

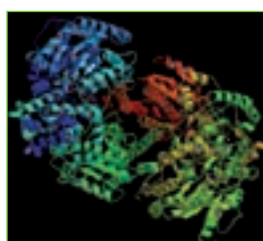


Chair:
Prof. Tiziano Faravelli

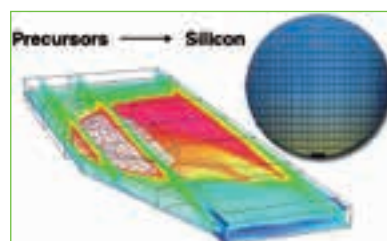
DOCTORAL PROGRAM IN INDUSTRIAL CHEMISTRY AND CHEMICAL ENGINEERING

The Doctoral Program in Industrial Chemistry and Chemical Engineering (**CII**) is designed for students aiming to get a deep expertise on chemical processes and on material processing either as the inherent *research* or in the *process design and development* activities.

The program is the ideal extension of the *Laurea Magistrale* degrees in *Chemical Engineering*, *Safety and Prevention Engineering*, *Materials Science*, *Material Engineering*, *Industrial Chemistry* and *Chemistry*, but it is also open to graduated in other scientific disciplines.



Structure simulation of
Nitrogenase enzyme for N_2
conversion to NH_3



Simulation of a chemical vapor deposition
reaction for silicon films deposition

The general topic for the doctoral program in Industrial Chemistry and Chemical Engineering is the application of the chemical and physical knowledge to all the activities related to the synthesis, design, production and transformation of chemical substances and materials (like advanced inorganic, polymers and biomaterials). These studies involve not only the synthesis processes but also the related plants, here analyzed starting from the laboratory tests and the pilot plant experiments up to the industrial size ones, always including the careful evaluation of the related energetic, safety and environmental issues.

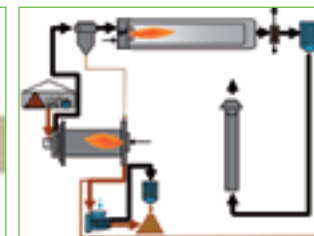
The final goal is to provide to the PhD student the tools and the skills: (1) to design and manage industrial processes at any size scales; (2) to develop new technical applications and (3) to create and to characterize new products and services.

The **CII** program covers three years for an overall amounts of 180 credits. The responsibility of the organization and of the contents of the doctoral program is attributed to the Professor Committee (PC). At the beginning of the Doctoral program, a tutor and a thesis

advisor is assigned to each student. The tutor has a supervisor function during the whole doctoral program, whereas the thesis advisor is responsible for the thesis work.

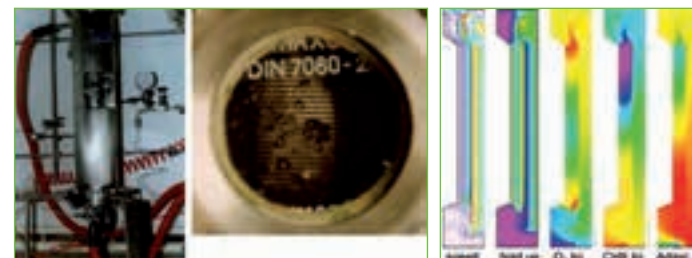


Hazardous gas dispersion simulation
from an industrial accident



Contaminated soil remediation
process

The PC defines a specific curriculum for each student, on the basis of the tutor suggestions. The curriculum has to be designed in order to both cover deficiencies in the student scientific formation and to give a high-quality technical and scientific preparation. Since 2001 (XVII cycle) the **CII** program graduates more than 100 students, being the 80% now working in industry and the remaining in the university or government research centers. These data demonstrate the great link existing between the performed researches and the industry. In fact, more than 70% of the research topics were directly supported by industrial companies, like ENEL, LPE Epitaxial Technology, Bracco, Flamma, Mapei, Solvay Specialty Polymers.



Lab-scale air-lift gas-liquid reactor and simulation of flow field, gas hold up
and concentrations of main reactants (cyclohexane oxidation to adipic acid)

THE REFERENCE COMMITTEE

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POLYMER NANOPARTICLES FOR THE DELIVERY OF HYDROPHOBIC DRUGS

Claudio Colombo - Supervisor: **Davide Moscatelli**

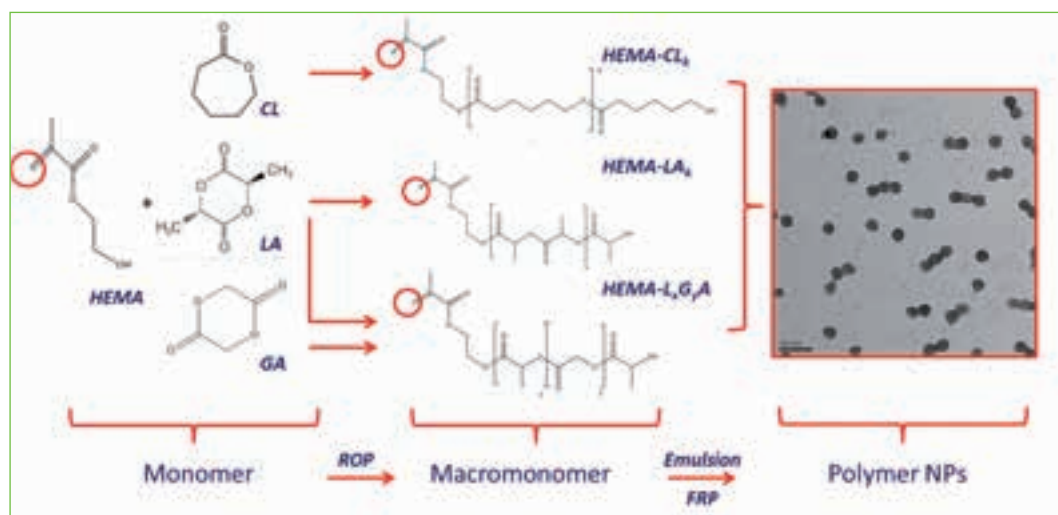
The term “drug delivery” refers to a practice in which an active compound is protected and delivered by a carrier with defined properties whose dimension usually belongs to the nanoscale. Several types of carrier have been developed for this purpose, among which liposomes, micelles and polymer nanoparticles (NPs). In particular, latter carriers are considered especially promising due to their ability to convey a wide range of active compounds and good stability. Biodegradable polyesters such as poly(lactic acid) (PLA), poly(lactic-co-glycolic acid) (PLGA) and poly(caprolactone) (PCL) are the materials of choice for

the production of polymer nanoparticles, due to the nature of these compounds NPs are produced through physical methods such as nanoprecipitation or solvent evaporation. From a clinical point of view, NPs can be seen a revolutionary way for the delivery of pharmaceuticals, particularly in anticancer therapy. In fact, they can act as a way to solubilize hydrophobic drugs without the use of toxic excipients but they can also lead to an higher accumulation of the drug in the target tissue, enhancing the efficacy of a treatment and reducing its side effects. Consequently a great number

of publications focusing on polymer nanoparticles for biological applications has been published since the 80's but only very few formulations reached clinical trials or the market. This discrepancy is due to the necessity of characterizing the formulation not only in terms of therapeutic efficacy and safety but also in terms of biocompatibility and biodegradability of the polymer nanoparticles themselves. For all these reason the possibility to tune the characteristics of the nanoparticles is an important feature in the design of these carriers. The aim of this thesis is the development and biological

validation of a nanoparticles library based on biodegradable polyesters (PLA, PLGA, PCL) with easily tunable proprieties in terms of composition, dimension and surface functionalization. This result was obtained through the use of functionalized polyester-based macromonomers obtained via Ring Opening Polymerization (ROP) of cyclic esters. These materials are then polymerized in an emulsion polymerization process to obtain polymer NPs with tunable proprieties in terms of dimension, composition, surface charge and degradation time. If the macromonomers are co-polymerized with suitable PEGylated methacrylate compounds it is possible to obtain NPs with covalently bound PEG chains. This result is particularly significant for biological applications due to the protein-repellent proprieties of PEG, which ensure a long circulation time in the bloodstream. A library of PEGylated NPs was synthesized with a dimension range comprised between 80 nm to 150 nm, suitable for the exploitation of the enhanced permeability and retention (EPR) effect in solid tumor. Several tests were carried out both *in vitro* and *in vivo* for the study of the toxicity and biodistribution of the produced NPs after intravenous injection and no

relevant toxicity was found. The produced NPs have been employed for the delivery of Paclitaxel, an anticancer compound which requires the use of excipients to be injected intravenously due to its poor water solubility. In particular the standard formulation of Paclitaxel is based upon the use of Cremophor, a steric surfactant whose usage is correlated to severe side effects, such as allergic reactions, hepatotoxicity and neurotoxicity. The efficacy of Paclitaxel-loaded NPs was compared to the standard formulation in mice bearing a xenograft breast cancer model, showing a similar regression of the tumor weight, thus confirming the possibility to use the produced NPs as drug delivery carriers.



1. Synthesis of polyester-based NPs via emulsion free radical polymerization. In the first steps functionalized oligomers are produced via ROP; these macromonomers are then polymerized in water to obtain polymer NPs.

REACTIVITY OF PERFLUOROPOLYETHER PEROXIDES ON CARBON BASED MATERIALS AND THEIR APPLICATION IN PROTON EXCHANGE MEMBRANE FUEL CELLS

Massimo Gola - Supervisor: Prof. Walter Navarrini

In the field of renewable energy, Proton Exchange Membrane Fuel Cells (PEMFC) are the devices which mostly have benefited of the unique characteristics of fluorinated materials. Many fluorinated sulphonic membranes have been developed for PEMFC and, in addition, fluorinated polymers are present in many other parts of the cell, such as the catalytic layer (CL) and the gas diffusion layer (GDL). The main function of the GDL is to promote the distribution of the gaseous reagents from the bipolar plates to the catalyst layer. However, GDL has other important functions: it allows the electric contact for conduction of electrons, it works as mechanical support for the catalytic layer and the membrane, it helps to remove the combustion heat, and it plays a key role in the water management. In fact, the overall fuel cell performances can be improved by a correct water management; on the contrary performances can be dramatically limited by the accumulation of liquid water inside the cell. Therefore, a correct water management is needed to reach power and current densities required for commercial applications. Thus, the conductive carbonaceous materials composing the GDL are usually coupled with a hydrophobic fluorinated material, usually polytetrafluoroethylene

(PTFE), in order to obtain a performing water management. Fluorinated materials are suitable for this purpose because one of their core characteristics is the very low surface tension that means low water polymeric surface interaction and therefore a very high hydrophobicity. Actually, carbon-based materials are the reference class of materials used for GDL, because they have high gas permeability, good stability in acid environment and good electric conductivity. An innovative methodology to confer a stable hydrophobicity to carbonaceous materials is the by the chemical linkage of perfluoropolyether (PFPE) chains through the chemical treatment with PFPE peroxides. PFPE peroxides are industrially available perfluorinated polymers whose structures are characterized by the alternation of fluorinated carbon-based units and oxygen units. A thermal treatment at 150-200°C can link PFPE chains to carbonaceous materials by a radical pathway. PFPE chains have the typical properties of perfluorinated polymers, like chemical stability, thermal stability and high hydrophobicity, and also some peculiar characteristic such as liquid physical form and high gas permeability. These modified carbonaceous materials are super hydrophobic and show surprisingly high conductivity compare to carbons fluorinated

with F₂. During this work, the reaction of functionalization of highly graphitic carbon black by perfluoropolyether peroxide was studied and the possible application of PFPE functionalized carbonaceous materials was investigated. Carbon cloth (CC) and carbon black (CB) were functionalized by decomposition of PFPE peroxide and the resulting materials were chemically and physically characterized. The PFPE functionalization of carbonaceous materials was applied to Vulcan XC72R CB and SEAL CC in order to evaluate their wetting and electrical properties for their possible application in fuel cells as materials for GDLs. The chemical treatment of CB with PFPE peroxide led to high hydrophobicity and contact angles over 150° were measured. The determination of the resistivity in function of the applied pressure allowed to characterize the electrical properties of each sample. Resistivity of treated CB samples remained very close to the values of the native CB (Figure A1), even if a significant increment due to the insulant properties of fluorinated materials was expected, as occurs with a PTFE coating. Similarly to CB, the carbonaceous structure of

CC contains condensed aromatic cycles, suitable for the hydrolytically stable linkage of perfluorinated chains due to decomposition of PFPE peroxide. Following this approach, a polymeric PFPE layer was chemically linked to CC structure and not simply deposited like the standard hydrophobization by PTFE-coating. PFPE chains on the CC surface allowed to obtain a suitable superhydrophobic effect even if the amount of PFPE linked on a CC was significantly lower than the typical 10%_{wt} of PTFE. PFPE functionalization led to a 1% linked PFPE with a water contact angle of 172°, while 10% PTFE allows to obtains angles lower than 150°. The single layer GDL is made of a macroporous substrate which is usually based on a carbon cloth. Two CC samples were functionalized with PFPE peroxide and XPS analysis confirmed that the functionalization with PFPE peroxide occurred mostly on the CC surface. PFPE coating resulted uniform along the surface of CC fibers and wrapped singularly each fiber of CC without filling the matrix porosity. On the contrary, the commonly used PTFE-based methodology forms a solid insulant barrier that includes many fibers, covers the empty spaces between them and

decreases the porosity needed for gas diffusion. The steady state current density-potential and current density-power curves of the cell assembled with PFPE-hydrophobized GDLs were registered and compared to standard GDL treated with 10% PTFE. The presence of PFPE improved the electrical performance of the fuel cell at each operating condition of temperature and humidity. In particular, the higher the content of PFPE, the better the performance in terms of maximum power density and slope of polarization curve. The PFPE-functionalized GDL is able to reduce the ohmic resistance of the whole system, increases the mass transport and improve the ionic conductivity of the membrane at low relative humidity. PTFE on the microporous layer of a dual layer GDL works as hydrophobizing agent, but even as a binder to keep the CB on the backing layer. A PFPE based ink with similar characteristics was developed and coupled with PFPE functionalized CC to obtain a dual layer GDL. The PFPE-functionalized dual layer GDL was tested and compared with a PTFE standard, resulting in better overall performances and especially largely improving the water removal.

The high resistance of PFPE to oxidative environment was used as new solution to the problem of the electrochemical corrosion of the carbon black that supports Pt catalyst in PEMFCs. This corrosion causes severe losses of precious metal catalyst and shorter cell lifetime. A PFPE-functionalized carbon black was used as a catalyst support subjected to an accelerated electrochemical corrosion. While the performances of the standard carbonaceous material were largely decreased after the accelerated degradation, the catalyst layer made of PFPE-functionalized carbon black suffered only minor effects. The introduction of PFPE functionalized materials in PEMFCs resulted to be a great improvement of the key parameters which characterize these electrochemical devices. Indeed PFPE-functionalized GDLs allow to reach higher currents as well as power density. Furthermore the catalyst layer based on PFPE-functionalized CB minimize the electrochemical degradation effects obtaining a longer fuel cell lifetime. The introduction of PFPE-functionalized carbonaceous materials improved the overall PEMFC performances by focusing on the requirements for their upcoming widespread commercial application.

PURIFICATION OF NATURAL GAS BY MEANS OF A NEW LOW TEMPERATURE DISTILLATION PROCESS

Stefano Langé - Supervisor: **Laura Annamaria Pellegrini**

Natural gas is a fossil fuel containing mainly light hydrocarbons and other non-hydrocarbon compounds considered as impurities. As the other fossil fuels, its origin comes from the bacterial degradation of organic materials going back to geologic eras ago, under the effect of high temperatures and pressures that typically occur in subsurface deposits of many geologic formations.

Natural gas is a resource that is widely used nowadays in different industrial sectors. Its main uses are related to the production of energy (38 %) and the industrial sector (60 %). In recent years, natural gas has started to be used also in the transportation sector, even if it just covers a small portion of the uses of natural gas.

The discovery of new natural gas reservoirs with high CO₂ and/or H₂S content and the increasing energy demand compel industries to design new process solutions for the profitable exploitation of these kinds of gas reserves, to meet the market demand while satisfying the commercial grade requirements. Recent studies have shown that more than 40% of the remaining natural gas reservoirs are sour and/or with high CO₂ contents. Low temperature technologies have been studied to this purpose.

These kinds of processes have shown higher performances and economic profitability when compared to the more traditional gas sweetening units (such as amine scrubbing or physical absorption) when the CO₂ content in the natural gas feed stream is high. During low-temperature operations, CO₂ can freeze in the equipment and precautions have to be adopted. To face this issue, several solutions have been adopted in the low-temperature natural gas purification processes proposed in literature. The Ryan-Holmes process consists in an extractive distillation, where a third compound (typically n-butane) is used to shift at low temperatures and pressures the freezing points of the binary CH₄-CO₂ mixtures. The CFZTM process by Exxon Mobil allows the solidification of CO₂ in a proper section of the distillation column and the subsequent re-melting of dry ice on a designed melting tray. Total and IFPEN have proposed the Sprex[®] process, coupling a pressurized low-temperature distillation, for the bulk removal of acid gases, with a more traditional alkanolamine unit to purify the gas stream to commercial grade. In this work a new low-temperature distillation process has been studied. The process is based on a dual pressure distillation operation to bypass

freezing points and to avoid the formation of a solid phase in all the parts of the process. The solution has been studied and optimized in terms of energy savings. A commercial process simulator (Aspen Hysys[®]) has been used for the study of process performances. Different gas compositions have been considered as potential gas feeds (CO₂ from 5 up to 65 mol% and H₂S from 0 to 15 mol%) to cover the largest possible range of real gases streams. Its performances have been assessed basing on case-studies and its profitability determined against more traditional MDEA units in terms of energy operating costs, showing the relative trade-off between the two technologies depending on the geographic area where the gas reserve is located. The proposed solution is able to purify natural gas to commercial grade, avoiding the formation of dry ice in all the parts of the process. For the cost analysis, a proper function has been built to quantify in a simple way the ratio between the energy costs required by a traditional MDEA unit (low-pressure steam for the solvent regeneration) and the studied low-temperature distillation process (electric energy to drive the compressors of the refrigeration cycle). This function relates the ratio between the two energy costs

to the ratio between the price of fuel and the price of electricity. Generally, it is more convenient than a more traditional MDEA unit when the CO₂ content of the natural gas feed is higher than 20 mol% for most of the considered geographic areas (Europe, USA, Saudi Arabia), while, for the case of Saudi Arabia, the proposed solution is more profitable starting from a gas feed having 8 mol% of carbon dioxide. The obtained results have been used for the design of the industrial unit and the pilot plant for the further test of the process on a lab-scale facility.

To allow a good process design and optimization, reliable thermodynamic tools are needed. Experimental data are of paramount importance to properly set up equations of state for both phase behavior and volumetric properties calculations. Since in low-temperature processes for natural gas upgrading a solid phase can be formed, experimental data are necessary to determine pressure, temperature and phase compositions when phase equilibrium involves the presence of a solid phase, formed mainly by CO₂. In this way, it is possible to properly set up a model to predict the conditions for solid formation and define the optimal process operating conditions, depending on the adopted technology. Literature data for the CO₂-CH₄, CO₂-H₂S and CH₄-H₂S binary systems are available to define the PT, the Tx or the Ty diagrams for the SLE, SVE or SLVE loci. On the contrary, experimental data for phase equilibria involving a solid phase in the CH₄-CO₂-

H₂S ternary system are few and almost only PT data. A good number of TPxy experimental data to describe the SLV loci of the CH₄-CO₂-H₂S system has been provided. A proper experimental procedure has been designed to obtain these measurements and data have been compared with the results obtained with a suitable thermodynamic model. The procedure consists in a synthetic, non-visual technique to measure triple points as pressure and temperature conditions where solid decomposition occurs. Phase compositions at triple point have been analyzed using gas chromatographic analysis and equilibrium conditions have been checked in detail by repeating measurements several times during the day. Obtained results have been applied for the thermodynamic validation of the process object of this thesis, showing that, also in the presence of hydrogen sulfide, no solid phase can be formed in the process. For the thermodynamic modeling both the classic approach (SRK and PR equations of state coupled with Gibbs free energy of melting for the calculation of the solid phase fugacity) and the Yokozeki analytic equation of state for the direct calculation of both fluid and solid phases fugacity have been considered. The obtained results and the experimental data have been used to validate the thermodynamic framework used for process simulations in Aspen Hysys[®] (SRK equation of state and the CO₂ Freeze-Out tool for the calculation of CO₂ freezing points), in order to give a good reliability to the obtained results.

As future developments of this work, a detailed investment costs analysis have to be done to better define the profitability indexes for the process. The plan of the experiments for the pilot plant has to be designed and a better assessment of its configuration is required. Procedures for the start-up and the shut-down of the process, together with the dynamic simulation of the plant layout, are required to test possible operating scenarios. A detailed study about the downstream separation processes for the recovery of NGLs is needed to assess the impact of C₂₊ on the profitability of the process. Process optimization and further energy savings can be investigated for the applications to LNG production. The integration of the process with EOR or CCS systems can be studied. Regarding the thermodynamic part, new experimental campaign can be performed in order to better describe the complex phase behavior of the ternary system and to study the effect of C₂H₆ and N₂ on the ternary system. For the modeling part, the binary interaction parameters for the CO₂-H₂S system need to be improved by mean of a more detailed optimization, to reduce the error in the representation of the eutectic point of the SLV locus of the system.

EXPLORING DIFFERENT CATALYTIC ROUTES FOR CO₂ VALORIZATION

Michela Martinelli - Advisor: Prof. Luca Lietti

Carbon dioxide is the primary green-house gas (GHG) arising from life and human activities. In recent years, the growing consciousness of the dramatic impact of its atmospheric concentration on the climate has brought to the conclusion that the reduction of CO₂ emissions from all anthropogenic processes is mandatory. In addition to the improvement of the efficiency of energy conversion and utilization processes, GHG reduction strategies proposed in the last decades include also secondary measures such as the carbon dioxide capture and the storage (CCS) or carbon capture utilization (CCU). In CCU technologies, CO₂ is no more considered as a waste to be dumped, but it is used as feedstock (C₁ building unit) to produce highly added-value products such as chemicals or fuels. In this thesis, the routes for CO₂ hydrogenation to hydrocarbons or light olefins were investigated on Fischer-Tropsch catalysts. The catalysts were prepared, characterized and then tested in a lab-scale plant.

Cobalt and iron based are the active phases during Fischer-Tropsch synthesis. However, the reactivity and reaction mechanisms of these two systems could be different during the hydrogenation of pure CO₂ stream or mixture

CO/CO₂. Therefore, a cross-comparison between the CO and CO₂ hydrogenation processes were carried out on representative iron (100Fe/10Zn/2Cu/4K on atomic basis) and a cobalt based (15 wt.% Co/γ-Al₂O₃) FT catalysts. On cobalt based catalyst CO₂ is easily hydrogenated with a reactivity higher than CO, however the selectivity of the two processes is completely different because during CO₂ hydrogenation the main product is methane, whose selectivity higher than 90%, but the same mechanism (H-assisted CO hydrogenation) occurs and the products are obtained by the same intermediate. The different selectivity of the mixture CO/H₂ and CO₂/H₂ is due to a different adsorption ability of CO and CO₂, which strongly affects the H/C atomic ratio on the catalytic surface. The higher H/C obtained during the CO₂ hydrogenation inhibits the chain growth, hence favoring the methanation reaction. In presence of CO, CO₂ is hardly hydrogenated and behaves as an inert species because of a competition between CO and CO₂ for the adsorption. On the contrary, on iron catalyst CO₂ hydrogenation rate is slightly slower than that of CO, but the product distribution does not change dramatically when switching from CO to CO₂,

even though the chain growth probability ($\alpha_{C_3-C_{10}}$) decreases from 0.71 to 0.65, as well as the fraction of unsaturated hydrocarbons in the products. This behavior can be explained considering that in the presence of CO₂ some of the catalytic sites active in the chain growth process (iron carbides) are transformed in sites active in the hydrogenation reactions (iron oxides / reduced iron centers). Another explanation is the different adsorption strengths of CO and CO₂, which would result in H/C ratios in proximity of the active sites very different for CO and CO₂ mixtures. During CO₂ hydrogenation, CO is detected in the pool of products, suggesting a first step of RWGS on the catalyst and a second step where CO is converted to hydrocarbons through the FT reaction with an H-assisted or un-assisted CO hydrogenation. In presence of CO, CO₂ is not hydrogenated, but the net CO₂ production is zero, this suggests that CO₂ is adsorbed and that this inhibits the un-assisted route where the oxygen is discharged as carbon dioxide, this behavior improves the atom efficiency of the process as all the CO is converted to hydrocarbons. To complete the study, the effect of potassium loading has been investigated by testing catalysts with K/Fe atomic ratios equal to 0.02, 0.04

and 0.1. Potassium has a minor effect on the catalyst activity, but it can dramatically change the selectivity in the presence of CO₂. High K-loading were found able to promote the chain growth process and the formation of primary olefins. Observed results were explained both in terms of K-effects on the stability of the iron carbide species and in terms of K role as electron donor, able to modify the adsorption strengths of H₂, CO and CO₂.

The selectivity to desired products on iron based catalyst can be controlled by modifying the process conditions and the catalyst formulation. At this purpose, iron based-catalyst, prepared by thermal decomposition of ammonium glycolate complexes and followed by impregnation with a potassium, was investigated for the production of light olefins. The duration of the thermal treatment has a dramatic effect on the surface area and crystal structure. In order to obtain a catalyst with high surface area (66 m²/g) and a spinel structure (Fe₃O₄-related), a calcination time of 15 min has to be adopted, otherwise the area decreases and the spinel structure is progressively transformed to a corundum-type (α -Fe₂O₃ related) phase. The obtained material was found to be a good catalyst in CO₂ hydrogenation (CO₂ conversion higher than 40%) to light olefins (selectivity of 38%) at mild process conditions. The analysis of the effect of the process conditions pointed out that by a fine tuning it was possible to enhance both the catalyst activity and C₂-C₄ selectivity. High temperatures (at

least 300°C) were required to increase the CO₂ conversion and to improve the Fischer-Tropsch activity. Medium pressure (5 barg) was instead needed to establish a Fischer-Tropsch regime. The prepared catalyst has higher CO₂ conversion rate and C₂-C₄ olefins selectivity than those of reference materials (Fe₂O₃ and Fe₃O₄), ascribed to its higher surface area and spinel structure that facilitate the reducibility and the carburization and therefore the catalytic activity.

In the thesis work the water-gas-shift reaction has also been investigated as well. WGS is a key reaction occurring in the investigated reacting systems since the CO/CO₂ transformation plays a role in the complex chemistry of the CO₂ or CO/CO₂ mixture hydrogenation. Aiming at a better understanding of the reaction and in the optimization of the catalyst in the low temperature range, new catalytic systems have been prepared and investigated. These systems consist of ZrO₂ doped with different levels of yttrium (0.1-0.9) in order to increase in the number of defects and so the oxygen mobility.

Y-doped zirconium oxide materials were characterized by high surface areas (150-200 m²/g). A combination of XANES and EXAFS were used to show that ZrO₂ exhibited the tetragonal phase, while the Zr_{0.5}Y_{0.5}O_{1.75} support displayed the cubic phase. A slight increase in d-spacing observed in HR-TEM for the Zr_{0.9}Y_{0.1}O_{1.95} support relative to undoped ZrO₂, along with a shift to lower 2θ in XRD, provide evidence that Y-doping caused macrostrain. STEM imaging confirmed that

the Pt clusters ranged from 0.5 to 2 nm over all three supports. Catalyst reducibility was explored by H₂-TPR, XANES at the Zr K-edge, and TPR-XANES at the Pt L_{III} edge. A higher concentration of surface defects for the 0.5%Pt/Zr_{0.9}Y_{0.1}O_{1.95} catalyst relative to 0.5%Pt/ZrO₂ was confirmed by DRIFTS of adsorbed CO, while a greater surface mobility of surface formate was suggested based on forward formate decomposition experiments in steam. The Y-doped Pt promoted catalysts displayed higher water-gas-shift activity relative to the 0.5%Pt/ZrO₂ catalyst when the Y content was at or below 50%, with the best catalyst being 0.5%Pt/Zr_{0.9}Y_{0.1}O_{1.95}. Indeed, at 300°C CO conversion for 0.5%Pt/ZrO₂ was 44.8% and it increases from 50% to 74% by decreasing the yttrium loading from 50% to 10%. So the increase of activity for the yttrium doped zirconia is strictly correlated to the higher concentration of defects and higher oxygen mobility. Indeed, when Zr⁴⁺ cations are substituted by Y³⁺ cations, oxygen vacancies are formed to maintain charge neutrality.

UNDERSTANDING CADHERIN MEDIATED CELL-CELL ADHESION AT THE MOLECULAR LEVEL: A STRUCTURAL APPROACH

Valentina Nardone - Supervisor: **Dr. Emilio Parisini**

A key biological process in the life of multicellular organisms is the establishment of proper adhesion between cells, to form at first tissues and then organs. Cell-cell adhesion is provided by macromolecular complexes localized in specific region of the cellular membrane. They comprise transmembrane proteins capable of establishing cell junctions via interactions between their extracellular domain while, at the same time, they are intimately linked to a series of cytoplasmatic proteins that ultimately connect them to the actin microfilaments and microtubules. The connection between the cell-cell junctions and the cellular cytoskeleton implies a reorganization of the latter following the formation of cellular adherens junctions, without which tissue morphogenesis and stability would not be possible.

The intriguing mechanism of cell adhesion is the result of several protein-protein interactions that take place either at the cell-cell interface or at the cell-matrix interface, with high tissue variability and specificity. The diverse set of molecules that are involved in this process belong to a number of different protein superfamilies, of which only some specific members are expressed in the different types of cells and tissues, to properly confer selectivity to

cell-cell interactions and tissue morphogenesis..

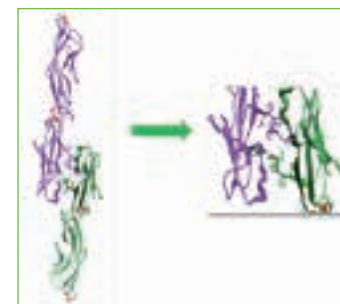
In this context, structural biology is a potent tool to understand the molecular bases of the adhesion process. In general, a high resolution structural analysis provides details about intra- and inter-molecular contacts that drive the formation of proteins assembling, often elucidating the mechanistic details of biological events. Our current understanding of the cell-cell adhesion mechanism is mostly based on a wealth of X-ray diffraction, NMR, electron tomography and other biophysical data, which have so far provided a detailed, yet incomplete, picture of this process at the molecular level. However, as in most fields, with the progression of knowledge always new and more sophisticated questions arise. Most of the work I did for my Ph.D. thesis is focused on the structural characterization of members of the large superfamily of Ca^{2+} -dependent cell adhesion proteins called cadherins, and in particular on the subfamily of classical cadherins. These transmembrane proteins interact with each other through their extracellular domains in a strictly homophilic fashion, to ensure the contact between two adjacent cells. At the same time, in the cytoplasm their intracellular portion forms

a number of interactions with proteins called catenins, which ultimately link the cadherins to the actin microfilament. Despite the good understanding of cadherin structures, functions and behaviour reached nowadays, more detailed studies are in progress in order to further elucidate the dynamics of the interactions, the mechanical features, and the heterophilic contacts of cadherin ectodomains with other proteins and small molecules acting as adhesion modulators.

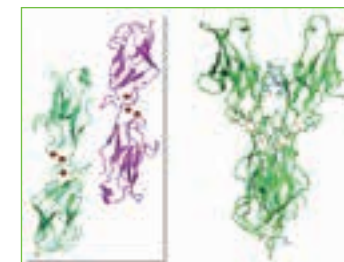
With the research projects described in this thesis, we attempted to approach a series of unresolved issues in the cadherin field, related to the molecular events that guide homodimerization, which is the key mechanism in cadherin-mediated cell-cell adhesion. To do so, we used single crystal X-ray diffraction analysis on different sequences of the extracellular domain, spanning from short oligopeptides (three amino acids) to almost the entire ectodomains (400 amino acids). The final, adhesive homodimer forms as a consequence of the swap of the N-terminal strand of the first extracellular domain, which has a well conserved sequence: this strand is usually called adhesion arm and present a series of molecular details essential for the dimer formation (fig.1). Our analysis of

the crystal structures of tri- and tetra peptides, fragments of the adhesion arm, allows the identification of short carbon-carbon contacts, which can be transient contacts important to mediate the recognition of the arms of two closed cadherins in the intermediate stages of the dimer formation. The characterization of these contacts is essential to identify a proper surface that can be target by small molecules to inhibit the dimerization, for drug design and drug delivery purposes. *In silico* studies from our collaborators have identified small molecules with a structure that mimics the N-terminal residues of the adhesion arm as possible hit compounds; the affinity for type-I cadherins has been evaluated by *in vivo* and *in vitro* experiments. The aim of my work, in this field, has been the biotechnological production of different sequences of type-I cadherin ectodomain and the crystallization alone and in presence of the hit compounds. These studies have led to important results in the cadherin field, such as the first characterization of the closed monomer of a type-I cadherin (the human P-cadherin) and the first co-crystal structure of a cadherin in presence of a inhibition compound, which allows the identification of a new target surface for the development of specific

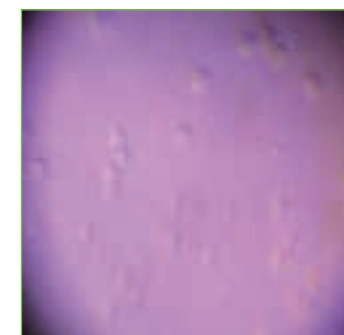
cadherins' ligands (fig.2). The results obtained for the type-I cadherins are also very useful for the studies in type-II cadherins (in particular cadherin-11), which are less structural characterized even representing an important pharmacological target; our structural studies have provided the crystallization conditions for cadherin-11 ectodomain, to be further optimized (fig.3). The combination of these different analyses provides novel details and opens new scenarios in the debated topic of cadherin dynamic, paving the way to a better comprehension of possible cadherin/small molecule interactions, which is an important issue in medicinal and toxicological chemistry due to the role of members of the cadherin superfamily in different pathological states such as cancer metastasis and rheumatoid arthritis.



1. the high resolution crystal structure of human E-cadherin shows the strand-swap mechanism of homodimer formation.



2. on the right, the crystal structure of human P-cadherin in closed, monomeric conformation: the two monomers in the packing are in an antiparallel arrangement, primed for adhesion; on the left, the structure of E-cadherin in the X-dimer conformation in presence of the inhibitor compound (in blue).



3. cubic crystals of cadherin-11 domains 1-4

PERFLUORINATED MATERIALS AND PHOTOCATALYTIC TITANIUM DIOXIDE: SYNERGIES AND CHEMICAL INTERACTIONS IN ENVIRONMENTAL APPLICATIONS

Federico Persico - Supervisor: Walter Navarrini

The main focus of this research has been the study of the interactions between TiO_2 and fluorinated materials. The stability of oxygen containing perfluoropolymers on UV activated anodized titanium, the photodegradation of perfluorocarboxylic acids, in particular perfluorooctanoic acid (PFOA), and the development of a TiO_2 -embedded fluorinated transparent coating for oxidation of hydrosoluble pollutants in turbid suspensions have been the specific research areas of my PhD study.

Protective Coating Evaluation

Three amorphous perfluorinated polymers (Hyflon® AD60, Fluorolink® S10 and Fluorolink® F10) were tested as protective coatings for anodized titanium. The effect of their application on the photoactive surface was studied by comparing stearic acid photodegradation rates promoted by coated and uncoated TiO_2 . All three coatings promoted a decrease in the TiO_2 surface wettability, thus potentially reducing greasy material deposition on the substrate and preserving its photocatalytic properties. AD revealed a good adhesion to the anodized titanium substrate, conferring to it both hydrophobicity and oleophobicity. Differently from S10 and F10, AD was

chemically stable towards the photocatalytic couple UV light/ TiO_2 . Furthermore, all the applied coatings did not block photocatalytic reactions, although a reduction in photoefficiency was observed. This undesired phenomenon was less effective in the case of AD. The evaluation of the optimal protective coating for anodized titanium led to hypothesize the existence of a straightforward methodology to decompose perfluorinated carboxylic acids into carbon dioxide and hydrofluorocarbons in the presence of photocatalytic TiO_2 .

PFOA Degradation

In order to verify the presence of a straightforward methodology to decompose perfluoro carboxylic acids into CO_2 and hydrofluorocarbons in the presence of photocatalytic TiO_2 , degradation of PFOA was studied by using TiO_2 -slurry as a catalyst. In order to evaluate the effects of oxygen excess/defect in the reaction environment different kinetic tests were realized and the results were compared. The degradation intermediates concentrations were monitored by HPLC-MS analysis; the observed trends appeared to be in agreement with the presence of two possible competitive degradation pathways: the photo-redox $\text{C}_n \rightarrow \text{C}_{n-1}$ chain

length decrease mechanism and the β -scission pathway. The mechanism based on β -scission reactions appeared to be dominant in O_2 -enriched solutions; in these conditions, especially during the first hours of photoabatement, the highest mineralization rate and the fastest release of fluoride ions were observed. On the contrary, in O_2 -poor solution conditions, the photo-redox $\text{C}_n \rightarrow \text{C}_{n-1}$ chain length decrease mechanism appeared to be prevalent, as low F^- release and low concentrations of shorter chain perfluorinated acids as degradation intermediates were observed. These hypotheses were confirmed by ^{19}F -NMR analyses. In order to study the effects promoted by fluoride ions on the catalyst surface, TiO_2 samples collected before and after the photodegradation treatment were characterized. XRD results revealed that the bulk crystal structure of the photocatalyst was preserved during the photoabatement of PFOA. Still, the formation of highly fluorinated and hydroxylated $\text{TiO}_{(2-x/2-y/2)}\text{OH}_x\text{F}_y$ species on the catalyst surface was revealed by XPS analysis. The F^- -induced chemical modification of the catalyst surface could be the cause of the observed lowering in the photocatalytic performances of TiO_2 for PFOA degradation.

Photoactive Coating Development

In order to avoid losses in photocatalyst and to enhance quantum yield and quantum efficiency of the photoabatement process, a TiO_2 -containing perfluorinated multilayered transparent coating able to promote photocatalytic degradation of hydrosoluble organic pollutants was developed. The multilayered coating composition and the catalyst content were optimized to promote the coating structural stability during time and to obtain the highest photoactivity. The photoactive coating was developed by applying a TiO_2 -containing fluorinated ionomeric dispersion and a perfluorinated amorphous polymer in an appropriate sequence directly on the UV source. The peculiar configuration of the photoactive coating allowed even the treatment of turbid dispersions, thus broadening its potential applicability. Immobilized TiO_2 particles, in fact, were not deactivated by slime interposition between the UV source and the photoactive coating and avoided onerous separation of the catalyst from the purified water. The coating photoactivity towards hydrosoluble organic pollutants was evaluated by monitoring the photoabatement rates of two dyes (Rhodamine B-base -RhB; Crystal Violet -CV) and a persistent pollutant (4-Chlorophenol -CP). The comparison of photodegradation and absorption trends of dyes and CP highlighted a direct relation between these two phenomena; whenever the hydrosoluble pollutant was

effectively absorbed into the photoactive coating, rapid photodegradation occurred, causing the complete removal of the organic compound from the aqueous solution. In these cases, in both clear and turbid conditions, TiO_2 -embedded transparent coating revealed higher photocatalytic activity than dispersed TiO_2 , this behavior being particularly evident at low pollutant concentrations. On the contrary, in the case of non-absorbed pollutants (CP), lower photoabatement rates were observed in the presence of the photoactive coating. Hence, due to the basic nature of RhB and CRY, a synergic effect between the ionomeric material and the embedded TiO_2 particles was observed. RhB and CRY photoabatement trends were almost overlapping both in the absence and in the presence of inert dispersed particles in the reaction environment. Furthermore, similar absorption trends were observed for the two tested organic dyes. The comparison of the apparent kinetic parameters allowed us to hypothesize that in the case of basic pollutants, the apparent kinetic constant values were independent from the molecular structure of the organic pollutant. These results could be interpreted by theorizing that the observed dye abatement rates were controlled by pollutant phase-transfer phenomena. Thus, an optimization of reactor mass-transport parameters could cause further increase in the degradation efficiency of the photoactive system. Photoactive coating physical and chemical stability were monitored by ATR

and TGA analyses on pristine and used (100 h) samples of photoactive coating. As no significant variations in the ATR and in the TGA spectra were observed, it appeared that no chemical modification of the perfluorinated matrix occurred during the degradation of pollutants. In view of a possible industrialization of the TiO_2 -containing coating its mechanical characterization would be useful. The actual and potential characteristics of the TiO_2 -containing photoactive coating make it suitable for industrial employment for both sequential batch and continuous water management. The photoactive coating could be also tested in the presence of gaseous pollutants. The use of short side chain ionomers in the photoactive layer can promote autohumidification of the TiO_2 -containing coating in the presence of air humidity. This phenomenon could be sufficient to guarantee the synergic effect between the ionomeric phase and the photocatalyst. Furthermore, the application to the photoactive coating of studies on TiO_2 doping could make this project extremely promising for green-chemistry purposes. In fact, the use of a visible light-activated catalyst into the coating could allow its direct *in situ* applications for environmental remediation.

ONE-POT MULTICOMPONENT FREE-RADICAL REACTIONS MEDIATED BY TITANIUM SALTS

Bianca Rossi - Relatore: Prof. Carlo Punta

Multicomponent reactions (MCRs) represent a green approach towards the synthesis of polyfunctionalized molecules by promoting multiple bond-forming mechanisms in a one-pot synthesis. Likewise, the development of radical-mediated, C–C bond-forming transformations has also attracted increasing interest. These protocols usually afford good selectivity, are highly compatible with common functional groups, and often require mild operative conditions. The combination of this two synthetic tools opens the way for the cheap and simple synthesis

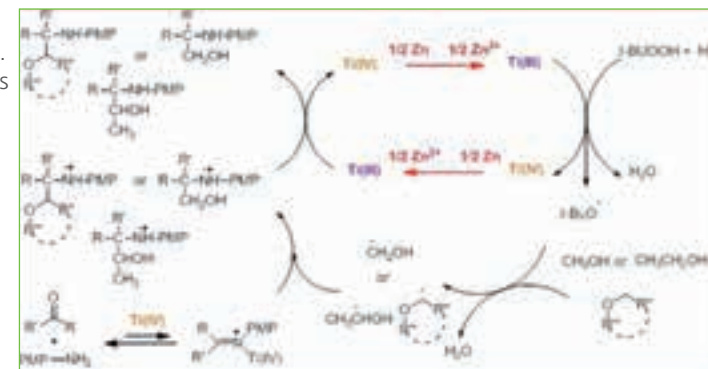
of poly-functional molecules and for the grafting of polymers and materials (Figure 1). The main goal of this work consisted into the optimization and application of a multicomponent protocol for the nucleophilic free radical addition to imines generated in situ, using the new $\text{TiCl}_4\text{-Zn}/\text{tert-BuOOH}$ catalytic system. As shown in Figure 2, in a proposed reaction mechanism Titanium promotes the formation of imine in situ and activates its reactivity towards nucleophilic addition. The research activity followed two consecutive steps. At first, the application of the

multicomponent free-radical approach was optimized and extended to alcohols and ethers as nucleophilic sources. The new explored conditions allowed to obtain a wide range of desired final products, with high conversion and selectivity, inhibiting the competitive domino side-reactions. In this part of activity, three applications were considered:

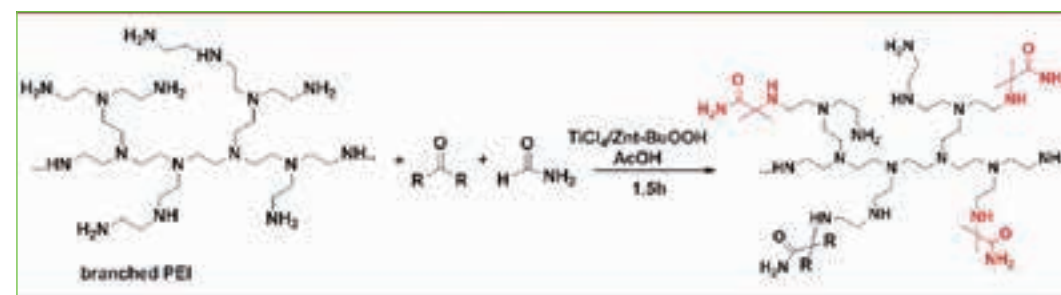
- Synthesis of β -amino alcohols via nucleophilic radical hydroxymethylation of ketimines;
- β -aminoalkylation of ethers;
- Nucleophilic radical hydroxyalkylation of ketimines with ethanol.

On the bases of the good results obtained by protocol optimization, the new methodology was applied for the grafting and formulation of non-cytotoxic cationic polymers. The efficiency of the new materials as *non-viral* vectors for gene delivery was verified. In particular, I focused on the grafting of branched polyethyleneimine 25kDa (25kDa bPEI), a cationic polymer bearing primary amino groups, which is one of the most widely used among *non-viral* vectors in gene delivery. Considering the positive effect of hydrophobic groups in increasing the efficiency of transfection, different types of modified 25kDa bPEI were synthesized, by introducing

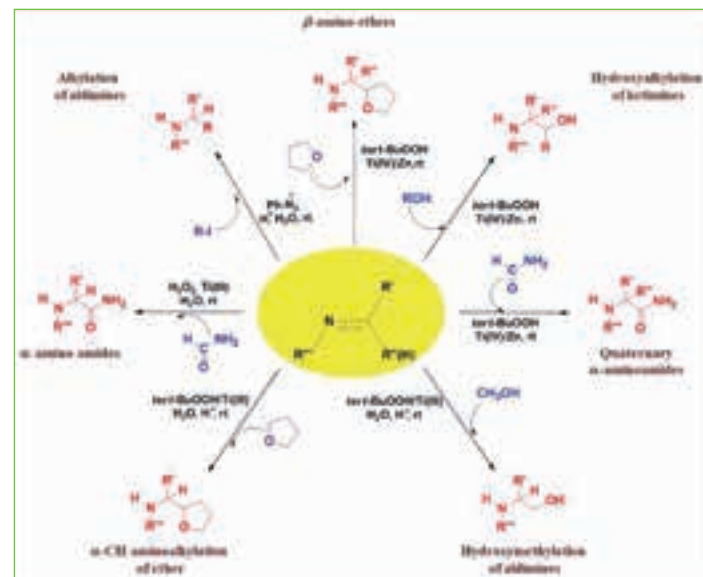
selected moieties on the pristine backbone (Scheme 1). Derivatives obtained by means of this one-pot free-radical approach were biologically tested in terms of cytotoxicity and transfection efficiency.



2. Nucleophilic addition to ketimines promoted by the $\text{TiCl}_4\text{-Zn}/\text{ROOH}$ system



Scheme 1. Radical addition of formamide to ketimines generated in situ from primary amino groups of 25kDa bPEI and ketones.



1. Radical addition to imines triggered by TiCl_3 or $\text{TiCl}_4\text{-Zn}/\text{ROOH}$ systems

DETAILED KINETIC MODELING OF SOOT FORMATION IN COMBUSTION PROCESSES

Chiara Saggese - Adisor: Prof. Tiziano Faravelli

Combustion is present in many large-scale processes, including internal combustion engines, power stations, waste incineration and residential burning of wood and coal. These, with field burning of agricultural wastes and forest and vegetation fires, are the main sources of airborne species, such as Polycyclic Aromatic Hydrocarbons (PAH) and Particulate Matter (PM or soot).

As by-product of fuel combustion, flame-generated carbon nanoparticles not only lower the efficiency of many combustion devices but also can adversely impact global climate, air quality and human health. In particular, smaller the particles more dangerous they are, because the exposure to such particles can affect both the lungs and the heart. Therefore a strong reduction of fine particulate matter emissions from combustion sources is needed and a fundamental understanding of soot formation process is required for the development of future clean combustion devices. Studying soot morphology and composition as well as its formation process in flames remains an intriguing problem in combustion chemistry research and significant progresses have been made over the last few years both experimentally and

numerically.

Soot formation occurs at high temperature and in rich conditions and includes different processes: particle nucleation from the combustion of the initial gas phase mixture, surface growth by gas-surface reactions with C_2H_2 and PAHs, oxidation and dehydrogenation reactions. Moreover, along with chemical growth in a flame, soot particles can also coalesce or aggregate. The development of a reliable soot kinetic model is an ambitious task and involves not only a proper description of the gas phase kinetics and its coupling with solid phase but also a correct understanding of the experimental setup necessary for obtaining soot data to validate the model. The aim of this thesis work is to have more insights on particle inception and growth through an improvement of a soot kinetic model based on the discrete sectional method and an experimental activity has been carried out at Stanford University to measure soot produced under controlled flame conditions and investigate fuel dependency on the soot formation process. The modeling activity is mostly focused on developing and further refining the soot kinetic model on the basis of recent experimental and theoretical evidences on aggregates formation in flames. Specifically,

fractal aggregates are added to the mechanism with their proper reaction kinetics and this allowed to better describe the evolution of soot morphology along the flame axis. In fact, particle-particle coalescence, particle coalescence on aggregates and particle aggregation are considered in the kinetic model. The model validation is performed in terms of comparisons with data obtained by many groups in laminar premixed ethylene flames.

Among them, the configuration of the Burner-Stabilized Stagnation (BSS) flame, shown in Fig. 1, is considered as main case study. Soot is generated in a 16.3% ethylene–23.7% oxygen–argon flame (equivalence ratio $\Phi = 2.07$) with cold gas velocity of 8 cm/s (STP) and stabilized on a water-cooled flat flame burner at atmospheric pressure. The soot is sampled in situ along the centerline of the flame at the stagnation surface, which also defines the downstream boundary condition of the flame. First, a proper one-dimensional method to describe the stagnation-surface configuration is defined through a set of conservation equations and boundary conditions. The approach consists in simulating it as a counterflow flame with zero velocity on the oxidizer side. It is very important to

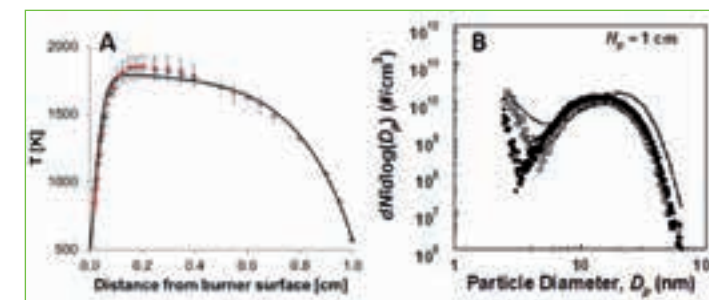
define correctly the boundary conditions, especially those for the species. In particular, for gaseous species, the sum of the convective and diffusive terms is zero on the air side, while for particles it is equal to the thermophoretic flux. This allows to take into account the flux of soot particles depositing on the water-cooled surface and to obtain a good agreement between experimental data and model predictions. Fig. 2 shows an example of comparisons for the measured and computed temperature profile and particle size distribution function (PSDF) at a fixed distance between the burner and the stagnation surface, $H_p = 1.0$ cm. The cooling effect of the stagnation plane is evident; the temperature cools down quickly to the value measured on the water-cooled plate. The temperature profile has been computed taking into account gas and soot radiation and the computed profile is within the experimental error. The predicted PSDF shows a tail on the small size side along with a lognormal-like PSDF on the large size site, both are in close agreement with the experimental data. Model uncertainties are also analyzed by means of sensitivity analysis on the kinetics of the various reaction classes inside the mechanism. Mobility measurements are interpreted

through the development of a new technique to measure simultaneously soot mass and size distributions. The goal of the experimental activity is to investigate the fuel dependency on the soot formation process. Soot has been sampled and measured in BSS propylene flames using a Scanning Mobility Particle Sizer. Similar flame operating and stoichiometric conditions have been chosen to compare soot volume fraction and size distributions from propylene with the one from ethylene. Afterwards, the model capability to predict soot formation under different conditions is tested through comparisons with experimental data from these measurements in laminar premixed propylene flames. Finally, the model reliability is tested also in benzene and cyclohexane premixed flames and discussed by means of the

rate of production analysis. A deeper knowledge of the mechanisms underlying PAHs and soot formation would allow for a better design of combustion systems with improved energy efficiency and a simultaneous reduction of particulate emissions.



1. Schematic representation of the burner-stabilized stagnation flame configuration: flame layout and illustration of the main characteristics of the system. x and r are the axial and radial coordinates, respectively. u is the axial velocity and v radial one.



2. Comparison of model prediction (solid line) and experimental data (symbols) in the BSS ethylene flame at $H_p = 1.0$ cm. Panel A) Temperature profile along the flame axis. Panel B) Soot particle size distribution function.

CFD MODELING OF ACCIDENTAL FIRES IN CONGESTED SCENARIOS

Silvia Tavelli - Advisor: **Marco Derudi**

Tunnel fires play a relevant and peculiar role in transportation safety: historical records have seen a number of accidents and near misses in tunnels, some of which characterized by catastrophic magnitude of the consequences and great public resonance, such as the Mont Blanc Tunnel fire (1999, 39 deaths). In the majority of cases mechanical or electrical failure in a vehicle or an accidental collision between two or more vehicles are at the origin of tunnel fires.

Since vehicles have a role in the initiation phase, they will always be present close to the fire and could influence the evolution of the fire phenomenon. However, the effect of the presence of relevant obstacles on the tunnel fires evolution was not previously investigated. Therefore, the focus of this thesis has been the simulation with a computational fluid dynamics software - the Fire Dynamics Simulator (FDS) - of complex systems and congested fire scenarios, with particular attention to the study of tunnel fires and the analysis of the consequences of the evolution of fire effluents in presence of large obstacles.

After the simulation of empty tunnel fire configurations, a systematic study of the effect of obstacles and their location on the critical

ventilation velocity, a key design parameter, was performed using experimental data from the literature to validate the simulation procedure and to highlight the best strategy for the identification of the critical velocity from simulation results. Henceforth, several obstacles configurations were analyzed in order to identify meaningful trends and strategies in order to rationalize the congestion modeling.

To account for the intrinsic complexity of the fire phenomenon, a thorough analysis should take into consideration the effect of thermal loads on structures, as well as of exposure to heat, toxic and irritating gases on the tunnel users' capability to reach a safe place. A comprehensive methodology providing a synthesis of the information regarding various threats to survival in a tunnel fire scenario in a number of Key Hazard Indicators (KHIs) and in an overall Key Performance Indicator (KPI) was then proposed. Its application is not limited to the consequence analysis, as the methodology can be useful to compare different configurations and strategies of fire prevention and protection, therefore becoming a tool useful for design purposes. The effect of complex geometrical features on real

scenarios - such as bypasses located in proximity to the fire - could also be relevant and has been addressed by analyzing and simulating in the experimental data obtained from full scale experimental tests.

Finally, the performances of the CFD code used for the simulations, FDS, were compared with the ones obtained from a zone model, in order to evaluate the potential use of the more simplified approach as a screening tool for this kind of scenarios, as well as those obtained using a different CFD code, FLACS, to highlight how the different approximations of the codes influence their applicability and reliability.

In summary, the underlying goal of the thesis has been to provide tools for a rational approach towards an effective and safe design, which could benefit from the results of predictive and reliable numerical simulations in order to shift from generic guidelines and prescriptive requirements towards the implementation of the conclusions obtained from the analysis of specific configurations and scenarios.

HIGH EFFICIENCY SCR PROCESS FOR STATIONARY APPLICATIONS: AN EXPERIMENTAL AND MODELING STUDY

Nicola Usberti - Advisor: Prof. Alessandra Beretta

The objective of this work is to improve the comprehension of the chemical processes that take place over traditional SCR $V_2O_5/WO_3(MoO_3)/TiO_2$ catalysts; focus has been on one side on the identification of the role of NH_3 oxidation within the $NH_3/NO/O_2$ reacting system in the case of High Efficiency SCR configuration (NH_3/NO inlet ratio higher than 1), on the other side on the kinetics of mercury oxidation.

Both experimental and modelling studies have been addressed at this scope, in cooperation with industrial partners (ENEL, Johnson Matthey). NH_3 -SCR, NH_3 -oxidation and Hg^0 oxidation were tested over commercial catalysts, exploring a very wide range of scales and conditions. Data were in fact collected both at the laboratory scale and in pilot scale facilities both on powders and on monoliths or plates, and were then analyzed with dedicated reactor models. The interplay of chemical reactions and inter- and intraporous mass transfer limitations required in fact the medium and methods of the chemical engineering analysis to extract intrinsic kinetic information and derive guidelines for the reactor design.

The $NH_3/NO/O_2$ reacting system was studied under conditions of $NH_3/NO \geq 1$ and temperature

up to 400°C, where some ammonia oxidation is expected. It was found that NO conversion passed through a maximum at increasing temperature, as commonly observed in SCR tests at the onset of ammonia oxidation; however, since the experiments were performed under excess ammonia, the high temperature decrease of NO conversion could not be attributed to a lack of surface NH_3 . The experiments were thus interpreted as the evidence of an unselective NH_3 -oxidation route, giving rise to some NO production. NH_3 -oxidation tests showed low selectivity to NO (in line with the current literature) which could be interpreted as the evidence of a selective ammonia oxidation route; however, a quantitative analysis of data showed that the observed product distribution was fully in line with an indirect-consecutive reaction scheme from NH_3 to N_2 , wherein NO is formed by NH_3 oxidation and is then rapidly converted to N_2 via NH_3 -SCR. Preliminary evaluations suggest that the impact of NH_3 -oxidation on the integral performance of full scale monolith reactors (operating at NH_3/NO ratios close to 1) is not negligible, and that the correct identification of the reaction stoichiometry is crucial. The extent of Hg^0 oxidation over V-W-Ti monoliths was

investigated performing lab-scale and pilot-scale tests. A model of the SCR reactor with honeycomb monoliths was developed to analyze the data, evaluate the rate of the chemical process and then comprehend the impact of NH_3 inhibition on Hg oxidation by examining the concentration and reaction rate profiles inside the monolith wall. It was found that, under typical operating conditions, both the DeNO_x and the Hg oxidation processes are affected by external and internal mass transfer limitations; NH_3 concentration drops very rapidly across the radial direction, but Hg^0 profiles are similarly concentrated in a thin superficial layer. Thus, the main operating parameter which affects the extent of NH_3 inhibition is the Area Velocity, that is the sizing of the full scale reactor.

The kinetics of Hg oxidation was further deepened by a dedicated experimental study on a plate-type V-Mo/Ti catalyst. Experiments at varying HCl concentration and varying temperature seemed to suggest that the activation of HCl is kinetically limiting at concentrations below 3 ppm; no temperature dependence of Hg conversion was in fact observed under these conditions. A positive, though weak, T-dependence was instead observed at 10 ppm HCl where the process tends to become

insensitive to HCl concentration, likely due to the reach of surface saturation.

As a first stage towards the comprehension of the complex interaction between SCR-DeNO_x process and Hg oxidation, experiments were performed with NO co-feed. At low-medium temperature, NO was found to have a promoting effect on mercury oxidation; this was observed also at low down to no HCl content. Instead, NO exerted a negative effect at temperatures above 350°C and such a negative effect worsened at decreasing HCl concentration and increasing temperature. This could be explained by assuming that NO interacted with the V sites differently at varying temperatures. Highly oxidizing NO-related surface species could be responsible for the promotion of Hg oxidation at temperatures below 350°C. On the opposite, the interaction of NO with the active sites at high temperature hindered the activation of HCl and thus the formation of chlorinated V-sites.

In general, these data showed that the rate of Hg oxidation is extremely sensitive to the surface coverage of the chemical species from the gas-phase, which likely influences the activation of HCl. This sensitivity produces very different values of the apparent activation energy, depending on the composition and evolution

of the gas-phase within the reactor.