



DOCTORAL PROGRAM IN INDUSTRIAL CHEMISTRY AND CHEMICAL ENGINEERING

Chair:
Prof. Tiziano Faravelli

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*.

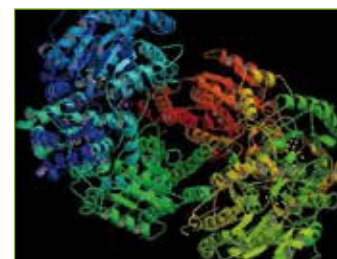
The program is the ideal extension of the *Laurea Magistrale* degrees in *Chemical Engineering, Safety and Prevention Engineering, Materials Science, Material Engineering, Industrial Chemistry and Chemistry*, but it is also open to graduated in other scientific disciplines.

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.

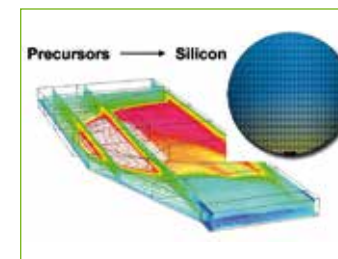
The **CII** program covers three years for an overall amounts of 180 credits. The responsibility of the organization and of the contents of the doctoral program is attributed to the Professor Committee (PC). At the beginning of the Doctoral program, a tutor and a thesis advisor is assigned to each student. The tutor has a supervisor function during the whole doctoral program, whereas the thesis advisor is responsible for the thesis work.

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.



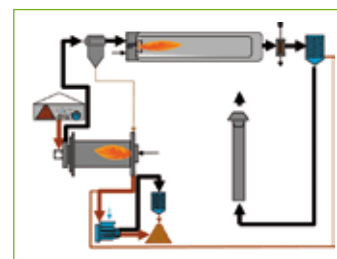
1. Structure simulation of Nitrogenase enzyme for N_2 conversion to NH_3 .



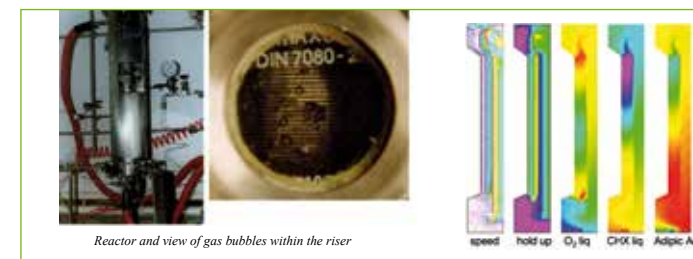
2. Simulation of a chemical vapor deposition reaction for silicon films deposition.



3. Hazardous gas dispersion simulation from an industrial accident.



4. Contaminated soil remediation process.



5. 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)

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MODELING, SIMULATION AND EXPERIMENTAL INVESTIGATIONS OF DUAL-REFLUX PRESSURE SWING ADSORPTION PROCESS

Bhatt Tushar Shankarlal - Supervisors: Prof. M. Morbidelli; Prof. G. Storti

Pressure swing adsorption (PSA) is widely used for the separation and/or purification gaseous mixtures. Its popular industrial applications include hydrocarbon separation, hydrogen purification and air drying/ separation. For processing binary feed gas mixtures, PSA systems can be categorized as: (i) stripping, (ii) rectifying and (iii) dual-reflux. The purity of Heavy product (A) is thermodynamically constrained in stripping PSA whereas, rectifying PSA systems have thermodynamic constraint on the purity of light product (B). In contrast, the purity of both products is thermodynamically unconstrained in dual-reflux pressure swing adsorption (DR-PSA): consequently, DR-PSA processes are capable of achieving complete separation of binary feed gas mixture. A typical DR-PSA unit comprises of a combined two-bed system with feed injection position (Z_F) along the axis of the column. Depending on the column operating pressure (high, P_H , or low, P_L) to which the feed is supplied and the type of gas (A or B) used for pressure swing, different cycle configurations can be identified, such as: DR-PL-A: Feed to P_L and pressure swing with A; DR-PH-A: Feed to P_H and pressure swing with A; etc. Literature survey revealed

that DR-PSA is recent and intriguing technology, therefore, in this PhD activity, my aim was to dwell further on DR-PSA process via mathematical modeling, detailed simulation and experimental investigations.

Mathematical modeling:

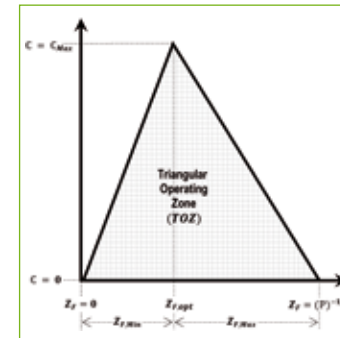
Modeling approach via equilibrium theory offers basic insight into the system behavior. Based on equilibrium theory, a numerical code in Matlab® was developed for calculating the evolution of wave profiles inside the column in DR-PH-A configuration. On the basis of this mathematical model, an optimal design procedure for DR-PH-A units was proposed. 3 parameters were identified as key to the effective design: Z_F , capacity ratio of the purge step (C) and light recycle ratio. An algebraic expression to compute optimal value of feed position ($Z_{F,opt}$), that assures complete separation and full adsorbent utilization, was evaluated:

$$Z_{F,opt} = \left[\frac{Y(y^*)}{\beta} + (P)^{1/\beta} \right]^{-1}$$

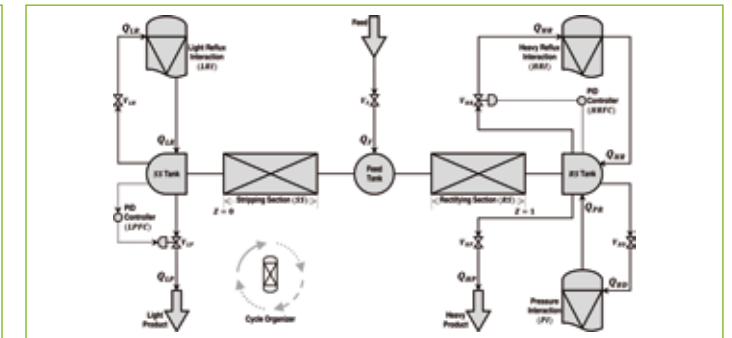
A region of complete separation was also found inside $Z_F - C$ plane: it has triangular shape and has been called 'Triangular Operating Zone' (Fig. 1). Additionally, the effect of different process parameters: adsorbent selectivity, feed

composition and pressure ratio; on the design parameters was investigated.

Detailed simulations: For simulating realistic DR-PSA process scenarios; detailed modeling approach is required that accounts for: nonlinear adsorption equilibrium along with pressure drop and temperature effects. Since none of the literatures aimed to validate the predictions of a detailed mathematical model of the DR-PSA process against some dedicated experimental data, a model for the detailed simulation of DR-PL-A process (Fig. 2) was developed in Aspen Adsim®. To validate the model, 19 experimental runs reported in literature considering the separation of $N_2-C_2H_6$ were simulated for 1500-3000 cycles each. At cyclic steady-state (CSS), model predictions were found to be in good agreement with experimental results (in terms of product purity and recovery values). Simulation and reported experimental trends obtained by analyzing the effect of operating parameters (feed composition, feed/purge step time, heavy product and light reflux flowrate) on process performance are also comparable. Additional simulations were performed to assess the effect of changing Z_F on process performance.



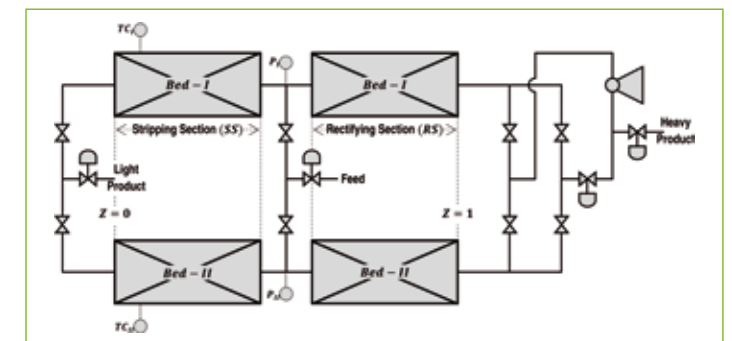
1. Qualitative representation of 'Triangular Operating Zone' (checked region)



2. Schematic representation of DR-PL-A process simulation flowsheet

Experimental investigations:

A lab-scale DR-PSA process unit (Fig. 3) was built and tested for concentrating dilute gaseous feed of CH_4 in N_2 . An intricate 4-step DR-PH-A cycle was employed. 9 experiments were performed for 200-500 cycles each, which revealed that the change in: heavy product flowrate, blowdown/pressurization and feed/purge time, did not have significant effect on process performance (in terms of product purity and recovery values). However, the process performance was found to be quite sensitive to change in light reflux flowrate. In these runs, the process unit was able to concentrate 5% CH_4 to an average of over 55% using moderate pressure ratios of 4. Additionally, the Aspen Adsim® model mentioned above was employed for detailed simulation of these experiments. At CSS, model predictions were found to be in good agreement with experimental results. The simulation and experimental trends obtained by analyzing the effect of operating parameters on process performance were also comparable. Overall, the model exhibited reliability and



3. Simplified schematic of lab-scale experimental setup depicting: adsorption beds, solenoid valves, flowmeter/ flowrate controllers, diaphragm pump, thermocouples, pressure transducers, input and output streams

versatility, thereby serving as an effective tool for process design, cost diminution of laboratory and/or plant trials, and enhanced process understanding.

BIOCATALYTIC PRODUCTION OF CHIRAL AMINES

Lorenzo Cerioli - Supervisor: Prof. Stefano Servi

Biocatalysis is the science that studies the use of natural catalysts, e.g. enzymes, to catalyze chemical reactions. Thanks to their characteristics of chemo-, enantio- and diastereoselectivity these types of catalysts, can often allow the synthesis of products not available or not obtainable in an efficient way with common approaches used in classical chemistry. Nowadays numerous biocatalytic processes for the production of fine chemicals are successfully adopted by industry. Biocatalysis is one of the starting points for the development of an environmentally sustainable chemical industry.

A very important part of pharmaceutical, chemical and agrochemical industry is constituted by chiral amines and amino acids. They play key roles in the preparation of biologically active molecules and in the resolution of chiral acids. The stereoselective production of amines can be accomplished both by chemical and biocatalytic synthesis. A lot of effort have been done to develop an efficient chemical asymmetric synthesis, but this still remains a challenge. Harsh reaction conditions, insufficient stereoselectivity for the pharmaceutical use and the presence of toxic or environmentally problematic transition metals are severe

drawbacks of the conventional chemical approach. Because of their high stereoselectivity and the possibility to carry out the reactions in mild conditions, biocatalysts are gaining consideration as a valuable alternative to the standard chemical synthesis. Different enzymes belonging to the families of hydrolases, oxidoreductases, and transaminases have been reported to be used in the production of chiral amines. During my PhD I focused my attention on two projects regarding the production of enantiopure amines; the former has been oriented on the production of a novel ω -transaminase, the latter one was a study of dynamic kinetic resolution and its applications.

Project 1

ω -Transaminases play a central role in the biocatalytic preparation of enantiopure amines for their generally high turnover rate, great stability, broad substrate specificity and no requirement of external cofactors. In this study we expressed a putative transaminase identified in the genome of the bacteria *Halomonas elongata*: this is a moderate halophile which evolved an organic-osmolyte strategy to overcome the high osmotic pressure of its natural

environment.

The *spuC* gene was identified, cloned into the vector *pRSET B*, expressed in *E. coli* BL21(DE3) and purified by metal affinity chromatography. The enzyme was characterized at different temperatures, pH and salt concentrations and in the presence of different cosolvents and additives. The best operating conditions were found at pH 8-9 and 45 °C. High salts concentrations and the presence of cosolvents decreased the enzymatic activity but showed almost no effect on the stability of the enzyme.

The substrate specificity of the transaminase was studied against a library of amino donors and amino acceptors. High enantioselectivity, large substrate spectra and stability in organic solvents make this enzyme a highly suitable catalyst for biotechnological applications in the production of chiral amines. Moreover, its acceptance of isopropylamine as amino donor is an advantage in asymmetric synthesis and a cost-effective benefit for industrial applications. The uncommon ability to accept α, α' -dihydroxyketones as amino acceptors looks promising for the application in the synthesis of chiral amino alcohols. Future work will involve studies on the enzyme activity in organic solvents and applications in

the production of chiral amino alcohols.

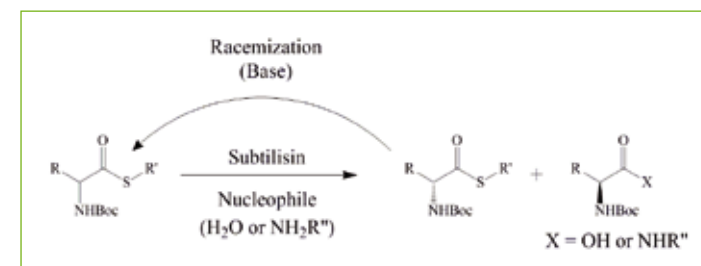
Project 2

Non-proteinogenic α -amino acids (AAs) are a group of required building blocks for the preparation of new bio active compounds and peptide mimetics.

Kinetic resolution of racemates is the most common method used for their production. The racemization of the undesired enantiomer, which is essential to preserve a high atom efficiency, could be done in a separate step, increasing however the complexity of the process, or *in situ* which is by far a more efficient procedure. The racemization catalyst can be a base, a transition metal catalyst or an enzyme.

Dynamic kinetic resolution (DKR) is a method in which a resolution process is coupled with an *in situ* racemization of the unconverted enantiomer. This approach presents many advantages by bypassing the tedious recycling steps of the undesired remaining enantiomer and increasing the enantiospecificity of the process. The combination of the enzymatic resolving step with a base catalyzed racemization is a better alternative with respect to transition metals catalyzed reactions, but the substrate has to be racemized by the base while the product should not racemize in the same conditions.

Compounds with these properties are hydantoines, oxazolones and thioesters from which the corresponding α -AA can be obtained by enzyme catalyzed hydrolysis while the base catalyzed racemization



1. Deracemization of *N*-Boc-amino acid-thioesters with subtilisin.

occurs only on the substrates and not on the products. In this study we have dealt with the set up and optimization of a DKR process for the production of enantiopure amino acids derivatives. This process consists of an *in-situ* chemical racemization coupled with an enzymatic hydrolysis (Figure 1). We carried out substrate and reaction engineering achieving a general protocol for the DKR of α -AA-derivatives of different nature. The general procedure provided selectively the hydrolyzed L-*N*-Boc- α -AA starting from the L-*N*-Boc- α -AA-thioester of the racemate while the D-thioester was continuously racemized by an organic base. The reaction medium for the α -AA-derivatives with an aromatic ring bound directly to the α -carbon was a biphasic (water/MTBE) system. For these substrates the catalyst was a protease soluble subtilisin and the racemization was due to the base triethylamine. For compounds with a lower proton acidity on the α -carbon the racemization was carried out with a stronger base such as 1,8-diazabicyclo[5.4.0]undec-7-ene in *t*-butanol. The hydrolysis in this case was performed by exploiting the catalytic activity of CLEA-subtilisin which was

completely stable in organic solvents and in the presence of the base. The CLEA-subtilisin is a cross-linked version of the enzyme and can be easily recovered and recycled. In all cases the absence of racemization on the product of hydrolysis (L-*N*-Boc- α -amino acid) in presence of the base was confirmed. All reactions occur with very high isolated ees and yields. Enzyme-catalyzed ammoniolysis and aminolysis reactions with complete deracemization of the racemate and amide formation were equally effective when the process was carried out in presence of an amine as nucleophile. In these cases the corresponding L-amides were obtained with excellent enantiomeric purity; all above 98% ee and in good yields.

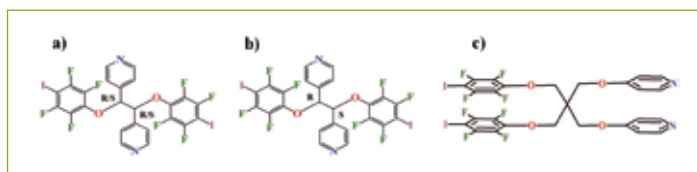
SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF NEW HALOGENATED SUPRAMOLECULAR MATERIALS FOR ADVANCED APPLICATIONS

Luca Colombo - Supervisor: Dott. Giancarlo Terraneo

In this thesis work, starting from the hypothesis that the cooperation between different interactions can help in crystal engineering for the construction of materials with new properties and applications, the possible cooperation between halogen bonding (XB) and other supramolecular interactions, namely hydrogen bond (HB) and coordination bond (CB), for the synthesis of purely organic and metal-organic frameworks has been investigated. Three new ligand molecules possessing suitable chemical and geometric features to be involved in HB, XB and CB have been designed and synthesized (Figure 1). Perfluoroiodinated aromatic rings have been selected as strong XB donor, while pyridyl rings have been chosen as hydrogen bond (HB) acceptor and for their ability to form strong coordination bonds (CBs).

In the first section the use of XB in a complementary and cooperative way with (HB) for the synthesis of new robust supramolecular organic frameworks (SOFs) is described. In order to break the self-complementarity of the ligands hydriodic acid has been selected as source of both protons, for the formation of HBs, and iodide anions as good XB acceptors.

The efficacy of the proposed methodology has been proved by the obtainment of an open



1. Ligand synthesized and used in the thesis. a) Ligand R2. b) Ligand M2. c) Ligand L1.

SOF by self-assembly of ligand **R2** and hydriodic acid. Protons act as linear bidentate HB donors and iodides act as bidentate XB acceptors resulting in a 1:1 ligand/HI stoichiometry. Ligand **M2** has been then employed to further validate the proposed methodology and to investigate the effect that small variations can have on the final structure. By self-assembly of **M2** with HI several supramolecular isomers with different topologies have been obtained. Finally ligand **L1** was employed to investigate more in the detail the stability of the networks and the possibility to form SOFs with others halogenidric acids (HBr and HCl). Remarkably the connectivity observed in **RN1** is conserved in all the networks obtained with ligands **M2** and **L1**. The robustness of the obtained frameworks has been proved via SCSC guest exchange reactions. In the second section, taking advantage of the strengthening of XB caused by the fluorination of the aromatic rings, the cooperation between XB and CB has been exploited in

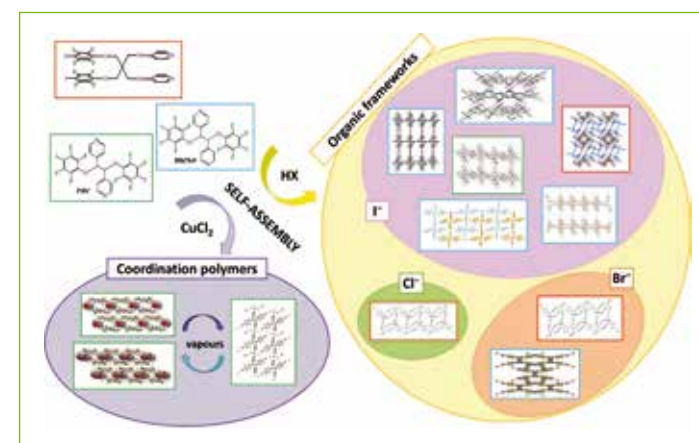
the synthesis of fluorinated coordination polymers (CPs). Self assembly of ligand **R2** with copper chloride resulted in the formation of the coordination polymer $[Cu(R2)(Cl)_2]_n$ (**F1a**) as violet crystals. Compound **F1a** is made out of 1D coordination chains arising from the alternation of copper cations and ligand molecules. The metal centres adopt a square planar geometry and the four coordination positions are occupied by two pyridyl groups belonging to two different ligands and two chloride anions in a *trans* arrangement, while an unsaturated coordination site remains available on the apical position. Each of the two chloride ions coordinated to the metal centre is involved in XB with the iodine of one fluorinated ring belonging to a ligand of an adjacent chain, in this way 2D layers are formed. Despite no free volume is present in the network, the new CP exhibits selective and reversible vapour absorption properties that come with a strong vapochromic effect (Table 1). The vapour absorption is driven by the

presence of the unsaturated copper centers that can coordinate a molecule on the free apical coordination position.

is exploited to allow the entrance of the guest molecules. Finally the new CP exhibits strong mechanochromic behaviour.

SOLVENT	ABSORPTION	NEW COLOUR	TIME SCALE
Water	No	-	-
MeOH	Yes	light blue	hours
EtOH	No	-	-
1-PrOH	No	-	-
CH ₃ CN	Yes	light blue	seconds
Acetone	Yes	light blue	minutes
AcOEt	Yes	blue	hours/days
1,4-dioxane	No	-	-

Table 1. Vapochromic behaviour of F1a.



2. Scheme of the thesis development. Three new ligands were synthesized (left top corner) and self-assembled with halogenidric acids to obtain purely organic frameworks (right) and with copper chloride to obtain coordination polymers (left bottom corner).

As demonstrated by structure solution of the adducts with methanol and ethyl acetate from powder X-ray diffraction data, absorption occurs through intercalation of the guest molecules between the layers. Remarkably these layers are not destroyed by the absorption of vapours, but the flexibility of XB

In conclusion this thesis demonstrates the possibility and the advantages to use XB in cooperation with HB and CB in crystal engineering. Starting from new ligands able to be involved simultaneously in different interactions two smart approaches for the synthesis of purely organic and metal-organic

frameworks have been proposed and their efficacy demonstrated. Cooperation and complementarity between HB and XB allowed for the synthesis of several open SOFs. The combination of pyridines and iodotetrafluorophenyl rings in the same scaffold, along with the coordination of HI may develop as a general strategy for the orthogonal self-assembly of new supramolecular co-polymers that can be tuned by various external stimuli through addressing HB and XB separately.

Cooperation between XB and CB allowed for the synthesis of a fluorinated CP showing selective and reversible vapochromism, a dynamic breathing behaviour, mechanochromism, and superhydrophobicity. The proposed methodology, which exploits the fluorinated part of the ligand in the network construction, paves the way towards a new class of fluorinated metal-organic frameworks.

ELECTRONIC NOSES FOR AIR QUALITY MONITORING: DEVELOPMENT AND TESTS

Licinia Giovanna Dentoni - Supervisor: Prof. Selena Sironi

During the last decades several studies have proven that air quality may affect human health. For this reason, several studies have been carried out in order to evaluate different methodologies to monitor air quality and to improve it, by reducing pollutant emissions. Historically, the first studies focused on outdoor air quality, as it was perceived as more polluted and potentially toxic. In more recent years, the air quality problem involved also indoor air quality: given that, in general, people spend the majority of their time indoor, the quality of indoor air is important, as well. Among other air pollutants, also odour is considered as a factor that may affect air quality. Especially regarding indoor air quality, among all possible types of pollution, olfactory annoyance has been considered as one of the causes of different symptoms of the Sick Building Syndrome. The research conducted during this 3-years PhD focused on different aspects of air quality monitoring: the monitoring at receptors, the emission monitoring and the monitoring of indoor air quality. More in detail, different instrument have been developed and tested in order to obtain electronic noses for odour monitoring at receptors, for odour monitoring at emissions and for indoor odour monitoring. Since the first

instrument developed mainly for laboratory use (EOS 835), during the last years an innovative electronic nose was realized (EOS 507), designed with the aim of guaranteeing better performance in the field under variable meteorological conditions and with diluted odours. Moreover, an electronic nose for indoor air quality monitoring, the so called EOS 101, has been developed too.

The PhD project involved the development of different instruments specifically designed and set up for different applications: (i) environmental odour monitoring at receptors, (ii) odour monitoring at emissions and (iii) indoor odour monitoring.

The first part of the research involved the study and the development of a new electronic nose, including several innovative features with respect to other commercial electronic noses, specifically designed for outdoor applications.

A primary research step involved the optimization of the innovative regulation devices introduced in this new instrument. More in detail, this part of the research focused on the possibility to use a reference substance different from clean air (or "neutral" air), which is actually used in almost all commercial electronic

noses. Tests were performed in order to evaluate different pure substances that could be considered as a reference for the EOS 507 electronic nose. The results prove some solid (at room temperature) substances like Coumarin and Maltol to be suitable for this purpose, due to the sensors sensitivity and sensor response linearity towards these compounds.

A second research step involved the in-depth study of the sensor responses towards changes in the humidity of the analysed air, with the aim of evaluating the possibility to compensate humidity variations by means of a specific algorithm rather than using a specific apparatus that physically changes the humidity content of the analyzed mixture, which entails an increase of the instrument complexity. The test results demonstrate that most sensors have an analogous behaviour and that sensor resistance decreases when humidity content of the analysed air increases, as expected by theory. Two sensors present a different trend, that might be attributed to a different reaction path for the odorous compounds on the sensor. The next step provided to describe the sensor response trend in function of the sample humidity by a suitable adsorption model. Both the Langmuir adsorption model and an empirical model derived from

the scientific literature proved to be effective in describing such trend accurately.

Besides the optimization of the instrument technical features, other studies were conducted in order to test the EOS 507 and maximize its performances in two different applications involving the continuous monitoring of odours at receptors or at emission, respectively.

Laboratory tests conducted to optimize the electronic nose for odour monitoring at receptors involved the analysis of samples prepared using pure substances and they proved the new instrument to be able to discriminate the different odours being tested, and to estimate the odour concentration of samples between about $50 \text{ ou}_\text{e}/\text{m}^3$ and $300 \text{ ou}_\text{e}/\text{m}^3$, giving correlation indexes (R^2) of 0.99 and errors below 15%. Moreover, a field test, consisting in a 10-day monitoring of an area where different odour emitting plants are present, was then conducted to verify the effectiveness of the innovations introduced in the EOS 507 with respect to the EOS 835. The new electronic nose guarantees a better clustering of training data and, as a consequence, a more reliable classification of the perceived odours. Moreover, the EOS 507 electronic nose is more user-friendly, due to the presence of specific devices that reduce the need of operator actions. As far as the optimization of the EOS 507 for odour monitoring at emissions, the performed tests show that the EOS 507 is able to quantify the odour concentration of samples of pure compounds and of real samples. If opportunely

trained, the capability of the system to estimate the odour concentration turned out not to be influenced by the use of mixtures of different pure compounds in air instead of gaseous samples of pure compounds in air. Tests performed with real samples demonstrate that the system is capable to estimate the odour concentration with the same accuracy using only a training dataset obtained with samples belonging to the same olfactory class as the sample to be quantified, as well as using a "complete" dataset, which contains data relevant to different olfactory classes. This of course is an important information, meaning that the use of one single "complete" dataset will be sufficient in order to quantify the odour concentration of the monitored emission during all the phases within a satisfying level. The error relevant to the odour concentration estimation of real samples is comprised between 2 and 37%.

Future studies will be carried out in order to verify the electronic nose performances directly in the field. Moreover, the instrument will be tested with different samples, collected on other odour sources, in order to evaluate its performances with different emissions.

The last part of the research involved the study of a "simplified" instrument (EOS 101) meeting the requirements of reduced cost and dimension for indoor application. The laboratory tests conducted with 4 different typical indoor allowed the determination of a "threshold" value to optimize the instrument sensitivity by

making it as much as possible similar to human sensitivity. The optimal "threshold" value was established and set for the subsequent indoor monitoring phase carried out inside a public office. The monitoring proved the simplified electronic nose EOS 101 to be effective in the detection of odours in an indoor environment. The effectiveness of the instrument was verified by comparing its results with the results obtained by means of the more complex electronic nose EOS 507 designed for environmental odour monitoring, whose accuracy and reliability has been proven in previous studies.

The comparison of the results obtained with the two instruments showed that they were substantially overlapping: the correspondence between odour detections by the EOS 101 (i.e., exceeding of the "threshold" by at least one sensor) and odour detections by the EOS 507 (i.e., classification of the analysed air as different from "neutral air") turned out to be above 99%, thus proving the effectiveness of the new instrument for the desired application.

SYNTHESIS, CHARACTERIZATION AND APPLICATIONS OF NOVEL MACROMONOMER-BASED BIODEGRADABLE NANOPARTICLES

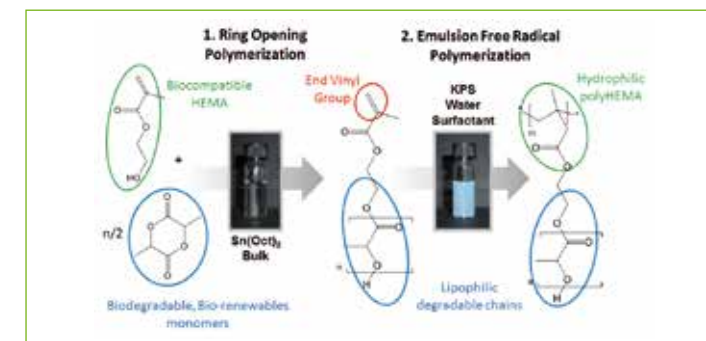
Raffaele Ferrari - Supervisor: Davide Moscatelli

Among the huge number of polymer formulations proposed in the literature for drug delivery applications, only few of them reached the market. While hundreds of publications address to the opportunities opened by targeted drug delivery, the only formulations reached the market were accepted mainly for their reduced toxicity profile. As a matter of fact, there is still a lack of optimization in this field, further studies aimed to assess and investigate problems such as biocompatibility, biodegradation and biodistribution are required. Commonly, drug delivery accounts for a system in which an active compound is protected and delivered by a carrier with tailored properties. Such systems have been developed for a huge category of application ranging from delivery of RNA, drugs, proteins and monoclonal antibodies. The concept of targeted drug delivery is attractive because it summarizes the advantages of drug applications: high local concentration and low systemic exposure of the active compound. Basically, the main target is to modify the biodistribution of the drug, not to be governed by the drug itself but by the delivery system. Hence, the main function of the biomaterial (nanocarrier) becomes to selectively transport and release the drug to the site

of action. Drugs are protected from interacting with other molecules (i.e. macrophages present in the blood) which could change its chemical structure or sequester the active ingredient. As a consequence, these systems aim to modify several parameters of the drug: the release profile and capacity to cross biological barriers, biodistribution, clearance, and stability. Such nanocarriers offer numerous advantages over conventional dosage forms. Increasing the therapeutic activity and decreasing the side effects, it becomes possible to reduce the number of drug dosages required during a treatment. Moreover, when the natural distribution of the drug causes major side effects due to its interaction with other tissues (i.e. necrotic tissues in the case of docetaxel injection), these are avoided. Starting from the 1970s many efforts have been done to design carriers, specific for different applications, able to efficiently trap active compounds. However, as one of the most devastating diseases with more than 10 million new cases every year, cancer is the main field where the development of biomaterials for drug delivery is addressed. In this light the drug delivery purpose is to formulate selective drugs, able to either passively or actively target cancer cells. Polymer NPs are the most

common delivery system reported in the literature; their nature makes them ideal candidates to deliver hydrophobic molecules, drug, peptides or proteins. In particular, they can be a useful tool to deliver drugs into cells since they permit a good loading efficiency due to their lipophilic characteristics and they can possess a tunable drug release in time as a function of their chemical-physical properties (e.g. surface charge, degradation kinetics, drug-affinity, biodistribution). In this work, a new material library based on different functionalized polyesters, the most used biodegradable polymers, has been developed responding to the following criteria and aimed to overcome the checkpoint a nanocarrier faces, as: (i) colloidal stability, (ii) biocompatibility (iii) biodistribution (iv) internalization in cells (v) biodegradation and elimination. The NP library has been optimized through the continuous feedback obtained from *in vitro* and *in vivo* experiments, giving a proof of effectiveness of the NPs as carriers for drug delivery. The aim of the work is then to solve the issues rising from the method for polymer NPs synthesis nowadays reported in the literature by developing a system: (i) made of low polyester MW (ii) easy adaptable to different polyester and relative

copolymers as poly(lactic acid) (PLA) poly(caprolactone) (PCL) and poly(lactic-co-glycolic acid) (PLGA) (iii) with an increased solid content in the final latex (iv) which avoids the use of organic solvents (v) that significantly decrease the average NP degradation time (vi) constituted of NP with tunable degradation time (vii) easy tunable in terms of NP size, surface charge and easy functionalizable, (viii) constituted of a NP library, optimized through the feedback obtained from *in vitro* and *in vivo* experiments. All these requirements have been fulfilled by developing a two-step process combining Ring Opening Polymerization (ROP) with emulsion Free Radical Polymerization (FRP). First, the synthesis of new macromonomers based on polyesters functionalized with a vinyl-end group has been developed using ROP reaction. Here, 2-hydroxyethyl methacrylate (HEMA) has been used as co-catalyst since it possess a vinyl group that can be preserved by ROP and used for further reactions, in particular in free radical polymerization. The living nature of ROP is exploited to produce polyesters with short and controllable average chain length (n) from 1 to 10 units and composition, terminating with a vinyl group and then suitable for FRP. More detailed, due to their relatively low MW they possess



1. Different steps used to obtain PLA-based NPs. The final polymer is composed of a poly(HEMA) backbone grafted with PLA side chains of controllable length.

a slight water solubility, making them amendable for emulsion polymerization which allows to obtain from the macromonomer, NPs and polymer. The final NP are then constituted of hydrophilic poly(HEMA) chains grafted with n polyester units, tunable in terms of material (PLA, PLGA or PCL simply by changing the cyclic monomer for ROP), average chain length and composition as reported in Figure 1 in the case of PLA-based NP. The two reactive steps are both solvent free; ROP is performed in bulk conditions, while the emulsion FRP takes place directly in aqueous phase without the use of solvent. As a remark, this second step is a conventional emulsion polymerization, allowing to obtain NP latex with a solid content up to 10% w/w, ten or more times the possibility provided from the conventional

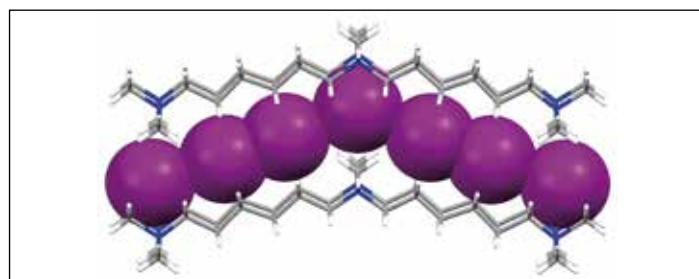
NP synthetic method, limited from the fluid dynamic processes. The NP degradation occurs through the hydrolysis of the side chains leaving hydrosoluble poly(HEMA) which can be easily disposed; moreover the possible modification of the grafted chains ensures the possibility to tune the degradation time and the lipophilic properties of the final NP system.

HOST-GUEST CHEMISTRY OF TAILORED ORGANIC IODIDE SALTS FOR MOLECULAR DEVICE AND FOR IMPROVED STORAGE, SEPARATION

Jingxiang Lin - Supervisor: Dr. Giancarlo Terraneo

Halogen bonding (XB), is a noncovalent interaction that occurs between electrostatic positive potential region on covalently bonded halogen atoms (halogen-bond donor, Lewis acid) and electron density from halogen bond acceptor (Lewis base). Researches have showed that halogen bond is directional, strong and predictable bonding tool for construction of supramolecular assemblies. In order to explore and expend the utility of halogen bonding tool in more diversified fields for practical application, a series of tailor-made organic iodide salts as halogen bond acceptor were synthesized and evaluated as host materials to interact with guest molecules via halogen bond. The scope of the research lies in the usage of iodide anion as halogen bond acceptor, in the template effect of specific cation, to selectively bind halogen bond donor, studying their host-guest chemistry, and evaluating them for potential application.

Polyiodides are attracting continuing interest due to their fascinating structural chemistry and, more important, their diversified properties allowing for useful applications. A strategy in the synthesis of solid polyiodides with a given composition and crystalline structure is the use of organic



1. Representation of an I_7^{3-} polyiodide (in space filling) encapsulated in the cavity defined by four organic trications (in sticks). Color code: carbon, gray; white, hydrogen; blue, nitrogen; purple, iodine.

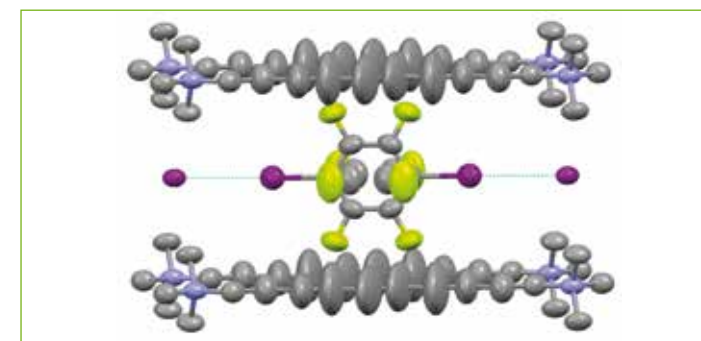
iodide which, on crystallization, can robustly template the formation of architectures possessing domains with a specific dimension and geometry tailored to accommodate the pursued polyiodide. In line with this strategy, 2,2,9,9,16,16-hexamethyl-2,9,16-triazoniaheptadecane triiodide ($HMTAHD^{3+}\cdot 3I^-$) and dodecamthonium diiodide were synthesized and used as host material to capture and store diiodine (I_2) molecules via halogen bond. Researches showed that organic alkyl ammonium iodides containing programmed cations, on reacting with iodine can template the formation of specific polyiodides that formed via halogen bonding. For example, in cocrystal between $HMTAHD^{3+}\cdot 3I^-$ and iodine molecules, three iodide anions are well positioned by triammonium cation

via electrostatic interaction between iodide anion and ammonium group. These well positioned iodides allowed the incorporation of two size-matched iodine molecules by strong halogen bonds, leading to the formation of $I\cdots I\cdots I\cdots I\cdots I\cdots I$, which is the first and only example of discrete I_7^{3-} polyiodide species ever reported in literature. The rare V-shaped I_7^{3-} polyiodide is encapsulated and stabilized by a bent cavity defined by four symmetry related $HMTAHD^{3+}$ trications thanks to good structural complementarity between the charged moieties (Figure 1). The protocol method proved that the organic iodides are reliable host materials for reversible storage and release of iodine. Which demonstrated that organic alkyl ammonium iodide could be an ideal sorbent for treating radioactive iodine waste.

A molecular gyroscope is a molecular or supramolecular device consisting of molecular frame (stator) and an intrinsically barrierless rotating molecular component (rotator) that emulates the macroscopic systems. In order to develop a supramolecular gyroscope driven by halogen bonding, decamethonium iodide was selected as host material to cocrystallize with potential rotator molecules of 1,4-diiodobenzene as well as its derivative. The resulting cocrystal structures were obtained by single crystal structure analyses. Studies revealed that decamethonium diiodide is able to form gyroscope-like crystal structure with a series of 1,4-dihalobenzene as well as its derivatives. For example, in cocrystal of decamethonium iodide @1,4-diiiodoperfluorobenzene (Figure 2), the $[Me_3N^{(+)}\cdot (CH_2)_{10}\cdot N^{(-)}Me_3]$ cations arrange in parallel fashion and define arrays of spatial cavities, in which superanionic rotator constructed by two iodide anions entering each end of 1,4-diiiodoperfluorobenzene via halogen bonds were encapsulated. The dynamic behavior of rotator was investigated as a function of nature of rotator and the size of cavity. Different behaviours of rotator were observed in the effect of difference in 'rotator' molecule and dimension of cavities. Iodoperfluoroalkanes (IRf_n) are important chemical intermediates, versatile synthetic reagents widely utilized to introduce the perfluoroalkyl functionality into organic substances. In industry, they are

usually produced as a mixture containing iodoperfluoroalkane analogues with different length of perfluoroalkyl chain. They are usually separated by using fractional distillation to obtain iodoperfluorohexane (IRf_6), iodoperfluorooctane (IRf_8), and iodoperfluorodecane

fluorine-fluorine interaction, leading to the separation of iodoperfluoroalkanes. Researches revealed that absorption effects between N-substituted perfluoroalkyl pyridinium iodide and iodoperfluoroalkanes are critically dependent on the



2. Cavity defined by four cations, wherein 1,4-diiiodoperfluorobenzene rotator was encapsulated, halogen bonds are depicted as dotted lines, hydrogen atoms were omitted. Color code: carbon, gray; fluorine, green; blue, nitrogen; purple, iodine.

(IRf_{10}), according to their physical properties. However, iodoperfluoroalkanes with longer perfluoroalkyl chain can not be separated in this way. Therefore, it would be meaningful to develop a new more inexpensive and efficient separation method for iodoperfluoroalkane mixture. Solid phase extraction and solid vapor extraction using 1-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptafluorodecyl) pyridinium iodide, (short as $pyC_{17}Rf_8\cdot I$) as sorbent were evaluated as potential separation method for IRf_n mixture. Investigations showed that N-substituted perfluoroalkyl pyridinium iodide, as solid absorbent, can selectively bind iodoperfluoroalkane both from solution and vapor via halogen bond and

interplay of several factors, including, extraction time, the amount of pyridinium salt used as absorbent and medium solvent (solvent effect). Researches have shown that the tailor-made organic iodide salts promising host materials for molecular device and for improved storage, separation. The template effect of cations, especially size matching effect and structural complementary effect, in halogen bond formation between iodide anion (as halogen bond acceptor) and selected halogen bond donor were evident. The research also demonstrated again that the halogen bonding can in general be used by rational design in all fields where non covalent bond interactions play a key role.

MOLECULAR MODELING OF MACROMOLECULAR SYSTEMS

Evangelos Mavroudakis - Supervisor: **Davide Moscatelli**

One of the most commonly used and versatile polymerization processes for the production of macromolecular materials is free radical polymerization. The full knowledge of all the reactions of the kinetic scheme of the process is not an easy task. However, the synthesis of proper polymers with specific properties, chain length distribution, and morphology requires that knowledge. Nevertheless, many important reactions cannot be estimated experimentally. For instance reactions like cross-propagation during copolymerization or secondary reactions like backbiting, β -scission, and intermolecular chain transfers, which affect the final product by changing the molecular weight and the material properties cannot be studied separately through experiments. The development and the continuous progress of the experimental techniques which are used nowadays led to important improvement of the obtained experimental values for polymerization processes. Techniques based on pulsed laser polymerization used for the investigation of reaction kinetics of many systems but it was mostly focused on acrylates. Techniques like those can estimate only the overall kinetic rate of the process at

the narrow temperature range in which they can be used. It is clear that despite the efforts, experimental advances are still not sufficient to provide a detailed characterization of individual reaction nor to provide estimations at a wider temperature range. On the contrary, there are many computational methods based on quantum mechanics which can be applied to the study of individual reactions without restriction on temperature. Through these relatively easy and cost-effective methods can be provided useful results for many important reactions which are not accessible by experiments. In the present dissertation, *ab initio* quantum chemistry methods have been adopted for the study of free radical polymerization processes. Polymer systems of industrial relevance and systems with bio-applications were the focus of this quantum chemistry investigation. Specifically, the rate coefficients of the studied reactions have been estimated through methods based on density functional theory adopting the classical transition state theory. The first step was to apply well established methods for the study of copolymer systems adopting the penultimate unit effect model instant of

terminal model. That was a try to provide more information about the copolymerization and the copolymer properties. However that extension proved not to be straightforward. The penultimate unit effect model requires long molecules that added two sources of uncertainty to the simulations. In particular, led to intramolecular interaction during the simulations as well as increased the possibility of the selection of a wrong initial structure for the simulations. A procedure that includes an extensive structural optimization has been proposed in order to overcome these difficulties and to avoid the uncertainties. Later, the same method and the proposed procedure have been applied to more complicated copolymerizations. Copolymer systems that exhibit great difficulties during their experimental study and thus there are few or none experimental data for them have been studied. Additionally, the increase of the computational power and of the potentiality of Polimi's cluster during the run of the Ph.D. enabled the study of the copolymer systems at a higher level of theory. The improved computational approach has been used for the rest of the studied systems. Afterwards, the investigation

has been focused on the study of the secondary reactions during free radical polymerization. Monomolecular reactions such as backbiting and β -scission have been studied first. Acrylate homopolymer systems have been used for the study of a wide range of monomolecular secondary reactions. Later, acrylate-based copolymer systems have been used in order to examine the kinetics of the same reactions in a copolymers. The obtained results can be used to describe the physicochemical behavior of the monomolecular secondary reaction and to provide a reasonable prediction for the reaction kinetics. Moving forwards, the study has been extended towards bimolecular secondary reactions such as chain transfer to monomer and chain transfer to polymer. Even in this case acrylate-based homopolymer and copolymer systems have been used for the study. The importance of such reactions on the overall propagation kinetics as well as the role of the chemical environment have been investigated. The obtained results provide a comprehensive overview of the intermolecular hydrogen abstraction reaction kinetics during bulk free radical polymerization and can improve the understanding of the kinetics in such systems.

The last of the secondary reactions that has been studied was the chain transfer to agent reaction. The proposed computational approach has been used to investigate the reactivity of acrylate polymer radicals towards common chain transfer agents. Different radical kinds and lengths have been adopted for the investigation. This study shed light on the mechanism that controls the decrease of branching degree when a chain transfer agent is added in a bulk polymerization. The computational study proved that the mechanism of mid-chain radical patching which could explain the lower branching degrees is not relevant to the decrease of branching. Particular attention was paid to the relevance of the quantum tunneling effect whenever hydrogen transpositions were taking place during the studied reactions. The role of this effect on the determination of the kinetic constants has been highlighted and proper factors have been used for the estimation of the reaction rates. Summarizing, quantum chemistry has been proved a powerful tool for the study of the individual reactions that compose the kinetic scheme of free radical polymerization. Computational approaches, like the one proposed in this thesis,

are in many cases the only way to determine the reaction kinetics especially when it comes to the study of reactions that are inaccessible through experiments. The computational results can support the experimental efforts as well as improve the understanding of the complex kinetic scheme of free radical polymerization

NOVEL ENVIRONMENTS FOR METAL IONS: COORDINATION COMPLEXES OF AZAHELICENES AND METAL-CONTAINING IONIC LIQUIDS

Daniele Mendola - Supervisor: Prof. Andrea Mele

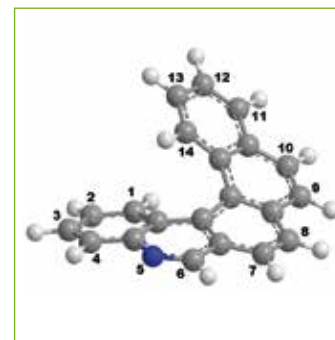
In the past few years, it was found that a class of newly synthesized molecules - aza[5]helicenes - (vide ultra) showed improved luminescence properties when confined inside nanometric cavities in the presence of lanthanides ions. This was actually done by segregating the azahelicenes in the polar core of the reverse micelles generated Yb(III) sodium bis(2-ethylhexyl)sulfosuccinate - Yb(DEHSS)₃- and dissolving the whole material in CCl₄. The effect of the nanosegregation of the π -system in close contact with a metalcation was to enhance greatly the photoluminescence of the helicene, probably for a mechanism of electron transfer-back transfer between the helicene and the metal ion. These observations led to the decision of improving such mechanism by exploiting the presence of the N atom on the azahelicenes (Figure 1) and to use them as ligands for a coordination complexes of transition metals. This is the object of the first part of this work: *the coupling of extended and helicized π -electron frames to transition metals by the synthesis of coordination complexes.*

A natural extension of this idea – forcing the π -system and the metal ion to interact by putting them in contact – was to dissolve transition

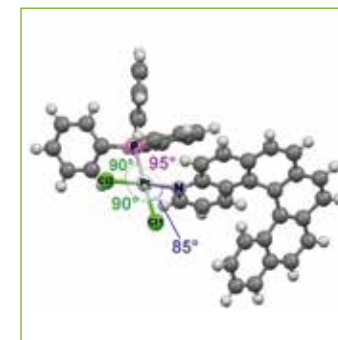
metal ions in ionic liquids (ILs) based on π -electron containing cations, such as the widespread imidazolium-based ILs. The rationale of this relies upon some distinct facts: i) ionic liquids provide a nanostructured environment with noanalogue in molecular solvents; ii) the existence of void spaces in the cation-anion pattern within the liquid was recently highlighted, leading to the concept of “cage like” structure. Thus, ILs provide naturally the nanosized cavity able to confine the interacting species; iii) although the typical anions present in the most common ILs are considered as “non-coordinating”, remarkable cases of formation of coordination complexes between metal ions and the anions of the ILs are reported. In the cases considered, the formation of the complex between the IL's anion and the metal ion takes place inside the solvent cages, thus in strict proximity to the π -electron system of the IL's cation. This is the second object of this work: *generating, uncovering and interpreting the interactions between the metal center (or complex, if formed) and the adjacent π -system of the IL's cations in some selected metal-containing ionic liquids.*

The main purpose of this work was to investigate the physico-chemical properties and the spectroscopic behavior

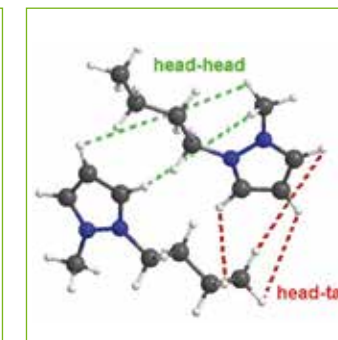
of selected transition metals framed in previously unexplored molecular environments. Two possible routes were identified. The first one was based on the formation of coordination complexes by using a collection of aza-[*n*]helicenes as ligands, thus obtaining complexes with unprecedented properties. An exploration of the electronic and physical properties of aza-[5]helicenes was started, obtaining useful indications on their electron density availability and racemization energy. Then, the target was to synthesize helicene/metal complexes and 4 new ones with platinum were obtained, using 5 and 6 membered helicenes with the N atom in position 4 and 5 in both cases (Figure 2). This gave the opportunity to observe very different intermolecular arrangement, simply depending from a slight variation in nitrogen position on the helicene ring, as proved by crystallographic data. With the aim to prepare chiral metal complexes, the reaction with separated enantiomers of the 4-aza[6]helicene was attempted, observing that, depending on the starting helicene ligand (enantiopure or racemic), the reaction led to different complexes (*cis* or *trans*) with different spectroscopic and chiroptical properties. This represented an unprecedented



1. Tridimensional helical structure of 5-aza[5]helicene



2. TX-ray molecular structure of the complex *cis*-PtCl₂(4-aza [6]helicene) (PPh₃)



3. Specific head to tail and head-to-head aggregation motives for pyrazolium cation.

use of chirality in transition metal complexes. The second route regarded the investigation of metal ion solutions in Ionic Liquids, which represent an innovative field of study. The properties of a well-known class of ILs, based on imidazolium cation, were compared with a brand new one, based on pyrazolium, structurally analogous to the imidazolium ILs, but with a different position of the nitrogen atoms in the heteroaromatic ring. Information on these new systems were obtained through NMR and DFT calculations (Figure 3). Then, the binary systems ILs/transition metal salts was investigated in both ILs classes, imidazolium and pyrazolium. Two main findings can be mentioned: i) the formation of stable association between the metal cation and the IL's anion

and ii) some remarkable cases of transfer of spin density from the metal to the IL's cations, as evidenced by NMR spectroscopy and thoroughly simulated at DFT level. These results confirm that the dissolution of metal ions in ILs is a complex process, with intermediate steps consisting of, inter alia, the formation of coordinated metal ions, the spin density transfer from the metal to the π -system of the IL and ligand exchange phenomena.

HIGHLY CONDUCTIVE STRUCTURED CATALYSTS FOR THE METHANOL SYNTHESIS

Andrea Montebelli - Supervisor: Prof. Gianpiero Groppi

From the industrial point of view, methanol synthesis from $H_2/CO/CO_2$ mixtures over $CuO/ZnO/Al_2O_3$ catalysts (ICI process, 1966) is a mature and well-developed process. The synthesis is carried out at 503-543K, 50-100 bar and is highly exothermic. At these conditions, the selectivity to methanol is very high, but the process yields are limited by thermodynamic equilibrium.

Fixed-bed reactors with quench or, more commonly, multitubular cooling are mostly used. For both reactor configurations, one direction towards process intensification concerns the accurate control of the temperature profile in the catalytic bed, in view of maximizing the syngas conversion per pass (in the direction of minimizing recycle ratios and therefore investment and operation costs) and the catalyst lifetime (i.e. to minimize the number of shut-downs) as well as minimizing the selectivity towards byproducts. Indeed, sintering of $CuO/ZnO/Al_2O_3$ catalysts starts at 573K, but the onset of selectivity loss is already observed at 543-553K.

In particular, in commercial externally-cooled multitubular packed-bed reactors the dominant convective heat transfer mechanism requires the adoption of high flow rates to grant acceptable heat transfer

coefficients and properly control the hot-spot in the reactor. This typically implies the use of long (i.e. several meters) tubes, which poses a serious limit to the possibility of developing compact reactor configurations. In this respect, thanks to their outstanding heat transfer properties, structured catalysts like washcoated honeycomb monoliths and open-cell foams, made of highly conductive substrate materials such as aluminum or copper, could be adopted for intensifying the methanol synthesis process. In particular, featuring a prevailing conductive heat transfer mechanism, independent of gas flow rates, conductive structured catalysts could enable the operation of compact multitubular methanol reactors, which is appealing for the exploitation of any type of feedstock available in limited amounts (e.g. syngas from biomass or stranded/associated gas reservoirs), otherwise unfeasible with conventional packings.

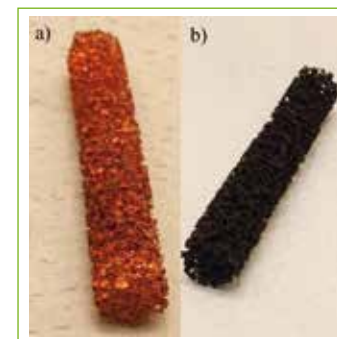
Nevertheless, the application of conductive structured catalysts to the methanol synthesis has been scarcely investigated in the literature and no industrial solution has been proposed so far.

In this context, the present work was devoted to investigate the potential associated with the

adoption of highly conductive structured catalysts in multitubular methanol reactors, within a collaboration with Total, France. By simulating the synthesis loop, the performances of three mathematical reactor models, namely the packed-bed (PB) (representative of the industrial units), the washcoated copper honeycomb monolith (HM) and open-cell foam (OF) reactors, were compared upon changing the fresh feed gas composition (i.e. the stoichiometric number) and the tube length at constant fresh feed flow rate to catalyst weight ratio. The latter study was specifically aimed at a preliminary assessment of compact reactor configurations with short tubes. It was found that, thanks to the effective convective heat transfer mechanism boosted by the high gas mass flow rates in full-scale reactor, higher radial heat transfer rates and lower hot-spot temperatures are granted by PB reactors, while this is not the case of structured reactors (SRs), wherein heat transfer is primarily governed by heat conduction in the thermally connected substrate. PB reactors exhibit, however, poor heat transfer performances in the case of short (i.e. 2-meter) tubes, where low gas flow rates are employed. On the contrary, SRs show nearly constant

heat transfer coefficients on reducing the tube length, as their dominant conductive heat transfer mechanism is flow independent. Contrary to PB reactors, therefore, compact SRs can be operated with lower recycle ratios and more limited hot-spot temperatures, which seems promising in perspective for small-scale MeOH synthesis processes for the valorization of feedstocks available in limited amounts.

Typical PB catalyst loads, however, are hardly feasible on structured catalysts according to the actual coating technology. Nevertheless, it was shown that compact multitubular reactors loaded with washcoated copper HM and OF could be also operated efficiently with lower catalyst volumetric fractions (i.e. down to $0.30 \text{ m}^3 \text{ catalyst/ m}^3 \text{ reactor}$), once the coolant temperature was suitably incremented to compensate the lower catalyst load: an optimal value for this temperature was found to be around 518K. Similarly, novel catalysts with enhanced activity could be used to increase the conversions per pass, thus making compact SRs configurations with low catalyst loads more appealing. Interestingly, the advantages of operating such compact SRs are eventually emphasized by the adoption of larger reactor tubes, in view of reducing the



1. Sample of 45 PPI, $\epsilon = 0.936$ copper open-cell foam a) before coating and b) after coating (14 wt.% washcoat load).

investment costs. Indeed, thanks to the effective conductive radial heat transfer, hot-spot temperatures as well as recycle ratios in compact SRs with larger (i.e. with diameters up to 63 mm) tubes can be kept limited. In the second part of the work, prototypes of washcoated copper open-cell foams (45 PPI, $\epsilon = 0.936$) were prepared by slurry-coating a commercial $CuO/ZnO/Al_2O_3$ powdered catalyst (Fig. 1). Washcoated copper foams (14 wt.% washcoat load) were then tested in the methanol synthesis at relevant industrial conditions to verify that the washcoating procedure does not significantly alter the catalytic activity. These data were collected in Trondheim, Norway, within a collaboration with the Norwegian University of Science and Technology (NTNU).

The coated foams proved active in catalysing the methanol synthesis reaction. This result, together with the previous findings, paves the way for the development of a novel compact multitubular reactor for the methanol synthesis loaded with conductive structured catalysts. Their activity was however lower than that of the original powdered catalyst. Chemical testing of slurried powder pointed out that the slurry deposition step does not affect the final catalytic activity of the structured system, being instead the slurry preparation step responsible for the activity loss. These results were confirmed by running RWGS experiments at atmospheric pressure. The qualitative accordance between CO_x conversion/MeOH productivities collected during high pressure tests and CO_2 conversion values collected during low pressure tests leads to conclude that the RWGS reaction can be considered as a representative probe reaction for ranking the intrinsic activity of $Cu/ZnO/Al_2O_3$ methanol catalysts without requiring operation under the high pressures and with the long transients typical of commercial methanol synthesis process.

IMPROVING INDUSTRIAL SAFETY BY NOVEL TRAINING AND ASSESSMENT METHODS (development, testing and validation)

Salman Nazir - Supervisor: Prof. Davide Manca

Improving profits and keeping the systems/processes safer are of paramount importance for all industries around the world. This work addresses the both, specifically for process industry. This study develops with interdisciplinary approach by combining expertise from Human Factor studies, Cognitive Sciences (Organizational Psychology, Training, Human Error, Situation Awareness, and Distributed Situation Awareness), Information Technology, Experimental Psychology, and indeed Chemical Engineering. Every year several injuries, fatalities and loss of millions of euros take place on account of abnormal situations and accidents in process industry. In this work, a training and assessment tool is proposed whose significance in terms of improving safety is demonstrated experimentally. In the first phase technical details of the tool are focused and later the details of experiments are reported. The aim of experiments was to study the impact of different training methods on the performance of operators in distinct scenarios. The results of the study conducted in this PhD work reveals the benefits developing performance indicators, automated assessment methodology, and of training in immersive environment. It was found that the participants who received training in immersive

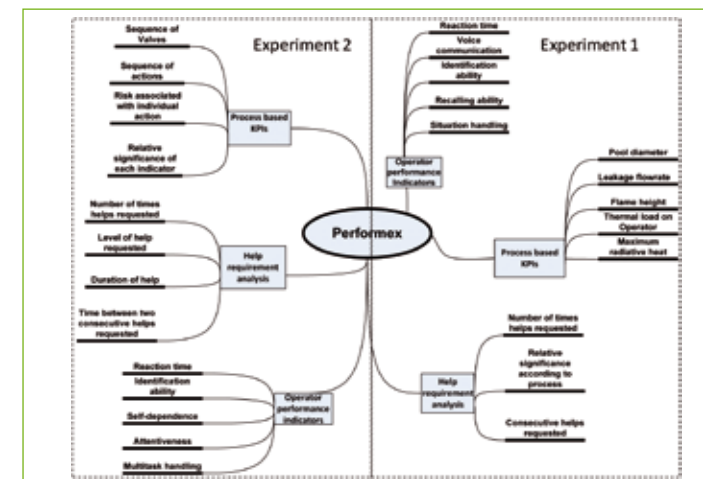
environment were able to reduce the impact of a simulated accident scenario as compared to the participants trained with conventional training methods. Moreover, the Distributed Situation Awareness of the former was better than the later. In the second experiment a variation in training within immersive environment was made and the results showed the effectiveness of a trainer in immersive environment. The thesis incorporates the relational and social complexity that industrial operators face. The training gap is identified based on existing learning theories and subsequently a comprehensive training syllabus is devised as a step towards implementation of the findings of this work in the process industry. The main findings of this work are as follows:

1. Industrial safety cannot be guaranteed by only focusing on conventional methods of approaching and analyzing it.
2. The application, adaption and implementation of Distributed Situation Awareness and Situation Awareness for industrial operators possess immense benefits in terms of improving safety, team work, communication and mitigating accidents. Further, the need for practitioners and designers to consider such concepts and theories is emphasized (Nazir et al. 2012; Nazir et al., 2014).

3. Proposed automated assessment methodology is an effective and efficient way of evaluating operators' performance. Developing hierarchy (see Figure 1) allows the trainee and trainer a tool for better training session and subsequent performance in training sessions and as well as in real plant (Manca et al. 2012a; Nazir et al., 2013c; Nazir et al., 2014b).
4. The ability of human beings to enhance their skills, understanding, comprehension, responsiveness, attention allocation, mental modeling and mental associations can be improved by different training methods (Salas et al. 2001; Nazir et al. 2012a; Nazir et al., 2013b). One of the contribution of this PhD work is the emphasis on training and the impact it can bring to the performance of industrial operators during normal operations and as well as abnormal conditions. Proposed training method (i.e. Immersive Training, see Figure 2a and 2b) resulted in improved and safer performance of the operators (Experiment no. 1a) and improved DSA (Experiment no. 1b) during a simulated accident scenario and as well as for a normal operating procedure (Experiment no. 2) (Nazir et al., 2012c; Nazir et al., 2013b; Nazir et al., 2014b; Manca et

al., 2013b).

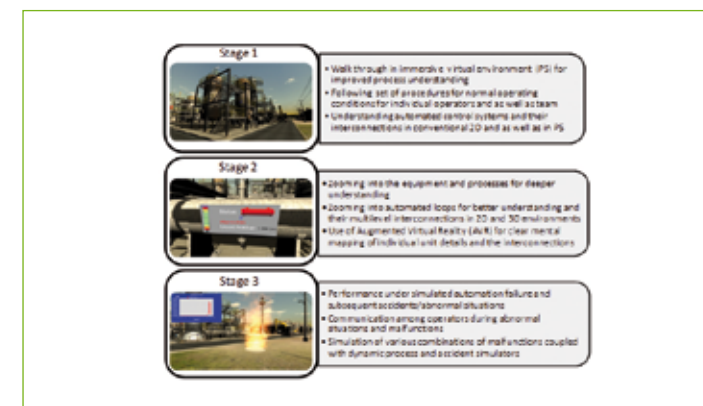
5. Synergizing expertise from different field of study, in this case; cognitive sciences, organizational psychology, human factors and chemical engineering results in most suitable method of training of industrial operator (as far as current literature is concerned) leading to safer operations, reduced accidents and eventual resources losses (financial and human) (Nazir et al., 2012a; Kluge, Nazir and Manca, (accepted).
6. Implementing the findings in order to develop training methods focusing on instilling operators with skills to handle automation challenges is introduced and elaborated in this work (Nazir et al., 2014c).
7. A Training Syllabus (see Figure 3) which incorporates some of the findings on this work is proposed as a step towards improvement in the conceptualization and rationalizing of Training in process industry, which is believed to be effective in reducing the abnormal situations, accident, non-routine shutdowns and increasing the profitability with higher safety. The proposed training syllabus is composed of three stages of increasing complexity (interconnectivity and dynamics) and is mainly aimed at inexperienced operators. The training for the understanding of the process components is also centered around the handling of real-time operations, but it "zooms in" to certain part/units of the plant in order to explain the general functionality. The introduction of unique nature of experiments in the Department of Chemical



1. A broad representation of assessment methodology for both experiments



2. a). Conventional Training. - b). Immersive Training.



3. The Hierarchical Training Syllabus.

Engineering may have long lasting impact in trending the new research activities and approaches. I believe that the outcomes of this PhD work has opened new horizons in the world of Industrial Safety and

provided CMIC (POLIMI) with new opportunities/perspectives to progress in the field of industrial safety with new collaborations developed during this PhD work under supervision of prof. Manca.

GREEN PROCESS INTEGRATION: INNOVATIVE PATHWAY OF BIOMASS TO METHANOL/DME SYNTHESIS

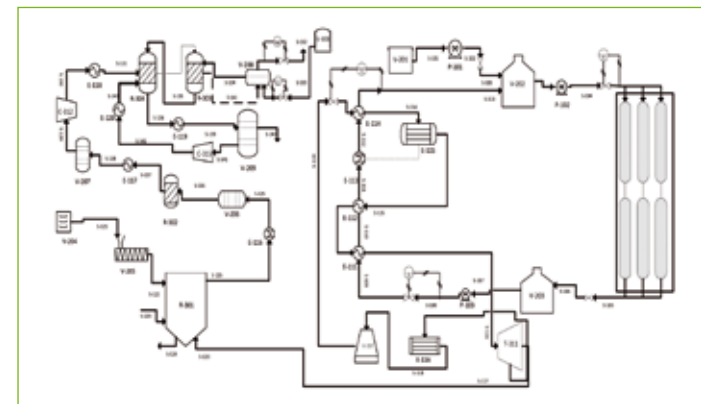
Zohreh Ravaghi Ardebili - Supervisor: Prof. Sauro Pierucci

The overall process of methanol/DME synthesis is modeled, simulated and integrated in unit process, initiating from a concentrated solar power (CSP) plant aimed to generating the low-temperature steam and in effect, supporting a low-temperature steam biomass gasification process with sustaining it towards syngas production. According to the application of syngas in this work designed to synthesis methanol/DME, H₂:CO ratio is adjusted relevantly by steam reforming to be adequate for mentioned application. All these considered, the entire process is integrated as a unit plant providing the green, sustainable process to fulfil the above-mentioned purposes. To the end that, starting from the ability of a process engineer to design, adjust and combine the units, and especially applying the green and renewable sources of energy through the process motivated this work to provide the innovative green pathway of methanol/DME synthesis. The main issues in modeling and study the practical feasibility of a novel solar-driven route from biomass to methanol/DME are related to the need of different tools and interdisciplinary competences. Actually, the discontinuous nature of CSP and the intrinsic dynamical behavior of TES technologies unavoidably

leads to the development of dynamic simulations. Conversely, steady state-models for biomass gasification and methanol/DME synthesis are enough to characterize such systems. Nevertheless, in these latter cases there is the complexity of considering either multi-phase, multi-scale and multi-step models (gasification process) easily leading to large-scale nonlinear systems or to handle networks of tubular reactors subject to very tight operating conditions (methanol synthesis process). Specifically, available commercial packages have been selected whenever the simulation can be carried out with existing models already implemented in these suites, whereas dedicated models have been developed when high reliability is required for the model prediction as local viewpoint as well as for the overall feasibility study. PRO/II steadystate simulator by Simulation Science is adopted for the steam methane reformer that processes the effluent of the biomass gasifier and for the heat exchange network to rationalize utilities in the unified plant. DYNSIM dynamic simulation suite by Simulation Science is selected to model the CSP and the direct TES technology. The selection of DYNSIM is dictated by two main reasons: the need of having the

best compatibility among all the selected tools; the flexibility of the dynamic simulator in exchanging data in realtime with the other tools and models to ensure the data synchronization during the calculations. MS Visual C++ and BzzMath library, with the possibility to exploit objectoriented programming and parallel computations, are selected for the modeling and simulation of the biomass gasifier and the methanol/DME synthesis reactors. Also, MS Visual C++ is adopted to improve some models in the simulation of CSP, with integration of the models into the DYNSIM environment. In this embedded context, MS Excel is selected as IT hub to collect the information of each system and make all of them consistent each other. This work presented and demonstrated the feasibility of an innovative green pathway in synthesis of methanol/DME in one step from low-temperature steam biomass gasification. In first step of this work, the concentrating solar power plant was modelled, simulated, optimized in order to generate the constant power through the 24-hours of a day in spite of intermittent nature of solar. Afterwards, the low-temperature steam is applied to drive the biomass gasification process, which was needed to investigate and demonstrate the

feasibility of low-temperature condition for the further unit. Therefore, all effective conditions such as: pre-treatment of feedstock, re-designing the gasifier were taken into account as the effective operating conditions. In this step, this green route produced syngas, is integrated into the methanol plant to synthesis methanol/DME. In addition of presenting an innovation in production process of a chemical (methanol/DME), overcoming on the complexity of design and integration of mentioned units in different software tools was the other remarkable achievement of this activity. Integrating the process in less energy-intensive and clean route was the other approach of this work to demonstrate the potential of renewable energies coupled with traditional units and processes. Therefore, this achievement in new models, simulation tools and information consistency as well, for this innovative pathway for biomass to energy carriers provided the feasibility of the entire plant from academy scale and gives the opportunity to extend in the industrial scale. Open issues are still the global optimization and energy integration of the utilities as well as the possibility to consider different technologies (for instance, different TES technologies in the CSP) and



1. One-step methanol/DME synthesis flowsheet in a green pathway.

process lines (for instance, the possibility to recover pure hydrogen) to make the overall system further appealing.

STUDY OF THE REACTION KINETICS OF GASSES WITH SURFACES

Stefano Valerio Ravasio - Supervisor: **Prof. Carlo Cavallotti**

This work is focused on the study of advanced kinetic mechanisms in several systems where there is an interaction between some components in a gas phase and an activated surface. Basically the gaseous reagents enter in a reactor where they undergo various chemical reactions. The energy necessary to promote such reactivity is supplied through a solid surface, located inside the area where the conversion takes place. Also material exchanges occur at the interface and a considerable part of the gaseous precursors might be deposited on the active surface. The control of the growth of such solid is a key aspect both in case that product is the target of the process, and when it is the result of an undesired side conversion. Hence the transport phenomena between the two phases act an important role in determining the performances of these systems, as well as the reaction kinetics.

The industrial applications of this type are actually countless, including the huge branch of chemical vapor deposition and a consistent part of catalysis. The reactors are designed on the basis of classical chemical engineering and the operative parameters should be selected in the best way to optimize the global performances. In particular, in

this study were analyzed three different processes where it is valid what stated above. The first one is a technology still in phase of investigation for the future use in the industrial scale that is the non oxidative conversion of natural gas in atmospheric non thermal plasmas. The others instead have been applied for decades to produce semiconductor materials, which are the chemical vapor deposition (CVD) of polycrystalline silicon and the metal organic vapor phase epitaxy (MOVPE) of gallium nitride. In all of the processes mentioned above, despite the wide interest for the large scale production, the kinetic mechanism has not yet been clarified and the reactors are actually managed following the results of a trial and error approach. Thus a better understanding of the fundamental chemistry and of how the kinetics is influenced by the heat and material exchanges can potentially lead to significant advantages. Indeed it should be a very useful tool for the optimization of the operative conditions and the reactor design with the final purpose to enhance the productivity of those systems, but also to limit the energetic costs, or to improve the quality of the products. The aim of this phd thesis is

to investigate the most critical aspects in the systems cited above, focusing in particular on their kinetics and fluid dynamics. The main issue was to develop a general methodology, which can be extended to other cases. As final result the method should provide useful guidelines to improve the global performances. Such approach was applied to describe three different processes of interest from the industrial point of view. The approach adopted was thus conceptually the same. The initial part consisted in assembling the kinetic scheme. A preliminary set of reactions was determined including what already proposed in the literature. Moreover a thermodynamic analysis helped to identify the most stable intermediates, which may have a significant role in the mechanism. After that, additional new classes of conversion routes were hypothesized for the first time. Accurate ab initio calculations were performed to evaluate the kinetic parameters of such new reactions, based on transition state theory. The precision of the computational techniques herein used was higher with respect to those previously utilized in the earlier articles for the processes object of the present study. Indeed the general tendency in the literature is to use the

density functional theory (DFT) for the estimation of the kinetic constants. At least that is what was found for the systems of interest. The methods based on that principle imply a limited computational effort, but on the other hand, the error on the activation energies could be very conspicuous (even 10-15 kcal/mol). The approach followed in this work instead combines the advantages of fast DFT with those of more rigorous techniques. The maximum error on the activation energies is around 2 kcal/mol. When relevant the low vibrational frequency associated to torsional motions was replaced by a 1D hindered rotor model. This improved the prediction of the pre exponential factors. Therefore also the constants taken from the literature were re evaluated in order to avoid comparing reaction pathways using kinetic constants calculated at different levels of theory. All the reactions were considered as reversible. Then the whole kinetic scheme was combined with a literature surface mechanism and tested with a program simulating a simple bi phase PSR reactor model. With that micro kinetic analysis was possible to find the most sensitive reaction pathways and to discard from the mechanism those without any noticeable effect on the global conversion rates. Once achieved the final set of reactions, the estimation of the pre exponential factors was further refined. However the transport phenomena in fact heavily influence the performances of real reactors. Thus fluid dynamics models were developed and finally solved

including the new proposed mechanism. The methodology described was applied to all the three processes, but paying more attention at different aspects in each of them, depending on the respective focuses and background of knowledge. The first part of the work was dedicated to the non oxidative valorization of natural gas through non thermal plasmas. The simulations are consistent with the results reported in the literature, that have demonstrated the possibility to achieve elevated acetylene yields with energy efficiencies comparable with those of thermal processes. Moreover one of the main findings of this study is that the temperature evolution in the plasma volume plays a key role in determining the system reactivity and its energy consumption. Among the conclusions of this study are included a set of guidelines that may be useful to improve the energy efficiency of plasma methane conversion. Then it was studied the silicon CVD from trichlorosilane. A micro kinetic analysis revealed that a radical chain mechanism, never proposed before in the literature, should be predominant in the gas phase of industrial Siemens reactors. These conversion pathways have lately been proved to be effective also during SiC growth. Furthermore it was pointed out a strong inter relation between the reactivity in the two phases because of the consumption of the corrosive HCl in the gas, produced during the deposition. Thus operating Si CVD in conditions in which the gas phase reactivity is favored (i.e. at high gas phase temperatures)

should enhance the precursor conversion and the film growth rate, though at the expense of an increased production of tetrachlorosilane. Finally this research was also focused on GaN MOVPE. Such project was in cooperation with two groups in TODAI and part of the phd thesis was spent in Tokyo. During that period the more strict collaboration has been crucial to coordinate the modeling work with the aimed experimental campaign. A good agreement between simulations and experiments was achieved. With the hypothesis proposed it has been possible to clarify the various phenomena that take place in the reactor during the film growth and to explain the effect of several operative parameters. Thus the model can be used as a means to achieve higher growth rates, as well as to reduce the powders drop on the substrate. In conclusion the methodology here proposed was successfully proved to be a useful tool to optimize the operative conditions for different type of processes with a subsequent improvement of their global performances.

NO_x STORAGE-REDUCTION (NSR) CATALYTIC PROCESS FOR NO_x REMOVAL FROM MOBILE SOURCES

Laura Righini - Supervisor: Luca Lietti

Nowadays lean-burn engines (e.g. Diesel fuelled) are achieving approximately 50% of European market share and are gaining interests in the US as well, due to their superior fuel economy and lower CO₂ emissions. The main concern related to their application is the NO_x removal under oxidizing atmosphere since the current Three-Way-Catalysts are effective only under stoichiometric conditions. Consequently SCR (Selective Catalytic Reduction) and LNTs (Lean NO_x Traps) technologies have been introduced and extensively studied to cope with the upcoming restrictive legislations (Euro VI and Tier 2 Bin 5). LNTs, also referred to NO_x Storage Reduction (NSR), has been developed by Toyota in '90 and has revealed more suitable for light duty cars. These catalytic systems mainly comprise: precious metals (Pt, Rh, Pd) to catalyze oxidation and reduction reactions, a storage component (an alkali or alkaline-earth metal like Ba or K) and additives (Ce, Zr), supported on a high surface area material, as γ -Al₂O₃. The LNT concept requires a catalyst that works cyclically, alternating a fuel lean phase, occurring under normal engine operation, during which NO_x are stored (as nitrites and nitrates), with a short fuel rich phase of few seconds, when the exhausts are deliberately made

rich to reduce the stored species into harmful compounds, like N₂, along with by-products, as NH₃ and N₂O. This technique has been already studied and commercially applied on diesel engines, but there are still many open issues regarding understanding of storage and reduction mechanisms as well as the role of the catalytic components. Currently numerous studies are carried out to optimize the operative conditions and to improve the catalytic formulations. The aim of this PhD thesis is to provide a deepen comprehension of the storage/reduction mechanisms along with a better understanding of the role of catalytic components. For this purpose an experimental activity has been developed, concerning preparation and characterization of catalytic materials, followed by testing their catalytic reactivity. The synthesized catalysts have been characterized by BET surface area measurements, precious metal dispersion with H₂ chemisorption, XRD along with XPS and in situ FT-IR analysis in collaboration with other research groups. Information about reaction steps sequences and mechanisms have been gained through transient techniques, by imposing changes of

temperature or concentrations to the reactant system and continuously following products and intermediate species. The activity has been mainly focused over PtBa/ γ -Al₂O₃ catalyst and comparison between results of different catalytic formulations let to obtain information concerning the role of active elements and thus how to improve catalytic formulations. According into recent interests towards regeneration mechanisms, the reduction is generally believed a Pt catalyzed process that it implies at first the NO_x release from the catalyst surface in the gas-phase (1st step), followed by the fast reduction of the released NO_x to N₂ or other by-products (2nd step). Concerning the NO_x release, driving forces have not been clearly identified and investigations about the NO_x release are lacking mainly because this step can be hardly separated from the subsequent reduction processes. Hence ¹⁵N/NO isotopic exchange technique has been used to decouple NO_x release and subsequent reduction processes. Data of this Thesis have pointed out that the NO_x release is the rate determining step of the reduction process and it has a chemical nature, driven by reduced Pt sites, while no thermal decomposition of the

stored species has to be invoked. The following reduction of the released NO_x to N₂ proceeds through different pathways depending on the applied reductant, e.g. H₂, CO, HCs (mainly C₃H₆ and C₃H₈). Formation of N₂O by-product is also recently gaining interests, being one of major greenhouse gas. In the case of regeneration with H₂, it has been proposed a two-step in series mechanism, involving at first the fast reduction of stored species to obtain NH₃, followed by the slower reduction of the stored NO_x by NH₃ to N₂. Nevertheless, many issues still remain open concerning the molecular pathways leading to N₂ and N₂O as long as factors ruling the selectivity of the regeneration process. Moreover, most published work focused on the regeneration in the absence of gaseous NO, while on real systems it is present also under rich fuel periods. Isotopic labeling experiments, by means of ¹⁵NO+NH₃, have been employed in this work to point out pathways leading to formation of N₂ and N₂O. Results have suggested that once NO reaches Pt sites, the molecule dissociates, leading to a pool of N, O, H ad-species. These ones along with undissociated NO and NH_x molecules populate noble metal sites and their concentration is ruled by the temperature and gas phase composition. Hence if Pt is not efficiently reduced NO dissociation is prevented and the resulting NO can: i) be released; ii) combine with a N atom (either coming from NO or NH₃) to give N₂O; iii) react with NH_x fragment to form N₂ via a SCR-like route. If Pt is reduced, NO is dissociated

and N ad-atoms statistically self-condensate over Pt sites with another ones, coming from NO or NH₃ molecules, to form N₂. High H/N ratio promotes the hydrogenation of N ad-atoms to NH₃. In this picture the presence of gaseous NO does not alter pathways to form N₂ or N₂O but the selectivity of the process, by changing the relative abundance of NO undissociated molecule over Pt sites and by decreasing the efficiency of Pt sites reduction. In order to study reduction mechanisms also with molecules representative of the HCs present in the exhausts, the reactivity of n-heptane with gaseous and stored NO_x also in the presence of H₂O and O₂ has been deepened. The collected results have pointed out that the n-heptane is able to reduce NO_x (either gaseous or stored species) and no intermediates, as NCO, have been evidenced. Accordingly, also in this case, the HC keeps Pt reduced and N, H, O along with C_xH_y fragments populate Pt sites, whose recombination explains products evolution. In the presence of H₂O and O₂, respectively, parallel reduction routes via H₂ (formed via Steam reforming and Water Gas Shift) and via CO (formed by HC oxidation) are effective, but not relevant. Hence in the presence of O₂ trace amounts of NCO have been detected, whose formation is likely related to the presence of CO (NCO are typical intermediates in the regeneration with CO). Commercial catalytic converters contain also Ce as a promoter or support, mainly due to its oxygen storage capacity (OSC), its redox properties (Ce⁴⁺/Ce³⁺), its ability to stabilize

alumina and to increase Pt dispersion. Previous studies collected opposite trends about the role of Ce in the improvement of the storage capacity, of the selectivity to N₂ and of S resistance. Up to now Ce optimum loading and its role in the storage and reduction processes still have to be identified. According to the here collected results, improved catalytic formulation could be obtained through addition of Ce as a promoter. Finally, increasing attention towards K storage compound has been shown recently for high temperature applications, although issues concerning the K stability has to be still overcome. Some authors reported promising application of potassium titanate based LNTs systems, where the mobility of K has been decreased through the reaction between K and TiO₂, nevertheless their storage properties, stability along with adsorption/reduction mechanisms have to be rationalized. Research activity performed abroad at PNNL (Richland, WA, USA) has evidenced that K improves high temperature performance, even if many issues concerning the stability of K phase are still open.

SYNTHESIS OF NEW LEAD COMPOUNDS WITH FUNGICIDAL ACTIVITY

Manuela Riservato - Supervisor: **Dott. Giampaolo Zanardi**

The aim of lead generation both in agrochemical and in pharmaceutical research is the discovery of molecules which cause a specific biological effect. In the case of agrochemicals, this means control of weeds (herbicides), fungi (fungicides) or insects (insecticides). Lead generation is the earliest stage in the discovery process of agrochemicals. Although terminology differs from company to company, lead is understood to be a chemical compound with defined biological activity against an agronomically important target species. Pharmaceutical leads are usually defined as having inhibitory activity against an enzyme or (ant)agonistic activity against receptor, i.e. *in vivo* activity. The emphasis on *in vivo* activity reflects the fact that agrochemicals can be screened directly against the target organism. Early *in vivo* activity studies of agrochemical leads are done under glasshouse conditions or even in highly artificial *in vivo* high-throughput-screening (HTS) set-ups. The transition to field tests represents a significant hurdle which a large proportion of leads fail, even after optimization work. In addition to activity in the field, the (biochemical) mode of action of agrochemicals has to be established as part of the registration process for

new products. This may require isolation and characterization of the molecular target, i.e. enzyme or receptor. Hence, it could be argued that *in vitro* activity studies are carried out at a later stage with *in vivo* activity being used as initial filter. Both pharmaceutical and agrochemical lead discovery use rational and random methods to generate compounds for screening. Compounds for random screening can come from historic compound collections, combinatorial chemistry, natural products or often imitative approaches (me-too chemistry). Rational design of compounds for screening refers to methods which pre-select or design compounds on the basis of information about the target site of action - structure-based design - or on the basis of structural similarity to known active compounds. Aim of this project is to find a new broad spectrum fungicide mainly active on the diseases of cereals, being inspired by chemical structures found in nature. As a result of constant monitoring of the scientific literature on this topic, we first identified new lead compounds from natural sources, with some antifungal activity. On this basis we hypothesized new classes of molecules, patentable and endowed with biological activity

for use in the agronomic field. Convenient method of synthesis for a number of molecules belonging to each class were selected and applied in our group laboratories. The synthetic intermediates and the final molecules were analyzed by the common analytical methods used in organic synthesis such as HPLC, LC-MS, GC, GC-MS and NMR. The products thus obtained and characterized were sent to biological evaluations, including both *in vitro* and *in vivo* studies. Data from *in vitro* activity carried out on a variety of fungi highlight the intrinsic activity of the molecules, and allow assessing the sensitivity of a certain strain towards the compounds under exam. In order to assess the spectrum of activity of our molecules, they were tested *in vivo* in greenhouse on the main diseases in preventive and curative tests. The first section of our research work was carried out starting from natural products, focusing on simplification of their chemical structures. Our research activity took the structure of tautomycetin, a natural molecule, as its initial model. Tautomycetin is a highly potent and specific protein phosphatase inhibitor isolated from *Streptomyces*

griseochromogenes. Inspired by unusual dialkylmaleic anhydride moiety shared by tautomycetin and tautomycin, we expanded our search for a simplified structure, found in chaetomelic acid A. This class of alkyl dicarboxylic acids that were isolated from *Chaetomella acutisetata*, are potent and highly specific farnesyl-pyrophosphate (FPP) mimic inhibitors of Ras farnesyl-protein transferase. Himanimides, other natural molecules, were isolated from basidiomycete culture as new maleimide derivatives which inhibit the growth of bacteria and fungi. In particular, the structure of himanimide C, possessing the N-hydroxylated maleimide moiety, was investigated by us as a lead compound. Ultimately the use of 3,4-disubstituted maleimide derivatives was patented as plant growth regulators, characterized by low rates of application. According to previous results, we decided to address our project to the discovery of fungicide molecules preserving the structure of maleic anhydride and imide and to introduce two different substituents in the 3,4 sites of the anhydride/imide ring. Natural product maleic anhydrides and maleimides have attracted the interest of several groups exploring their biological activity. The best synthesis path to diphenylmaleic anhydride was a Perkin condensation of benzoylformic acid as the mixed K-Na salt with phenylacetic acid by acetic anhydride. The synthesis of the maleimide was performed by treatment of anhydride with urea. Similarity, the treatment of the

anhydride with N-Hydroxylamine hydrochloride gave the N-hydroxylated product. Greenhouse data evidenced that our compounds had promising activity but showed drop in persistence, i.e. reduced activity over time, probably due to chemical degradation. In order to obtain more stable chemical structures and consequently improved persistence, we undertook the synthesis of compound belonging to the class of natural fimbrolide analogues, and their screening for biological activity. Fimbrolides, which have been isolated from red marine algae *Delisea fimbriata*, are bromobutenolides with interesting antifungal and antimicrobial properties. In the second section our studies continued on the synthesis of structurally natural and unnatural products using cyclic anhydrides as precursors. We concluded that diphenylmaleic anhydride structures, together with the fimbrolide analogues, can be used as potential precursors for the synthesis of several bioactive compounds. All of the compounds were evaluated in our biological screening against the major plant pathogens, but in contrast to the obtained data, we evidenced the main drawback related to the stability of the molecules and the activity persistence. The preparation of additional compounds belonging to this class is currently under evaluation and the project will be continued in our chemistry department. We then continued our exploration on a parallel branch, in an effort to further increase

the activity and transfer the data on a large scale, in order to obtain an active product to be applied in field tests. The third and final part was dedicated to a molecule proposed for development, its chemical synthesis study and its application on pilot plant. We pursued the synthesis of a series of analogues starting from the andrimide structure. Andrimid is a pseudopeptide antibiotic, first discovered from the culture broth of an intracellular symbiont of *Nilaparvata lugens*. Its chemical structure includes β -phenylalanine and L-valine groups. Our purpose was to exploit the portion of L-valine, an amino acid which is common in nature and readily available as chemical. Dipeptide compounds are known, having high antifungal activity, consisting of the L-valine conjugated through its carboxyl group with a β -aromatic amino acid, whose free carboxy and amino functions may be suitably derivatized and whose structures can be attributed to a single general formula. The synthesis of several analogues and their biological evaluation led us to extract a synthetic study of a best candidate molecule and its final application on pilot plant intended to produce about 120 Kg of product per batch. The optimization carried out so far has had as its main effect in the preparation of a macro sample with satisfactory reduction of the costs and number of steps.

EXPERIMENTAL AND MODELING INVESTIGATION OF NH₃ SCR REACTIONS OVER V-BASED AND FE-, CU-PROMOTED ZEOLITE CATALYSTS

Maria Pia Ruggeri - Supervisor: Prof. Isabella Nova

NH₃-SCR is a well-established technology for NO_x abatement from stationary sources, such as power plants. However, compliance of upcoming standard pollution regulations for Diesel engines both in European countries and in USA, requires the development and the application of aftertreatment systems which can effectively reduce NO_x in transient conditions. Among the available technologies, the Urea/NH₃-SCR has been successfully adapted in the last decades as a promising solution for NO_x abatement, from both heavy duty and light duty Diesel vehicles.

This technology implies the use of a catalyst and of a reducing agent provided in the form of a urea solution which rapidly decomposes, generating NH₃, above 180 °C.

Typical catalysts used in the SCR aftertreatment systems are extruded monoliths of V₂O₅ supported on TiO₂/WO₃ and wash-coated honeycomb catalysts in which the active phase consists of a metal exchanged zeolite. In particular, Cu- and Fe- promoted zeolites exhibit good deNO_x performance with good potential in increasing low temperature activity and catalyst stability at high temperatures. Since exhaust gases contain for the greater part NO, the main reaction occurring in this

systems is the Standard SCR reaction, in which NH₃ reacts in a stoichiometric 1:1 ratio with NO to give N₂ and H₂O as products.

However, considering realistic aftertreatment configurations, a DOC (Diesel Oxidation Catalyst) device is always placed upstream the SCR converter thus determining an increased NO₂ content in the exhaust, due to the occurrence of NO oxidation to NO₂.

This greatly enhances the deNO_x performance of the whole combined system, as onto the SCR catalyst the Fast SCR reaction (in which NH₃ reacts with equimolar amounts of NO and NO₂ to give N₂ and H₂O) becomes dominant, being well known as very active already at low temperatures (180-250°C). The mechanism of the Fast SCR reaction has been widely discussed in literature and a general agreement on a three-step mechanism has been achieved: i) NO₂ disproportionates to nitrites and nitrates; ii) NO reduces nitrates to nitrites; iii) NH₄NO₂, formed by interaction of NH₃ and nitrites, decomposes to N₂ and H₂O.

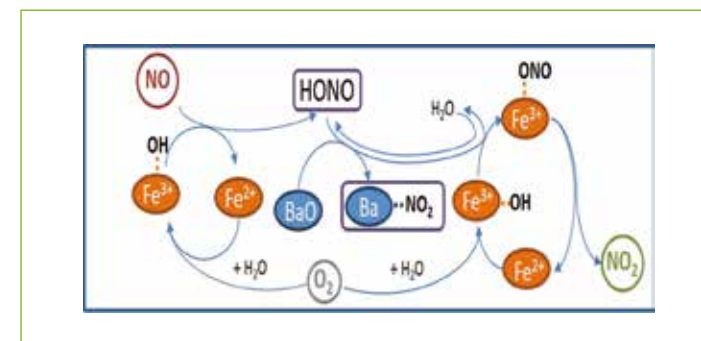
On the contrary, the Standard SCR mechanism is still object of debate. Indeed, a mechanistic proposal supported by several authors in literature, implies a two-step mechanism in which i)

NO is oxidized by O₂ to NO₂ and ii) NO₂ reacts with additional NO according to the Fast SCR. Since Fast SCR is much faster than NO oxidation, the latter becomes the rate determining step of the whole Standard SCR process. This mechanism is consistent with the fact that SCR catalysts are reported to be active in NO oxidation. However, scattered experimental evidence available in literature contrasts with this hypothesis. Investigation of such fundamental aspects is, of course, of crucial importance for a better understanding of the SCR process and could provide important information for the development of improved catalysts, thus having a positive impact on the overall performance of SCR systems. Moreover, despite being already commercially available and successfully applied, the NH₃-SCR technology still presents few aspects which could be improved from a practical point of view. As an example, the need for accurate predictive simulations of SCR converters behavior during the development of aftertreatment systems requires the applications of mathematical models accounting not only for catalytic activity, but also for physical phenomena such as mass transfer effects and diffusional limitations. Another important issue

regards catalyst ageing. Indeed, the understanding of ageing phenomena could lead to improvements in catalysts formulation. Furthermore, ageing phenomena, possibly occurring during real SCR applications, should be taken into account by effective mathematical models of SCR converters.

Finally, the upcoming stringent emission limits lead to a growing interest in expanding the operational temperature window of SCR catalysts. In fact, the need for urea injection sets a technological limit of utilization of this technology above 180°C. On the other hand, at low temperatures, namely at the engine start up, considerable amounts of NO_x are emitted and exhaust temperature levels will become lower and lower with increasing fuel efficiency of the combustion engines.

The aim of the present PhD thesis is the investigation and the elucidation of the abovementioned aspects related to the application of the NH₃-SCR technology for Diesel exhaust aftertreatment. Research activities have included the experimental and modeling investigation of SCR reactivity over different catalytic commercial systems: V-based catalyst, Fe zeolite, Cu zeolite. A study performed on a commercial V-based extruded



1. Mechanism of NO oxidation on the mechanical mixture of Fe-ZSM-5 and Ba/Al₂O₃

monolith revealed that mass transfer limitations resistances affect NH₃ and NO_x conversions to an extent depending on temperature and on the NO₂/NO_x feed content. A very simplified approach was developed for the model description of hydrothermal ageing of a Fe zeolite commercial catalyst: a mathematical correlation between catalysts deactivation and ageing conditions was established and could be effectively used to generate model predictions of the SCR activity of aged catalysts. Phenomena occurring at the engine start up were successfully reproduced at the lab scale on a Cu zeolite commercial SCR catalyst. The set of dedicated lab-scale experiments, addressing the individual mechanistic steps, provided a full

rationalization of the peculiar cold start phenomena observed in engine test bench runs. The mechanism of NO oxidation and Standard SCR was investigated by means of steady state data and in-situ DRIFT technique on a Cu-CHA catalyst. Moreover, an original technique, Chemical Trapping, was developed for the ex-situ mechanistic investigation of the same reactions on a Fe zeolite catalyst. A comprehensive mechanism for both NO oxidation and Standard SCR was formulated (§ Figure 1), which is able to account for all the phenomena observed experimentally.

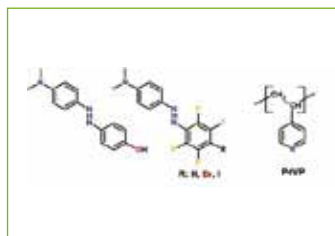
ENGINEERING EFFICIENT MATERIALS FOR OPTOELECTRONIC APPLICATIONS THROUGH HALOGEN BONDING

Marco Saccone - Supervisor: Prof. P. Metrangolo

The vast majority of supramolecular systems used for materials applications is based on the most common non-covalent interaction, namely hydrogen bonding, however in recent years another non-covalent interaction has been studied and applied in these systems, becoming more and more relevant: the halogen bonding (XB).

Halogen bonding could be defined as an attractive interaction between an electrophilic region associated with a halogen atom in a molecular entity and a nucleophilic region in another, or the same, molecular entity. Recent applications of XB in materials science includes for example the self-assembly of liquid crystal from starting molecules that don't display any mesomorphic behaviour, magnetic or conductive crystals and even luminescent materials. Even more recently, halogen bonding has been used for the assembly of supramolecular photoswitchable materials that proved to be more effective than their hydrogen bonded analogues.

Photoresponsive hydrogen bonded supramolecular polymers were extensively investigated by Priimagi and Vaapavuori. Very interesting results from a comparison between supramolecular



1. The chemical structure of the azobenzenes used by the Italian-Finnish collaboration and the structure of the poly(4-vinylpyridine).

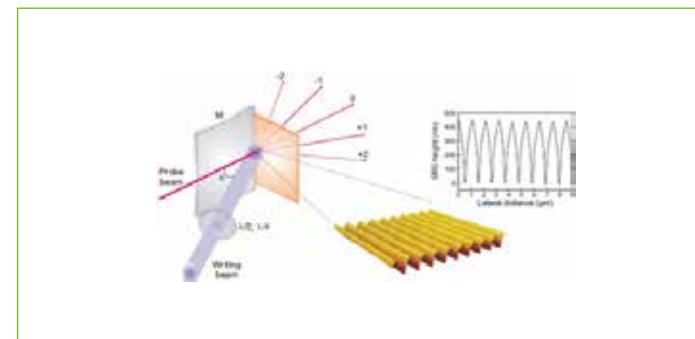
polymers having hydrogen and halogen bonding donor azobenzene molecules were reported in 2012 by an Italian-finnish collaboration. In Fig. 1 are reported the materials used in that paper. Given the fact that it has basic sites that could interact with both hydrogen and halogen bonding donors, the poly(4-vinylpyridine) was used as polymer matrix. A new class of *push-pull* azobenzene molecules were designed and synthesized, having a fluorinated ring with a halogen atom in para position (para in respect to the azo group). The molecule with the H atom para to azo was also prepared as a control molecule. In these molecules the phenomenon of surface relief grating (SRG) formation was investigated. The SRG formation is a kind of photoinduced motion occurring mainly in a thin film is irradiated with an

optical interference pattern, the material starts to migrate and move away from high-intensity areas to form a replica of the incident irradiation in the form of a surface-relief grating (Fig. 2).

It was found that the SRG formation efficiency develops in the order $I > Br >> H$ and also the surface modulation depth was superior in the iodine containing azobenzene. The non-fluorinated azophenol was used to compare an hydrogen bonded azobenzene with the new halogen bonded systems, and quite surprisingly, the halogen bonded azobenzene with the iodine atom was superior to the azophenol, despite the fact that the latter is much strongly bound to the polymer matrix.

In this thesis I discuss about three topics.

The first deals with halogen bonded photoresponsive polymers: the objective is to extend the work that has been done in this direction and that is described previously. This extension features a more appropriate and consistent comparison between perfluorinated azobenzene molecules containing halogen atoms (Fig. 1 center) and the perfluorinated equivalent of the azophenol dye (Fig. 1 left). By comparing the SRG formation



2. Experimental setup for the inscription of surface-relief gratings. $\lambda/2$ and $\lambda/4$ denote wave plates that are used to control the polarization of the irradiation beam, and M refers to a mirror that reflects half of the incident beam onto the sample to form the interference pattern.

efficiency in the polymer-dye complexes I demonstrated that halogen bonding unequivocally surpasses hydrogen bonding in driving surface patterning phenomena.

The second topic is related to the first and is totally new: I designed and obtained the first supramolecular small-molecule complex capable to display not only highly efficient SRG formation but also an high degree of photoalignment. This complex displays a nematic liquid crystalline phase that is known to enhance the degree of photoinduced anisotropy (photoalignment). The complex is assembled combining the perfluoro-azobenzene bearing a iodine atom reported in Fig. 1 and a derivative of the 4-alkoxystilbazole which is a known promesogenic molecule.

The complex is thus halogen bonded and, as I said previously, halogen bonding promotes an efficient photoinduced mass transport on thin azobenzene films upon irradiation with an interference pattern of light.

The third topic consists in the halogen bonding driven self-assembly of novel supramolecular architectures for application in the field of liquid crystals and photomechanics. For this purpose, molecules such as 1,2,4-oxadiazole heterocycles and perfluorinated azobenzene derivatives, were employed.

To accomplish these objectives, a wide range of methodologies were employed. I started with the synthesis of all the molecules used in these studies, followed by a complete spectroscopic characterization that includes

also single crystal and powder x-ray diffraction. I investigated the optical properties at the department of Applied Physics in Aalto university together with Dr. Arri Priimagi and under his supervision. Atomic force microscopy was employed to probe the SRG formation in polymers and liquid crystals and polarized optical microscopy was used to assess the features of the mesophases.

OPTICAL CORRELATION TECHNIQUES IN GELS AND BIOLOGICAL SYSTEMS

Eleonora Secchi - Supervisor: Prof. Roberto Piazza

The characteristic microscopic length scales comparable to the wavelength of light makes “soft” materials like colloidal sols and gels suitable to be investigated by optical methods. While earlier structural and dynamic investigations have mostly relied Dynamic Light Scattering (DLS), in the past few years real-space visualization methods have provided novel insights about colloidal structures. Whereas a DLS setup require a laser and sophisticated electronic units, one of main advantages of microscopy studies is that they can be carried on using widespread commercial instrumentation. Yet, several concepts in Fourier and statistical optics on which static and dynamic light scattering are based can be profitably exploited to turn a microscope into a much more powerful instrument than a simple visualization tool. Two recently developed techniques, Photon Correlation Imaging (PCI) and Differential Dynamic Microscopy (DDM), have helped bridging the gap between real-space imaging and DLS. In PCI, the image of the sample is formed on a 2D detector by the laser light scattered in a narrow range of scattering vectors; this configuration allows to study the sample dynamics by means of a correlation analysis quite similar to DLS, but retaining at the

same time the spatial resolution typical of imaging techniques. DDM, conversely, allows gaining dynamic information equivalent to that obtained in DLS experiments by processing microscopy images using Fourier optics. Both techniques basically measure statistical fluctuations, describing them in terms of correlation. Correlations and fluctuations are related to the concepts of spatial and temporal coherence of an optical radiation field, which are exploited in this PhD thesis to develop particle velocimetry techniques, and to apply them to the investigation of three distinct subjects in soft matter science. Combining of the power of a well-established intensity correlation technique like DLS with standard microscope imaging, we have developed a new velocimetry technique, named **Ghost Particle Velocimetry (GPV)**. This new approach is based on imaging the scattering speckle pattern generated by a flowing suspension, wherefrom the full velocity field can be reconstructed by evaluating spatial cross-correlations of the difference of two images acquired at closely related times. The novelty of this approach is that we track the motion of the speckle pattern rather than that of “seed” particles: hence, the size of the seeded particles,

which just play the role of scatterers can be much smaller than the resolution limit of an optical microscope. The addition of tracers is not even necessarily required, since the speckle pattern to be tracked may be directly generated by sufficiently strong refractive index fluctuations in the investigated system. Thanks to the partial coherence of the white light source, which limits the longitudinal spatial coherence, only a limited region of the sample along the direction z of the optical axis is probed, which in fact yields a rather good 3D spatial resolution of the velocity field even along z . Besides, such a limited longitudinal coherence of the source makes the technique suitable to investigate turbid sample with negligible multiple scattering effects. GPV can readily be performed using a standard optical microscope, but a setup suitable to investigate much larger samples can also be implemented by simply illuminating the sample with a LED source, and collecting the transmitted light through a stopped down optics. As I shall explain in detail in the remaining part of this report, these very generic requirements allow to apply the technique manifold systems. The subject of the first part of my work is an experimental analysis of the **sedimentation**

of colloidal gels, an extensively studied topic for both fundamental and practical reason. Colloidal gels are viscoelastic systems that yield under a weak stress, due for instance to their own weight. Aim of the investigation has been obtaining a comprehensive description of the structure and restructuring kinetics under gravity of weak colloidal gels using a combination of several optical techniques, (DLS, PCI, polarimetry, and video imaging) allowing to access complementary information about the sample. We first mapped the phase behavior of the system, and in particular the region where a liquid-liquid (L-L) separation is observed. Within the L-L coexistence region, a kinetic arrest of the spinodal decomposition process leads to the formation of disordered gels, whose susceptibility to gravity was found to depend on the location within the phase-separation region. At low particle and/or depletant the gel network breaks into free-falling clusters that re-compact into a dense, slowly restructuring amorphous solid. A novel evidence concerns the shape of the kinetic sedimentation profile, showing two distinct columns where the particle concentration is roughly uniform and characterized by completely different internal dynamics. At higher MFA or surfactant concentration, the gel compresses uniformly, forming a column with increasing particle concentration, surprisingly behaving as a solid, rather than a fluid-like structure. Optical correlation methods were then used to investigate **ionic-bond polymer gels**

made of **alginate**, which typify a large class of bio-gels stabilized by non-covalent cross links that display, after they are synthesized, a consistent spontaneous restructuring kinetics. In order to understand gelation kinetic and subsequent restructuring effects, a detailed optical study of alginate gels generated by slow perfusion of CaCl_2 , was performed using PCI. Since the macroscopic elasto-mechanical properties of the gel keep trace of the evolution of the microscopic dynamics, this optical analysis was supplemented with uniaxial compression test and stress relaxation tests, performed on samples kept in the gelation bath for variable times. The gelling kinetics displays a peculiar non-diffusive behavior, and the subsequent restructuring of the gel structure shares several features in common with the aging of colloidal gels, in particular for what concerns the occurrence of heterogeneous dynamics effects. The comparative analysis of the gel macroscopic mechanical properties at different aging stages further highlights distinctive effects arising from the non-permanent nature of the bonds. In the third part of this thesis, I have investigated systems made of “self-propelling” Brownian particles, namely, **concentrated suspensions of bacteria**. A suspension of motile bacteria is the simplest realization of “active” matter and represents a convenient experimental and theoretical model to examine fundamental aspects of collective behavior, such as that exhibited by swarming microorganisms, fish

schools, flocks of birds and even pedestrian crowds Concentrated bacterial suspensions often exhibit emergent patterns and self-organization that are not shared by “passive” systems, such as swarms and vortices, which shed light on the subtle interplay between hydrodynamic interactions, oxygen consumption, chemotaxis, diffusion of nutrients and mixing. Nontrivial properties come from the collective dynamics, including dynamic instability, nontrivial stress-strain relations and viscosity reduction. We obtained a detailed characterization of bacterial flow patterns using GPV, without tracers addition. In particular, we have investigated the effect of flow on a concentrated suspension in accurately controlled laminar flow conditions generated in a microfluidic channel. The effect of a shear flow has been tested on concentrated active and inactive suspensions at different concentrations. The shape of the average velocity profile changes in time, displaying an intermittent-flow behavior, which is detected only for suspensions of living bacteria and can be ascribed to the formation of coherent structure and local reduction of the solution viscosity.

SURFACE MODIFICATION OF CARBON-BASED MATERIALS BY FLUORINE-CONTAINING REAGENTS

Sadaf Talae Mashhadi - Supervisor: Prof. Walter Navarrini

Carbon nanotubes (CNTs) are chemically stable and a mechanically hard material due to their delocalized π electron systems. Nevertheless, their application has been limited in some cases by the difficulty in dispersion and compatibility with different media, especially in fluorinated phases. Therefore, we attempted to functionalize CNTs in order to improve their dispersibility and facilitate their manipulation.

Linear (Z) and branched (Y) perfluoropolyether (PFPE) peroxides were used for the functionalization of the sidewall of multi-walled and single-walled carbon nanotubes (**MWCNTs** and **SWCNTs**), because highly reactive PFPE radicals formed during its thermal decomposition could react with the π -electron systems of CNTs. The chemical treatments of CNTs with PFPE peroxides led to the formation of non-peroxidic PFPE layers covalently bonded to the CNTs surface. Products and by-products were evaluated by mass balances of decomposed portions of PFPEs residues, PFPEs chains bonded on carbon nanotubes and PFPEs fluids obtained by homocoupling side-reactions.

Fluorination with elemental gaseous fluorine is a quite effective method to perturb the π -electron system of

carbon-based materials and this methodology can provide a strong hydrophobicity to the carbonaceous surfaces. The direct fluorination of CNTs with elemental fluorine is associated with a sp^2 to sp^3 change of carbon hybridization. In our research, the fluorinated samples were obtained by heating **MWCNTs** and **SWCNTs** under a pure fluorine gas atmosphere at a temperature ranging between 25 and 80°C. These conditions are considered mild, and it was expected that fluorination occurred mainly on the CNTs surface. Thus, the bulk of **MWCNTs** sample could remain unchanged and the formation of fluorinated sp^3 -hybridized carbon atoms was expected to be achieved only on their surface. The properties of fluorinated CNTs were analyzed in order to describe the differences and analogies with the CNTs functionalized with PFPE chains.

Functionalized CNTs were characterized by X-ray photoelectron spectroscopy (XPS), ^{19}F solid state MAS-NMR spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), thermogravimetric analysis (TGA), X-ray diffractometry (XRD), contact angle (CA), surface area and porosity measurements. The effects of the chemical treatment on

the conductive properties of CNTs were studied by resistivity measurements at different applied pressures. The XPS data confirmed the presence of fluorinated moieties on the CNTs surface after chemical treatments with PFPE peroxides and elemental fluorine. XPS analysis showed also that the fluorine contents increase as the amount of PFPE peroxide in the chemical treatments increases. After treatments with PFPE peroxides as well as with elemental fluorine, the higher fluorine content was measured on the surface of treated **SWCNTs**. Since **SWCNTs** have small diameter than **MWCNTs**, they are characterized by a high reactivity towards linear PFPE radicals as well as fluorine atoms. The covalent nature of F-C bonds was confirmed by high resolution XPS analysis in the typical zone of F-bonds: signals in the region of 687 and 689 eV were observed for all samples treated with PFPE peroxides and in the region of 687 eV for samples treated with elemental fluorine. The main effect on CNTs due to the chemical treatments with linear and branched PFPE peroxides and fluorination with elemental fluorine was the modification of the wetting properties, until the exceeding of the threshold of

superhydrophobicity. Water droplets on pellets of CNTs without any treatment were adsorbed in few second (2-4 s) by the carbonaceous matrix of CNTs. On the contrary, droplets of water on functionalized CNTs were enduringly stable and CA measurements with water were easily determined. The increase in the amount of fluorine content on the surface of CNTs had a fundamental role in determining this property. The electric characterization of the samples treated with PFPE peroxides and elemental fluorine consists in the determination of the resistivity in function of the applied pressure (from 0.9 to 13.6 MPa). **SWCNTs** treated with PFPE peroxide and elemental fluorine showed the highest electrical resistivity among all samples because of the higher PFPE chains and fluorine content on their surface. Conductivity measurements show that the covalent linkage of PFPEs chains weakly modifies the electrical properties of conductive CNTs. Conversely, the covalent linkage of fluorine atoms by fluorination with elemental fluorine had a deeper influence on the conductive properties of CNTs. However, the conductivity measurements under higher pressure (*i.e.* 13.6 MPa) suggested that the fluorination occurred mainly on the surface of **MWCNTs** and for **SWCNTs** preferentially on the amorphous carbonaceous portion. Overall, the reactions of functionalization with PFPE chains and fluorination were relatively nondestructive to the electronic structure of CNTs. TGA analysis revealed that the higher the amount of linked PFPE chains on the CNTs, the

higher the weight loss measured in the typical temperature range of PFPE thermal decomposition. These results are additional evidences of the linkage of PFPE chains on CNTs surface. TGA of fluorinated samples of CNTs also determined that weight loss increases if the fluorine content on the CNTs surface is increased. On the basis of weight losses measured by TGA, the degrees of coverage were higher than 1 (DOC > 1) in all the samples. This result confirmed that the functionalization with PFPE chains and elemental fluorine occurred mainly on the surface of CNTs and that the bulk of **MWCNTs** remained partially unaltered.

X-ray diffraction studies on CNTs were performed to detect the changes in crystalline domains which can be referred to the delocalized π -electron systems of the graphitic portions of carbon-based materials. The XRD analysis revealed that CNTs structures were preserved in all the samples treated with PFPE peroxides and partially in samples fluorinated with elemental fluorine. The chemical treatments with PFPE peroxide and elemental fluorine had a weak influence on the average crystallite size (D_{002}) of **MWCNTs**. Defects were generated during the chemical functionalization of **MWCNTs** with PFPE peroxides and elemental fluorine influenced the crystallinity of nanotubes. In this research the chemical functionalization with PFPE peroxides was also compared with the physical adsorption (physisorption) of inert linear and branched PFPE fluids. Inert PFPE fluids Fomblin® M03 and Fomblin® YHVAC

18/8, which do not contain peroxidic moieties and are characterized by linear and branched structures, respectively, were used for the preparation of these comparative samples. Physical adsorption of PFPE fluids conferred to CNTs approximately the same surface properties observed after functionalization by PFPE peroxides. However, no chemical linkage of the fluorinated chains occurred by physisorption of PFPEs and simple washings with solvent removed the PFPE molecules. Conversely, the surface properties due to functionalization of CNTs by PFPE peroxides were considerably stable. This difference can be considered as a further experimental evidence of the chemical linkage of PFPE chains on CNTs by treatments with PFPE peroxides. In summary, the functionalization of CNTs with PFPE peroxides could be an important and powerful methodology to modify the surface, electrochemical, and morphological properties of carbon nanotubes, as alternative approach to the direct fluorination with elemental fluorine.

Keywords: Carbon nanotubes, chemical functionalization, superhydrophobicity, conductivity, perfluoropolyethers, radicals.