



Coordinator:
Prof. Carlo Alessandro Cavallotti

DOCTORAL PROGRAM IN INDUSTRIAL CHEMISTRY AND CHEMICAL ENGINEERING

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 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 researches 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, Flamma, Isagro, LPE Epitaxial Technology, Mapei, Pirelli, RSE, Solvay Specialty Polymers, Tecnimont.

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TOWARDS NET-NEGATIVE EMISSIONS METHANOL SYNTHESIS: INTEGRATION OF NOVEL REFORMER CONCEPTUAL DESIGN WITH PROCESS ELECTRIFICATION AND OXYFUEL STEAM MODERATED COMBUSTION

Filippo Bisotti - Supervisor: Prof. Flavio Manenti

Recent studies showed that the current production methods are not sustainable, and the chemical and energy sectors should re-think technologies and feedstocks. Electrification and waste recycling (including CO₂) are the new trends in chemical engineering for effective decarbonisation and greener technologies. The reforming (i.e., syngas production) is one of the most polluting processes, but the resulting syngas is the most versatile mixture exploited to make the largest volume of chemicals. The reforming negatively impacts on the environment due to a large amount of CO₂ emissions coming from fuel combustion to sustain endothermic reactions at high temperatures. Generally, the reformer burner consumes the oxygen in the air as the comburent and the nitrogen acts as a thermal buffer. The resulting flue gas contains a large amount of nitrogen which is toughly split from the generated CO₂. It is remarkable that CO₂ capture (CCS) is an energy-starved process and the sequestration efficiency is limited to 90-95%, thus a CO₂ release is unavoidable. The thesis work aims at developing the conceptual design of a novel reformer system where oxyfuel combustion is

applied instead of air. High-pressure steam guarantees thermal dilution. Several recent experimental works showed the benefits of steam-moderated oxyfuel combustion (SMOFC) such as (1) lower fuel consumption, (2) easy separation of the flue gas compounds, and (3) higher temperature in the combustion chamber. Thanks to the SMOFC, it is possible to reduce the combustion chamber volume while the exiting flue gas is mainly constituted by steam and CO₂. The generated CO₂ is then reduced with green hydrogen (i.e., electrolysis using renewable energy). Other hydrogen sources are not accounted for since (1) blue hydrogen is generated from fossil fuels and the thesis aims at decarbonising the entire production system, and (2) turquoise hydrogen is energetically unsustainable as stated in several reports of the IEA and Norwegian Petroleum Ministry (despite even Norway has a large surplus of renewable energy). The work analyses several process configurations which are not here reported since they are objects of shared patents (with NTNU). The different sensitivity analysis and process integration prove that the novel reformer enables to reduce the emissions (up to net zero

emissions) and the generated CO₂ is consumed within an internal chemical loop. Thus, the novel conceptual reformer results in a close-system where the flue gas is a waste any longer, but a valuable source of carbon to be converted into e-fuels. The conversion to e-fuels requires an effective system for the generation of green-H₂. Solid oxide electrolytic cells (SOEC) are investigated as ideal H₂ generation system. The choice of these innovate electrolyzers arises when you would like to preserve the enthalpy of system at high temperatures. Solutions such as alkaline electrolyzers and PEM are not optimal due to large energy dissipation and large entropy generation which reduce the global second principle efficiency of the overall system. Remarkably, the thesis presents a novel self-consistent and thermally independent SOEC-based module for green H₂ production. This novel system is interesting since (1) reduce the electrical energy demand, (2) it is modular, and (3) it is flexible; thus, it enables to select different operative process configurations according to the desired performances (i.e., maximum hydrogen production or maximum energy recovery, for instance). Due to patent

pending, it is not possible to disclose the novel technology module and integration with the aforementioned novel reformer configuration.

Finally, the novel reformer is integrated within the methanol synthesis loop. The thesis considers the methanol as final target, however, other chemicals can be produced just by modifying the catalyst and the operating condition. To quote a few, DME, higher alcohols and FT hydrocarbons are gaining more and more interested since they are valuable chemicals (and intermediate building blocks) and ideal substitutes of the fossil fuel for conventional engines. The methanol has a well-established market and large production volumes, and these are the main reasons that drives the selection of this molecule as ideal candidate. The methanol reactor is designed according to Lurgi technology (boiling feed water) adopting a refitted and updated Graaf-type kinetic validated both on experimental data and industrial observations (on several industrial reactor alternatives).

The coupling of the novel reformer with the novel hydrogen production module shows that:

- 1) The electrification of syngas production is possible and paths the way to several alternatives that should be investigated.
- 2) Under specific operating conditions, the methanol reactor lacks CO₂. Thanks to this peculiar situation, the process includes an exogenous CO₂ make-up

coming from any hard-to-abate industry (cement, steel, and so forth), or, alternatively, pure CO₂ generated in electro calcination or direct air capture (DAC). The latter two are becoming appealing for industrial applications.

- 3) The novel process enables to fix CO₂ into a valuable chemical by reducing the emissions, however, an increment in the electrical consumption is unavoidable. Anyway, the proposed flowsheet provides a potential candidate for reducing the emissions in this energy transition period since the chemical sector urges disruptive solutions to achieve sustainability and environmental tasks.
- 4) The novel green H₂ production system opens to several interesting applications. First, it is a module which can be easily replicated and produced in series. The replicability it a key feature for the industrial implementation (production cost reduction and transportation). In addition, the novel electrolyser configuration paths the way to high-temperature electrolyzers and it enables to feed the SOEC with high temperature steam without any consumption of additional fossil fuels to keep the optimal operating conditions. This is reflected in lower fossil fuel and electricity consumption as well. The last task is achievable thanks to energy integrations. Nevertheless, the module can be installed as it is to produce

green H₂ competing with current industrial solutions for the hydrogen production. respect to current SOEC implementation and low-temperature electrolyzers such as alkaline and PEM.

- 5) The novel process configuration proves the feasibility of CCU instead of CCS. The CCS considers just the sequestration of the CO₂, while the CCU tries to produce valuable chemicals starting from the CO₂ as feedstock. The thesis moves in this direction and provides a complete overview of different reforming alternatives which enable successfully reforming (bio)-methane into different chemicals. The novel approach considers only a small production scale due to the electrical (renewable) energy demand. However, this could represent an advantage since small-scale sites enable the development and implementation of distributed and integrated production sites (at the national and European levels) where renewable energy and e-fuels are shared. The main strength of distributed and pervasive grid lies in a dense interconnection leading to a progressive reduction in the production and distribution costs. This may be a winning solution for the European countries to break their dependence on natural gas (from Russia, for instance) and energy exporters as claimed in recent published articles.

DEVELOPMENT OF NEW BIOCATALYSTS FOR APPLICATIONS IN ORGANIC SYNTHESIS

Danilo Colombo – Supervisor: Prof. Maria Elisabetta Brenna

Nowadays, Biocatalysis is a deeply investigated field and its importance is well established also for chemical industries. With the aim of developing more and more efficient synthetic strategies, enzymes represent now a reliable solution due to multiple factors. Enzymes are biodegradable and non-toxic, moreover are able to catalyze a wide range of reactions with excellent chemo-, regio-, and stereoselectivity. Their ability of working under mild conditions (room temperature, pH and atmospheric pressure) and producing low amount of wastes and by-products (effectively fitting in modern green chemistry and sustainability guidelines) is greatly appreciated, especially for the production in the field of fine chemicals and bioactive molecules. In addition, the enzymes, with respect to classical catalysis, are generally suited to be integrated in cascade processes, since they operate typically in very similar reaction conditions. Last but not least, the set-up of multi-enzymatic processes is appealing because avoids possible substrate/product inhibitions. The aim of my PhD research has been the exploitation of biocatalysts (microorganisms and isolated enzymes) both for

the production of various fine chemical products (such as pharmaceutical ingredients, flavors and fragrances) and for developing more sustainable synthesis strategies with respect to traditional organic chemistry, avoiding the use of metal-based catalysts, toxic reagents and harmful operative conditions. The bioreduction of "activated" C=C bonds, i.e. those conjugated to one or more electronwithdrawing groups, is a widespread activity in nature and its applicability to preparative organic synthesis has been early recognized in last decades. Most of the enzymes responsible for this kind of activity that have been identified in the last years belong to the well-known and thoroughly characterised family of ene-reductases (ERs), nicotinamide-dependent flavoproteins which mediate the addition of a hydride and a proton to the C=C bond, with an anti mechanism. New applications of ERs for the stereoselective synthesis of active pharmaceutical ingredients and fragrances (or their key precursors) have been reported in this thesis work, in order to add such bioreductions to the toolbox available for asymmetric synthesis and to implement them in industrial manufacturing processes. Different classes

of substrates have been investigated, gaining insight into the stereoelectronic factors that control the reactions. In multiple cases, ERs have been exploited in cascade reactions with other classes of enzymes (in particular alcohol dehydrogenases), in order to design even more appealing and promising synthetic applications of these biocatalysts. Considering modern needs and trends in industrial manufacturing processes, primary attempts of using ERs as immobilized biocatalyst, or in continuous-flow reactor, have been reported too, furtherly establishing the great flexibility of these enzymes in productive contexts. The limited availability of non-renewable petroleum-based sources and the increasing attempts to reduce waste and energy consumption (all key aspects of the modern concept of Sustainability) have prompted the international community to move towards the optimization of greener manufacturing processes, recovering unavoidable waste and promoting the market of secondary raw materials and by-products. Fats and oils represent an important class of renewable feedstock from which the so-called oleochemicals are obtained. They are abundant

in nature, biodegradable, and possess nontoxic properties. In collaboration with an industrial partner, new chemo-enzymatic strategies for the valorization of soapstock, the by-product obtained from the refining process of vegetable oils, have been successfully developed, achieving the production of carboxylic and dicarboxylic acids of high commercial value.

ENVIRONMENTALLY AND PUBLICLY ACCEPTABLE SEPARATION PROCESSES FOR LIMITING THE NUCLEAR WASTE HAZARDS IN THE LONG-TERM

Greta Colombo Dugoni – Supervisor: Prof. Andrea Mele

The global energy demand is estimated to grow at a CAGR of over 4% in the next five years. Given the depletion of fossil fuel resources and the need to reduce greenhouse gases in the atmosphere, nuclear energy is considered to be one of the most viable options. Limited emissions are generated during the entire nuclear power plant life, from construction to decommissioning, including the fuel fabrication stage. Nuclear energy can be considered an environmentally friendly and green energy source. However, one of the problems is the production of high-level radioactive waste (HLW). Spent nuclear fuel (SNF) is characterized by a long-term radiotoxicity (~300k years), for the presence of long-lived radioelements, in particular plutonium and the “minor” actinides, MA (neptunium, americium and curium). The PUREX (Plutonium and Uranium Reduction EXtraction) process is currently used in many plants to recover uranium and plutonium from spent nuclear fuel to use as new fuel. One of the most important goals should be the selective separation (partitioning) of MA from the PUREX raffinate. The goal is challenging, because the separation of MA from

lanthanides (Ln) is a difficult task for their similar chemical and physical properties (such as size and coordination capabilities). Once removed, MA may be converted by fast neutrons into less radiotoxic or even stable elements (transmutation). This strategy, known as partitioning and transmutation, permits to reduce the environmental footprint and improve the sustainability of nuclear energy production also for the treatment of the existing HLW. One of the most promising classes of processes is referred to as SANEX (Selective ActiNide EXtraction) processes. Two variants should be mentioned: a) i-SANEX (innovative Selective ActiNide EXtraction): co-extraction of Actinides and Lanthanides using a lipophilic ligand followed by the stripping of the Actinides with a hydrophilic ligand; b) 1c-SANEX (1 cycle-Selective ActiNide EXtraction): it is a solvent extraction process aimed at extracting the Actinides with a lipophilic ligand from a PUREX raffinate. Basically, a lipophilic ligand is exploited to selectively extract MA(III) from an acidic aqueous solution containing also Ln(III). So far, hundreds of polydentate S and N-donor ligands have been tested. Soon, the highly selective

and efficient dithiophosphinic acids were abandoned, since they do not contain just C, H, O, N atoms (CHON principle), i.e. they would imply secondary waste generation as they are not fully incinerable. In this context, the bis-triazinyl-pyridine (BTP) class of ligands showed outstanding extraction capability and in particular CyMe₆-BTP showed chemical and radiolytical stability, that would favour longer lifecycle and easier recyclability. However, it was affected by slow extraction kinetics and too strong ligand-cation complexation. A real breakthrough has been the discovery of the extraction and stability properties of the pyridine-bis-triazolyl (PyTri) class of ligands. Unfortunately, shows some drawbacks, i.e. the complex synthesis for its industrial application. Here are summarized the characteristics to satisfy the industrial constraints:

- selectivity towards An,
- reversible binding between the ligand and An,
- solubility in a suitable solvent (i.e. kerosene or 1-octanol),
- fast kinetic complexation of An,
- stability to hydrolysis and radiolysis,
- compliance to the “CHON principle”.

Given this background, I worked on the development of new systems with a good performance in the extraction of actinides to have new fuel and reduce waste. I decided to follow two different strategies: a) to improve the performance of the most promising system 1c-SANEX and b) to design new ligands that respect all the industrial constrain and with a good extraction capability and selectivity. To reach the first goal, I studied the extraction system with CyMe₆-BTP and I speculated on the use of co-solvents to increase the kinetics and reduce the time of the process. I designed a new class of choline acetate based DESs, in order to respect the industrial constraints, in particular the CHON rule. DESs are eutectic mixtures of Lewis and Brönsted acids and bases, usually obtained by mixing a quaternary ammonium salt (HBA) with a hydrogen bond donor (HBD)

species. DESs were prepared and characterised by studying their physical properties (density/viscosity vs temperature), their chemical stability (NMR), radiolytic stability (25-50-100kGy) and their behaviour in presence of water. They were tested as co-solvents in 1c-SANEX in the reference system with CyMe₆-BTBP. The addition of DESs permits to decrease the processing time and improve the selectivity of the process. The synthesis of new ligands was the second goal of my thesis. I studied the characteristics and the properties of the already known ligands. I identified the techniques of studying the chelation of metals: a) NMR spectroscopy, to discover the stoichiometry of the complex, b) X-ray diffraction of powders and c) single crystal X-ray analysis, to know the structure of the molecule and its complex in the solid-state.

I used this information to study the Pytri family (PTD-PTEH), in particular the metal-ligand stoichiometry and the solid phase structure of the ligand and its complex using lanthanum nitrate as a model. Then I focused on two families: bispidine and di(2-picoly)amine. Bispidine is a diazabicyclononane, used as a chiral base or ligand for asymmetric synthesis, simply synthesizable by Mannich condensation. I introduced the triazole moiety on the core of bispidine to increase the coordination number. A small library was synthesized and analysed by NMR, X-ray diffraction and catalysis using the complex as catalyst. Only two molecules have proven to be suitable for SANEX like processes, but the preliminary extraction tests do not have good results. Di(2-picoly)amine (DPA) is a secondary amine with two picolyl substituents, commonly used as a chelating agent. I decided to introduce a triazole moiety obtaining a small library of click DPAs. Their chelation capability was tested using Zn, Cu, and La. I used NMR and ESI-MS spectrometer to characterize the complex. Starting from the information about the complexation, some preliminary tests about the solubility in suitable solvents were performed. Only three molecules showed good solubility and stability in the extraction system, but due to lack of time, they have not yet been tested.

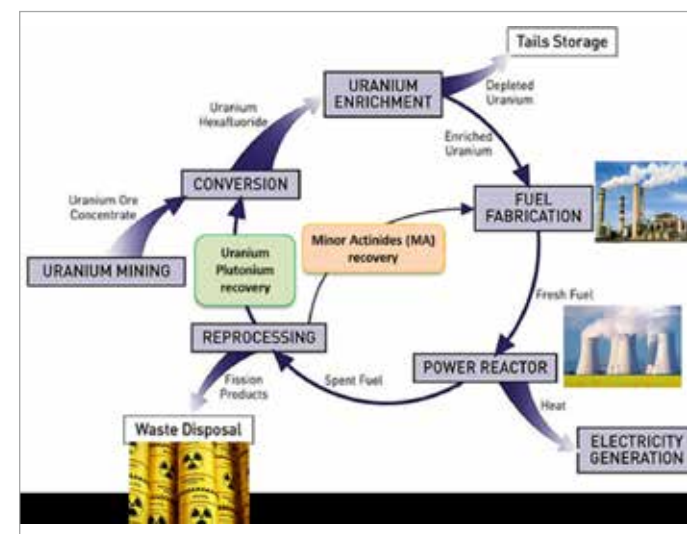


Fig. 1

STUDY OF STRUCTURE AND DYNAMICS OF PROTIC IONIC LIQUIDS (PILS) AS ELECTROLYTES AND COMPONENTS FOR POLYMER ELECTROLYTES

Giselle de Araujo Lima e Souza - Supervisor: Prof. Andrea Mele

The use of energy storage devices is exponentially growing, especially for mobile devices and the transportation sector, therefore the development of optimized systems is the key to the successful and entire transition to renewable energy sources. Nowadays, lithium-ion batteries (LIBs) are the technology of choice for most electrochemical applications thanks to their high specific energy, high efficiency, and long cycle life. However, safety is still an issue, and some electrolyte components must be improved. Recently, protic ionic liquids (PILs) emerged as potential electrolyte components in LIBs. When replacing flammable and volatile organic solvents, PILs are expected to improve the safety and performance of electrochemical devices. For implementing PILs as electrolyte components, a challenging task is still to understand the key factors governing their physicochemical and transport properties. To this end, this PhD work deeply investigates the effects of the structural features and intermolecular interactions on the properties of promising PILs based on the 1,8-diazabicyclo-[5,4,0]-undec-7-ene (DBUH⁺) cation and the (trifluoromethanesulfonyl-

nonafluorobutylsulfonyl) imide (IM14⁻), trifluoromethanesulfonate (TFO⁻) and bis(trifluoromethanesulfonyl) imide (TFSI⁻) anions. Here, a complete characterization of the PILs by using multinuclear NMR methods and different physicochemical analyses provided a comprehensive understanding of the features governing the properties of the selected PILs. The initial results unveiled the peculiar behavior of DBUH-IM14 in terms of macroscopic properties, which may be related to the structural characteristics of IM14⁻ anion, such as the presence of a C4 perfluorinated chain, the asymmetric distribution of the F atoms at the side of the sulfonylimide functional group, the steric hindrance, the capability of establishing fluorinated domains in the bulk liquid, etc (Fig. 1).

Yet, to promote the application of the PILs as electrolyte components, an in-depth understanding of the role played by the ions in the bulk system became crucial to scaling their transport properties. In this regard, both neat PILs and PIL⁻ based electrolytes (DBUH-IM14, DBUH-TFSI and DBUH-TFO doped with lithium salt containing the

same anion, i.e., LiTFO, LiIM14, and LiTFSI) were investigated by conductivity, diffusion and relaxation NMR. These techniques allowed the achievement of a broad overview of the ion dynamics of these systems. Accordingly, the presence of Li⁺ showed a peculiar effect on the dynamics of DBUH-IM14, and from the molecular point of view, DBUH-IM14 electrolytes deserve further investigation. It is known that polymer electrolytes can further improve the safety issues of the LIBs. Besides, polymer electrolytes are shapable materials and can improve the volumetric design concerns associated with liquid electrolytes. Then, to expand the application of PILs as innovative

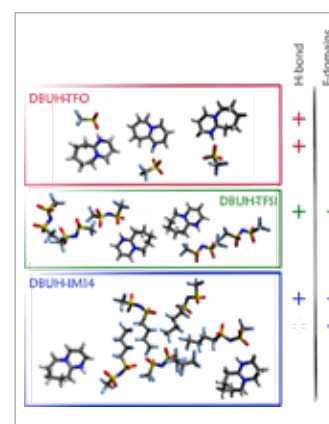


Fig. 1 - Sketch of the main intermolecular interactions in the studied PILs responsible for their peculiar behaviour.

electrolyte components, the selected PILs were confined into a polymeric matrix using poly(methyl methacrylate) (PMMA) as a polymer host (Fig. 2). Through the thermal analysis and solid-state NMR, this work could probe the structural features and molecular level interactions between the ions and the PMMA. The combined approach showed that (i) even when housed by the polymeric matrix, the PIL retains some internal mobility, and (ii) DBUH-IM14 has a stronger interaction with the polymeric matrix than DBUH-TFSI and DBUH-TFO.

The unpredictable behavior of DBUH-IM14-polymeric system prompted to further investigate the transport properties of DBUH-IM14-based polymer electrolytes. Then, the effect of PILs confinement onto their transport properties was probed by pulsed field gradient NMR and fast field cycling NMR. When

blended with PMMA, a marked slowing of the overall dynamics was observed. In the case of the polymer electrolyte system, Li⁺ showed a minor effect on the DBUH⁺ dynamics, whereas rotational and translational dynamics of the IM14⁻ anion was quite responsive to the presence of Li⁺. Still, a descriptive model is currently being developed to fully explain the transport properties and relaxation profiles of these systems.

From all the achievements of this PhD work obtained from the multifaceted experimental characterization of the molecular/atomic properties (multinuclear NMR, diffusion, relaxation and electrophoretic NMR) and the macroscopic behavior (density, viscosity, conductivity and thermal analyses), I can certainly state that DBUH-IM14-based electrolytes are of interest in LIB application and the structural features and nature of the intermolecular interactions in the

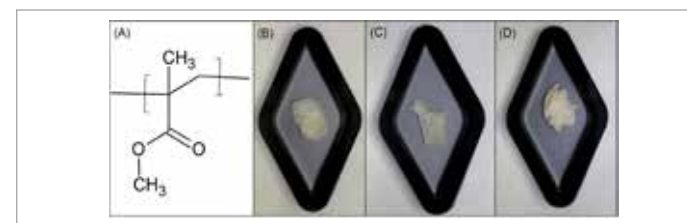


Fig. 2 - Structure picture of the (a) PMMA; picture of the solid materials (b) (PMMA + DBUH-IM14), (c) (PMMA + DBUH-TFSI), and (d) (PMMA + DBUH-TFO)

IM14⁻ anion play a crucial role in their molecular and macroscopic properties.

DESIGN, PREPARATION, AND CHARACTERISATION OF COMPLEX NANOMATERIALS FOR BIOMEDICAL APPLICATIONS

Nicolò Massironi – Supervisor: Prof. Elena Vismara

Nanotechnology is one of the key sciences of the 21st century and it is clear that the interest in nanoworld (from the Greek word “nano” meaning dwarf) has been rapidly increasing over the past few years.

We can safely say that nanotechnology is playing a key role in the development of different scientific areas such as materials science, communications, medical science, biomedical imaging, chemical engineering, and computing. One of the most important applications of nanotechnology are drug delivery and diagnosis, leading to the development of new and more effective medical treatments (nanomedicine). Looking back at the past two years, with the covid pandemic, it is clear how colloidal gold nanoparticles played, for example, a crucial role in the development of rapid antigen the latter being just one of the plenty of applications.

The purpose of the work was to develop complex nanosystems, whether inorganic (iron oxide nanoparticles with organic coating) or organic (nanocellulose fibrils) for applications towards human health in a direct (drug delivery and diagnostics) or indirect way (water remediation of pharmaceutical pollutants

mediated by nanocellulose or wound dressing). Starting from a rational design, which involves the usage of biocompatible materials like iron salts and cellulose, the study proceeded with the synthesis of iron oxide nanoparticles with an organic heparinic coating and nanocellulose through simple and cost-effective procedures. Shortly, synthesized nanoparticles were composed of an iron-oxide core (Fe_3O_4 -OA) and an organic layer made of LMWH (Low Molecular Weight Heparin) obtained by nitrous acid depolymerization starting from porcine mucosa UFH (Unfractionated Heparin), BSA (Bovine Serum Albumin) imposing biocompatibility and acting as a drug carrier in virtue of hydrophobic pockets, and DA (dopamine) acting as anchoring moiety between the core and LMWH/BSA via catechol group coordination. Nanocellulose was obtained via a top-down approach starting from industrial cotton waste by either hydrolysis or TEMPO-mediated oxidation, followed by chemical functionalization with glycidyl methacrylate or allyl appendages. Both systems were characterised in terms of morphology (TEM, SEM), stability in aqueous media (DLS), and chemical

structure (ftIR, NMR). Biological and relaxivity tests such as cytotoxicity on HeLa cells, heparanase inhibition assays (a novel chemotherapeutic target), and TD-NMR were carried out on iron oxide nanoparticles to ensure in-vitro biocompatibility and the ability to act towards the desired scope (theranostics). A chemotherapeutic agent, paclitaxel, was successfully included in the nanoparticles systems increasing its water solubility and its potency probably by mediating cellular uptake. The final systems were proved to be non-toxic, effective in inhibiting heparanase enzyme, and capable of being used as contrast agents given the relaxivity values in line with commercial preparations. Moreover hydrolyzed and oxidised nanocellulose fibrils functionalised with glycidyl methacrylate or allyl group were shown to adsorb amoxicillin (AM), vancomycin (VC), ciprofloxacin (CP), and chlorhexidine (CHX) and effectively act as an antibacterial substrate. This latter nanosystem could, for the aforementioned reasons, be exploited in water remediation of hospital or domestic wastewater and wound dressing. Those results highlight how the application of nanotechnology could deliver exceptional benefits to society

(more specifically human health) and how it could effectively broaden the tools, knowledge, and therapies currently available to clinicians. Even though nanomedicine is still commercially a niche application of nanotechnology, this work aims to prove the potentiality of this approach by presenting two different complex nanosystems and their characteristics.

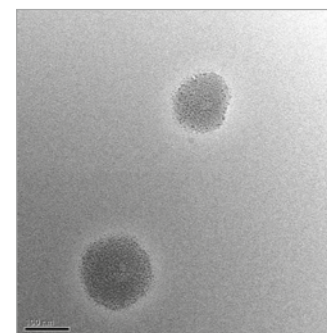


Fig. 1 - TEM image of the superparamagnetic iron oxide nanoparticle system (10.3390/molecules27207116)

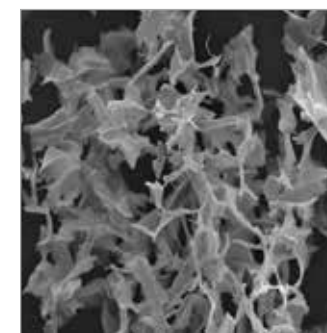


Fig. 2 - SEM Image of oxidised nanocellulose (10.3390/nano11020476)

UNRAVELING CARBON DEPOSITION MECHANISM AND ITS KINETIC CONSEQUENCES IN CATALYTIC DRY AND STEAM REFORMING OF METHANE BY COMBINED *OPERANDO* SPECTROSCOPY AND MICROKINETIC MODELING

Gianluca Moroni – Supervisor: Prof. Matteo Maestri

The catalytic reforming of methane with CO_2 (MDR) represents a promising path for the valorization of biogas and remote natural gas reservoirs rich in CO_2 . The process produces syngas with a high content of carbon source, useful for the manufacturing of useful value-added products. Since carbon formation represents one of the main issues for the industrial development of the process, understanding the phenomenon of carbon deposition and its kinetic consequences on the MDR reaction is pivotal in the continuous attempts of rational catalyst design. In this work, the mechanism of carbon formation on Rh and Ni based catalysts was studied by a combination of *operando* spectroscopic investigation of the working catalyst and microkinetic analysis. The tests performed in the *operando* Raman annular reactor and in a classic packed bed reactor were aimed at the comprehension of the effect of operating conditions (i.e., CO_2/CH_4 ratio, reactants concentration, and temperature), nature of the co-reactant, active phase, and catalyst support on the mechanism of carbon formation during CH_4 reforming processes. In the light of the kinetic data collected and the information

obtained with both *operando* and *ex situ* characterizations, a detailed mechanism for carbon formation during MDR was proposed (Figure 1). According to this mechanism, as soon as the reactants are introduced in the system, CH_x^* intermediates of reaction (simplified with C^* in Figure 1), which were recognized as carbon precursors, start to be formed at the catalyst by the catalytic cycle. The lower the CO_2/CH_4 ratio or the higher the reactants concentration, the higher the concentration of the intermediates CH_x^* at the catalyst, and faster the catalyst deactivation. These CH_x^* interact with each other over the metallic surface forming aggregates that represent the nuclei for more complex carbon species formation. The higher is the concentration of the intermediates, the more nuclei are formed on the metal surface, and the higher is the decrease in catalyst activity (nucleation phase). Based on the catalyst and on the concentration of the CH_x^* aggregates at the surface, the nuclei formed on the metal surface may evolve into two main carbon structures. In the case of Rh/ $\alpha\text{-Al}_2\text{O}_3$ catalyst, the carbonaceous nuclei represent the foundation for carbon filaments growth. The

difference in the CH_x^* chemical potential between the free catalytic surface and the nuclei generates a diffusional flow of CH_x^* intermediates towards the filaments foundation that start to grow over the Rh nanoparticles according to a base growth mechanism. When the growth of carbon filaments prevails over the creation of new nucleation centers, the catalyst activity reaches a stationary condition. Conversely, Ni/ $\alpha\text{-Al}_2\text{O}_3$ catalyst and BN supported catalysts (both Rh and Ni) showed a monotonous decreasing trend in catalyst activity for all the duration of the tests. This was due to the higher CH_x^* concentration at the catalyst surface that favor the continuous formation of new nuclei. These latter progressively cover more and more metal surface, forming a carbon film that finally encapsulate the metal nanoparticles. The different carbon formation mechanism showed by these catalysts is due to the lower metal dispersion reached by these catalysts and to the higher occurrence of RWGS reaction that increases the concentration of CO in the products, thus enhancing the occurrence of Boudouard reaction. Hence, according to this theory, the mechanism is ruled by the concentration of CH_x^*

at the catalyst surface and can explain both the temporal and spatial trend of carbonaceous species detected with the spectroscopic techniques as well as the kinetic data. As confirmed by UV-Vis spectroscopy, the carbon structures formed at the catalysts surface are made of benzene rings, whose conjugation depends on the operative conditions. These species organize themselves in more complex amorphous or graphitic structures. Usually, lower is the CO_2/CH_4 ratio, the more graphitic and less reactive are the carbon deposits. Time and temperature variations play an important role in defining the morphology of carbonaceous species, too. In fact, the carbon structure may evolve under the influence of these two parameters, especially in the case of temperature increase. This latter modifies the conformation of C-deposits, making them more graphitic and thus less reactive, according to a sort of aging process. The kinetic data collected

on Rh/ $\alpha\text{-Al}_2\text{O}_3$ catalyst in the *operando* Raman annular reactor were used to refine the microkinetic model developed by Maestri et al. with the specific aim to extend its validity under a wider range of operating conditions. The refined model was used to conduct a microkinetic analysis of the kinetic results to obtain a quantitative rationalization of the deactivation process during CH_4 reforming reactions. This represents the first attempt of including carbon formation and its kinetic consequences into the atomistic description of the MDR reacting system, paving the way towards the development of structure-dependent microkinetic modeling, able to take into consideration the "living" nature of heterogeneous catalysts in reacting environment. This work proposed a new methodology for the investigation of those heterogeneous catalytic reactions whose intrinsic kinetic is hindered by a deactivation process. This novel approach, which combines reliable

kinetic study of the reaction with *operando* and *ex situ* characterizations of the working catalyst and detailed first-principles microkinetic analysis, represents a successful way to gain a deeper understanding into the working fundamentals of heterogeneous catalysis and to enable rigorous mechanistic interpretations by theory. This methodology was fundamental to elaborate a detailed mechanism for carbon deposition. In fact, it enabled the possibility to directly observe for the first time in literature the process of carbon formation and growth at a molecular scale. This generalized mechanism represents an important breakthrough in the detailed comprehension of catalyst deactivation during MDR that paves the way towards a rational design of the catalytic material and of the process itself.

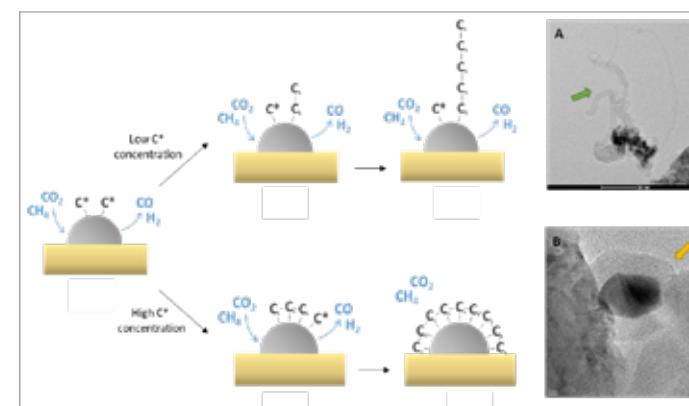


Fig. 1 - Sketch of the comprehensive carbon formation mechanism during Methane Dry Reforming reaction together with Transmission Electron Microscopy (TEM) images of the spent catalyst material where carbon filaments (A) and encapsulating carbon (B) species were identified.

THEORETICAL AND KINETIC MODELING OF THE COMBUSTION OF AROMATIC HYDROCARBONS

Luna Pratali Maffei – Supervisor: Prof. Tiziano Faravelli

The increase in the world energy demand and the unstable geopolitical scenario call for short and medium-term sustainable alternatives for energy production, including high energy density fuels for transportation. This motivates the research on biomass-derived biofuels, which satisfy net zero- CO_2 balance (Fig. 1). However, the large amounts of soot emissions related to their high content of aromatic hydrocarbons raise both environmental and health concerns. The presence of aromatics in fuel mixtures may also be exploited for the formulation of anti-knocking additives, the upgrade to high-value chemicals, or the synthesis of carbon nano-materials. Kinetic models are used to evaluate the combustion properties of a fuel mixture in terms of compatibility with existing engine infrastructure, emission control, and new applications. In the last 30 years, *ab initio* theoretical calculations significantly helped to predict thermochemical properties and rate constants, and have recently become the standard practice, thanks to automated codes for electronic structure (ES) calculations and theoretical kinetics, the availability of higher computational power, and the

increasing accuracy of theoretical methods. In this thesis, state-of-the-art *ab initio* theoretical methodologies are exploited to build a more consistent kinetic model for the combustion of monocyclic and polycyclic aromatic hydrocarbons (MAHs, PAHs). Model compounds here addressed theoretically are C5 unsaturated rings and benzene, key building blocks in PAH growth, and substituted oxygenated MAHs (OAHs) representative of biomass-derived biofuels. Despite the interest in the combustion kinetics of MAHs/OAHs, several aspects are still unclear. Therefore, systematic approaches for model organization, widely spread for reference components of conventional fuels (e.g., alkanes), have not been developed for aromatic systems. Additionally, theoretical calculations for MAHs/PAHs are challenging due to the large species size and the poor assessment of the accuracy of ES methodologies for these compounds. Finally, complex multi-step reactions of MAHs/PAHs occur via a large number of intermediate species, that are difficult to integrate in existing global combustion kinetic mechanisms without preventing their use

for practical applications, thus often discouraging *ab initio* calculations. This thesis addresses some of the challenges listed above. The subset of C5 and aromatic species reactivity of the CRECK kinetic mechanism is organized systematically and hierarchically according to the reaction classes formulated in this work. Similar kinetic parameters are adopted for compounds with the same chemical functionality. State-of-the-art theoretical calculations for relevant reactions of C5, benzene, and substituted MAHs are carefully performed. The appropriateness of the theoretical methodologies adopted is assessed by comparison with microkinetic experimental data. The present results also highlight that while many reaction types are

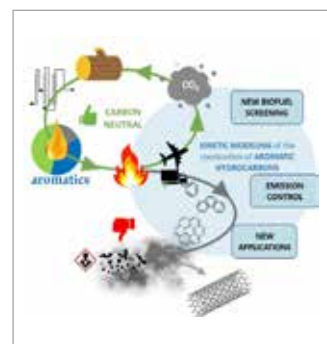


Fig. 1 - Kinetic modeling of aromatic hydrocarbons in the context of clean energy production

successfully automated, human intervention is still required in many cases to avoid large errors in the predictions. Theoretical calculations for a large number of H-atom abstraction and ipso addition-elimination reactions for benzene and substituted MAHs/OAHs reveal systematic trends and guide rate rule development for aromatic systems. For instance, the behavior of the aromatic ring sites is found to be very similar, while more complex functional relations are derived

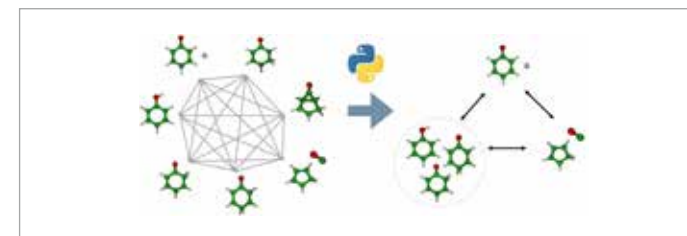


Fig. 2 - Schematic representation of the master equation-based lumping approach

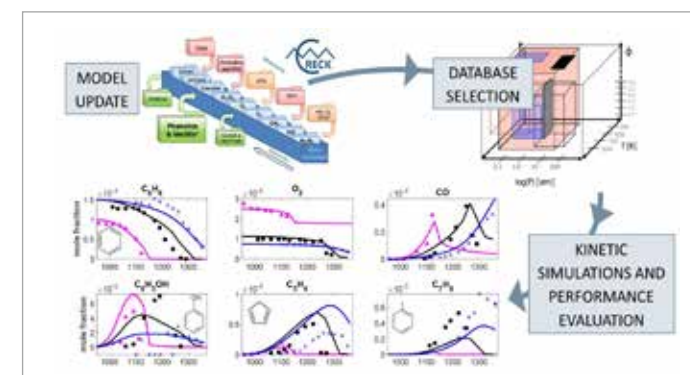


Fig. 3 - Workflow for model update and kinetic simulations

to account for the effect of lateral substituents. The chemistry of relevant aromatic species in the CRECK kinetic mechanism is updated with theoretical calculations from both this thesis and from the literature, focusing on oxidation kinetics. Complex multi-step reactions are simplified with a lumping approach specifically developed in this work for the integration of theoretically-derived rate constants into kinetic mechanisms, called

master equation-based lumping (MEL, Fig. 2). The ability of MEL to significantly reduce the system size while simultaneously retaining the macroscopic reactive behavior is proved with several examples. MEL also constitutes a more general tool for the simplification of kinetic mechanisms based on first principles. The final updated kinetic mechanism is tested against a wide range of experimental reactor data, as exemplified in Fig. 3. A class-based heat map flux analysis, implemented in this work, provides a general overview of relevant reaction classes at different operating conditions and helps to identify the reasons for model shortcomings. The kinetic model thus obtained shows overall reasonable performances. This work sets the grounds for future consistent, simple and physically meaningful kinetic model development for MAHs and PAHs combustion. Methodological aspects related to theoretical calculations, uncertainty estimates, master equation-based lumping, and reaction class organization will contribute to future integrated and automated workflows for systematic kinetic mechanism development.

VALORISATION OF GALACTARIC ACID AND ITS DERIVATIVES FOR THE SUSTAINABLE SYNTHESIS OF BIOBASED MOLECULES

Grazia Isa Carla Righetti – Supervisor: Prof. Cristian Gambarotti

Nowadays, in the pressing need to find more sustainable chemical processes to reduce our carbon footprints, biomass valorization has gained much attention, not only as renewable feedstock for the production of energy and biofuels, but also as starting material for the production of high value-added bio-based chemicals that, currently, mainly derive from petrochemical routes.

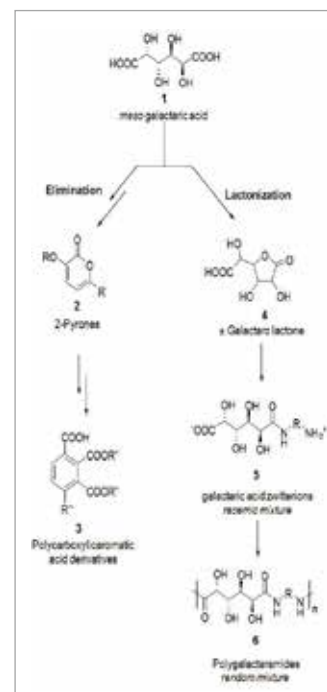
Aldaric acids are polyhydroxy dicarboxylic acids that formally derive from oxidation of aldose at both termini. They can be obtained from sugars by reaction of the substrate with strong oxidizing agents. The importance of the investigation of the reactivity of this class of compound is also underlined by the fact that they have been classified as six-carbon platform chemicals due to their potential to be precursors of high value added molecule.

The aim of this PhD project is to investigate the reactivity of galactaric acid (**1**, **scheme 1**), also known as mucic acid, as a model molecule of the aldaric acids class of compounds. The choice fell upon mucic acid for several reasons: (a) it can be obtained from food waste such as fruit peels which are rich in pectine whose main component is made

of a galacturonic acid chain; (b) little is known about the reactivity of this molecule; (c) it has a symmetric structure. Galactaric acid (**1**) was reacted to give 2-pyrone derivatives (**2**), moieties present in molecules with a peculiar pharmacological activity. Those were then employed to obtain bio-sourced polycarboxylic aromatic acid derivatives (**3**) through a sustainable pathway. Due to the importance of 2-pyrones both in medicinal and synthetic chemistry, the optimization of the developed process was performed by means of a statistical design of experiment and this was transferred to a continuous flow reactor in order to open easy and fast access to those molecules. On the other hand, galactaric acid was manipulated to obtain new monomers (**5**) for the synthesis of hydroxylated polyamides (**6**).

To sum up, in this PhD projects mucic acid was efficiently converted to obtain two main class of compounds: 2-pyrones and new zwitterionic monomers. An efficient synthesis of 2-pyrones (**2**) from mucic acid (**1**) was found. The 2-pyrones synthesis was then optimized by performing a design of experiment obtaining a 99%

yield in the desired product. The reaction protocol was scaled up from a 500 mg to a 100 g scale still maintaining a 99% yield. A recyclability study of the solvent was also performed and it was found that the solvent can be recycled up to 5 times without compromising the efficiency of the process (99% yield). A new decarboxylation protocol to open access to 3-hydroxy-2-pyrone was developed. Nowadays, the



Scheme 1 - General scheme of all the reaction products obtained from **1**; the nature of R, R' and R'' will be specified in the dedicated chapter

market price of this molecule is 500 euros/g. It was estimated that the production cost of 3-hydroxy-2-pyrone through the synthesis developed in this thesis is less than 50 euros/g. The 2-pyrone syntheses were then also transferred to a continuous flow reactor in order to reduce the reaction time and improve the productivity. This system resulted to be highly efficient. In fact, the *space-time yield* for 3-acetoxy-2-oxo-2H-pyran-6-carboxylic acid was 3 times higher in flow than in batch and the *space-time yield* for the synthesis of 3-hydroxy-2-pyrone was 10 times higher in flow than in batch.

Biobased polycarboxylic aromatic acids (**3**) were obtained in high yield using the obtained 2-pyrones as starting material. Usually the syntheses reported in the literature for these products starting from 2-pyrones involve the loss of carbon dioxide. The protocol developed in this thesis shows how the aromatic compound can be obtained through a one-pot base promoted domino reaction which proceeds with elimination of water only preserving all the carbon atoms presents in the substrate.

Lastly, mucic acid was employed to obtain new zwitterionic

monomers (**5**) for the synthesis of polyhydroxy polyamides (**6**). These polymers are highly interesting as they show good degradability in soil with respect to nylon, they are also currently under study for their potential applications in medicinal chemistry as drug delivery systems. The reactions performed with the zwitterions showed that these molecules are able to give a comparable or higher degree of polymerization with respect to the data reported in the literature.