Chair:
Prof. Tiziano Faravelli

DOCTORAL PROGRAM IN INDUSTRIAL CHEMISTRY AND CHEMICAL ENGINEERING

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

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

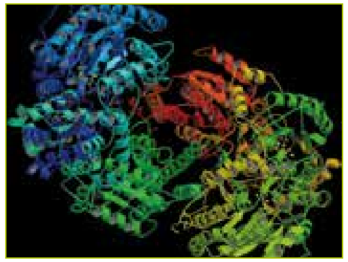
The general topic for the doctoral program in Industrial Chemistry and Chemical Engineering is the application of the chemical and physical knowledge to all the activities related to the synthesis, design, production and transformation of chemical substances and materials (like advanced inorganic, polymers 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.

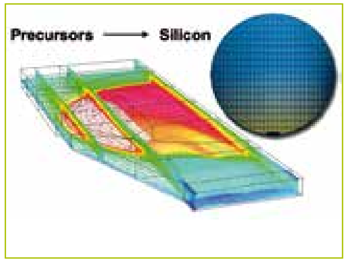
The ***CII*** program covers three years for an overall amounts of 180 credits. The responsibility of the organization and of the contents of the doctoral program is attributed to the Professor Committee (PC). At the beginning of the Doctoral program, a tutor and a thesis advisor is assigned to each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

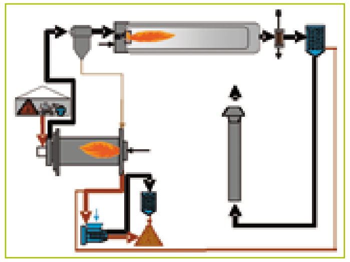


1. Structure simulation of Nitrogenase enzyme for N_2 conversion to NH_3.

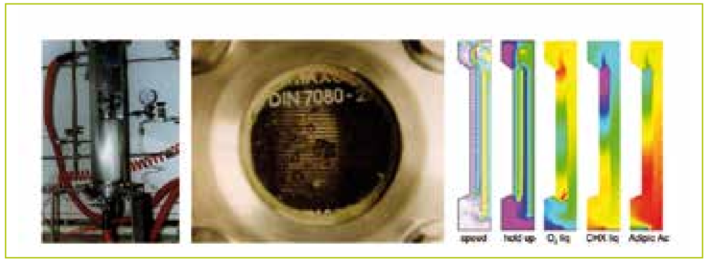


2. Simulation of a chemical vapor deposition reaction for silicon films deposition.

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 aci.

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CATALYTIC REMOVAL OF NOX AND SOOT FROM MOBILE SOURCES

Nancy Artioli

Commercial vehicles and diesel passenger cars will be subjected in a near future to very stringent emission regulations regarding nitrogen oxides (NO_x) and particulate. To handle these limits the use of exhaust after-treatment technologies is required.

Different strategies have been proposed for lean-burn engines; one such strategy is the Diesel Particulate NO_x Reduction (DPNR) system that accomplishes the simultaneous removal of NO_x and particulate. In this thesis work the behaviour of these systems has been investigated by the use of different techniques. Model DPNR catalyst (such as Pt-Ba/Al_2O_3 and Pt-K/Al_2O_3) has been prepared in our labs using standard wetness impregnation technique and have been characterized with B.E.T, TPD/R/O and XRD analysis. Then catalyst-soot mixtures have been prepared using a synthetic soot (Printex U) and their reactivity has been addressed both in the soot oxidation and NO_x reduction performing lean-rich cycles by imposing stepwise changes in the reactants concentration at constant temperature in the presence of water and CO_2.

The results obtained during the lean NO_x adsorption over the Pt-Ba/Al_2O_3-soot mixture showed that the presence of soot decreased the NO_x storage capacity of the catalyst. Moreover soot leads to an appreciable decrement of the rate of NO_x adsorption: these effects are seen also at different temperatures (200-350°C) and with different values of the NO inlet concentration (250-1000ppm). During NO_x storage, soot oxidation also occurs, thanks to the presence of NO_2 formed upon NO oxidation over Pt sites. In fact the NO_2 concentration at the reactor outlet in the presence of soot is significantly lower than that observed without soot, thus pointing out the involvement of NO_2 in soot oxidation. The decrease of the NO_2 concentration may explain also the observed decline in the NO_x storage properties of the catalyst. In fact, in line with the occurrence of a "nitrate" pathway for the storage of NO_x (i.e., NO oxidation to NO_2 followed by NO_2 adsorption in the form of nitrates via a disproportion reaction), Ba and soot compete for reaction with NO_2, leading to the observed decrease in the NO_x storage properties. On the other hand, the reduction of the stored NO_x is not significantly affected by the presence of soot, although some minor changes in the N_2 selectivity (a slight increase in the presence of soot) have been observed.

Worth to note that the adsorbed NO_x oxidize soot at temperature well below those corresponding to their thermal decomposition originating NO_2 in the gas phase. This has been shown by TPD /TPO experiments in which the reactivity / thermal decomposition of nitrates has been investigated in the presence and in the absence of soot. It has been found that the presence of soot favors the decomposition and the reduction of the stored nitrates, while soot is oxidized.

In fact the presence of soot shifts the decomposition/reaction of the stored nitrates at lower temperatures, and the stoichiometry of the released products reflects the occurrence of a partial reduction of the initially stored NO_x, as well as the oxidation of soot. This reaction possibly involves the surface mobility of the stored nitrates, soot particles being the driving force for the process and acting as reduced centers.

Pt-Ba supported on Al_2O_3 is one of the most common formulation of LNT catalytic system, but also potassium based catalyst is gaining attention for its storage capacity. For this purpose De-NOx and De-soot activity has been investigated over a model Pt-K/Al_2O_3 by performing lean-rich cycles at constant temperature. The interaction between soot and the stored NO_x has also been investigated by temperature programmed methods (TPD and TPO). It has been shown that the pathways for the adsorption and the reduction of NO_x are similar for the Pt-Ba/Al_2O_3 and Pt-K/Al_2O_3 catalytic system. The presence of soot affects the NO_x storage capacity and the stability of the adsorbed species of both samples. However, it has been observed an higher mobility of the K-containing surface species involved in these reactions since their decomposition/reduction is achieved at lower temperature compared to the ones reported for Ba based catalyst.

Finally mechanistic aspects involved in the formation of N_2 and N_2O during the reduction of NOx stored over the model PtBa/Al_2O_3 NSR catalyst have been investigated by means of isotopic labeling experiments.

A combined use of MS, UV-Vis and GC analysis has been adopted allowing the complete quantitative analysis of the reaction products. The reduction of the stored labelled nitrites species with ^{14}NH3 leads to the selective formation of N_2 and very small amounts of nitrous oxide. The formation of all possible nitrogen isotopes has been observed (i.e. $^{15}N^{14}N$, $^{15}N_2$ and $^{14}N_2$), although the single labeled isotope $^{15}N^{14}N$ dominates (49%). This points out that N_2 formation cannot be uniquely explained on the basis of the selective coupling of NH_3- and NO-derived species, as observed in the case of the NH_3-SCR reaction over vanadia-based catalysts and transition metal exchanged zeolites as well. An additional route is likely operating in this case: based on the suggested pathways for the NO and NH_3 reaction on Pt-based catalysts, the recombination of N-atoms formed by dissociation of NOx- and NH_3-related intermediates should be invoked to explain the observed isotopic distribution of the produced nitrogen.

Isotopic labeling experiments also provide indications on the pathways involved in the formation of N_2O by-product.

Another important part of this thesis work was focused on the study of the elementary steps involved in NO oxidation on Rh and Co catalysts. Kinetic experiments were carried out to study the effect of NO, O_2, and NO_2 pressures on turnover rates. It was observed that turnover rates increased linearly with NO and O_2 pressures and were inversely proportional to NO_2 pressure, as also observed on Pt and Pd catalysts. NO oxidation rates are limited by O_2 activation on isolated vacancies (*) on surfaces of Rh and Co oxides saturated with oxygen (O*). RhO_2 and Co_3O_4 as the stable active phases during NO oxidation throughout the temperature and concentration ranges relevant to catalysis.

Turnover rates increase with increasing cluster size, because the formation of kinetically-relevant vacancy sites becomes more facile on larger clusters, with more coordinatively saturated surfaces. NO oxidation turnover rates on RhO_2 and Co_3O_4 are higher than expected from oxygen binding energies on the respective metals or from the two-electron reduction potentials of Rh^{4+} or Co^{3+}, but fall in line with the reactivity of Pt and PdO when one-electron reductions (accessible for Rh and Co, but not for Pt or Pd) are used to predict turnover rates.

NO oxidation has been studied also on siliceous micro and mesoporous materials like Silicalite-I, Beta and Chabazite zeolites that are effective catalysts for this reaction.

This feature involve van der Waals interaction between the framework of the zeolite and molecules adsorbed in the intracrystalline space. These interactions are responsible for the confinement effects which govern the behavior of zeolites as catalysts. Kinetic effects of NO and O_2 pressures on NO oxidation on siliceous zeolites have been investigated in a wide temperature range (15-350°C) and kinetic parameters were estimated using Transition State Theory. It was noticed that NO oxidation on siliceous zeolites proceed with apreciable rate at temperatures below 58°C. In this regime, the reaction has a negative activation energy of approximately -30 kJ/mol for the three zeolites investigated and is second order in NO and first order in O_2, as the gas phase NO oxidation. The possibility that in the zeolite the reaction proceeds through similar reaction intermediates was considered, but the calculated entropy and enthalpy of formation of the transition state are inconsistent with this hypothesis.

DETAILED KINETIC MODELS FOR THE THERMAL CONVERSION OF BIOMASS

Emma Barker Hemings

In the PhD activity detailed kinetic model for the thermal decomposition of biomass have been studied. The work originates from the evidence that a growing interest around biomass and its conversion processes exists. The world energy demand is currently in the range of 32 quadrillion BTU, and projections indicate a trend of growth for the upcoming decades. The major contribution to meet the energy demand is nowadays represented by fossil fuel, however this picture is expected to change in the near future. The growth in the energy demand, together with the depletion of fossil sources, is expected to result in a rise of the oil price. Environmental concerns, together with the introduction of more restrictive regulations on pollutant emissions, pose an issue of sustainability of fossil fuels as well. In addition, diversification and decentralization of energy supplies is a strategic step in the light of energy self-sufficiency, at least at a local, regional, and eventually national level.

In this framework, biomass is a promising alternative source of energy, with an availability of 220 billion oven-dry ton per year (equivalent to 4500EJ), no net CO_2 emissions and lower emission of detrimental gases (e.g. sulphur and nitrogen oxides). Cellulose, hemicellulose and lignin are generally acknowledged as the major components of biomass material, which also contains inorganic constituents (ashes) and water. Major considerations on the economic sustainability of biomass processing have been repeatedly addressed, together with the need for standard specifications and procedures.

From the technological point of view, a major distinction exists between thermal and biological pathways of conversion of biomasses. Given their higher efficiency, thermal processes are considered to be more relevant. Combustion, pyrolysis and gasification represent the most attractive options. The limited exploitation of biomass potential to date is mainly related to the poor understanding of biomass itself, and its behavior in conversion processes. Therefore, the opportunity of sheading some lights on the several uncertainties is interesting.

With respect to thermal treatments of biomass, the interplay of kinetics and transport phenomena is considered determinant. The description of the thermal conversion of biomass thus represents a very complex problem, which is defined as multicomponent, multiphase and multiscale. The first issue is in the characterization of the biomass material, for which a definition in terms of some major reference species is proposed, starting from the elemental composition.

The chemistry of the system is described by means of two kinetic mechanisms. A model for the solid phase, including lumped stoichiometries that account for the reactivity of the reference species in the solid matrix, is proposed.

The competition between cross-linking, devolatilization and decomposition reaction pathways is highlighted. The volatile species released from biomass primary decomposition are likely to undergo further decomposition, which is accounted for in a dedicated detailed kinetic model for the gas phase. The description of the chemical phenomena occurring in the system is coupled with a model for the solid particle, which deals with heat and mass transfer limitations within the solid particle, and a reactor model. The coupling of all these elements concurs to the definition of a comprehensive mathematical model for the thermal conversion of biomass.

The model is tested under conditions of fast pyrolysis. Yields of the major product fractions are evaluated and simulated results are compared with experimental data found in literature. The comparison shows a satisfactory agreement and offers the opportunity to analyze the role of the original composition of biomass and of operating parameters, such as the residence time in the gas phase and the particle diameter, in the definition of the final product yield. The optimal conditions for the maximization of the bio-oil yield are therefore individuated. An attempt to characterize the composition of the bio-oil is also performed. The comparison is not satisfactory, especially with reference to the overestimation of carbohydrates in the simulations, and the underestimation of phenolics.

The kinetic model for the gas phase, including the reactions of biomass primary devolatilization products, is therefore revised and extended.

Given the limited information available on the reactivity of the lignin devolatilization products, a kinetic model for the pyrolysis and oxidation of anisole has been developed and tested.

Anisole has been chosen as the simplest aromatic having a methoxyl substituent, which is characteristic in many lignin structures. The reactivity of the system is largely determined by the highly resonant phenoxy radical, which undergoes radical recombinations to form phenolics, decomposition to cyclopentadiene and CO and addition on other resonant radicals to build PAH and soot precursors. Comparisons between simulated and experimental results (from literature) are encouraging, even though the chemistry of the phenoxy radical is not completely understood and therefore represents an interesting opportunity to extend and improve the kinetic description of the system.

Similarly, a detailed kinetic model for the decomposition of glycerol has been developed and tested. Glycerol is an interesting component, as it can be representative of poly-alcohols derived from the decomposition of carbohydrates in biomass.

Acetol and 3-hdroxypropanal have been defined as major reactive intermediates. The role of H-abstraction reactions, whose reaction rates are interestingly influenced by the presence of hydroxyl groups, has been highlighted. Molecular dehydrations have also been studied and a rapid reaction of the intermediates to form aldehydes has been registered.

Comparisons between model simulations and experimental results from literature have been successfully performed.

The growing interest in biochar, which finds many interesting applications in soil amendment, waste management, and mitigation of the climate change, has moved the last part of the work, which has been devoted to the analysis of slow pyrolysis conditions.

Under low temperatures and long residence times, the yield of biochar can be optimized.

The kinetic model for the solid phase has been tested in this set of operating conditions and some extensions appeared necessary. Particularly, cross-linking reactions accounting for the slow escape of tars from the solid matrix, and their eventual decomposition within the pores of the solid, have been introduced. These reactions account for the formation of the secondary char, which grows on primary char and contributes to the occlusion of pores in the solid matrix. This can compromise the performance of biochar in several applications, and is therefore relevant.

Another class of reactions which was extended is representative of the desorption of functional groups from the solid matrix at high temperatures. Experimental evidence of a slow and persistent release of gases form the solid at high temperatures has been interpreted in terms of the devolatilization of fragments absorbed on the solid surface.

In conclusion, the present work aims at consolidate and extend the kinetic mechanism for the reactivity in the solid and gas phase which determines the evolution of the thermal conversion of biomass.

Improvements in the modeling tools, with the extension of the gas phase kinetics to new compounds and the insertion of new reaction classes in the solid phase kinetics, has been reached. Open opportunities for further improvement of the present work are many, and include the study of heterogeneous gas-solid reactions to better describe the formation of secondary char.

Similarly, the description of the reactivity in the gas phase could be improved by adding new components to the kinetic mechanism.

STRATEGIES FOR THE ENHANCEMENT OF LOW-TEMPERATURE CATALYTIC OXIDATION OF METHANE EMISSIONS

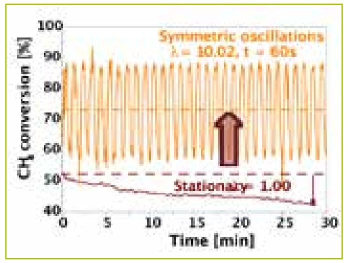
Djamela Bounechada

The replacement of gasoline and diesel with natural gas as fuel for cars allows achieving a reduction of CO_2 per MJ emissions, due to the higher hydrogen/carbon ratio of CH_4. However, the presence of unburned methane in the exhausts of natural gas vehicles (NGVs) represents a major drawback because of its high Global Warming Potential (GWP). At present the most common strategy for the abatement of methane emissions is catalytic combustion. Ceramic monoliths coated with palladium and platinum based catalysts are recognized to be the most promising materials for this purpose. However, these noble metals present major drawbacks which could limit their use in real applications. Despite its high activity under lean conditions, palladium is very sensitive to the presence of water or sulfur in the exhausts, which may lead to catalyst deactivation. On the other hand the performances of sulfur resistant platinum based catalysts are limited under lean conditions due to oxygen inhibition. In this context, gaining further understanding in the mechanisms of CH_4 oxidation promotion, in the nature of the active sites and in the role played by noble metal-support interactions is mandatory to be able to design more active catalysts.

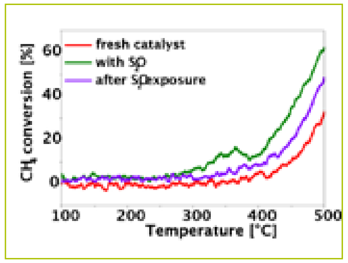
In this work different strategies for the enhancement of low-temperature catalytic activity towards methane oxidation were investigated over a commercial Ce-Zr promoted Pd-Rh/Al_2O_3 catalyst and SiO_2, Al_2O_3 and CeO_2 supported Pt catalysts for NGVs applications.

The behaviour of a commercial Ce-Zr promoted Pd-Rh/Al_2O_3 catalyst for the abatement of methane from the exhausts of NGVs was studied under stationary stoichiometric ($\lambda = 1.00$) and lean ($\lambda = 1.02$) conditions in the presence of large amounts of water. In both cases, after prolonged exposure to the reaction mixture catalyst deactivation is observed. The introduction of rich pulses ($\lambda = 0.98$) in a constant lean feed gas ($\lambda = 1.02$) results in the stabilization of catalytic performances. The performance of a specular experiment, i.e. the introduction of lean pulses ($\lambda = 1.02$) in a constant rich feed gas ($\lambda = 0.98$), evidences that a higher methane conversion is obtained under stationary reducing than stoichiometric or oxidizing conditions. The analysis of reactants conversion and products distribution suggests that different chemistries are involved under lean and rich conditions. Total oxidation reactions mainly occur under excess of oxygen, whereas under rich conditions NO reduction, CH_4 steam reforming and water gas shift also occur. Forced oscillations of gas composition around stoichiometry were also performed by periodically switching the feed from slightly rich to slightly lean compositions with different oscillation amplitudes (0.01, 0.02 and 0.03). The cycle average methane conversions are more stable and higher than those obtained working under stationary stoichiometric conditions (Fig. 1), proving that the perturbation of the feed gas composition by periodic oscillations around stoichiometry is an effective strategy for the enhancement of methane combustion over this catalyst. Since a markedly higher CH_4 conversion is observed at $\lambda = 0.98$ than at $\lambda = 0.97$, when oxygen is absent, O_2 should plays a major role in CH_4 oxidation under slightly rich operations. The establishment of a more active mixed PdO/Pd° state, possibly promoted by the presence of Ce-Zr mixed oxides, might be responsible for both the higher CH_4 conversion observed during the rich than in the lean phase and the stabilization of catalytic performances under periodic rich pulses.

On the basis of the analogy between SO_2 and NO oxidation on Pt based catalysts and SO_x/NO_x storage properties of the support materials, sulfur promoted and NO_x assisted low-temperature methane oxidation were studied by comparing silica, alumina and ceria supported platinum catalysts with the purpose to gain further understanding on the mechanisms of methane oxidation promotion. Transient flow-reactor and DRIFTS experiments in presence/absence of SO_2 and NO_x show that the catalytic activity is strongly dependent on the nature of the support material. An inhibiting effect is observed in presence of SO_2 (or NO_2) on the Pt/silica sample, due to a competition between CH_4 and SO_2 (or NO_2) adsorption on the same active sites as a first step for the respective subsequent oxidation (or disproportion) reactions. These results evidence that methane oxidation occurs exclusively on platinum sites for the silica supported platinum.



1. Enhanced catalytic performances under periodic operation over Ce-Zr promoted Pd-Rh/Al_2O_3 (T_{oven}= 450°C, GHSV = 50000 h^{-1}).



2. Sulfur promoted CH_4 oxidation over 4% Pt/Al_2O_3 (0.05% CH_4+0.15% O_2 in presence/absence of 20ppm SO_2, GHSV = 15000 h^{-1}).

On the contrary, the oxidation of methane is promoted over Pt/alumina in presence of SO_2 through formation of sulfates at the noble metal-support interface, which work as highly active sites for methane dissociation. The promoting effect partially remains even after sulfur exposure due to migration of some ad-SO_x species from interfacial locations to the support (Fig. 2).

The importance of interfacial active sites in the promotion mechanism is confirmed by the temporary enhancement of methane conversion observed when introducing NO_x in the feed gas at 500°C. Similarly, new active sites in the form of a polarized couple ($Pt^{\delta+}$ $NO_3^{\delta-}$) are proposed to be formed. Finally, exposing Pt/ceria to SO_2 (or NO_2) leads to a temporary promotion of the methane oxidation, likely via formation of sulfates (or nitrates) at the noble metal-support interface. Since ceria may contribute to the overall oxidation kinetics via spillover processes, the promoting effect observed on Pt/ceria is stronger than on Pt/alumina. Accordingly, the long-term deactivation after sulfur exposure might be due to the blockage of the oxygen mobility and the active sites on ceria by nearly complete sulfation (surface and bulk) of the support. Similarly, catalyst deactivation after NO_x exposure is likely induced by the formation of stable bulk carbonates readily formed after reaction of nitrates with dissociated methane.

In summary, the presence of coadsorbates, e.g. sulfates and nitrates, is proved to be of major importance in the enhancement of low-temperature methane oxidation, likely through the promotion of the first H abstraction. In this picture, the choice of the support material on the basis of its adsorption proprieties and its ability to interact with the noble metal is crucial in the design of more active catalysts.

MECHANISM, KINETICS AND MODELING OF AUTOMOTIVE NH3-SCR AFTERTREATMENT SYSTEMS

Massimo Colombo

Emissions regulations for internal combustion Diesel engines have become more stringent over recent years and in many cases the required emission levels cannot be achieved just by improved combustion technologies. The strict limits imposed by international legislations requested automobile manufacturers to undertake an intensive research work in order to develop effective aftertreatment systems to meet emission standards of NO_x and particulates.

One of the most promising techniques for removing NO_x in the presence of the excess of oxygen, as typical of the combustion processes in Diesel engines, is the selective catalytic reduction (SCR) with ammonia/urea as a reducing agent. The NH_3-SCR technology has been applied since the '70s in industry to reduce NOx emissions from stationary sources (e.g. from power plants). One of the first articles describing an SCR system to be applied in a vehicle was published in 1990, suggesting the use of non-toxic urea as the reducing agent, from which ammonia could be released under hydrothermal conditions. The application of the SCR technology to mobile emissions control is however a rather complex task, due to the difficulties of using the right amount of urea as a function of continuous changes in NOx emissions, catalyst activity, temperature and ammonia stored on the catalyst. The process has been improved step by step in the last decade, and NOx reduction efficiencies in the range of 80–90% or even higher have been demonstrated.

The catalysts used for SCR in stationary applications are based mainly on TiO_2-supported V_2O_5, promoted with WO_3. This catalyst type has also been used since 2005 for heavy duty diesel vehicles in Europe. Nowadays, NH_3/Urea SCR is universally recognized as the most relevant technology for the abatement of NOx emissions from heavy duty Diesel vehicles, and is also studied for passenger cars applications. Notwithstanding the commercialization of SCR equipped vehicles, research and development on this technology is not only still ongoing but it has been acquiring growing interest in both the scientific community and industry in the last few years. The research on this technology involves the design and improvement of configurations capable to assure high performances in terms of $DeNO_x$ efficiency, improved low temperature activity and minimized ammonia emissions. Within this framework, research lines involve the development of new catalysts, the elucidation of the reaction mechanisms, the control of NH_3 emissions, the development of reliable and chemically consistent mathematic models and, last but not least, the integration of NH_3/Urea-SCR in complex after-treatment systems (i.e. combination with Diesel Oxidation Catalysts and Diesel Particulate Filters).

The present Ph.D. project was devoted to the development of the NH_3/Urea SCR technology following the research lines just mentioned, with a substantial part of the work carried out within a long-lasting collaboration between the Catalysis group of Politecnico di Milano and Daimler AG, Stuttgart, DE.

The NH_3-SCR and the NH_3 oxidation reactivity were investigated according to a multiscale approach, both from the experimental and from the modeling point of view. Starting from the lab scale, the catalysts were first tested in the form of powder to identify the chemistry and the mechanism of the prevailing reactions. Additionally, the catalyst in the form of powder enabled collection of experimental data in the chemical regime, to be used for kinetic modelling purposes. Then, in a second lab rig, the same catalysts were tested in the form of small core monoliths accounting also for the effects of heat and mass transfer. In both laboratory rigs synthetic gases from high pressure cylinders were dosed to the reactors by mass flow controllers. Finally the full scale monoliths were tested in an engine test bench facility at DAIMLER AG using real feed gases from Diesel engines.

The same data were used for validating the developed mathematical model of SCR/ASC (Ammonia Slip Catalyst) converters.

Within the general topic of new SCR catalysts, a part of the work was devoted to the study of the catalytic activity in the NH_3-SCR reactions of copper and iron promoted zeolite SCR catalysts, with the aim of developing chemically consistent kinetic models. With respect to the iron-based catalyst, the copper zeolite system showed a higher ammonia storage capacity, a higher activity in the ammonia oxidation reaction and in the Standard SCR reaction, and in general its $DeNO_x$ activity was found less sensitive to the NO_2 feed content. As opposite to the iron zeolite, over the copper zeolite no inhibiting effect of ammonia on the standard SCR reaction was observed, while formation of some N_2O was detected even in the absence of NO_2 in the gas feed mixture.

Specifically focusing on the problem of extending the operative temperature window of SCR systems towards low temperatures, different topics were covered, ranging from the analysis of the interaction of NH_3 and NO_2 with the catalyst surface, to the study of SCR reactions mechanisms in presence of NO_2. The bulk of transient experiments addressing the mechanistic features of the NH_3/NO_2-NO reacting system over the considered catalyst, namely a Cu-zeolite, was found consistent with a scheme based on the key role of surface nitrates/nitrites species. Accordingly, a dual-site micro-kinetic model was developed on the basis of such a scheme, accounting in principle for the description of Fast- and NO_2-SCR reactions. The intrinsic kinetic scheme was fitted to the collected experimental data and validated against an additional transient data set.

The developed model provided an overall good qualitative and quantitative description of all the dynamic features associated with the NH_3-NO_2-NO SCR chemistry, thus lending substantial support to the proposed Fast- and NO_2-SCR reaction mechanisms. Additionally the developed model has significant practical implications: the use of a model accounting for the complex NH_3 and NOx storage phenomena and related transient behaviors is indeed mandatory to adequately simulate the SCR behavior at low temperatures, a condition of particular interest for vehicles during their cold start transient.

Regarding the control of NH_3 emissions from mobile SCR devices, a big effort has been put into the development of a mathematical model for novel dual-layer NH_3 slip catalysts. An original heterogeneous 1D+1D dynamic mathematical model of a single monolith channel with dual-layer washcoat was specifically developed for the simulation of ASC catalysts.

Such a model involved first the study of the chemistry and the kinetics of the individual ASC components, namely a PGM washcoat for highly efficient NH_3 oxidation and an SCR washcoat, coated on top of the PGM catalyst to improve the selectivity towards N_2. The rate parameters derived from the kinetic analysis of the powdered catalyst data were incorporated, together with the relevant geometrical and morphological catalyst properties, into the ASC converter model, which was eventually validated by simulating the SCR runs performed over core honeycomb samples of the SCR, PGM and dual-layer ASC catalysts. The final model validation was performed against data from engine test bench runs over a full scale dual-layer ASC monolith catalyst.

Finally, the possible integration of the SCR functionality within Diesel Particulate Filters was investigated by means of a modelling study, performed during a period at the Aristotle University of Thessaloniki, Greece. The study pointed out a competition between soot oxidation and DeNOx processes involving NO_2. Indeed it was found that soot presence can lead to the alteration of the local NO_2/NOx molar ratio, thus affecting both the DeNOx performances and the filter regeneration process.

DETAILED KINETICS OF PYROLYSIS, GASIFICATION AND COMBUSTION OF BIO-FUELS

Roberto Grana

The current demand for energy in the world is approximately 120 quadrillion kcal and expected to grow by 50% in the upcoming 20 years. The major energy resource is represented by fossil fuels, which account for more than 95% of the overall consumption in the automotive field. However, fossil fuels are inadequate to cope with the foreseen demand, both for availability and sustainability problems. The combination of supply depletion and environmental remediation expenses are expected to increase the effective cost of oils, thus introducing the problem of new energy resources.

Given the above mentioned scenario, biomass is generally acknowledged as an interesting and convenient alternative to oil. Biomass can be converted into useful forms of energy (solid, liquid, or gaseous fuels) as well as useful products (polymers, bio-plastics, char, pellets, and acids). Biorefinery process technologies include thermochemical (gasification, pyrolysis), biochemical (fermentation), or chemical (chemical synthesis) pathways.

Among the possible products, bio-alcohols show significant potential to be an alternative to conventional gasoline. Alcohols are renewable fuels because they can be produced either from biomass fermentation or by Fischer Tropsch processes.

There is considerable interest in promoting the use of butanol (C_4H_9OH) as an alternative to ethanol. Butanol can be derived from lignocellulosic materials and it has some advantages, as transportation fuel component, when compared with ethanol: it is less corrosive, has a lower vapor pressure, higher energy density, and its octane rating is similar to that of gasoline. Thus, it can be blended with gasoline at much higher proportions than ethanol without compromising efficiency.

Another promising product obtained from biomass is biodiesel. Biodiesels are complex mixtures of multi-component alkyl esters of long-chain fatty acids, generally produced by trans-esterification of soy and rapeseed oil with methanol. These biofuels are mostly composed of unsaturated methyl esters, methyl oleate ($C_{19}H_{36}O_2$) and methyl linoleate ($C_{19}H_{34}O_2$), with minor quantities of saturated components such as methyl palmitate ($C_{17}H_{34}O_2$) and methyl stearate ($C_{19}H_{38}O_2$). Relevant amounts of methyl linolenate ($C_{19}H_{32}O_2$), characterized by three double bonds, are also present.

Pyrolysis and gasification of solid bio-fuels are nowadays promising alternative to direct combustion, both electric and thermal energy are viable products, together with chemicals. Gasification is a robust proven technology that can be operated either as a simple, low technology system based on a fixed-bed gasifier, or as a more sophisticated system using fluidized-bed technology.

The mathematical description of such processes is rather difficult due to the complex phenomena involved, such as modelling solid devolatilization, gas-solid interactions and secondary gas phase reactions. However, a mathematical model is a powerful tool for process design, prediction of the gasifier performances, understanding of evolution of pollutant and a dynamic description of the system could provide strategies for an optimal process control.

The topic of this dissertation is the mathematical modelling of the combustion, pyrolysis and gasification of bio-fuels, both in gas and solid phase. Therefore, this work has two sections. The first one deals with the development of a detailed kinetic model of pyrolysis and oxidation of the four isomers of butanol and of methyl esters up to methyl decanoate. A detailed approach is employed in the development of the kinetic scheme of the four butanol isomers. The validation of the mechanism is carried out by means of comparisons with experimental data taken from literature.

Very different conditions are tested (e.g. perfectly stirred reactor, premixed flame) and the model predictions fairly agree with experimental trends. Detailed kinetic analyses show the different combustion behaviour of butanol isomers in premixed flame conditions.

Further investigation and kinetic analysis are required to model tert-butanol oxidation. The observed large deviations when comparing model predictions to shock tube and premixed flame data demand further kinetic studies.

The lumped approach employed for methyl esters is necessary to reduce the number of species. Indeed, the possible isomers are lumped in one correspondent reference species and intermediate C6-C10 methyl esters are modelled as a mixture of the reference components, methyl butanoate and methyl decanoate, by means of the lever rule. Model comparisons show the feasibility of such an approach. Reactivity and products distribution during pyrolysis and combustion in different conditions have been analysed and properly described.

In the second section, a theoretical model able to describe solid fuels combustion and gasification at the particle and the reactor scale is described. This is a complex multi-scale, multi-component and multi-phase problem.

The coupling of reactor and particle models with a detailed kinetics (both in gas and solid phase) represents the novelty of this approach. Such a model is able to describe the dynamic behaviour of the system taking into account mass and thermal diffusion along the reactor. The particle model provides an internal description in order to account for intra-particle heat and mass resistances. The accuracy of this description depends on the number of discretization sectors. This feature becomes fundamental for the analysis of the gasification of thermally thick solid fuel particles.

Material balance accounts for diffusive and convective fluxes (Fick's and Darcy's laws) and the reactive term involve solid fuel devolatilization and char reactions as well as secondary gas phase reactions.

Analogously, the energy balance settles the particle temperature and accounts for conduction and convective contributions as well as the heat of reactions involved in the solid phase. This particle model together with the kinetic models previously described is embedded in the fixed bed reactor model.

The reactor is considered as a series of elemental units which exchange mass and heat to each others. The single unit accounts for gas-solid interactions with particular attention to the inter-phase resistances. The balance equations refer to a perfectly stirred reactor in dynamic conditions. It is worth to note that reactor model calls for a detailed gas phase kinetic. More than one thousand balance equations are obtained, when considering ~10-15 solid species, 100 gas-phase components, 10 reactor layers and 5 discretizations of the solid particle. Fast pyrolysis of biomass to produce bio-oil is the first step in the model validation.

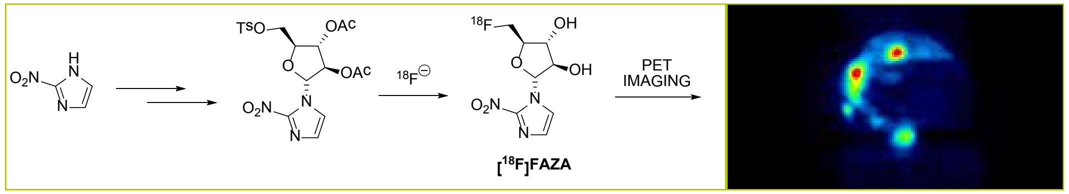
In these processes, secondary gas-phase reactions concur with biomass devolatilization to determine bio-oil yields. Model predictions reasonably agree with experimental data. The relative role of the kinetics of solid devolatilization and gas-phase reactions are analyzed.

Finally, preliminary gasifier model applications are discussed in detail. These simulations require several hours of CPU time, due both to the stiff nature of the gas phase kinetics and to the dynamic approach to the steady solution. Despite the computational difficulties, the approach developed in this work allows an overall and comprehensive understanding of the problem. Indeed, only the coupling of detailed kinetic models, like the ones developed in the first part of this thesis, with the models at particle and reactor scales allows to distinguish and to analyze the role of chemical kinetics and transport phenomena and to properly design industrial units.

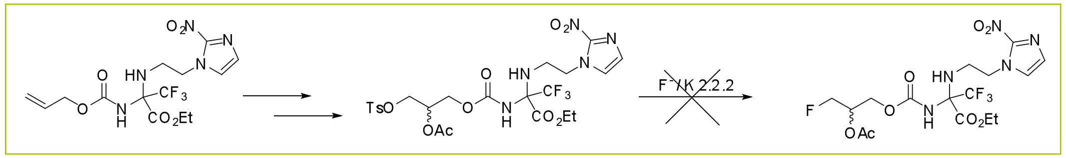
SYNTHESIS OF ^{18}F-LABELLED COMPOUNDS AS TARGETS FOR APPLICATION IN PET RADIOCHEMISTRY

Giovanni Pinna

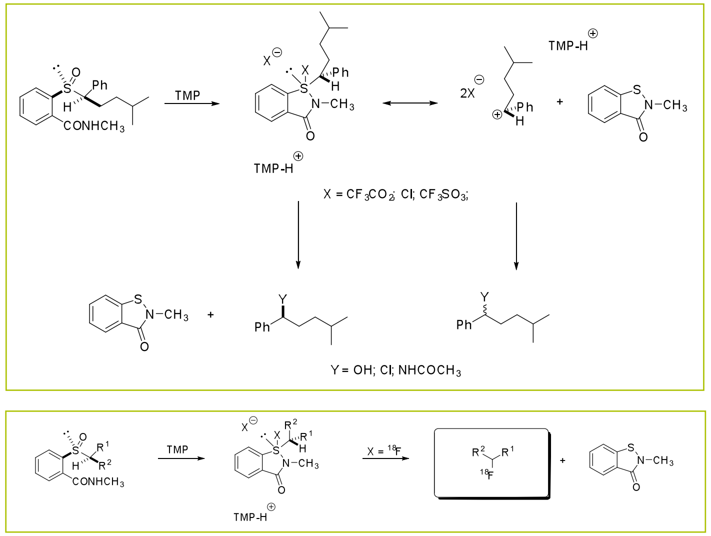
The work herein presented aimed at investigating several synthetic approaches for the introduction of ^{18}F-fluorine into selected target molecules and synthesising new ^{18}F-containing compounds to be tested as radiotracers for positron emission tomography (PET).
Positron emission tomography (PET) is a highly sensitive molecular imaging technique which allows the visualization and investigation of *in vivo* biological processes occurring at the molecular level or cellular level by detection of radiopharmaceuticals labelled with positron-emitting radionuclides. PET may be used for the early diagnosis, characterization and "real time monitoring" of disease as well as for the investigation of the efficacy of drugs.
The radioactive compound (tracer) is commonly administered to the subject by intravenous injection of a sterile saline solution (the amount of administered tracer is typically 10^{-10} g). The radiosensitizer for PET is labelled with a radioactive isotope, which decays by emitting a positively charged particle, the positron (β^+). The positron, after travelling a short distance in the body, collides with an electron in the surrounding matter, thus giving rise to an annihilation event, which produces two high energy (511 KeV) gamma (γ) ray photons that travel out through the body at 180° with respect to each other. The simultaneous detection of these two gamma ray photons by a PET scanner and the subsequent computer elaboration allow to calculate the spatial distribution of the radiotracer within the body's patient and the production of a 2D or 3D image of the area where the tracer is localized. Many millions of annihilation events are required for the construction of a PET image.
The radioisotopes for PET are produced by a cyclotron, where accelerated beams of protons or deuterons are generated and used to irradiate a target material (e.g. N_2, Ne, $H_2{}^{18}O$, etc), giving rise to the desired radioisotope through a nuclear reaction.
The radioactive isotopes commonly used for the production of the PET probes are represented by short-lived radionuclides such as ^{11}C ($t_{1/2}$ = 20.4 min), ^{13}N ($t_{1/2}$ = 9.97 min), ^{15}O ($t_{1/2}$ = 2.04 min), ^{18}F ($t_{1/2}$ = 110 min). ^{18}F is the most used PET radionuclide, because of its favourable physical properties, namely a high half-life ($t_{1/2}$ = the period of time over which half of the radionuclide undergoes disintegration) and a low positron energy (0.64 MeV, which allows a better quality of PET images).
2-Nitroimidazole radiolabelled compounds are a specific class of PET tracers used for the detection of hypoxia, a condition associated to a deficiency in oxygen supply. Hypoxia has been found in several types of solid tumors and has demonstrated to decrease the efficacy of both radio- and chemotherapy. Radiolabelled 2-nitroimidazole compounds are selectively accumulated within the tumor cells, when there is a lack of oxygen, therefore, they are essential for the early assessment of tumor hypoxia by means of PET and evaluation of the response of a tumor to the therapy.
^{8}F-Fluoroazomycinarabinofuranoside ([^{18}F]FAZA) has demonstrated to be a suitable PET hypoxia marker, given its faster elimination from the body and low accumulation.
Given the increasing importance and diffusion of [^{18}F]FAZA as a PET hypoxia marker along with its high cost and low availability in PET centres, we aimed at achieving an efficient synthesis of the [^{18}F]FAZA precursor and its subsequent labelling procedure, in order to have satisfactory radiochemical yields (RCYs) of the [^{18}F]FAZA, to be finally used for pre-clinical and clinical PET hypoxia imaging experiments.
This project involved the synthesis of the precursor of [^{18}F]FAZA bearing a suitable leaving group on its structure, and the subsequent radiosynthesis of [^{18}F]FAZA, to be then tested on hypoxic animal models, and later on human patients with cancer.



Scheme I. Synthesis of FAZA and PET image of a transgenic hypoxic mouse (PTP1B).



Scheme II. Synthesis of a new potential PET-hypoxia tracer.



Scheme III. a) Proposed mechanism for the Pummerer reactions resulting in the formation of α-hydroxy- α-chloro- and α-acetamido derivatives, starting from alkylated N-methyl ortho-carbamoyl benzyl sulfoxides and b) potential synthetic strategy for the introduction of fluorine-18 and production of new PET-tracers.

The key step of this project was the radiolabelling procedure, which was performed under nucleophilic substitution conditions (S_N2) by using non-carrier added (NCA) ^{18}F-fluoride, produced by the nuclear reaction ^{18}O(*p*,*n*)^{18}F from ^{18}O-enriched water ([^{18}O]H_2O), and the phase transfer reagent Kryptofix 222 (K_{222}), which was crucial to improve the reactivity of ^{18}F-fluoride ion, in a polar aprotic solvent.
We achieved satisfactory radiochemical yields (RCYs) of [^{18}F]FAZA and successfully accomplished a PET-hypoxia imaging experiment on hypoxic animal models (Scheme I).
We have also developed a synthetic approach for the production of a new potential hypoxia PET-tracer and investigated several fluorinating conditions (nucleophilic substitution, S_N2) to introduce ^{18}F-fluorine atom into the precursor molecule (Scheme II).
We have furthermore investigated the role of several alkylated *N*-methyl *ortho*-carbamoyl benzyl sulfoxides as chiral auxiliaries for the synthesis of α-chloro-, α-hydroxy- and α-acetamido derivatives, obtained by "non-oxidative Pummerer" reactions.
The treatment of the aforementioned sulfoxides with different Pummerer promoters such as oxalyl chloride $(COCl)_2$, trifluoroacetic anhydride (TFAA) and trifluoromethansulfonic anhydride (Tf_2O), in the presence of *sym*-collidine (TMP) as the base, at different temperatures in DCM or MeCN, led us to suggest different reaction mechanisms by which the products took place.
We assumed that this mechanisms could be exploited to synthesise new specific ^{18}F-fluorinated products by using several ^{18}F-fluoride sources (Scheme III).

THE PLANT SIMULATOR: COUPLING ACCIDENT AND PROCESS SIMULATION WITHIN VIRTUAL ENVIROMNENTS

Roberto Totaro

In the last fifty years, a number of accidents have occurred with dramatic consequences, such as the loss of lives among population, responders, and operators, and the discharge of toxic chemicals in the environment. In addition, it is worth mentioning that chemical accidents entail costs for both the company liable for the accident and the community in the surrounding due to reconstruction costs, loss of production, court costs, fines, business interruption, reallocation of production to other sites, cost of on-site personnel and contractors, plant redesign, and costs for the civil and health authorities. Furthermore, accidents affect the company reputation. For instance, after the accident at the BP plant of Texas City in 2005, the company decided to implement and to invest in advertising the on new safety policy.

High-cost accidents share some common features: the lack of understanding and the incompetent management of the storage and/or of the process; the unawareness of the risks associated with the activities that can lead to accidents (perceived low risk); problems with isolation valves that are not remotely operable; the combination of inadequate and unreliable process control equipment; the loss of process control (*e.g.*, runaway reactions).

The U.S. Chemical Safety and Hazard Investigation Board (CSB) emphasizes also that it is common practice to adopt procedures that deviate from the protocols because they are not updated with the existent plant-layout or they are vague or impracticable. This practice can lead to accidents because non-investigated dynamics or deviations that the operators are not trained to face may occur.

The structured approach to conduct a hazard analysis can be described as follow: identification of potential failures; calculation of the quantity of hazardous material released in each failure; calculation of the impact of each release on plant equipment, people, the environment, and property.

This procedure can be applied to an entire plant or to one of its portions. Software tools can quantify and characterize the probable accident scenarios to support the decisions of many subjects involved at different levels in the emergency preparedness: the decision maker; the emergency responders; the local authorities; the emergency responders; the company liable for the accident.

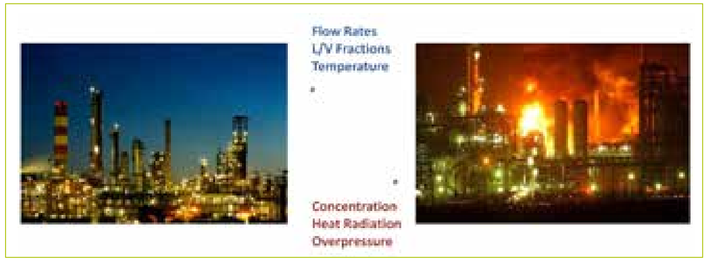
Accident simulators are defined as software tools that, starting from a set of input data, are able to quantify the consequences of an accident in order to determine the distances from the accident location where some risk thresholds are exceeded.

Literature, technical paper, users' manuals, and websites discuss a number of accident simulators differing in the input data they require, the output data they evaluate, and the models they adopt. In some cases, models are designed to simulate only one of the possible accident consequences, usually the dispersion of gases, and the user has to run more than one model to get a whole picture of the accident outcomes, iterating the procedures loosing pieces of information.

A hazard analysis requires the calculation of the impact of the possible accident on plant equipment, people, the environment, and property.

However, as far as the accidents occurring in chemical industries are concerned, a further step in the direction of increasing the safety can be achieved by considering not only the accident but also the interactions between the accident and the process because they influence each other (see figure 1).

The plant conditions and the intervention of operators and/or the control system determine a possible leakage flow rate, its thermodynamic state (pressure, temperature, composition, vapor/liquid fractions), and the outflow velocity and direction. These variables are input data that the accident simulator uses to evaluate the possible consequences of the accident. Both direct and indirect effects influence the plant dynamics. Indirect effects are those phenomena that do not allow the intervention of operators and/or the control system restoring the nominal operating conditions. Examples of indirect effects are the dispersion of a toxic or burning gas, and the presence of a flammable liquid on the ground. In case of fire, non-fireproof cables melt, and the control system cannot modify the process variables by, for instance, closing a valve. In all the aforementioned cases, the field operators may not be able to reach the remotely-operated valves.



1. Two-way interaction between the process, and the accident

These examples highlight the way the plant and the accident influence each other. In order to explore the consequences of an accident event and its interaction with the plant, it is possible to derive the data related to the dynamics of the process from a dynamic process simulator.

The simultaneous evaluation of process and accident conditions and their feedbacks is promising and advisable from the technical, safety, and financial points of view. In addition, it allows assessing the human factors issue because, from a safety management perspective, the data gathered on human behavior, under the simulation of the plant management, are much more revealing than desk exercises on emergency response. The simultaneous and coupled simulation of the process and the accident can represent an effective tool for implementing Operator Training Simulators (OTS), since in a virtual environment the operators are allowed to modify the process variables while quantifying the consequences on the plant conditions without incurring into real risks or compromising the production. With this support to training, it is expected that the operators will gain experience on the process, can face with malfunctions and deviations from nominal conditions, and become aware of the importance of implementing the prescribed operating procedures by understanding the consequences of their actions.

Therefore, to improve the safety, it is advisable to: develop new models that are capable of better characterizing the phenomena involved in chemical accidents; consider the influence that the accident has on the process dynamics and *vice versa*; apply the aforementioned solution to an OTS.

In particular, to develop the second aspect, two tools are mandatory: a dynamic process simulator, to evaluate the plant dynamics due to changes of process conditions; a dynamic accident simulator, to evaluate the consequences of the hazardous material release.

In order to build an OTS, these tools must be coupled into one program for a real-time simulation, so that the operators become aware of the time scale of occurring phenomena. In addition, the accident simulator must address the "dynamic" feature to deal with unpredictable input data, so it is not possible to evaluate the accident consequences from considerations on the source term because it is not known *a priori* and cannot be computed *a priori* (since it depends on the dynamic evolution of the process).