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PhD Yearbook | 2025

DOCTORAL PROGRAM IN INDUSTRIAL CHEMISTRY AND CHEMICAL ENGINEERING

Coordinator:
Prof. Carlo Alessandro Cavallotti

The Doctoral Program in Industrial Chemistry and Chemical Engineering (***CIIC***) is designed for students aiming to get a deep expertise in research activities related to the development and design of chemical processes.

The general topic of the doctoral program is the application of the chemical and physical knowledge to all the activities related to the design, production and transformation of chemical substances and materials (like advanced inorganic chemistry, polymers and biomaterials). These studies involve not only the synthesis processes but also the related plants, here analyzed starting from laboratory tests and pilot plant experiments up to the industrial size, always including the careful evaluation of the related energetic, safety, and environmental issues.
The final goal is to provide to the PhD student the tools and the skills to:
(1) design and manage industrial processes at any size scales;
(2) develop new technical applications;
(3) create and to characterize new products and services.

To provide a few examples, the research activity may be focused on one of the following topics:

- study of processes from the microscopic to the macroscopic scale, by analyzing the thermodynamic and kinetic aspects of the process at the fundamental and applied levels;
- methodologies and criteria for process and plant design and operation, considering the choice of raw materials, costs, safety issues, and sustainability;
- design and control of unit operations and of the whole plant through mathematical modelling and computer simulation techniques;
- synthesis, characterization, process technologies, and use of substances;
- development of innovative chemical processes;
- catalysis and bio-catalysis;
- innovative energy technologies, with particular attention to energy consumption;
- biotechnology and chemistry of natural compounds.

The abstracts reported in this Yearbook provide further examples of the topics covered in the CIIC doctoral program.

Students holding "Laurea Magistrale" degrees in *Chemical Engineering*, *Materials Engineering*, *Industrial Chemistry*, *Chemistry*, and *Safety and Prevention Engineering* are the natural CIIC PhD students, though the program is also open to graduates from other scientific faculties. The ***CIIC*** program covers three years during which, in addition to developing the research project, the PhD student follows courses offered by the PhD school, seminars, summer schools, and workshops. The courses offered in the CIIC program cover both soft skills as well as the some of the most advanced scientific subjects in the field of Industrial Chemistry and Chemical Engineering.

Since 2001 (XVII cycle) the ***CIIC*** program graduated more than 250 students. The number of enrolled students has risen steadily in the last 10 years, increasing from about 10 to more than 30. About ~80% of the CIIC graduated PhD students now work in industry, with the remaining employed in the university or government research centers. These data demonstrate the important interconnection existing between the performed research and the industrial application. In fact, during the years, numerous research topics were directly supported by industrial companies through the Industrial PhD program. Among the sponsors of these programs were Biochemtex, Bracco, ENEL, ENI, Flamma, Isagro, LPE Epitaxial Technology, Mapei, Mare, Pirelli, RSE, Solvay Specialty Polymers, Tecnimont.

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EXPLOITATION OF BIOCATALYTIC METHODS FOR THE ASYMMETRIC SYNTHESIS OF FLAVOURS AND FRAGRANCES

Maria Cristina Cancellieri - Supervisor: Francesco Gilberto Gatti

In recent years, enzymatic catalysis has emerged as a crucial player in meeting the growing demand for sustainable methods in chemical synthesis, particularly in industries like pharmaceuticals, bio-based polymers, flavors, and fragrances. By harnessing biological catalysts such as enzymes or microorganisms, biocatalysis enables the efficient production of enantiomerically pure compounds.
My research project focuses on leveraging enzymatic catalysis for the stereoselective synthesis of chiral flavors and fragrances. Enzymes offer significant advantages over traditional chemical catalysts by operating under mild conditions, thereby reducing the use of toxic substances and extreme reaction parameters like temperature and pressure. This not only enhances safety but also minimizes environmental impact.
Enzymes' remarkable chiral selectivity allows for precise transformations that are often challenging with conventional methods, making them indispensable for producing the highly pure compounds essential in pharmaceuticals and specialty chemicals. Through enzymatic processes, my work aims to improve the sustainability of manufacturing practices.
One aspect of my research involves the development of a novel colorimetric assay for detecting alcohol dehydrogenase (ADH) activity and stereoselectivity. This assay utilizes a resorufin dye that changes color during enzyme-catalyzed transformations, enabling straightforward detection of ADH activity and stereoselectivity by visual observation.
Another key focus of my work is the stereoselective synthesis of sandalwood fragrances using biocatalytic methods. By employing ene-reductases (ERs) and alcohol dehydrogenases (ADHs), I achieved the asymmetric synthesis of fragrances like Brahmanol®, Firmantol®, Sandalore®, and Ebanol®. This approach replaces less sustainable traditional hydrogenation techniques.
Additionally, I investigated the biocatalytic desaturation of γ-lactones catalyzed by Rhodococcus erythropolis. This enzymatic process offers an innovative pathway to obtain dehydrogenated compounds with high enantiomeric purity, showcasing both enantio- and chemoconvergent synthetic capabilities.
Together, these studies illustrate the potential of enzymatic catalysis to revolutionize the synthesis of complex molecules, advancing sustainability and efficiency in chemical manufacturing.

PD/SSZ-13 LOW-T NOX ADSORBERS: AN INVESTIGATION BY OPERANDO FTIR SPECTROSCOPY AND MICROREACTOR STUDY

Yusra Hamid – Supervisor: Luca Lietti

Air pollution from transportation accounts for a significant share of global pollutant emissions. Among these pollutants, nitrogen oxides (NOx), which are primarily emitted by internal combustion engines, present a serious threat to human health. NOx is particularly concerning due to its strong link to lung cancer and its role in the formation of tropospheric ozone, a harmful air pollutant. In response to these health risks, recent regulations have been implemented with the goal of reducing NOx emissions to nearly zero, reflecting the growing emphasis on minimizing the environmental and public health impacts of transportation.
Currently, nitrogen oxides emissions are managed using Three-Way Catalysts (TWC) for gasoline engines and Selective Catalytic Reduction (SCR) and Lean NOx Trap (LNT) technologies for diesel engines. These systems are effective but require a minimum operating temperature, typically above 200°C, to function efficiently. However, internal combustion engines, particularly diesel engines, frequently experience an extended period known as the cold start phase, during which the engine operates at temperatures below this threshold. Hybrid vehicles, which combine electric motors with internal combustion engines, also encounter significant challenges related to cold starts. The start/stop nature of hybrid operation, where the combustion engine frequently cycles on and off, intensifies these cold start issues. Addressing these cold start challenges is essential for several reasons; Improving cold start performance can significantly enhance the fuel efficiency, reliability as well as the durability of hybrid vehicles. Moreover, by reducing the emissions associated with cold starts, hybrid vehicles can better fulfill their potential as environmentally friendly alternatives to traditional vehicles.
One promising strategy for mitigating NOx emissions at low temperatures is the implementation of Passive NOx Adsorbers (PNAs). PNAs are specifically engineered to capture NOx during cold start conditions when traditional catalytic converters are less effective. They adsorb NOx at low temperatures and then release it at higher temperatures, allowing the NOx to be treated in downstream systems such as selective catalytic reduction (SCR) units or three-way catalysts (TWC). Among various materials evaluated for PNA applications, zeolite-supported Pd stands out due to its remarkable NOx storage and release characteristics. The integration of zeolite-supported Pd-PNAs into exhaust systems represents a significant step forward in the development of advanced aftertreatment technologies aimed at reducing vehicular emissions under real-world driving conditions.
This has motivated this PhD research where an investigation have been conducted using *operando* FT-IR spectroscopy in combination with microreactor studies to explore the mechanistic details of low-temperature NOx adsorption and desorption, and to assess the catalyst's performance at different temperatures and under the impact of the different species present in the exhaust gases like O_2, H_2O, CO, hydrocarbons (e.g. C_3H_6).
In particular, *Operando* FT-IR spectroscopy plays a crucial role in providing insights into catalytic reaction mechanisms and pathways by enabling real-time analysis of both the catalyst surface and the gas phase during catalytic reactions. By integrating gas-phase analysis with simultaneous FT-IR spectroscopic surface analysis, this approach contributes to a comprehensive understanding of reaction mechanisms and the behavior of surface species.
This research has investigated the mechanisms of NOx adsorption on Pd/SSZ-13, with particular emphasis on the characteristics, stability, and reactivity of the NOx species that are adsorbed onto the catalyst. For this purpose, a wet-impregnated Pd/SSZ-13 catalyst has been synthesized and characterized, and the adsorption/ decomposition of NOx has been analyzed under relevant conditions. Under all experimental conditions, the catalyst exhibits an effective capacity to store NOx and release them on heating.
Characterization of the catalyst using in-situ CO/NO adsorption experiments combined with FT-IR spectroscopy reveals the existence of isolated Pd^+ and Pd^{2+} species. These species are produced through ion exchange with the Brønsted acid sites of the zeolite, along with PdOx particles present on the external surface of the zeolite.
NO adsorption under standard conditions (i.e. in presence of water and oxygen) at all temperatures is accompanied by NO_2 evolution due to the reduction of Pd^{2+} to Pd^+ sites; following the reaction: $2[PdOH]^+ + 3\,NO \rightarrow 2\,Pd^+NO + NO_2 + H_2O$. The formation of Pd nitrosyls is observed, although the nature of the Pd species involved in the adsorption process remains debated, with possibilities including monomeric sites such as Pd^{2+} or $[PdOH]^+$, and Pd^+ as well as dimeric sites like $[PdOH\text{-}PdOH]^{2+}$, $[Pd\text{-}O\text{-}Pd]^{2+}$, or $[Pd\text{-}Pd]^{2+}$.
The investigation of various adsorption temperatures yield similar nitrosyl formations, with additional nitrate formation at lower temperatures. The thermal stability of the adsorbed species increases upon increasing the adsorption temperature.
The absence of oxygen does not significantly impact NO adsorption, with the formation of nitrosyls similar to that of the standard run. However, the presence of oxygen reduces the stability of adsorbed nitrosyls by promoting the reoxidation of Pd^+ nitrosyls to less stable Pd^{n+} species upon heating. At variance, H_2O strongly impacts the NO adsorption since in its absence no reduction of Pd^{2+} to Pd^+ by NO occurs and hence no formation of NO_2 is observed during the storage. Nitrosyls of Pd^{2+} are formed in this case, along with nitrosonium ions over the acid sites of the zeolite. This increases the storage capacity of the catalyst; however, the thermal stability of the adsorbed species is very poor, and they decompose at low temperatures.
The presence of CO and propylene was found to reduce the NOx storage capacity of the catalyst. NO was observed to adsorb as nitrosyls in the presence of CO and as $Pd^{n+}(NO)(X)$ complexes in the presence of propylene.
Finally, the performances of an ion-exchanged catalyst (IE-Pd/SSZ-13) has been compared with that of the wet-impregnated catalyst (as investigated above). Normalizing the results for the different Pd loading of the two samples investigated, very similar results have been obtained under standard conditions, i.e. NO reduces Pd^{2+} to Pd^+ and adsorbs in the form of nitrosyls. The ion-exchange catalyst showed a slightly improved NO adsorption capacity (normalized for the Pd loading) but a lower thermal stability of the adsorbed species. Very similar effect of the operating conditions (T, oxygen and water content) is observed on this catalyst with respect to the impregnated sample, if one exclude the higher formation of nitrosonium ions under dry conditions due to the higher amounts of zeolite acid sites not occupied by Pd.
In conclusion, this study highlights the critical role of water and oxygen in modulating NOx adsorption-desorption on Pd_1/SSZ-13 catalysts. Optimizing the balance of these components could improve passive NOx adsorber performance, especially during cold-start, advancing aftertreatment systems to meet stringent NOx emission standards and support sustainable automotive technology.

TOWARDS THE GREEN PRODUCTION OF BASE CHEMICALS

Andrea Isella – Supervisor: Davide Manca

Among the main emitters of greenhouse gases in the chemical industry, several base-chemical processes (*e.g.*, ammonia and methanol synthesis) stand out for their high hydrogen consumption. The present doctoral dissertation examines the opportunity of replacing such "grey" hydrogen (as it is typically synthesized from hydrocarbons: *e.g.*, natural gas and coal) with "green" hydrogen (*i.e.* produced via water electrolysis powered by renewable electricity). Nevertheless, major operational issues due to this approach arise from the need to reconcile non-dispatchable renewable energy sources (which inevitably affect the electrolyzer and therefore the production of green hydrogen) with the low flexibility of chemical plants (traditionally designed to operate in stationary conditions). Specifically, this work introduces new methodologies for the design of (i) systems producing green hydrogen (*i.e.* aimed at sizing the electrolyzer and its renewable power plant) and (ii) systems allowing the inherent discontinuities of renewable sources to meet the operational requirements of the downstream chemical plant through a material (*i.e.* tanks) or electrical (*i.e.* batteries) storage. Then, such tools have been applied to carry out feasibility studies on ammonia plants wherein the fossil hydrogen input is, partially ("hybrid-green ammonia") or totally ("green ammonia"), replaced with green hydrogen.

More specifically, this work starts analyzing today's chemical sector to understand what visions are leading the green transition in the industry. Also, it reviews the most widespread carbon-intensive processes worldwide to define what direction to take and which objectives to focus on to achieve the most effective results. Indeed, by ranking the most common chemical processes by their environmental impact, ammonia and methanol turned out to be in the top positions, hence the subsequent emphasis on replacing their fossil-based hydrogen feedstocks with renewable-based ones, to fully abate the carbon emissions associated with their synthesis. To do this, a novel methodology to identify the most sustainable designs for hybrid- or fully-green Power-to-Chemicals plants was developed. Indeed, although it was mainly applied to green ammonia production, this criterion has been elaborated to potentially refer to all those industrial processes calling for green hydrogen as feedstock.

Power-to-Chemicals plants are required to operate in unsteady-state conditions because of their inherent dependence on renewable energy sources, but also to feature mass and/or energy buffer systems mitigating the fluctuations introduced by such input discontinuities and thus allowing for smooth reconciliation of renewable energy sources with the steadiness of the process. Specifically, such storage systems must be operated flexibly to minimize their storage capacity, hence both capital and operative expenses. Accordingly, this work introduces two novel criteria to identify the optimal (a) mass or (b) electricity delivery schedule minimizing the design capacity of flexible (a) storage tanks or (b) battery energy storage systems. Specifically, in both cases, the material/energy balance of the storage system is enhanced with an additional term acting as a "memory" of all the limitations encountered in equaling the outlet mass/energy flows to the inlet ones. Such a formulation allows the discharge of the resulting hold-up whenever possible to fully satisfy the downstream demand and minimize the required storage capacity. Finally, regarding the general formulation of the problem, the proposed design framework also stands out for the multi-objective optimization it addresses. Indeed, our methodology aims to identify the best solutions according to each of the "three pillars of sustainability": economic, environmental, and social. In this regard, the adopted optimization methodology is based on the scalarization method. Namely, this technique aims to aggregate the different objective functions (in this case, three) into only one by a suitable scalarization function. In this way, a multi-objective optimization (MOO) problem can be converted to a single-objective optimization (SOO) problem. The choice of the scalarization function is the crucial point of this method: the simplest possibility is the linear combination (or weighted sum) of the objective functions. Indeed, solving MOO problems always requires some human decision-making, and, concerning the scalarization method, in this case, the choice of weight values represents the core of the decision-making process. In this sense, the user is allowed to solve an optimization problem either addressing one pillar only or even all three of them by simply imposing the weight each pillar should have in leading to the optimal configuration (*e.g.*, Economic = 60%, Environmental = 30%, and Social = 10%).

The present doctoral research led to the prominent conclusion that the electrification of ammonia and many other base chemicals represents a viable production route for their synthesis: both hybrid- and fully-green plants resulted in still higher production costs than conventional technologies, but more and more competitive, especially considering the almost monotonically decreasing costs of renewable power generation systems in the last few years. Fully understanding the paradigm shift where all the chemical processes traditionally featuring stationary regimes now need to be operated in dynamic conditions (*e.g.*, increasing process flexibility, optimizing material and energy storage systems, relying on resilient renewable energy networks, *etc.*) will represent the endgame of the chemical industry in the 21st century, as this is the only way to push the cost-effectiveness of renewable integration within the chemical industry to economically competitive levels.

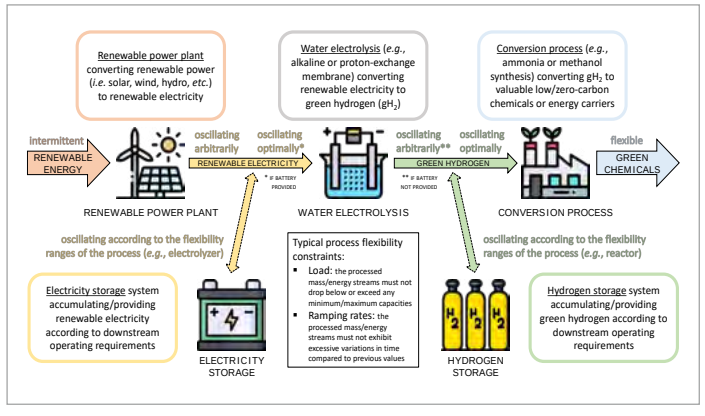

Fig. 1 - Typical scheme of a Power-to-X (applied to a Power-to-Chemicals) process. Electricity or hydrogen storage (or both) are needed to mitigate the intermittencies from renewable energy sources.

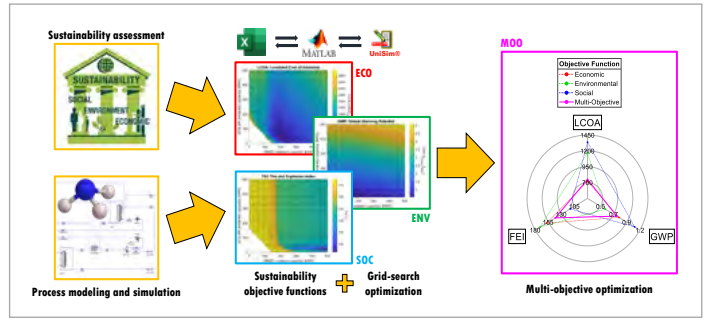

Fig. 2 - The proposed multi-objective optimization methodology to maximize the global sustainability of Power-to-Chemicals plants (here referring to the Power-to-Ammonia process).

NEW INSIGHTS INTO THE NH_3-SCR MECHANISM OVER CU-CHA CATALYSTS: AN EXPERIMENTAL AND KINETIC APPROACH

Nicole Daniela Nasello- Supervisor: Enrico Tronconi

Despite the recent strides in meeting the strict environmental regulations, nitrogen oxides (NOx) emissions from internal combustion engines still represent a concern. In this context, the Selective Catalytic Reduction process via urea/ammonia injection (*i.e.*, NH_3-SCR) is currently considered the best available aftertreatment technology for NOx emission control from Diesel engine exhausts. This usually occurs over typical SCR catalysts (e.g., metal-exchanged zeolites), where, after the injection of a urea-based solution, NOx are selectively converted into harmless compounds such as nitrogen (N_2) and water (H_2O). Notably, copper-based zeolite catalysts (e.g., Cu-CHA) are preferred for applications demanding high de-NOx activity, selectivity, and hydrothermal stability. Nevertheless, despite the effectiveness of this technique, some aspects still represent a huge concern: among these, a complete understanding of the SCR reaction mechanism is missing. In addition, together with harmless N_2 and H_2O outlet species, significant release of nitrous oxide (N_2O), a greenhouse gas (GHG) with high global warming potential, is also detected as an undesired by-product of the SCR reactions. In this context, the present PhD thesis work aims at investigating and broadening the fundamental mechanistic understanding of NH_3-SCR processes over Cu-CHA catalysts, focusing on two main fronts: i) unraveling the redox SCR scheme in which Cu active sites are involved; ii) investigating the mechanism of N_2O production to minimize its undesired release without affecting the deNOx efficiency.

It is commonly accepted that in Cu-CHA catalysts Cu ions are actively involved in a redox cycle, with their oxidation state transitioning from Cu^{II} to Cu^{I} during the reduction (RHC) and from Cu^{I} to Cu^{II} during the oxidation (OHC) half-cycles of the Standard SCR reaction ($4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$). To unveil the low temperature (≤200°C) Cu/redox scheme, in the first part of this thesis, the reduction and oxidation half-cycles are independently investigated over a reference model Cu-CHA catalyst by means of transient response methods (TRMs). In particular, the reactants are stepwise fed to the reacting section under isothermal conditions to analyze the interaction between the gas-phase species and the catalyst. Experimental and kinetic results reveal: i) the RHC to proceed via second and first-order kinetics in Cu^{II} and NO concentration, respectively, according to a Cu:NO=1:1 stoichiometry; ii) the OHC to proceed via second and first-order kinetics in Cu^{I} and O_2, respectively, being O_2 alone able to completely reoxidize Cu^{I} sites. These aspects underline the dominance of *dinuclear* Cu species in the low temperature SCR redox mechanism. The two half-cycles are then combined to describe the global process (RHC+OHC=STD-SCR), hence conclusively assessing the closure of the Standard SCR Cu/redox cycle.

Notably, these findings are also validated by varying the catalyst formulation as well as the reaction operating conditions. For instance, by applying the same transient approach on samples with fixed Cu loading and different silica-to-alumina ratio (SAR), we reveal: i) only a minor SAR effect on OHC; ii) an inhibiting effect of SAR on the RHC rate. As a result, a higher deNOx activity is achieved on samples with lower SAR. By comparing dry and wet experiments, the effect of water is also evaluated. Unexpectedly, results reveal the impact of H_2O to vary depending on the catalyst formulation. At high SAR, water inhibits the RHC and promotes the OHC: as a result, limited impact is observed on the steady state deNOx activity. With decreasing SAR, the H_2O effect on RHC gradually shifts from inhibition to promotion, while OHC is always promoted.

Concerning the RHC only, the adopted study is also extended to higher temperatures (up to 350°C) and to hydrothermally aged samples. In the whole T-range under investigation (135-350°C), results demonstrate the Cu^{II} reduction process to be unaffected by the aging level of the tested samples. In addition, as long as enough NH_3 is present on the catalyst surface and can mobilize the copper ions, the reduction transients are accurately predicted by assuming the same RHC rate law already adopted at T≤200°C. Remarkably, at least under wet conditions, this reveals the low-T Cu^{II} reduction mechanism to remain unaltered at high temperatures, at least up to 300°C.

In the last part of this thesis work, both steady state and transient experiments are performed to investigate the undesired N_2O production mechanism during NH_3-SCR reactions over commercial Cu-CHA catalysts. In line with literature, a *bimodal* trend is observed in the outlet N_2O profile, hence suggesting the existence of two different formation mechanisms depending on the reaction temperature. Focusing on T≤300°C, NO_2 and NH_3 are identified as the key species promoting the N_2O release, in line with a NH_4NO_3 formation and decomposition route. Under Standard SCR conditions (NO_2/NOx=0), however, this route has been challenged, suggesting instead N_2O to result from Cu redox reactions (e.g., unselective reduction of Cu^{II} sites). To mitigate the N_2O production, a novel approach based on the strategic injection of NH_3 is adopted. Remarkably, at temperatures exceeding 200°C, our data show that it is possible to limit the N_2O production by about ~11% while concurrently maximizing the catalyst deNOx efficiency (>99%). As expected, the N_2O make increases when ammonia is pulsed to the system, while it decreases when ammonia is cut-off. Surprisingly, the opposite trend is observed at lower temperatures. In line with recent literature findings, such a so far unreported observation suggests the existence of different controlling phenomena when dealing with the formation of N_2O, namely: i) the Cu/redox activity at low-T (≤200°C); ii) the NH_3 coverage at higher temperature. In this direction, additional mechanistic and kinetic experiments reveal a direct correlation between N_2O make and Cu oxidation state and suggest the N_2O formation at low-T, when under Standard SCR conditions, to derive uniquely from the reduction of Cu^{II} sites (RHC).

The present findings offer new insights on the nature of the redox NH_3-SCR reactions over Cu-CHA catalysts and on the release pathway of undesired N_2O, from both a fundamental and a more practical point of view. In view of the upcoming stricter emissions regulations, these results are an essential step to give guidance to the automotive industry for the development of new generations of aftertreatment systems and catalysts.

MODELING FORMATION AND OXIDATION OF CARBONACEOUS PARTICLES: TOWARDS AN IMPROVED DESCRIPTION OF THEIR REACTIVITY AND MORPHOLOGY

Andrea Nobili – Supervisor: Tiziano Faravelli

Carbonaceous particle formation from hydrocarbons combustion is of high interest not only for the study of pollutant (soot) emissions, but also in the field of advanced materials. In this regard, it is known that carbon nanoparticles (CNPs) possess quantum-dot behavior, and their optical and electronical properties, relevant for practical applications, significantly change with their size, morphology, and nanostructure. However, the understanding of main physical and chemical pathways governing carbonaceous particle evolution in high-temperature reactive systems is not complete.
Recently, there has been emerging evidence supporting resonance-stabilized radicals and open-shell multiradical aromatic structures as key players in the growth of large polycyclic aromatic hydrocarbons (PAHs) and carbonaceous particles. In this work, a quantum-chemistry study is firstly carried out to assess from a theoretical standpoint the behavior of large PAHs that may participate to the still obscure inception mechanism, i.e., the transition from gas-phase aromatics to CNPs. The results obtained suggest that, beyond a critical size, PAH reactivity can be assimilated to that of persistent radicals. In particular, odd-C-numbered PAHs embedding 5-membered rings rapidly lose a hydrogen atom to form resonance-stabilized radicals in combustion conditions, while even-C-numbered PAHs react as open-shell rather than closed-shell molecules independently of temperature, as usually assumed. Also, the concentration of large closed-shell and open-shell polycyclic aromatic hydrocarbons (PAHs) levels out with the increase of their aromatic structure and, contrary to conventional assumptions in existing soot models, their reactivity approaches that of persistent radical species.
Based on these findings, a detailed kinetic model for carbonaceous particle formation and oxidation is here developed. The proposed model is formulated based on a discrete sectional approach, through which large PAHs, carbonaceous particles and aggregates are described through lumped pseudo species. The model, coupled with the gas-phase chemistry of smaller hydrocarbons developed and iteratively updated by the CRECK modeling group at Politecnico di Milano, is full written in the CHEMKIN format. Compared to its previous versions, the proposed model accounts for the persistent radical behavior of large aromatic structures with > 100 C-atoms, consistently with the results obtained from the quantum-chemistry study. Furthermore, it explicitly incorporates the description of CNP polydispersity, which allows to better capture the evolution of carbonaceous particle morphology and, in turn, of their surface reactivity. In particular, the model considers various nanosized primary particles generated from liquid-like counterparts through a carbonization process. Such primary particles successively grow or aggregate forming fractal structures.
The model is validated against carbonaceous particle experiments available in the literature for more than 100 laminar flames, mostly fueled by ethylene and including counterflow diffusion, premixed Mc-Kenna burner and burner stabilized stagnation flame configurations. The validated targets comprise soot volume fraction, average primary particle diameters, particle size distribution functions (PSDF), average particle size, number density and particle H/C ratio.
A general good agreement between experimental data and numerical simulations at different pressures (P=1-10 atm), maximum flame temperatures (T_{max}~950-2790 K) and carbonaceous particle yields (f_v~0.01 to ~170 ppm) is obtained. Parity plots allow to identify systematic deviations of the present model from the experiments, while the comparison between all the flames included in the database highlights the relative contribution to particle formation and growth of the main reaction classes implemented in the model.
Significant improvements in the predictions of the proposed model are obtained with respect to its previous versions and, in some cases, with respect to other state-of the art soot models proposed in the literature and based on different approaches, such as the method of moments or the stochastic approach.
In particular, by accounting for the persistent radical character of CNPs, it is possible to reproduce data of nascent soot oxidation by O_2 in plug flow reactors under very dilute conditions. Under these conditions, surface-activating species such as Ḣ and ȮH are almost absent, and existing models which instead consider soot particles as closed-shell species that require an activation step, such as through H-abstraction reactions, before O_2 attack are unable to predict the oxidation measurements of the analyzed CNPs. Furthermore, the evolution of primary particle diameter and PSDF with residence time can be now reasonably described compared to previous versions of the model, which neglected CNP polydispersity for the sake of simplicity.
On the other hand, model limitations emerging in some of the investigated flames, such as the description of particle fragmentation in premixed flames under lean conditions, are discussed, with references to other mechanisms proposed in the literature in order to highlight possible future improvements of the model predictive capability. Overall, this work provides a novel and effective tool for the detailed modeling of carbonaceous particles chemistry in high-temperature combustion systems, which could help to better predict and interpret CNP reactivity and morphology.

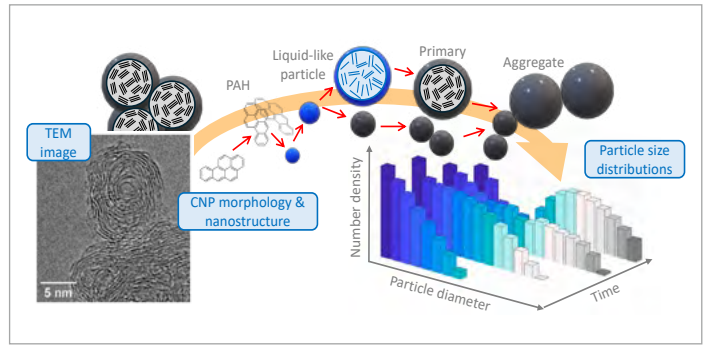

Fig. 1 - Schematic representation of carbonaceous particle formation and evolution

REACTION ENGINEERING AND MULTI-SCALE ANALYSIS OF UPGRADING PROCESSES ON TRANSITION METAL SULFIDE CATALYSTS

Anna Nova – Supervisor: Flavio Manenti

This work focuses on processes for the upgrading of waste or low-value products through a reaction engineering and multi-scale analysis approach. In particular, two processes were investigated, both characterised by their potential to benefit from the catalytic activity of transition metal sulfides (TMS): the hydrogen production via hydrogen sulfide (H_2S) decomposition and the selective ring-opening (SRO) of decalin.
The conversion of hydrogen sulphide into value-added products, namely hydrogen and elemental sulphur, represents a promising route for the treatment of H_2S, an hazardous waste, and for a sustainable production of hydrogen. The thermal decomposition of H_2S was first investigated, using a multi-scale approach, which included thermodynamic and kinetic analysis, reactor modelling, and process design. Experimental campaigns were conducted using a tubular reactor, with an H_2S partial pressure of 1.27 kPa, at temperatures ranging from 640 °C to 1100 °C, achieving a maximum conversion of 64% at 1107 °C. The measured H_2S conversion data were used to validate a kinetic model integrated into a customized simulation suite. The model accurately reproduced the experimental results, including the temperature drop observed at the reactor outlet. Based on these validated results, a process design was proposed and the simulation of a complete plant converting H_2S into hydrogen and sulfur was performed. The production of H_2 from H_2S has not yet reached an industrial-scale implementation due to several technical and economic issues, including the separation of H_2 from unreacted H_2S, the high energy demand of the regeneration step, and the management of sulfur vapor. The proposed process design addresses these challenges in order to develop an economically viable H_2 production process. An economic analysis was also carried out. The H_2 production cost for the simulated plant was compared to the current market prices. The analysis demonstrated the competitiveness of the proposed process and provided a preliminary assessment of its industrial feasibility.
However, for potential industrial applications, it is essential to operate at high flow rates to minimize residence time, making the study of the catalytic H_2S splitting essential. Among TMS catalysts, molybdenum disulfide (MoS_2) has proven to be one of the most efficient in promoting H_2S decomposition. Despite its potential, a comprehensive understanding of the reaction kinetics is still missing in existing studies. This work investigates the H_2S splitting over MoS_2, within a temperature range of 640 to 929 °C. At the highest temperature, a conversion of up to 40% was achieved. It was also determined that the system works in chemical regime. The characterization of the catalyst, both fresh and post-use, revealed that the total surface area, as well as the crystal structure, remained stable. This indicates that no sintering is occurring up to 929 °C. Moreover, the catalyst did not show any sign of deactivation or poisoning after 10 hours of operation. Experimental data enabled a kinetic analysis, leading to the development of various models. The first model employed a power-law approach and accounted for the reverse reaction by including the thermodynamic equilibrium constants. In addition, a four-step reaction mechanism was proposed, and the rate expression was derived using the Langmuir-Hinshelwood method. The kinetic parameters obtained for both models were consistent with those reported in the literature, where available, and confirmed the consistency of the proposed mechanism. The average reaction order across the tested temperature range was 1.09, while the apparent activation energy varied from 98 to 112 kJ/mol, depending on the model.
The catalytic reaction was compared with its thermal non-catalytic version, demonstrating notable advantages, especially at moderate temperatures. As reported in the literature, MoS_2 is one of the most effective catalysts for H_2S decomposition. Accurate kinetic modelling is fundamental for the scale-up of the process and for industrial applications. Therefore, these results provide a robust foundation for optimizing the efficiency of the process and support the integration of the catalytic H_2S splitting into industrial hydrogen production systems.
Another upgrading process in which TMS catalysts demonstrated to be particularly effective is the selective ring-opening of naphthenes, with decalin as a representative example molecule. This reaction contributes to the upgrading of low-quality fuel fractions, leading to a higher combustion efficiency and therefore to a mitigation of harmful emissions. The SRO of decalin was studied at 160 bar and 400 °C over a SiO2-supported Ni/W/Mo catalyst. Starting from the collected experimental data, the reaction was investigated. The yield in decalin skeletal isomers increased linearly up to conversion values of about 20%. Instead, the reactions of decalin cis-trans isomerization and of decalin dehydrogenation resulted to reach the thermodynamic equilibrium. The equilibrium seemed to favour the formation of trans-decalin and tetralin. However, as decalin started to undergo isomerization, tetralin reacted to regenerate decalin. Over time, the equilibrium of the whole system drove all the species toward cracking.
The experimental datasets also provided a starting point for the kinetic modelling of the reactions, which in turn provided insights into the reaction mechanism. To date, detailed kinetic models for decalin ring-opening on this or other TMS catalysts are lacking in the literature. In this study, several reaction mechanisms were evaluated, differing in the level of detail used to classify the ring-opening products and in the reaction steps involving these compounds. For each mechanism the specific rate constants were determined by fitting the model to the experimental data. The thermodynamics of the reversible reaction steps were included using equilibrium constants.

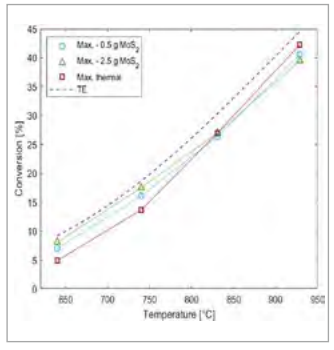

Fig. 1 - H_2S splitting: maximum conversions obtained without MoS_2, with 0.5 and 2.5 g of MoS_2, and conversion at thermodynamic equilibrium.

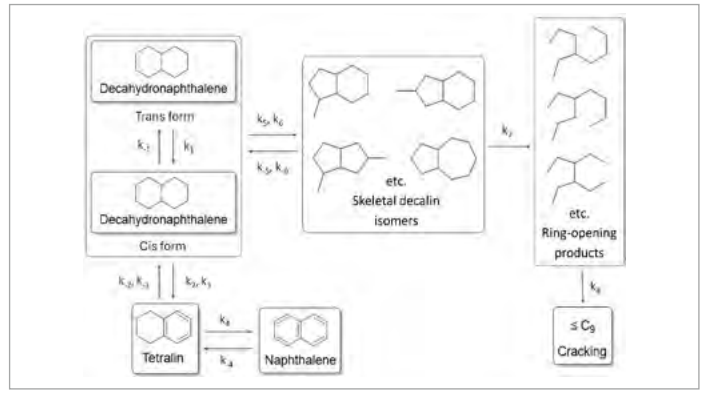

Fig. 2 - Reaction mechanism proposed for the decalin ring-opening on SiO_2-supported Ni/W/Mo sulfide catalysts.

BIOMASS TO FUELS: DEVELOPMENT OF THERMOCHEMICAL CONVERSION PROCESSES

Veronica Piazza – Supervisor: Alessandra Beretta

Within the current energy transition, the thermochemical valorisation of waste lignocellulosic biomass represents a key pathway for circular economy and a promising solution for the generation of valuable biochemicals and biofuels. In this context, pyrolysis, the thermal degradation of biomass in an oxygen-free atmosphere into a complex pool of products - consisting of a gas stream, bio-oil and biochar - emerges as a promising process for the production of liquid biofuels that can support the decarbonization of critical sectors, like aviation and marine markets. Beyond its standalone importance, the study of pyrolysis is important also because it constitutes the preliminary devolatilization stage of all thermal processes, including gasification and combustion. However, the complex multi-component and multi-phase nature of this process has hindered the obtainment of rigorous experimental data on biomass devolatilization, necessary for the refinement of kinetic schemes and technology optimization. Moreover, bio-oil streams currently contain unstable light oxygenates that do not meet the fuel quality standards.

This PhD thesis aims to contribute to progress biomass thermochemical valorisation with a dual research approach: the kinetic investigation of biomass pyrolysis and the study of catalytic C-C coupling reactions for the upgrade of light bio-oxygenates into fuel-like species. A figure of the process scheme composed by a first pyrolysis step and a second catalytic vapour upgrading stage is represented in *Figure 1*.

The study of biomass pyrolysis was addressed with a double strategy that combined experimental investigation and kinetic modelling. The initial goal was the development of an experimental methodology and setup in Polimi. A novel TGA-based experimental protocol was developed, where tests were performed with full control of operating conditions and multiple analytical methodologies allowed to precisely quantify pyrolysis products. A graphical representation of this TGA-based protocol is shown in *Figure 2*. During the PhD work, this methodology was applied to study the pyrolysis of biomasses of increasing complexity, starting from cellulose and progressing to three types of hemicelluloses – xylan, glucomannan and arabinoxylan – and mixtures of them. Experimental data were compared with the predictions of state-of-art lumped kinetic schemes, showing significant margins of model improvement, in particular in terms of products speciation. Therefore, this experimental methodology has proven a flexible and unique solution for the comprehension of biomass devolatilization chemistry and the tuning of kinetic schemes. Additionally, an improved version of the kinetic scheme of cellulose pyrolysis was elaborated, exploiting newly in-house experimental data as well as literature data for validation. Moreover, further pyrolysis experiments were performed on the same bio-feedstocks, in a fixed bed reactor in the laboratories of NTNU (Norwegian University of Science and Technology, Trondheim, Norway), testing larger and more representative scales, and validating the observations collected in the ideal TGA-system.

Besides, the study of the catalytic valorisation of pyrolysis vapours was addressed by investigating C-C coupling reactions of light oxygenates, the species that mostly lower the quality of bio-oil. These are chain-growth reactions that transform light oxygenates into species with longer C-chain and lower O-content, thus enhancing their stability and heating value. Among catalytic formulations, TiO_2 emerged as an active catalyst. The research involved the kinetic study of two model reacting systems on TiO_2: the ketonization of acetic acid (C_2, the simplest carboxylic acid) and the condensation of acetone (C_3, the simplest ketone). Catalytic activity tests were coupled with characterizations on both fresh and spent catalytic samples, associating activity to surface features. The experimental data were rationalized into a reaction scheme involving several consecutive and parallel reaction routes. The association of catalytic activity tests to a thermodynamic analysis and a study on dynamic trends has shown the presence of both thermodynamic and kinetic bottlenecks, that hampered the catalyst performance.

In conclusion, this research has advanced the understanding of biomass thermochemical valorisation. The development of an innovative experimental methodology for the kinetic study of pyrolysis has made available new but fundamental piece of information on model biomasses. Furthermore, the catalytic potential of TiO_2 for upgrading light oxygenates via chain-growth reactions has been deepened. Overall, these findings contribute to broadening the knowledge on thermal processes for the valorisation of waste lignocellulosic biomasses towards sustainable energy production.

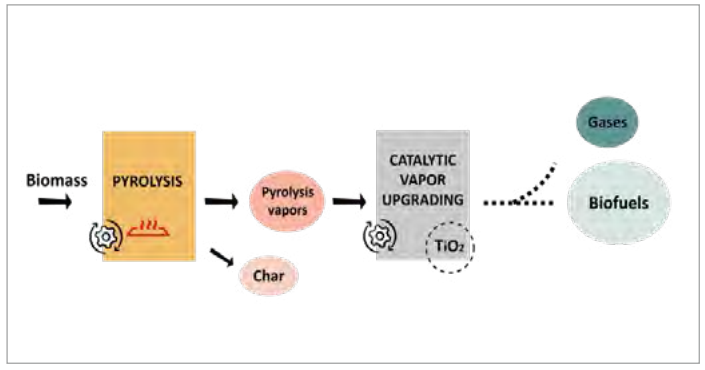

Fig. 1 - Schematic process scheme of biomass pyrolysis with consecutive catalytic vapour upgrading stage for the production of biofuel.

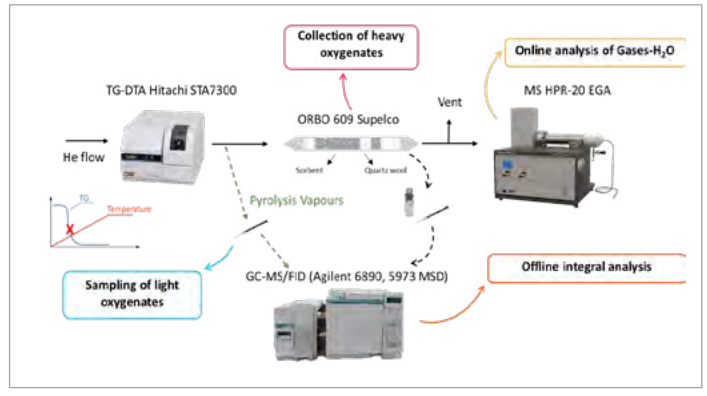

Fig. 2 - Novel TGA-based methodology for the kinetic study of biomass pyrolysis.

TECHNO-ECONOMIC EVALUATION OF OPTIONS FOR LARGE-SCALE HYDROGEN TRANSPORT

Federica Restelli – Supervisor: Laura Annamaria Pellegrini

Green hydrogen is expected to play an important role in tackling climate change. The transport of H_2 from regions rich in renewable energy resources, exploitable at a low cost, to countries with a high energy consumption, but limited resources, involves its conversion to a "hydrogen carrier", a substance capable of efficiently storing it. A techno-economic analysis was carried out on the value chains of ammonia (NH_3) and liquefied hydrogen (LH_2) for H_2 transportation. Two case studies were examined: a European scenario and an Asian scenario. The European scenario is representative of the early stages of green hydrogen delivery infrastructure development, with a moderate H_2 input flow rate (44 t/d), a relatively short sea transport distance (2500 km), and the use of conventional fuels, such as diesel or marine fuel, for transportation by ship and truck. The Asian scenario represents a future where large-scale hydrogen export projects are well established, with a high H_2 input flow rate (440 t/d), a relatively high sea transport distance (7500 km), and the consumption of hydrogen or ammonia as sustainable fuel for transportation by ship and truck.

The value chain involves H_2 conversion to the carrier, storage, maritime transport, distribution and carrier reconversion to H_2. For LH_2 the conversion and reconversion processes correspond to liquefaction and regasification, while for NH_3 they correspond to ammonia synthesis and cracking.

The first objective was to develop accurate simulations of the processes involved in the value chains of LH_2 and NH_3, to obtain the material and energy balances. From this analysis, the advantages and disadvantages of the investigated hydrogen carriers emerged as follows. For LH_2 one of its main advantages is the low reconversion cost, with the possibility of integrating the regasification process with a power generation cycle. Another advantage is that the liquefaction process requires only electric energy. Among the disadvantages, it has to be stored at extremely low temperature (-250 °C), necessitating high performance insulation and posing cryogenic hazards. The liquefaction process is expensive due to high electricity consumption, and large-scale liquefaction plants have yet to be constructed, as existing projects have only been demonstrated at the pilot scale. Moreover, managing the boil-off gas generated during storage and transport is crucial, requiring efficient recovery methods. NH_3, on the other hand, offers certain advantages over LH_2. It can be stored at a milder temperature of -30 °C and is already widely traded as a global commodity, transported via ship, truck, and pipeline. Its versatility is another key benefit, as it can be used as a hydrogen carrier, a chemical feedstock, and a fuel for power generation. Despite these advantages, NH_3 also has drawbacks. There are fewer opportunities for cost reduction in its synthesis, storage, and transport, since the value chain for its end use in the fertiliser production is already well established. Additionally, NH_3 presents toxicity hazard. Its cracking process is the most energy-inefficient step in its value chain, and large-scale cracking plants have yet to be constructed.

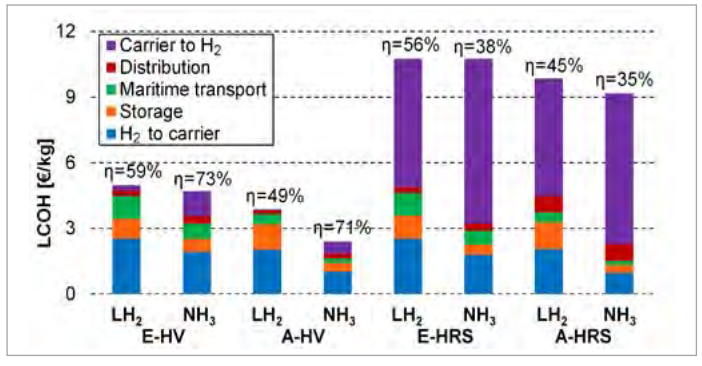

Fig.1 - LCOH [€/kg] and η [%] for the LH2 and NH3 value chain in the Hydrogen Valley (HV) and Hydrogen Refuelling Stations (HRS) cases for the European (E) and Asian (A) scenarios.

The second objective was the economic and energetic assessments of the hydrogen carriers, with the calculation of the Levelized Cost Of Hydrogen (LCOH) and efficiency (η). The LCOH accounts for both capital and operating expenditures, expressing the cost of H_2 delivery in €/kg. Efficiency is defined as the ratio of the H_2 flow rate delivered to the end user, net of the losses and H_2 consumptions to supply the energy required for the processes, to the total H_2 flow rate fed. The results of these assessments are graphically illustrated in Fig.1 for the investigated scenarios and assumed end uses of the delivered hydrogen, distinguishing between its application to the industrial sector (delivery to a Hydrogen Valley) and road transport sector (delivery to Hydrogen Refuelling Stations).

From Fig. 1, the following considerations arise: for the European scenario and H_2 application in the industrial sector, NH_3 incurs the lowest cost (LCOH of 4.6 €/kg) and highest energy efficiency (η of 73%); for the European scenario and H_2 application in the road transport sector, LH_2 and NH_3 present almost the same cost (LCOH of 10.7 €/kg), with LH_2 having the highest energy efficiency (η of 56%); for the Asian scenario and H_2 application in the industrial sector, NH_3 presents the lowest cost (LCOH of 2.4 €/kg) and highest energy efficiency (η of 71%); for the Asian scenario and H_2 application in the road transport sector, LH_2 and NH_3 exhibit low costs (LCOH of 9.8 €/kg and 9.1 €/kg, respectively), with NH_3 being the most cost effective, and high energy efficiency (η of 45% and 35%, respectively), with LH_2 being the most energy efficient.

In conclusion, this study revealed several insights. The optimal use of H_2 involves centralisation at a single hub operating at moderate pressure. This approach enhances safety, as H_2 is a hazardous substance with risks of flammability and explosion, allowing few, well-trained personnel to manage it, thereby reducing the risk of accidents. Ammonia would be more economically attractive if it could be used directly by the end consumer, thereby avoiding the additional costs of reconverting it back into H_2. The effect of scale on economic viability is more pronounced when considering the application of H_2 in the industrial sector, where centralised processes benefit from economies of scale. In contrast, this effect is less significant in the transportation sector, as refuelling station operations are not scalable. Due to the high cost of H_2 delivery as LH_2 or NH_3, hydrogen export is currently economically unviable and is expected to remain so, even with large-scale implementation in the future. While producing green H_2 in countries like Italy or Japan is more cost-effective than importing it, land-use constraints must be considered, as renewable energy plants require significant space. Therefore, while local production can avoid transport costs, it may not be scalable to meet future H_2 demand. Countries like Australia or Africa, with abundant renewable resources and vast uninhabited land, are well-suited for large-scale hydrogen export projects. Thus, the transition to green H_2 will require government policies that facilitate its import and export, ensuring a sustainable and economically viable hydrogen market.

NOVEL NANOCATALYSTS FOR SUSTAINABLE CHEMICAL PROCESSES

Vincenzo Ruta – Supervisor: Gianvito Vilé

The sustainability of chemical processes is increasingly recognized as critical today, driven by the growing awareness of climate change, energy crises, and environmental challenges resulting from human activities. Heterogeneous catalysis is deemed crucial in addressing these issues: the use of a catalyst allows the reduction of process energy consumption, simultaneously guiding the reactions towards the desired product, decreasing waste and byproducts. Moreover, the heterogeneous nature of the catalysts facilitates their recovery and reuse across multiple cycles, further minimizing the production of catalyst-derived waste. Thus, from this perspective, the design of heterogeneous catalysts with tailored nanostructures can increase the efficiency and sustainability of catalytic processes.

In this regard, the underlying concept of this thesis is the development of novel, tailored catalysts for the synthesis of pharmaceutical intermediates and fine chemicals. These reactions are often conducted with homogeneous molecular catalysts, which pose challenges for catalyst recycling and reutilization, and the need for external ligands, additives, or co-catalysts. Moreover, for complex organic transformations in the liquid phase, harsh reaction conditions in terms of time, temperature, and pressure, are often required. Thus, the use of heterogeneous catalytic processes for fine chemical and pharmaceutical synthesis can mitigate these conditions, increasing the sustainability of the processes by lowering waste production and energy consumption. In addition, heterogeneous catalysts avoid the use of external ligands or additives through rational catalyst design, furtherly simplifying downstream purification operations, and reducing the waste generated by these external additions.

Several industrially-relevant reactions have been targeted in this PhD thesis (Fig. 1).

For example, a single-atom copper-based catalyst has been formulated for the synthesis of diaryl ethers, where the metal is anchored to the support through polyaminic linker. In this case, combined catalytic and computational studies have shown how the polyaminic linker behaves as a ligand under reaction conditions, activating the metal atoms towards the reaction studied. Moreover, green metrics have been assessed for the preparation of the catalytic material, clearly demonstrating its eco-friendliness in terms of energy consumption, material efficiency, and waste generation.

In addition, a nickel-based single-atom catalyst has been proposed for the photocatalytic C-O cross coupling between ubiquitous aryl/alkyl halides and carboxylic acids. In this work, catalyst design studies allowed to elucidate that the integration of Ni single atoms in the catalyst generates a sole material capable to undergo simultaneously the photoredox and metallaphotocatalytic cycles.

In the case of trifluoromethylation of heteroaromatic rings, a photocatalytic protocol has been developed, studying the effect of rational catalyst design to establish precise structure-reactivity relationships that determine the most influential structural parameters of catalytic materials on the reaction, namely surface area and the non-metallic nature of catalysts. Furthermore, the protocol has been translated in continuous-flow mode, doubling system productivity, and facilitating recycling operations through catalyst packing in a fixed bed reactor. Finally, the thesis also explored catalysts for photocatalytic degradation of persistent pharmaceuticals ending in (waste)water, such as Gemfibrozil, emphasizing the importance of these catalysts not only to build complex synthetic molecules, but also to effectively break down challenging molecules that are difficult to abate.

Overall, this work opens new pathways for sustainable chemical production, demonstrating the potential of tailored heterogeneous catalysts for scalable applications in pharmaceutical synthesis and pollution mitigation. Through a combination of computational studies and practical experimentation, this thesis also provides a comprehensive approach to understanding these reactions and solving modern chemical challenges. From this perspective, this PhD opens new avenues for the development and application of single-atom catalysts (Fig. 1) in industrially-relevant reactions. The peculiar features of these materials can lead not only to an improvement in the efficiency, but also to a drastic increase of the sustainability of these processes.

Fig.1 - A compilation of reactions investigated in this thesis using heterogeneous single-atom catalysts (left) and a representative aberration-corrected STEM micrograph of the catalyst (right), illustrating the isolated nature of the active sites. This atomic-level precision in catalyst design not only enhances catalytic activity, selectivity, and stability, but also allows for greater tunability in reaction pathways.

DEVELOPMENT AND OPTIMIZATION OF SEPARATION/ PURIFICATION PROCESSES OF INDUSTRIAL GAS STREAMS BY ADVANCED ADSORPTION PROCESSES

Hamza Shafiq – Supervisor: Marco Derudi

Gas separation plays an integral yet complex role in the chemical industry, with application-specific needs dependent on feed composition. This encompasses an extensive scope spanning macro to micro processes. Among emerging methodologies, adsorption technology has demonstrated considerable promise across a variety of applications and scientific fields, necessitating deeper investigation to fully realize its potential uses and capabilities. Ongoing research is predominantly focused on adsorbent characterization and enhancing its capacity. Nonetheless, increased attention is required for overcoming limitations of adsorption process dynamics as well as the optimization of existing adsorption setup. Based on this two aspects were extensively researched during the tenure of PhD

i) Development of advanced adsorption process and
ii) Optimization of existing adsorption system for the industrial gas separation

Conventional PSA, due to thermodynamic limitation governed by the variable pressure sequence, is unable to separate both extract and raffinate at high purity simultaneously. Such limitation can be overcome by employing dual-reflux configuration i.e., dual-reflux pressure swing adsorption (DR-PSA).

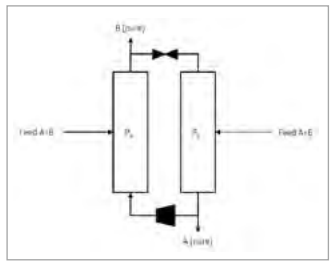

Fig.1 - Dual-reflux pressure swing adsorption configuration

Post-combustion carbon capture was assessed using the DR-PSA system. CO_2 separation was explored solely because of the exponential rise in CO_2 concentration. Robust theory model was numerically computed to evaluate the performance of DR-PSA system. The developed model employed in MATLAB® environment is capable to overcome the linear isotherm limitation of existing equilibrium theory. Using robust theory model, the performance of DR-PSA was then compared with the existing VPSA pilot plant for CO_2 capture using identical system and operating parameters. Using 5A zeolite the VPSA was able to recover 79 vol.% CO_2 with 85 vol.% purity from anhydrous flue gas comprising of 15 vol.% CO_2 at a power consumption of 2.37MJ/$kgCO_2$. While using the VPSA design specification, DR-PSA was able to recover the CO_2 product ≥96% purity at less stringent pressure ratio albeit at higher energy consumption of 2.58 MJ/$kgCO_2$. Sensitivity analysis study based on the pressure ratio and light reflux ratio demonstrated that energy consumption can be lowered to mere 1.67 MJ/$kgCO_2$ while constraining the CO_2 purity to ≤95%. The comparative results are quite encouraging to proceed with the economic feasibility of the DR-PHA configuration as well as the adoption of the DR-PHA system for carbon capture on an industrial pilot scale.

	Two-bed DR-PSA	Three-bed VPSA
Steps	Four steps	Seven steps
Pressure ratio	1.89	24
Feed time (s)	64	120
CO_2 purity (%)	95.457	85
CO_2 recovery (%)	95.46	79
Specific work (MJ/$kgCO_2$)	1.67	2.37
Productivity (mol/kg.h)	2.91	3.29

Tab.1 - DR-PHA vs. VPSA pilot plant performance comparison

For the latter, existing fixed-bed temperature swing adsorption system located at Settala Gas complex was focused for the olefin/paraffin separation. For quite some time, the Settala Gas operation team was not able acquire the desired purity of the end product. Multi-component fixed-bed adsorption model was mathematically designed to study the adsorption behavior of hydrocarbon feedstock with sulfur and moisture impurities. The dynamic model was constructed around the olefin and paraffin alongside the impurities such as mercaptans, sulfide etc. Upon investigation, it was observed that sulfur content approximately takes 12-13 days to breakthrough the adsorbent bed at a concentration exceeding their odor threshold. This translates identical to the Settala Gas operation of 25 days (12hr per day) till sulfur odor detection at the column outlet therefore augmenting the reliability of developed model results. Additionally, olefin breakthrough was monitored after ~1.7 days (24h operation) causing inability to meet the product requirement. At the moment, regeneration was being carried out for only 12h which was sufficient enough to only remove the sulfur odor but not the full bed regeneration. In initial meeting with Settala Gas management, it was concluded that adsorption sequence in series and regeneration condition due to energy restriction were the bottlenecks in the current operation strategy. The developed model was then used to simulate different scenarios to determine the optimal adsorption sequence to achieve the desired product purity as well as the regeneration conditions for the adsorption column while being within the energy constraints. Based on this parametric analysis, two strategies were formulated within the existing design specification of Settala Gas plant albeit at slightly higher energy consumption.

The strategies were proposed to the Settala Gas management for implementation to remove the bottleneck in current plant operation. The proposed adsorption sequence and new regeneration parameters with 25% higher energy consumption were accepted by Settala Gas in a positive manner for execution.

	Existing plant operation	Proposed plant operation	
Adsorption sequence	Series operation for olefin/paraffin	One column operation with other in standby/ regeneration	
Regeneration sequence	No regeneration for olefin/paraffin adsorption bed	Regeneration for adsorption bed	
Sweeping gas flowrate (l/h)	270	350	
Regeneration temperature (K)	490	590	525
Energy consumption (kWh)	0.0939	0.137	0.118

Tab.2 - Current vs. proposed operation scheme

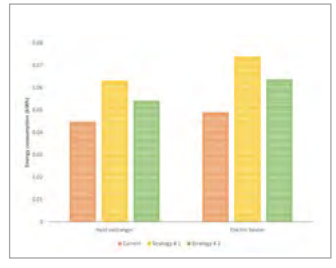

Fig.2 - Dual-reflux pressure swing adsorption configuration

SINGLE-ION CONDUCTING POLYMERS AS ELECTROLYTES AND INTERLAYERS FOR PREVENTING DENDRITE GROWTH IN LITHIUM METAL BATTERIES

Jiajia Wan – Supervisor: Elie Paillard

Lithium-ion batteries (LIBs) with high energy density and long cycle life are widely used today including in portable electronic devices, stationary energy storage systems and electric vehicles (EVs). However, the energy density of LIBs is reaching its theoretical limit. In this regard, Li metal batteries (LMBs) are reviving, primarily due to their potential to achieve higher energy density as lithium anodes have a high theoretical capacity of 3860 mAh g^{-1} (vs. 372 mAh g^{1} for commercialized graphite anodes). However, LMBs face critical challenges, including the inhomogeneous Li stripping/plating (e.g. dendrites growth), that leads to poor cyclability and raise safety issues and therefore limits their commercial application. To this end, the goal of this PhD thesis was to prevent the dendrite growth of lithium metal to improve the electrochemical performance and safety of LMBs.

Therefore, two strategies were adopted to address these challenges. On the one hand, artificial solid electrolyte interphases (art-SEIs), made from single-ion conducting polymers (i.e. Li^+ polyanions), were used to build interlayers to improve the homogeneity of the current density and suppress dendrite growth since they allow, in principle, to limit salt concentration gradients at the vicinity of the Li electrode by providing fixed anions. On the other hand, using solid polymer electrolytes greatly improves safety since they only contain low flammable and low volatile components contrary to liquid electrolytes with flammable organic solvents. A PEO/ionic liquid (IL)/lithium salt ternary solid polymer electrolyte (TSPE) with advantages such as low flammability, and high conductivity (vs. PEO/lithium salt electrolytes) was combined with a single-ion interlayer to benefit from their respective merits (i.e. a high conductivity and elasticity for good contact with electrodes for the electrolyte, limitation of salt concentration gradients near the electrode, and acting as a mechanical barrier for the art-SEI, as well as the presence of extra ions acting as supporting electrolyte for the TSPE), which allowed extending the cyclability of Li metal batteries. Also, to improve cell performances further, polyethylene oxide solid single-ion conducting polymer electrolytes (SICPEs) were used and optimized to achieve a balance of high lithium transference number, high ionic conductivity, and good mechanical stability, enabling better cycling performance of Li metal.

In this PhD thesis, three main achievements are reported. Firstly, single-ion polymer-based art-SEIs based on polystyrene (PSTFSILi) and/or polymethacrylate (PMTFSILi) backbones were prepared to improve Li deposition and suppress the dendrite growth. The improved effects of art-SEIs were confirmed by visual and SEM observation of plated Li electrodes and corresponding separators. The combination of these two polymers outperforms single polymer art-SEIs at higher current densities of 0.25 and 0.5 mA cm^{-2}, resulting from the synergy of properties, including their different solubilities in ether-based liquid electrolytes and the reactivity of the coating solution with Li metal. The mixed polymers art-SEI enables better cycling stability in both Li‖Li symmetric cells and $LiFePO_4$‖Li cells compared with cells using untreated Li. This likely results from improvements in lithium metal confinement and the homogeneity of the current density, as concentration gradients close to the Li metal are limited as well as the direct contact between the Li metal anode and the separator. To further improve the performance of LMBs, a crosslinked comb SICPE was prepared, using poly(ethylene glycol) methyl ether methacrylate (PEGMEM) as monomer, poly(ethylene glycol) dimethacrylate (PEGDMA) as a crosslinker, and lithium sulfonyl(trifluoromethanesulfonyl) imide methacrylate MTFSILi as monomeric Li salt with a PEGDMA:PEGMEM molar ratio of 1:10 and an O/Li ratio of 20 (O corresponding the ether oxygen onto the PEO chains). The as-prepared SICPE membrane was combined with the single-ion-based art-SEI, significantly enhances the long-term cycling performance of the Li metal anode and that of lithium metal polymer battery cells.

Secondly, a homogeneous and transparent crosslinked TSPE (PEO/1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl) imide ($PYR_{14}TFSI$)/bis(trifluoromethanesulfonyl) imide lithium salt (LiTFSI) electrolytes with a molar ratio of 10:1:1) was prepared. Although TSPE has relatively high conductivity, its low Li transference number leads to significant salt concentration gradients and Li depletion at the Li/electrolyte interface during plating. Furthermore, despite of crosslinked, its mechanical strength is rather low especially at 80 °C. This is detrimental for the good confinement of lithium metal and suppression of dendrite growth. Therefore, art-SEI with a high Li transference number and a high mechanical robustness was combined with TSPE to compensate the limitation of TSPE. The electrochemical results indicate that the art-SEI can help suppress the dendrite growth and resist short-circuits, enabling a cycling life more than double in Li|TSPE|Li cells. Also, in a $LiFePO_4$|TSPE|Li lithium metal polymer battery, the art-SEI layer significantly improves the cycling stability and reaches an 85% capacity retention after 350 cycles at 0.2C while the bare Li cells fast decay to 60% of the initial discharge capacity after 62 cycles.

Thirdly, although SICPEs are advantageous in excellent ability to suppress the lithium ions depletion at the lithium anode interface, their ionic conductivity is usually unsatisfactory. Accordingly, a series of SICPEs were prepared and optimized in terms of the content of plasticizer (poly(ethylene glycol) dimethyl ether, PEGDME), and the monomer/crosslinker ratios. Results show that all plasticized membranes exhibit a high lithium transference number ($t_{Li}+$) above 0.8 and an acceptable mechanical strength, allowing a long-term cycling of Li‖Li cells over 2000h at 0.1 mA cm^{-2} with 1 mAh cm^{-2} while the non-plasticized one ends up at 60h. The optimal membrane exhibits the highest Li^+ conductivity of 1.5×10^{-4} S cm^{-1} with a $t_{Li}+$ of 0.85, and a storage modulus of 8×10^{-3} MPa at 80°C. It was selected to be used in full cells, enabling an 80% capacity retention after 136 cycles in $LiFePO_4$|‖Li cells. The cyclability of the cells is further improved to 236 cycles when using a coated Li anode with an art-SEI.

During my thesis, art-SEIs with good adhesion to the Li metal surface and good chemical compatibility were developed and could be used in combination with various electrolytes, for instance, with soft polymer electrolytes that possess strong conductivity but that inherently cannot confine lithium metal. In this case, the art-SEI plays the role of a mechanically robust layer and, for non-single-ion conducting electrolytes, limit the salt concentration gradient near the anode. On the other hand, they could also improve the contact between rigid electrolytes such as glasses and ceramic, which usually require the use of a softer interlayer, either liquid or polymeric for improving the contact with the Li metal anode. Since they were prepared using a coating method that closely resembles the industry standard that consists in spraying liquid solutions onto freshly extruded Li metal foils, the road is open for mass-production of coated Li foils, not only to improve the performance of Li anodes in cells, but also to enhance the long-term storage ability of lithium metal, as an issue often encountered is the ageing of the foil and the uncontrolled growth of interfacial layers, which is detrimental for performance (and reproducibility). All the studies include tests in devices and therefore demonstrate the validity of the technologies and their combinations at TRL4. Further development would require the upscaling of the production of foils and cells to the pilot scale.