Chimica Industriale

IND-KN-01 New trends in biodiesel production

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Biodiesel production is increased exponentially in the last decade (2009 world production 16000 Ktons). Biodiesel is a fuel safe, renewable, non-toxic, biodegradable and much less contaminant for the environment than conventional diesel. Moreover, it represents a strategic source of energy especially for the countries that have not oilfields. For these reasons, even if the cost of biodiesel is still greater than diesel from petroleum, many governments sustain this production also considering the forecast of a strong increase of petroleum consumption due to the increasing demand from the underdeveloped countries. An European Directive, for example, impose a 10% volume of biofuels in the transport sector by 2020. The key problems in the production and use of biodiesel are: to reduce the costs of production and to avoid the competition between the production of energy and food. As a matter of fact, many vegetable oils are highly refined edible oils.

The cost of biodiesel is mainly affected by the cost of the feedstock for more than 85%, but also an improvement of the adopted technology can contribute in reducing the costs. Therefore, it is imperative:

1) To employ less expensive feedstock, that is, unrefined or waste oils. These last contain large amount of free fatty acids and the scheme of the process must be modified as a consequence.

2) To use not edible oil coming from alternative sources as, for example, algae or Jathropa Curcas. Jathropa is a plant growing with a high oil productivity in residual dry lands, while, Algae grow in water ponds with an extraordinary productivity. Therefore, all these oil sources are today object of very intensive studies.

3) To improve the actual technology based on the use of homogeneous alkaline catalysts through a better understanding of the reaction mechanism, the development of new biphasic kinetic models and the adoption of techniques of process intensification favouring the reactions occurring at the interphase and the mass transfer operations.

4) To introduce the use of heterogeneous catalysts, simplifying the continuous operation, possibly finding a catalyst promoting in one step both esterification of free fatty acids and transesterification of tri-glycerides. Moreover, the ideal catalyst must be stable to the poisoning and leaching effect.

5) To find new remunerative uses for the by-product glycerol contributing to the reduction of the overall costs.

In this lecture, all the mentioned aspects will be considered in detail by reporting the most relevant results obtained in the last years by both our research group and other researchers operating in the corresponding fields.

IND-KN-02 The role of catalysis in the heavy oil up-grading: past and present

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The unconventional oils will play a much larger role in the growth of fuel supply than is currently recognized. As a matter of fact, whereas the earth's conventional proven world oil reserves are 1.3 trillion barrels (bbl), extra-heavy plus bitumen resources amount to about 4 trillion bbl.

The unconventional oils are characterized by an API gravity lower than 10, high viscosity and an unusual high concentration of poisons such as sulphur, nitrogen, metals, and asphaltenes. For this reason, a key role for the full exploitation of these hydrocarbon resources is played by the downstream processes that are required to upgrade and convert them into valuable products.

To this purpose different technologies has been developed along with the years, all aimed to increase the H/C ratio, both by carbon rejection or hydrogen addition. Thermal processes like visbreaking and coking belong to the former, while the latter include the hydrocracking, with different catalytic reactor technologies: slurry, fixed and ebullated bed.

In the new scenario of oil supply, the hydrocracking processes are required to be well-suited for the conversion and upgrading of a variety of "black oil materials", from conventional vacuum residues up to extra-heavy oils and bitumen, avoiding the production of residual by-products, such as pet-coke or heavy fuel oil.

It is interesting to point out that since the beginning of oil industry, refiners faced the problem of heavy stuff upgrading. The first thermal cracker, realized by Dubbs dated back to 1919. The earliest hydrocracking was introduced later in the 1930s by the American Standard Oil, to produce gasoline and lubricants form heavy petroleum fractions. The process was developed jointly with the German I.G. Farbenindustrie, based on its knowledge for coal liquefaction.

Among the pioneers in this area we can also cite Mario Giacomo Levi at Politecnico of Milan and Giacomo Fauser at Montecatini/ANIC of Novara. The efforts of Levi and Fauser were addressed to find out a valuable route to upgrade the Albanian oil, an asphaltic crude with a very low yield of gasoline (<10%). In Novara research centre, Fauser developed up to the pilot scale an hydrogenation process yielding up to 80% of high quality avio gasoline. This process was than industrially applied at the ANIC refinery of Bari in 1938.

In this communication, a past and present outlook of the main catalytic aspects of the heavy oil upgrading will be discussed.

IND-KN-03 Efficient Palladium(II)-Catalysis. Oxidative Heck Couplings and Addition Reactions

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The aim of the work has been to discover and to study new efficient palladium(II)-catalyzed coupling reactions. Thus, a number of oxidative Heck reactions were developed, in which the aryl-palladium intermediate was formed through transmetallation of an aryl boronic acid, an aryl carboxylic acid or an aryl sulfinic acids to a palladium(II) catalyst.

The first open-vessel, room-temperature palladium(II)-catalyzed oxidative Heck reaction with arylboronic acids, using oxygen from the air as the reoxidant of palladium, was identified. In a further investigation, base-free conditions for the transformation were developed and suitable conditions for microwave-assisted oxidative Heck reactions were established.

A convenient and low-cost palladium(II)-catalyzed method for the synthesis of styrene derivatives, by coupling arylboranes with vinyl acetate, was developed. The reaction mechanism was studied using on-line ESI-MS, which enabled the detection of cationic palladium intermediates in ongoing reactions, and a plausible catalytic cycle was proposed. In an attempt to make the oxidative Heck and the styrene synthesis reactions more attractive from an industrial point of view, conditions for continuous flow synthesis and microwave-assisted flow synthesis were identified. The results were generally good and rapid synthesis of the desired products was obtained.

Finally, novel methods for synthesizing aryl ketones from benzoic acids or aryl sulfinic acids and nitriles, *via* palladium(II)-catalyzed decarboxylation/ desulfination of the aromatic acids, were established. Further, the reaction mechanisms were studied by ESI-MS and plausible catalytic routes were suggested.

IND-KN-04 Catalysis for sustainable chemistry: looking at the future

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Chemical industry has made a considerable effort in recent decades to reduce the impact on the environment, and consumption of raw materials, including energy, but mainly to comply with regulations. The fast evolving world scenario for energy and chemistry, however, has accentuated the need to put innovation at the core of the industrial competiveness instead of the financial aspects. However, it is necessary to rethink the development model of the chemical industry, by introducing new flexible and modular approaches. Catalysis, in combination with microreactor and process intensification, are the core and enabling factors to achieve above objectives and thus realize sustainability through chemistry [1].

However, it is necessary to reconsider catalysis from this perspective. In microreactors, for example, the usual approach by deposition of a thin film on the microchannels walls is not optimal in terms of amount of catalyst and fluidodynamic and safety aspects, particularly for gas-liquid reactions such as the case of the H_2O_2 direct synthesis from H_2/O_2, a good example of key reaction towards the goal of sustainability for chemical production [2,3]. Microchannel reactors offer various advantages to overcome current limits in this reaction, but it is necessary to develop nanofibrous catalysts, because they allow to increase the (i) wall-to-volume ratio for an effective quenching of the radical-type explosive reactions, (ii) surface to volume catalyst ratio and catalyst loading per volume of microreactor, (iii) microturbulence. A further possible extension is the passage from micro- to nano-reactors using the channels of nano-membranes to host the catalyst nanoparticles.

A second challenge that will be discussed regards the need to accelerate the introduction of renewables and to address by catalysis the issue of greenhouse gas emissions [4-6], but putting them in the general perspective of which sustainable energy scenario should be developed, and what are the opportunities and need of catalysis in relation to these scenario. In a short term, energy efficiency and valorization of the less conventional energy sources are the two critical elements. Aspects that will be discussed regard the opportunities for energy efficient processes, and the development of novel routes for using natural gas to produce liquid fuels. In the short-medium term, biomass conversion represents an opportunity, but it is necessary to define which strategies should be adopted. Some aspects of the opportunities and challenges for catalysis for biomass conversion will be presented. Finally, in a long term scenario it is necessary to use the solar energy. This would imply solving the issue of energy storage and transport, and find a sustainable solution to CO_2 emissions. The possible scenario for using solar energy and CO_2 will be commented.

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IND-KN-05 PLASTIC ZEOLITES

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The contribution is devoted to thermoplastic materials whose crystalline phases are able to host low molecular-mass guest molecules.[1] Particularly relevant are polymeric materials including co-crystalline host-guest phases that, by suitable guest extraction procedures (e.g., by carbon dioxide in supercritical conditions), produce nanoporous crystalline phases,[2] which are able to absorb guest molecules also from very dilute solutions. For instance, δ and ε crystalline phases of syndiotactic polystyrene (s-PS) present their nanoporosity organized as isolated cavities and channels, respectively.

It will be also shown that suitable processing conditions can lead to the unprecedented formation of films with three different kinds of planar orientations of the co-crystalline phase.[3] The availability of s-PS films with three different kinds of uniplanar orientation can be, of course, relevant also for practical purposes. For instance, it allows guest orientation control for co-crystalline phases and guest diffusivity (and hence permeability) control for the nanoporous δ and ε phases.[4]

Aerogels including the two nanoporous phases can also be easily obtained by solvent removal by carbon dioxide in supercritical conditions from s-PS physical gels.[5] Guest sorption measurements at low activity have shown that δ-form aerogels present the high sorption capacity characteristic of s-PS δ-form samples (due to the sorption of molecules as isolated guests of the host nanoporous crystalline phase) associated with the high sorption kinetics typical for areogels (due to the high porosity and hence high surface area). Thus, these new materials present a fast sorption kinetics while maintaining a good handiness.[5]

The final part of the presentation will be devoted to possible advanced applications of materials based on co-crystalline and nanoporous crystalline s-PS phases. In particular, applications of nanoporous films for molecular sensor,[6] for sensors of chirality[7] and for active packaging of fruit and vegetable (by removal of ethylene and carbon dioxide)[4] will be presented. Moreover, several possible applications of co-crystalline films will be presented. In particular, advanced optical materials being photoreactive or fluorescent [9] will be reported. Recent studies on dielectric[10] and magnetic[11] properties of co-crystalline materials based on s-PS will be also reported.

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IND-OR-01 CO_2 Capture Technology Applications to the Oil & Gas Industry

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The need to satisfy growing world demand for energy, among the emerging economies in particular, goes hand in hand with the need to tackle the risks to the climate stemming from increased production of CO_2. In the medium-long term, one of the solutions can be represented by CO_2 Capture and Storage (CCS) technology, used to geologically sequester CO_2 generated by fossil fuels, especially from large-point source emitters such as power plants, refineries, cement plants and steel mills. Typically, CCS is defined as the integrated process of gas separation at industrial plants, transportation to storage sites and injection into subsurface formations, either depleted hydrocarbon fields or saline aquifers. Here, attention will be focussed only to the CO_2 Capture step of the CCS technology. The dimensions of the Climate Change issue are such that substantial improvements are to be achieved in the technologies of CO_2 separation, thus representing an intriguing new challenge for industrial chemistry to improve processes very old in their nature. The main activities of *eni* on CO_2 Capture are briefly described in the following.

Since 2001, *eni* has been member of the international CO_2 Capture Project (CCP) consortium (www.co2captureproject.org), together with most of the oil majors. The CCP is a unique collaborative technology development program initiated in 2000 with the aim to advance development of new approaches to capture and store CO_2 and improve efficiencies of existing technologies. The overall objectives are to deliver major cost reductions for carbon capture and demonstrate geological storage is safe, measurable, and verifiable. Phase 3 of the CO_2 Capture Project began in 2009 and is continuing support of R&D work for capture technologies at multiple levels of development, from exploratory research to demonstration. Different scenarios for application have been selected: Steam production for extraction of heavy oils, Natural Gas Combined Cycle for power production, Oil refinery (capture from process heaters, fluid catalytic cracking, hydrogen plants)

New scenarios for cost analyses are being developed and are serving as the basis for comparison of the capture technologies under development. At least two next generation technologies being developed by CCP are planned for demonstration in the Phase 3: a) the regenerator of a large pilot Fluid Catalytic Cracking unit in a Brazilian refinery run by Petrobras is currently being retrofit to oxy-firing with CO_2 recycle; a demonstration test is running in 2011. b) The retrofit to oxy-firing of a commercial Once Through Steam Generator used in tar sands extraction operations in Canada is scheduled for 2012.

In addition, Eni is pursuing the development of other CO_2 capture technologies in a few selected fields and will be briefly mentioned.

IND-OR-02 BIO-ORGANICS FROM BIO-REFUSE AS SOURCE OF CHEMICALS FOR USE IN CHEMISTRY, AGRICULTURE AND ANIMAL HUSBANDRY

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Urban biowastes (UBW) have been proven source of bio-based products for many uses (www.biochemenergy.it). Indeed, soluble bio-organics (SBO) isolated from UBW processed by anaerobic and aerobic digestion have been found to have cost effective performance as auxiliaries for use in chemistry, agriculture and animal husbandry. The potential monetary value of the above SBO is estimated to span from 1 to 70 € kg^{-1} against a processing cost evaluated at 0.10-0.50 € kg^{-1}, depending on the degree of purity required by the intended application. Urban refuse are therefore viewed not as a cost, but as source of revenue. Agriculture and animal biorefuse are likely to contribute organics useful to make a wider range of finished products. A main problem to fully realize these expectations is that SBO however contain 25 % of inorganics which may affect critically the product performance in many applications. This paper reports the most recent results obtained by isolating SBO from different biomass residues and characterizing both inorganics and organics in UBW and SBO in order to understand the partition of the sourcing matter components into soluble and insoluble materials.

IND-OR-03 Hydrogen production by glycerol steam reforming with ruthenium based catalysts, effects of reaction conditions.

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Glycerol is the main byproduct of biodiesel production and it is expected to increase its availability keeping also low prices. Hydrogen production by steam reforming of glycerol/water mixtures was recently reviewed [1] and Ru based systems showed promising performances [1,2].

Catalysts based on Ru nanoparticles supported on Mg(Al)O mixed oxide, derived from hydrotalcite precursor, were tested in the steam reforming of glycerol at different reaction conditions. Namely the effects of reaction temperature and of glycerol concentration in the feed were studied. Particular care was devoted to the study of coke deposition, that is one of the main reasons of catalysts deactivation.

Ru/MG70 catalysts (Ru 0,6% and 1% wt.) were prepared by impregnation using $RuCl_3$ solution on Mg(Al)O mixed oxide, derived from Pural MG70 (Sasol) hydrotalcite-like compound calcined at 900°C. Supported Ru nanoparticles were obtained by calcinations and reduction. Catalytic tests were performed in a fixed-bed quartz reactor, T=450-650°C; feed: 10-40 wt.% glycerol/H_2O mixt. (0.06 ml min^{-1}); He carrier flow = 30 ml min^{-1}; 0.200-0,800 g catalyst (mesh 45-35).

The systems were fully characterized by CO-DRIFTS, TPR, HRTEM, Raman, TGA-DSC, etc.

Working at 550°C catalysts were stable up to 20 hours and reached excellent performances: conversion up to 100%; H_2 yield >95% and CO selectivity less than 5%. Such high stability can be ascribed to the high nanoparticles stability on Mg(Al)O supports and on the high activity in WGS and C gasification reactions that keep a clean and active catalyst surface avoiding excessive coke deposition, so preventing deactivation.

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IND-OR-04 HS- functionalized silica HMS as support for PdAu hydrodesulfurization catalysts

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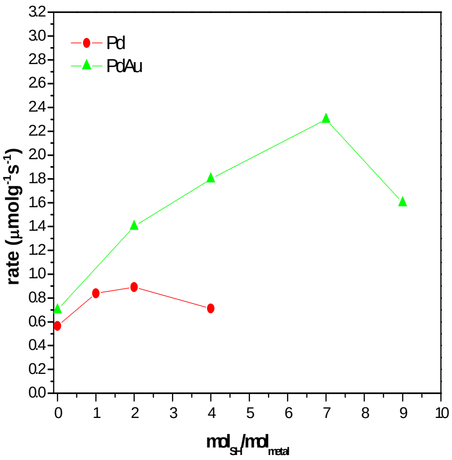
Environmental restrictions regarding the quality of the transportation fuels draw research toward more active and selective catalysts for hydrodesulfurization (HDS)[1]. As alternative to the CoMo or NiMo type of HDS catalysts, noble metal (Pd, Pt, Au) catalysts have been also investigated [2]. Moreover, ordered mesoporous silicas (MCM-41, HMS) have recently attracted much interest in hydrotreating processes due to their high surface area and controlled porosity [1,3].On the basis of a positive effect of the -SH functionalization of silica on the HDS activity of the supported CoMo catalysts [4], the investigation of similarly functionalised mesoporous silica on the hydrodesulfurization activity of the monometallic and bimetallic PdAu catalysts has been here undertaken. To this aim, mesoporous silica HMS was functionalized by suspending calcined silica in dry toluene and adding the appropriate amount of 3-mercaptopropyltrimethoxysilane (MPTMS). The mixture, refluxed for 24 h was recovered by filtration, washed several times with toluene and dried at 120°C overnight. The obtained products, functionalized with different amount of mercaptopropyl groups were labeled as HMS-xSH were x is the mol_{SH}/mol_{metals} ratio. Pd and PdAu catalysts were then prepared by deposition precipitation method using $PdCl_2$ and $HAuCl_4$ as metal precursors and urea as precipitating agent. The metal loading was 1 wt% of Pd in the monometallic Pd and 1 wt%Pd and 1wt% Au in the bimetallic samples. The samples were characterized by XPS and XRD analyses. Catalysts were tested in thiophene hydrodesulfurization (HDS). The reaction was carried out in the vapor phase using a continuous flow microreactor. An amount of 200 mg of catalyst (sieved fraction 210–430 mm), diluted with inert particles of SiC (in a weight ratio of 5:1 with respect to the catalyst) was used for each test. The samples were reduced in situ for 1h in flow of H_2 at 50 ml·min^{-1} and at 400 °C at a rate of 7 °C min^{-1} After purging with nitrogen, the HDS of thiophene was carried out at 340 °C with 5.3 vol. % thiophene in H_2 and WHSV = 7500 h^{-1}.

The reaction products were analyzed by online gas chromatography. The HDS catalytic activities of the monometallic and bimetallic series as a function of mol_{SH}/mol_{metal} ratio are given in Fig. 1. The amount of mercaptopropyl groups anchored on the support had a remarkable effect on the activity of the bimetallic catalysts. A maximum of the beneficial effect was achieved for a molar ratio $mol_{SH}/ mol_{metal} = 7$, therafter a decrease of the activity was observed. On the contrary a much milder effect was produced on the monometallic Pd catalysts. According to the XPS and XRD analyses, the enhancement of the activity is discussed in terms of an increase of the metal dispersion and on the structural changes of the active phase.



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IND-OR-05 Ceria-promoted Cu-based catalysts for the synthesis of methanol by CO_2 hydrogenation

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The synthesis of methanol from CO_2-rich syngas streams, produced by catalytic partial oxidation instead of energy-intensive reforming processes, would represent a decisive technological breakthrough with a remarkable improvement of the overall processes economics [1]. However, the "poor" performance of traditional methanol catalysts towards CO_2 activation [2] requires the discovery of alternative catalyst formulations [2-4]. This work is aimed at probing the effects of CeO_2 addition on the structure and CO_2-hydrogenation activity of Cu-based catalysts for methanol production. Characterization data revealed that ZnO acts as a structural promoter, while the replacement of zirconia carrier with ceria significantly depresses the extent of surface area of the Cu-ZnO system. Moreover, CO_2-hydrogenation data (Table 1) show that, in the range 453-513K, the activity pattern depends both on catalyst composition and activation atmosphere (pure or diluted hydrogen). In particular, the activation in diluted hydrogen enhances the surface functionality of ceria-promoted Cu-ZnO catalysts, understanding that higher surface methanol yields rely on the dual-site nature of the main reaction path which involves sites at metal/oxide interface.

Table 1. *CO_2 hydrogenation data (P_R, 3.0 MPa; GHSV, 8.8 NL g^{-1} h^{-1}).*

CATALYST	***T_R*, 453K** X_{CO2} - S_{MeOH} (%)		***T_R*, 473K** X_{CO2} - S_{MeOH} (%)		***T_R*, 493K** X_{CO2} - S_{MeOH} (%)		***T_R*, 513K** X_{CO2} - S_{MeOH} (%)	
	pure H_2	*diluted H_2*	*pure H_2*	*diluted H_2*	*pure H_2*	*diluted H_2*	*pure H_2*	*diluted H_2*
ZnCuZr	2.1 – 90	1.7 – 100	4.6 – 75	3.3 – 84	9.5 – 54	6.4 – 68	16.4 – 38	11.8 – 46
CeCuZr	1.1 – 100	1.0 – 99	2.1 – 71	1.9 – 76	4.7 – 58	3.4 – 62	9.4 – 39	6.8 – 42
ZnCuCeZr-1	2.9 – 97	3.2 – 92	5.7 – 88	6.4 – 82	9.9 – 74	11.4 – 65	14.7 – 57	16.9 – 51
ZnCuCeZr-2	1.7 – 100	2.2 – 93	3.6 – 80	4.8 – 86	7.1 – 65	8.6 – 74	11.3 – 46	13.3 – 56
ZnCuCe	0.6 – 100	1.6 – 100	1.8 – 87	3.6 – 89	3.5 – 77	6.0 – 79	6.4 – 62	10.7 – 59

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IND-OR-06 From waste biomass to levulinic acid, its esters and gamma-valerolactone: a high yield catalytic route to valeric biofuels

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The exploitation of waste biomass to produce electricity, biofuels and chemicals can represent a renewable energy source and a safeguard for environment. Recently we have studied some wastes as wood sawdust, paper sludge, exhausted lemon peels, tobacco chops, coffee tofferaction wastes, olive tree pruning, which are economically relevant for our country. A new process for the complete and efficient acid-catalyzed exploitation of the three components (hemicellulose, cellulose and lignin) of the above wastes has been optimized. This process allows us to convert the aqueous biomass slurry to furfural (yield up to 10 wt % with respect to dry biomass) and levulinic acid (4-oxopentanoic acid, LA, yield up to 25 wt % with respect to dry biomass) using a very dilute acid and a temperature of 100-200 °C. When the acid-catalyzed reaction is carried out in ethanol slurry, ethyl levulinate (EL) is obtained (up to 22 wt % yield).

The recovered lignin has been characterized by FT-IR, NMR and DSC: it resulted lignino-similar, with high content of functional groups and low molecular weight. These characteristics make this residue a valuable anti-oxidant and also a promising starting material for the synthesis of polymers.

Aqueous LA or EL were successively hydrogenated to γ-valerolactone (GVL) which is not only a sustainable liquid but also a valuable fuel additive and a precursor for the new platform of “valeric biofuels” which can deliver both gasoline and diesel components that are absolutely compatible with transportation fuels [1]. The bifunctional (acid and hydrogenating) performances of Ru heterogeneous catalysts and the optimization of the reactions conditions have been studied. The optimized catalytic system was recycled in successive runs and resulted completely stable. The inexpensive production of GVL directly from the biomass with an “one pot process” in water was also performed by adopting heterogeneous catalytic systems as well as very mild reaction conditions (only 5 atmospheres of hydrogen and temperatures of 50 °C are involved in the hydrogenation step).

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IND-OR-07 Optimization of the synthesis of 4'-nonafluorobutylacetophenone by metal catalysed cross-coupling reactions

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McLoughlin and Thrower[1,2] discovered the interaction between iodofluoroalkanes and iodofluoroaromatic compounds catalysed by copper in polar aprotic solvents to obtain a fluorinated organic compound having an aromatic group directly linked to a fluorinated alkyl group. This reaction was revisited by Chen and Tamborsky for bromoaromatics[3] and bromoheterocyclic[4] compounds. The results showed that the 4'-bromoacetophenone lead to the highest yield.

In this work, the synthesis of 4'-nonafluorobutylacetophenone (1) by the reaction between perfluorobutyl iodide and 4'-bromoacetophenone in the presence of N,N dimethylformamide (or dimethyl sulfoxide) as the solvent, was carried out with different transition metals as Cu^0, Cu(I), Cu(II), Fe^0, Fe(II), and Fe(III). Investigation on the effects of ligands, solvents, temperature and metal catalyst on the yields was optimized[5], with the purpose to find out the best conditions for the synthesis of the product.

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IND-OR-08 Palladium-catalysis to Dihydrodibenzoazepine Derivatives: Synthesis, Structure and Theoretical Calculations

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In the framework of our research aimed at developing efficient methods for the construction of complex molecules through a series of metal-controlled steps, starting from a pool of simple molecules [1] we have worked out a one-pot process for the synthesis of dihydrodibenzoazepines, an important class of seven-membered heterocycles with pharmacological activity [2].

The process consists of the reaction of one molecule of aryl iodide, one of a bromoaniline and one of norbornene at 105 °C in DMF under the catalytic action of palladium(0)/triarylphosphine. Several steps occur, including the initial oxidative addition of the aryl halide to palladium(0), norbornene insertion, palladacycle formation, new oxidative addition, this time involving bromoaniline, *o*-aminoaryl migration onto the norbornyl site of the palladacycle, azepine ring closure by reaction of the amino group with the palladium-bonded arene carbon [3]. All steps occur chemo- and regio-selectively and are compatible with a variety of substituents. Thus it has been possible to obtain compounds of the type reported in Figure 1 (R^1 = H, alkyl, alkoxy, R^2 = H, alkyl, Cl, carbalkoxy, R^3 = alkyl, Cl, F) in high yields.

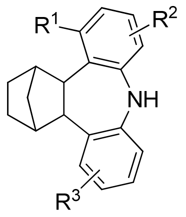

Figure 1

The structure of two members of this class (R^1 = Me, R^2, R^3 = H; R^1 = Me, R^2 = 7-Me, R^3 = H) has been determined by single-crystal X-ray diffraction [4].

Theoretical calculations indicate the critical role played by the chelating amino group in directing the reaction pathway to the seven-membered ring formation [5].

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IND-OR-09 Short Contact Time - Catalytic Partial Oxidation based technologies: recent advance in pilot- and bench-scale testing

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Eni R&D has been active in the field of Short Contact Time – Catalytic Partial Oxidation (SCT-CPO) processes for almost twenty years. The “main stream” activity is oriented to the definition and development of technologies for producing Hydrogen/Synthesis gas. However the SCT-CPO method, for its flexibility and simplicity, can be successfully applied to other fields. Among them, the production of light olefins starting from light hydrocarbons and/or naphtha, has recently re-gained attention thanks to very promising experimental results obtained with catalysts developed together with the Dipartimento di Ingegneria Chimica dell’Università di Napoli [1].

The experimental work devoted to Synthesis Gas production [2] is addressing either the fundamental principles or the technical and economical potential of the technology. Good experimental responses -achieved with peculiar technical solutions- were coupled to favourable techno-economical evaluations and promoted the progressive widening of the field of the investigations. The list of “processable” Hydrocarbons now ranges from Natural Gas (NG) to Liquefied Petroleum Gas (LPG) and Gasoils, including those characterised by high levels of unsaturated and sulphurated molecules and, lately, to other compounds with biological origin.
The defined technological solutions are grouped as follows:

Technology 1: Air Blown SCT-CPO of Gaseous Hydrocarbons and/or Light Compounds with biological origin
Technology 2: Enriched Air/Oxygen Blown SCT-CPO of Gaseous Hydrocarbons and/or Light Compounds with biological origin
Technology 3: Enriched Air/Oxygen Blown SCT-CPO of Liquid Hydrocarbons and/or Compounds with biological origin

Recently, the licence rights on a non-exclusive basis for the commercialisation of SCT-CPO based processes for H_2/Synthesis gas production from light hydrocarbons with production capacity lower than 5,000 Nm^3/h of H_2 or 7,500 Nm^3/h of syngas have been assigned to two external companies. In parallel, the development of a medium-scale demonstrative plant is progressing within the framework of an eni refinery. These activities are addressed to the utilisation of SCT-CPO for matching the variable Hydrogen demand in several contexts of oil refining operation.

This presentation will report on the current status of SCT-CPO based technologies for Synthesis gas and light olefins production with a focus on experimental results obtained, either at pilot- and bench- scale level.

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IND-OR-10 Reforming of the biomass gasification producer gas

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The gasification of lignocellulosic biomass is receiving increasing interest to produce syngas ($CO + H_2$), which can be further converted to substitute natural gas and via Fischer-Tropsch to liquid fuels [1]. The producer gas obtained by gasification contains CH_4, H_2, CO, CO_2, C_2-C_4, condensable hydrocarbons (tars) and some contaminants such as NH_3, HCl, H_2S and particulate (ash, alkali, soot). In order to generate a suitable syngas for chemical treatment the producer gas must be cleaned and upgraded. After the removal of the particulate by hot gas filtration, reforming or autothermal reforming processes can convert the hydrocarbons and increase the CO and H_2 content, making therefore the gas suitable for the production of biofuels by Fischer-Tropsch. The feasibility of these processes is dependent on the development of reforming catalysts active and stable in presence of the contaminants [2].

Ni- and Rh-based catalysts, commercial-type and obtained from hydrotalcite-type compounds, were studied for the reforming of the producer gas. In a first step, catalysts were tested in a laboratory rig by feeding a simulated producer gas and selected contaminants: model tar compounds (toluene and naphthalene), NH_3 and H_2S. Then, tests were performed under real conditions in a reactor placed downstream an oxygen/steam circulating fluidized bed gasifier. The effect of the biomass fuel composition and reforming temperature on the catalytic performances was studied. High temperatures (950-1050 °C) were required to achieve high hydrocarbon conversions (methane and tar) with Ni-based catalysts; whereas the presence of rhodium in the catalysts allowed to decrease the reaction temperature, even in presence of sulfur. The characterization of the used catalysts evidenced three deactivation mechanisms: sintering, chemical poisoning and fouling by physical deposition of carbon, soot or particulates.

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IND-OR-11 Ni-CeZrO$_2$ catalysts for low temperature steam reforming of methane

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The growing request for the development and diffusion of technologies based on renewable energy sources represents an important challenge for researchers working in catalysis. Steam reforming of methane (MSR) is a well known process for the production of syngas, a valuable feed for important industrial processes and for fuel cells. When the process is coupled to water gas shift reaction, after CO_2 removal hydromethane (a mixture of hydrogen and methane) can be obtained, to power hybrid automotive systems. If the temperature of the process is lowered by employing a proper catalyst, a low green-house impact fuel can be produced in solar powered plants, based on molten salt technology [1].

One of the most promising catalysts for low temperature MSR is based on Ni-Ce-ZrO$_2$ mixed oxide [2]. The primary difficulty associated with supported Ni catalysts is deactivation, either due to coke formation or to sintering of the metallic and support phases at high temperature [3]. CeO$_2$ is found to stabilize the catalyst against deactivation due to its redox behaviour and/or better dispersion of the active metal, while the addition of ZrO$_2$ should improve thermal resistance and the oxygen storage capacity of ceria.

In this work, a one step co-precipitation/digestion method [2] is employed to prepare a series of Ni-Ce-ZrO$_2$ catalysts with different Ni loading and Ce/Zr ratios. The preparation method has been optimized to obtain nanosized particles with high surface areas (75 – 180 m2/g). Structural and spectroscopic techniques (XRD, TEM, UV-Vis, FTIR) are employed to study the nature of NiO particles and their interaction with the support. The catalytic activity is tested in MSR reaction at 520 °C, varying steam to carbon ratio and spatial velocity, in order to obtain kinetic values for a possible upscale of the process. Comparison of the catalytic performances (conversion and stability) with characterization results is aimed at defining structure/properties relationships.

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IND-OR-12 ION EXCHANGER CATALYST MODIFICATION FOR REACTIONS INVOLVING LIPOPHILIC REAGENTS.

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Sulfonated poly(styrene-co-divinylbenzene) is an effective acid catalysts commonly used in several chemical processes. Conventional materials are fully or almost fully sulfonated. This makes them compatible with polar substances, but implies that lipophilic reagents can be used only when the porosity of the catalyst little (or not at all) depends on swelling or when a polar co-reagent, able to swell the catalyst, is involved and used in large excess. [1] In the latter case the combination of lipohilic and hydrophilic domains within the polymeric framework should give improved catalysts. [2] In this connection, the approaches employed sofar gave materials of limited performance or scope. [3-6] We have prepared new strongly acidic ion exchanger catalysts by partial acylation of common styrene-co-divinylbenzene polymers before sulfonation, [7] with improved catalytic performance in the esterification of stearic acid with MeOH. They are as active as conventional ion exchanger catalysts when the reaction mixture (stearic acid, alcohol, exhausted edible oil) is saturated with MeOH (20% wt), and much more active when the alcohol concentration is lowered to 5 % wt. The swelling behaviour of the acylated and conventional catalysts at relatively high and low MeOH concentrations are very similar and should equally affect them. This suggests that the better performance of the acylated ones is brought about by the presence of lipophilic adsorption domains which assist the activation of the fatty acid inside the catalyst.

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IND-OR-13 Photocatalytic Oxidative Dehydrogenation of Ethylbenzene to Styrene on Sulphated $MoO_x/\gamma\text{-}Al_2O_3$

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Styrene is one of the most important compounds in the chemical industry. It is industrially produced by catalytic dehydrogenation of ethylbenzene on iron-based catalysts. The main problems associated with the dehydrogenation process of ethylbenzene are the thermodynamic limitation, the low conversion rate, the energy demand due to the high endotermicity of the reaction, and the deactivation of catalysts by coke formation. As an alternative way, the oxidative dehydrogenation of ethylbenzene has been proposed. In most cases, the reaction temperature was above 500 °C. For this reason, the use of a photocatalytic process may be beneficial because of its mild reaction conditions that could reduce operating costs and increase selectivity. In this study sulphated $MoO_x/\gamma\text{-}Al_2O_3$ catalysts were used as photocatalysts for the oxidative dehydrogenation of ethylbenzene to styrene in gas phase. The influence of the Mo and sulphate load was investigated. Catalysts, prepared by incipient wet impregnation, were characterized by N_2 adsorption-desorption at -196°C to measure specific surface area, thermogravimetric analysis, Raman and UV-Vis spectroscopy.

A gas-solid heterogeneous photocatalytic reactor at high illumination efficiency [1] was utilized to measure the photoreactivity. It consists of a fluidized bed reactor irradiated by two arrays of UV Leds, emitting at 365 nm, positioned at its external transparent walls. The photoreactor is equipped with an electrical heater immersed within the catalytic bed to control the reaction temperature that was set at 120°C. Catalytic tests were carried out feeding N_2 stream containing an ethylbenzene concentration ranging between 1000 and 6000 ppm, with oxygen/ethylbenzene and water/ethylbenzene ratio equal to 1.5 and 1.6, respectively. The catalyst weight was 14 g diluted with 16 g of $\alpha\text{-}Al_2O_3$ or with 7 g of silica gel. Obtained results showed that it is possible to obtain styrene on MoO_x/Al_2O_3 catalysts with 100% selectivity. The molybdate surface coverage of 50 % gave the maximum photoactivity. An optimum in sulphate loading was found to be 2.4 wt%. The decreasing in catalytic activity at high sulphate load is due to lower accessibility of surface MoO_x species, decorated by sulphates when present in high amount. For all the operating conditions, no deactivation phenomena were detected.

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IND-OR-14 Towards the development of a new reactor technology for the Fischer-Tropsch synthesis

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The adoption of multitubular reactors loaded with washcoated structured catalysts having highly conductive honeycomb supports has been proposed as an alternative to conventional packed-bed reactors in order to approach the ideal plug-flow behaviour while (i) enabling isothermal operation of highly endo and exo-thermic reactions, (ii) facilitating the intraparticle mass-transfer, and (iii) limiting pressure drop.

A systematic study has been carried out in this work to assess the heat transfer characteristics of washcoated conductive structured catalysts for the Fischer-Tropsch synthesis. Following the experimental testing of 27 cpsi aluminum monoliths washcoated with a layer of a representative Co/γ-Al_2O_3 catalyst reported in a previous paper [1], in this work we have simulated the performances of a technical tubular reactor loaded with such catalysts by means a pseudo-continuous, heterogeneous, two-dimensional non-adiabatic numerical model. Lumped CO conversion kinetics, developed for the adopted Co-based FT catalyst, have been adopted. Heat generation by the FTS over the washcoated walls of the monolith channels, heat conduction along the longitudinal and the radial dimensions of the monolith, and heat exchange both with the gas phase flowing in the monolith channels and with the external coolant have been accounted for in the model.

Simulation results indicate that heat conduction in the aluminum support of the catalyst can be exploited to remove effectively the heat generated by the strongly exothermic FT reaction. Flat axial and radial temperature profiles have been found along the catalytic bed, showing the unique ability of the adopted structured catalysts to manage the heat removal issue and to guarantee an excellent temperature control without the need of recycling a fraction of the liquid reaction products. Moreover, due to the high void fraction of the structured support and the laminar flow in the straight washcoated channels, pressure drop has been found negligible at all the investigated process conditions.

These results make highly conductive extruded honeycomb monoliths, washcoated with a Co-based FT catalyst, very promising for the application at the industrial scale, in particular when adopting supports with high cell densities and catalysts with high activity. In fact, the excellent properties of such catalysts could afford new opportunities for intensification of existing processes in externally cooled multitubular fixed-bed reactors, where operation is limited by the onset of severe hot-spots, so that significant amounts of liquid products (at the process conditions) have to be recycled to the reactor to remove the reaction heat. Near-isothermal and isobaric behaviour of tubular FT reactors at high conversions per pass without the need of a liquid cofeed is in fact an interesting perspective.

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IND-OR-15 CATALYTIC LIQUID- AND GAS-PHASE OXIDATIONS FOR THE SYNTHESIS OF INTERMEDIATES AND SPECIALTY CHEMICALS: SOME EXAMPLES OF INDUSTRIAL RELEVANCE

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Nowadays, it is clear that the target of creating a sustainable future for the next generations requires to re-think the industrial application of chemistry. In this context, oxidation reactions play a major role, being the tool for the production of huge quantities of chemical intermediates and specialties.

Actually, in order to implement all these ideas into real projects, the development of more efficient reactions is one primary target. Yield, selectivity and space-time yield are considered the right metrics for evaluating the reaction efficiency[1].

Three reactions that are emblematic of the new approaches used in the chemical industry will be discussed.

The first one is a new process aimed at a more sustainable production of menadione (vitamin K3). The “greener” approach includes the use of hydrogen peroxide in place of chromate (from a stoichiometric oxidation to a catalytic oxidation), and the transformation of 2-methyl-1-naphthol using Nb_2O_5-SiO_2 catalysts prepared with the sol-gel technique. The study of the reaction mechanism was fundamental to get indications about the best operative conditions, and improve the selectivity to menadione [2].

In the second part, I explored the direct oxidation of benzene to phenol with hydrogen peroxide. Titanium silicalite-1 (TS-1) is the catalyst chosen for this reaction. Comparing the reactivity results obtained with some TS-1 samples having different chemical-physical properties, and analyzing in detail the effect of the more important reaction parameters, we could formulate some hypothesis concerning the reaction network and mechanism [3].

Finally, the last part deals with the study of a new process for the valorisation of glycerol by means of transformation of glycerol into acrylic acid, with the intermediate formation of acrolein; the latter can be obtained by dehydration of glycerol, and then can be oxidized into acrylic acid[4].

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IND-OR-16 A New Water Soluble Cationic Pd(II)-Allyl Complex Containing Sulfonate “Click” type Ligand

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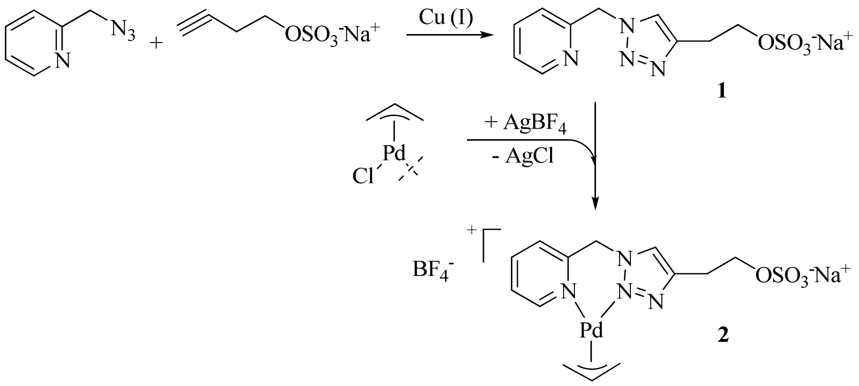
Nowadays, the chemistry that takes place in water receives considerable attention for environmental, economic and safety reasons, and also because it allows for unique reactivities not usually observed in organic solvents [1]. The use of the aqueous medium for metal-mediated synthesis has attracted large interest and there is a increasing demand of water-soluble ligands and metal complexes [2].

An intriguing and efficient method for the synthesis of ligands is the copper catalyzed [3+2] azide-alkyne Huisgen reaction, so called “click chemistry”. Recently we have been involved in this topic [3]. We wish to report here the synthesis of a novel water soluble chelating pyridyl-triazole sulfonate ligand **1** and of the water soluble cationic palladium allyl complex **2** (see Scheme 1).



Scheme 1. Synthesis of ligand **1** and of complex **2**.

NMR investigations in D_2O confirm the chelating behaviour of ligand **1** and reveals that **2** is stable up to 90 °C.

Preliminary investigations demonstrate that **2** is an promising catalyst in cross coupling reactions carried out in aqueous media.

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IND-OR-17 Synthesis and self-assembly of biodegradable poly(ε-caprolactone) /poly(ethyleneoxyde) "Y-shaped"copolymer for pharmaceutical applications by click chemistry and R.O.P

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Recently, hydrophobic biodegradable polyesters such as poly(ε–caprolactone) (PCL) and poly(lactide) and their amphiphilic block copolymers with poly(ethyleneoxyde) (PEO) have attracted much attention of pharmaceutical and biomedical applications [1]. These copolymers, due to their excellent biocompatibility and biodegradability, and the remarkable ability to self-assembly in aqueous solution with formation of "core (PCL)-shell(PEO)", micellar structures have been investigated as nanocarriers for controlled and targeted release of various bioactive molecules [2]. These nanocarriers are caracterized by very high thermodynamic stability, small size and biomimetic "stealth" properties provided by the crown of PEO. This allows a high residence time in the bloodstream necessary to the crossing of the blood vessels (extravasation) in tissues with high vascular permeability such as tumors or inflamed tissue (EPR effect). This work was aimed at the synthesis and characterization of copolymers "Y-shaped"wf-assembly in water. Chain-end bifunctional PCL segments were obtained by ROP of ε–caprolactone initiated by bis-azido alcohol. The coupling of the PCL with two PEO segments having a terminal alkyne group was accomplished by 1.3 Huisgen cycloaddition catalyzed by Cu (I).The obtained "Y-shaped" copolymers were characterized by NMR, DSC, DLS WAXS SEC and inherent viscosity measurements, showing high structural regularity and monomodal molecular weight distribution. The critical micelle concentration, CMC, was determined by fluorescence spectroscopy using pyrene as probe.. Different crystalline PCL and PEO phase were evidenced in bulk by DSC and WAXS. Their aggregation in aqueous solution produced micellar structures with hydrodynamic diameter in the 50-200 nm range and very low CMC values. Such systems are good candidate as biomimetic nanocarriers of lipofilic drugs.

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IND-OR-18 Synthesis and Catalytic Applications of Novel Thiolated and Sulfonated Polymers Resulting by Functionalization of Multiblock Syndiotactic Polystyrene-*co*-1,4-*cis*-Polybutadiene.

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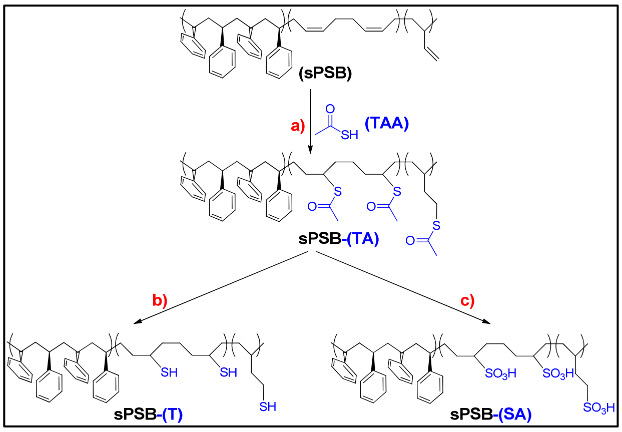

Scheme 1. Thioacetylation, thiolation and sulfonation of sPSB copolymers.

Hydrocarbon polymers carrying side chain functional groups are attractive materials because of their specific chemical reactivity or physico-chemical properties.

Their direct synthesis by copolymerization of suitable monomers is often impracticable because of incompatibility of the transition metal catalysts with the polar monomers; thus post-functionalization is often required to yield these polymer products of interest.

In this work the controlled radical thioacetylation of polybutadiene segments in multiblock copolymers syndiotactic polystyrene-*co*-1,4-*cis*-polybutadiene (sPSB) is described. sPSB are semicrystalline polymers (T_g = 100°C, T_m = 250°C) which exhibit, when shaped as thin film by spin coating, a phase separated morphology, ranging from irregular hard lamellae of sPS in PB to spheres of PB embedded into the sPS phase[1]. The selective functionalization of the PB domains by thioacetylation followed by thioester cleavage lead to thiol functionalized sPSB (sPSB-T). The direct thioester oxidation by *in situ* synthesized performic acid leads to sulfonated sPSB (sPSB-SA) in quantitative yield.

sPSB-SAs with high degree of sulfonation were successful tested as strongly acidic catalysts in esterification reactions.

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IND-OR-19 Dehydrogenation reaction of Ethanol to Ethyl Acetate in one step reaction by using copper chromite based catalysts.

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In the last years the worldwide interest to the use of biomass, as raw materials to obtain energy, is growing as a key technology towards sustainable development. In particular the bio-ethanol is a renewable source available to produce both bio-fuels and commodity chemicals of great interest such as ethylene, acetaldehyde and ethyl acetate. The bio-ethanol based processes have shown great advantages by the environmental and economics viewpoints [1]. In particular the ethyl acetate production by one step ethanol dehydrogenation reaction is a promising alternative process to the classical one that use acetic acid [2]. Therefore our research has been focused on the ethanol dehydrogenation to ethyl acetate in one step reaction using copper based catalysts. In the present paper, we have studied the behaviors of three different commercial catalysts: (i) a $CuO/ZnO/Al_2O_3$ catalyst (BASF-K-310) (ii) a $CuO/CuCr_2O_4$ catalyst (Sud Chemie T-4466) (iii) and a $CuO/Cu/CuCr_2O_4/Al_2O_3/BaCrO_4$ pre-reduced catalyst (BASF Cu-1234-1/16-3F).

The kinetic runs have been performed in a stainless steel tubular packed bed reactor (i.d. 1.8 cm, length 30 cm) by changing the temperature in the range 200-260°C and the pressure from 10 to 30 bars. The best catalytic results, in terms of activity, selectivity and thermal stability, have been obtained with a pre-reduced commercial copper chromite catalyst (BASF Cu-1234) supported on alumina and containing $BaCrO_4$ as promoter. The best results obtained for this catalyst, by operating at 220-240°C, 20 bars and 98 (grams hour/mol) of ethanol contact time, were 65% of conversion with 98-99 % of selectivity to ethyl acetate. One of the advantage of the examined process is the possibility to produce as main co-product pure hydrogen, a promising future energy vector. A depth study of the structural and chemical properties of the catalysts, realized with the common characterization techniques, has been investigated, with the aim to correlate them to their surprising results of activity and selectivity to ethyl acetate. In particular a very interesting study of the surface and structural has been realized using very sophisticated techniques such as the EXAFS, XPS and DRIFT measure. The promising results should be the base for the development of an industrial plant to produce ethyl acetate in a very simple and economic way [3].

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IND-OR-20 Ni based catalyst for Ethanol Steam reforming (ESR)

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ESR seems to be a promising way for the production of H_2 starting from a renewable source, provided that ethanol is produced from bio-mass (bio-ethanol). Verykios et al. studied H_2 production by SR of bioethanol, focusing on Ni as active phase loaded on different supports [1] or on supported noble metals [2]. The key issue was to reduce coke formation and to lower the reaction temperature. Other investigations on low temperature SR were carried out by Llorca et al. [3,4], using Co-based catalysts in microreactors.

In the present work, two different series of Ni-based catalysts were synthesized by Flame-pyrolysis [5] and tested for the low temperature ESR (≤ 500°C). TiO_2 and La_2O_3 were chosen as supports and the Ni loading was 5-15 wt% for each set of samples. Activity test were made focused the attention on H_2 productivity, CO/CO_2 ratio and the formation of coke. Comparing the activity of catalysts based on TiO_2 and La_2O_3 we found that the best support was La_2O_3 and that the catalytic performance improved as the content of Ni increased.

Therefore, a $LaNiO_3$ (Ni ca. 36 wt%) catalyst was tested, showing the highest H_2 productivity, with a low CO/CO_2 ratio and above all a very good resistance towards deactivation.

Conversion of ethanol was around 90% at 500°C, with a stable H_2 productivity and selectivity over 24 h-on-stream. The CO/CO_2 ratio was around 0.4 and it was stable for all the duration of the test. Even reducing 4 times the contact time, ethanol conversion was still around 80% after 24 h-on-stream with an increase of H_2 selectivity at the expenses of CH_4 as the conversion decreased.

Future experiments are planned to check the activity of this catalyst under different experimental conditions and to improve the catalytic performance using some metals as doping agent.

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IND-OR-21 TUNGSTEN-VANADIUM MIXED OXIDES FOR THE OXIDEHYDRATION OF GLYCEROL INTO ACRYLIC ACID

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Glycerol is considered one of the Bio-based Building Blocks (B^3) with the greater potential for the implementation of the biorefinery concept into practice.[1] One of the most studied reaction is the transformation of glycerol into acrolein,[2] whereas much less attention has been given to its direct transformation into acrylic acid. The reaction formally includes a first dehydrative step into acrolein, requiring Brønsted-type acidity, and a second selective oxidation step of acrolein into acrylic acid. The approach of a single bifunctional catalyst is aimed at combine several chemical steps into a single catalyzed transformation ("one-pot" and "cascade" reactions).

In the present work we report about an investigation of the properties of a bifunctional W-V-O system (as V-containing WO_x hexagonal bronzes), with the aim of understanding which are the key chemical-physical features needed for the direct transformation of glycerol into acrylic acid. We carried out preliminary experiments aimed at studying the acid-type behavior of WO_3 in the dehydration of glycerol into acrolein; tests were carried feeding also oxygen to reduce considerably the rate of catalyst deactivation due to heavy compounds accumulation on the catalyst surface, finally leading to coke. However, negligible selective oxidation properties were found, because of the absence of V ions. The catalyst was very active in glycerol dehydration, with maximum selectivity to acrolein of 50%, major by-products being heavy compounds and acetaldehyde.

The introduction of V did not increase the activity of the catalyst but the distribution of products changed considerably. Acrylic acid formed with 25% selectivity at 320°C; however, the increase of temperature led to a progressive decline of selectivity to the acid. CO and CO_2 were the major products in the entire range of temperature considered. Experiments made by variation of contact time demonstrated that the only primary products were acrolein and acetaldehyde; the two compounds, however, underwent a consecutive transformation into the secondary products, acrylic acid and acetic acid. The atomic ratio between W and V remarkably affected the catalytic behavior.

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IND-OR-22 Effect of water on NO decomposition over Cu-ZSM5 based catalysts

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The catalytic decomposition of NO into N_2 and O_2 represents the ideal process to remove nitrogen oxides in the presence of oxygen. Cu-exchanged ZSM5 zeolite is the most promising catalyst for this process and, although several limitations hinder practical applications, it was widely investigated to understand its unique behaviour of this zeolite [1,2]. One of the main drawbacks is the presence of water vapour in the feed which causes deactivation generally associated to copper shifting to inactive positions. Rare earth ions addition was reported to be effective to partially prevent catalyst deactivation [3].

In this study the effect of water vapour on the adsorption and decomposition of NO was studied by conducting adsorption, TPD and NO decomposition tests on both pre-reduced Cu-ZSM5 and LaCu-ZSM5 catalysts. The adsorption experiments were carried out at 125°C in the presence or in the absence of H_2O in the NO/He feed mixture. The original catalytic activity towards NO decomposition is totally recovered when water, previously adsorbed at low temperature, is desorbed before starting the reaction at 450°C. This result rules out the hypothesis that water could deactivate the catalyst even at low temperature. Nevertheless, the co-adsorption of water dramatically decreases the amount of adsorbed NO at 125°C under dry conditions. The addition of lanthanum to a Cu-ZSM5 catalyst increased the amount of NO adsorbed in the absence of water and significantly limits the decrease of NO adsorption in the presence of water. TPD experiments carried out after NO adsorption showed that the addition of lanthanum promotes the formation of nitrates which are considered as reaction intermediates in the NO decomposition [4].

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IND-OR-23 Sulfonic Acid Resin: an Useful Support of Palladium for the Direct Synthesis of H_2O_2

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Hydrogen peroxide is a versatile and environmental friendly oxidizing agent. Currently, H_2O_2 is produced on large scale preferentially by the anthraquinone auto-oxidation process which is associated with considerable consumption of energy. The direct synthesis of H_2O_2 from H_2/O_2 could represent a viable alternative.

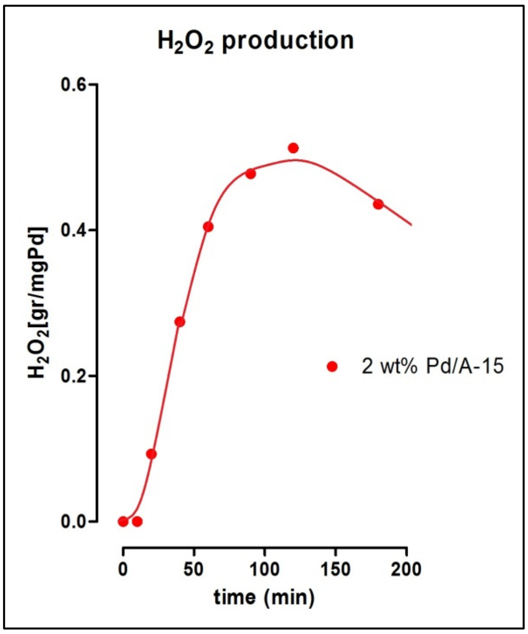
It's known that one of the most active metals for the synthesis is the Pd and it's important to find the best way to disperse it on a support able to enhance the performance in terms of productivity and selectivity. Acid polymeric resins can be considered a valid support [1] because they don't promote the hydrogen peroxide decomposition. In this work the commercial acid resin Amberlyst 15 was tested for the synthesis of hydrogen peroxide. The catalysts have been prepared by ionic exchange method mixing Amberlyst powder with an aqueos solution of palladium cloride.

The synthesis was carried out in a stainless steal autoclave at room temperature using CO_2 expanded methanol as solvent [2] at 30 bar of total pressure.

The catalytic activity is comparable with the most active catalysts reported in literature and moreover the leaching of palladium in reaction solution is less than 2%.

TEM analysis shows that the distribution of particles is homogenous and the average diameter is almost 15 nm.

The results will be presented in comparison with other catalytic systems of palladium based on oxides and carbon nanotubes.



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IND-OR-24 Effect of the support on Ni catalytic performances in glycerol steam reforming

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In the last years, the use of hydrogen as new energy vector has been widely encouraged, because it is clean and carbon-free [1]. Nevertheless, an effective solution of environmental problems such as the greenhouse effect and the global warming, as well as the decrease of the dependence on fossil fuels, requires the use of renewable sources. In this context glycerol, the main by-product in biodiesel production, has emerged as a promising source of hydrogen, because of its high hydrogen content and renewability, safeness and non toxicity [2].

Several catalysts have been proposed for glycerol steam reforming. In this work we report the catalytic performances of Ni-based catalysts at two different reaction temperatures. Moreover, the effect of the support (*i. e.* TiO_2, SBA-15 and ZrO_2) on the selectivity to hydrogen was studied.

TiO_2 and ZrO_2 were synthesized by a conventional precipitation method [3], whereas SBA-15 was prepared through a template synthesis [4]. Catalysts were prepared by incipient wetness impregnation of the supports with an aqueous solution of the Ni precursor in order to obtain a 10 wt% Ni loading and they were finally calcined. The physico-chemical properties of the catalysts were determined by nitrogen physisorption analysis (BET), temperature programmed reduction (TPR) and high resolution transmission electron microscopy (HR-TEM). The activity tests were carried out in a fixed bed tubular quartz reactor at atmospheric pressure at two different temperatures (500°C and 650°C), after reduction of the samples in H_2 flow for 1 hour at either 500 or 700°C respectively. A water/glycerol solution was fed (10 wt% solution of glycerol in water) at the constant flow rate of 0.06 mL/min. Data were collected up to 20 hours on each sample.

The Ni/TiO_2 sample exhibits negligible activity at 650°C because of the collapse of the support. Concerning Ni/SBA-15, our results indicate the insufficient hydrothermal resistance of the support, which leads to the progressive deactivation of the catalyst. However this support is able to stabilize the active phase in a rather efficient way, thus preventing Ni sintering. Ni/ZrO_2 exhibits the best performances: a stable glycerol conversion of ~72% and a hydrogen yield of ~65% were obtained. This is due to the almost full preservation of the structure of the zirconia support even after 20 h in the SR conditions; moreover, also the dispersion of the Ni active phase remained unchanged.

The different behaviour of the three catalysts can be then ascribed (i) to the chemical, thermal and mechanical resistance of the support in the reaction conditions and (ii) to the intensity of the interactions between the support and the active phase, which affects in particular the stability of the Ni nanoparticles. Our results highlight the importance of the nature of the support, which plays a key role in designing the catalytic performance.

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IND-OR-25 A Photomodulable organometallic catalyst

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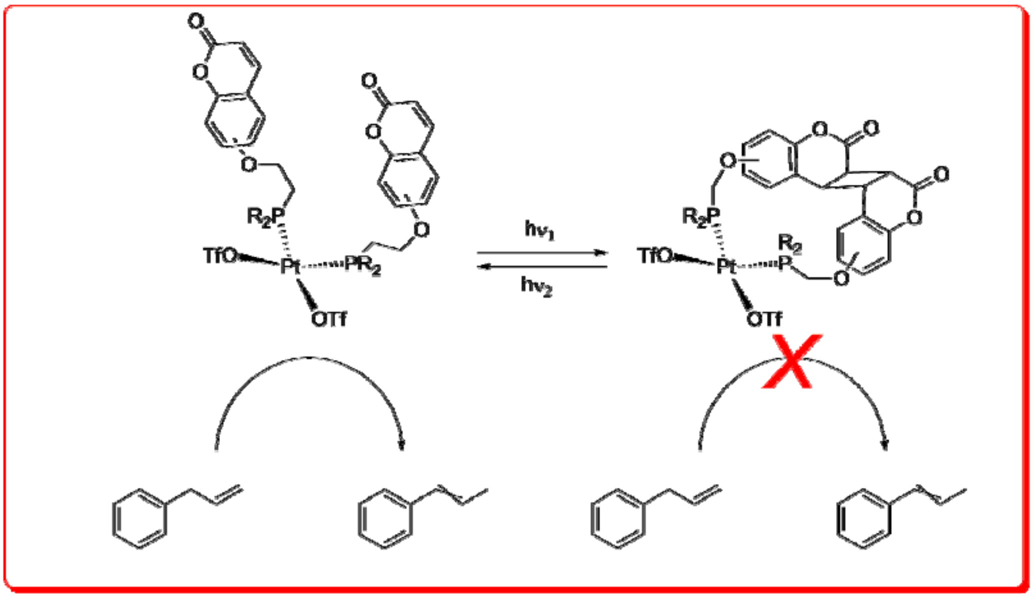
In homogeneous catalysis proper functionalization of a metal center with an appropriate ligand system often represents the most rewarding strategy to achieve the best performance, in terms of activity, selectivity and sometimes recycle. Alternatively the performance of a homogeneous catalyst can be modulated by means of interaction with external stimuli, mimicking what occurs in Nature where the activity of enzymes is triggered on and off as a function of the request of the organism. A possible approach exploits supramolecular interactions (*host-guest*) between the catalytic species and another chemical entity which interact as a second sphere ligand.[1] In this case the restoration of the original activity requires the addition of a third chemical species. A more simple system can be obtained if considering the light as effector in catalysis.[2] The preparation of an organometallic complex bearing a molecular tag that undergoes a photochemical reaction could deliver a new generation of homogeneous catalysts whose activity, selectivity and recycle properties can be tailored by employing an appropriate light source.[3]

In the present contribution are presented the synthesis, the light induced behavior and preliminary results in homogeneous catalysis of a series of new generation soft Lewis acid Pt(II) complexes bearing a coumarinic moiety in the phosphane ligand. Such species undergo reversible 2+2 photo-cycloaddition if irradiated at the proper wavelength changing both their steric and geometrical properties. One of these systems demonstrated a high catalytic activity difference between its light un-reacted and reacted forms in the alkene isomerization reaction.



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IND-OR-26 Screening of Pt-based bimetallic catalysts for the Ethanol Steam Reforming reaction

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The PEM fuel cells fuelled by pure H_2 are the leading candidate for various stationary and mobile applications. In order to ensure a sustainable power supply, ethanol has attracted some attention as a source for H_2 production, with the potential to replace fossil fuels, responsible for environmental problems. The steam reforming of bio-ethanol (BESR) may be considered more attractive since it is renewable, easy to store, safer to handle and transport and is produced from biomass, without net addition of carbon dioxide to the atmosphere. Above all, it is directly usable without water distillation since steam is necessary as a reactant. The involved reaction is strongly endothermic then favoured at high temperature, but to perform BESR reaction directly at low temperatures can favour CO minimization by promoting the CO-WGS reaction. It is important to know that in BESR reaction, the catalyst role is very crucial due to its strong tendency to fast deactivation linked to coke and by-products formation. [1,2,3]

In this work, the performances of CeO_2 supported-bimetallic Pt-Ni and Pt-Co catalysts for low temperature BESR reaction was investigated in a lab-scale plant, in very severe conditions in terms of ethanol concentration and steam to carbon ratio. The feed mixture that simulate the raw bioethanol is properly fed thanks to several optimizations of the feed system. An on line FT-IR multigas analyzer continuously and simultaneously monitors the gas-phase products distribution at the reactor outlet, in order to verify the carbon, hydrogen and oxygen mass balance and the by-products presence.

Preliminary results showed the effect of preparation method on the catalyst performances at different values of main operative parameters such as dilution ratio, temperature, water-to-ethanol molar ratio and GHSV. In terms of catalytic activity and agreement with equilibrium calculations, the Pt-Ni/CeO_2 catalyst prepared through impregnation seems to be promising for the low temperature BESR reaction, yet at low contact time values. Anyway, a deep investigation of deactivation and coke formation tendency together with the evaluation of the kinetic parameters will be crucial to select the best catalyst for the process. Based on preliminar economic evaluation, the process appears economically feasible.

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IND-OR-27 Metal-Binding Polysaccharides: New Bio-Generated Nanostructured Catalysts

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Bio-generated metal-binding polysaccharides may be novel sustainable materials with interesting catalytic properties for many synthetic applications and for supporting environment remediation and with potential application in medicine and as nutraceutical supplement of oligo metals. In this context we are currently investigating the preparation and uses of different metal ions and metal (0) species, such as for example iron, palladium, silver, gold, ruthenium, platinum and nickel, bound to an exopolysaccharide (EPS). These metal-polysaccharides (Me-EPS) are directly produced by a *Klebsiella oxytoca* BAS-10 during fermentation in the presence of suitable metal salts under anaerobic conditions, and/or by a following reductive step with hydrogen. Gel or semi-crystalline metal-binding products may be easily recovered and characterized. An eptameric unit with 4 α-rhamnose, 2 β-glucuronic acids and 1 β-galactose is repeated to form long polysaccharide molecules of several million Dalton; metal species should be located mostly in the proximity of the two glucuronic acids molecules. Very recently, Fe-EPS has been used as fine catalyst in oxidation reactions with 35% H_2O_2 to transform phenol into a mixture of catechol and hydroquinone [1]. At the moment we are studying the catalytic activity of the species Pd-EPS in the aqueous biphasic hydrogenation of some representative compounds as styrene, benzaldehyde and some (E) α,β–unsaturated aldehydes as 2-methyl-3-phenyl-propenal, 3-(1,3-benzodioxol-5-yil)-2-methyl-propenal [2] and 2-methyl-3-[5-(2-isopropyl)-thiophen-2-yil)]-propenal, these two last substrates being precursors of the valuable fragrances Helional® [3, 4] and Lioral® [5], respectively. Preliminary results showed that the catalytic system was very active and selective, working under very mild reaction conditions, and its activity was maintained practically unchanged in some recycle experiments.

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IND-OR-28 Impact of sulphur poisoning during the partial oxidation of methane on Rh-based structured catalysts

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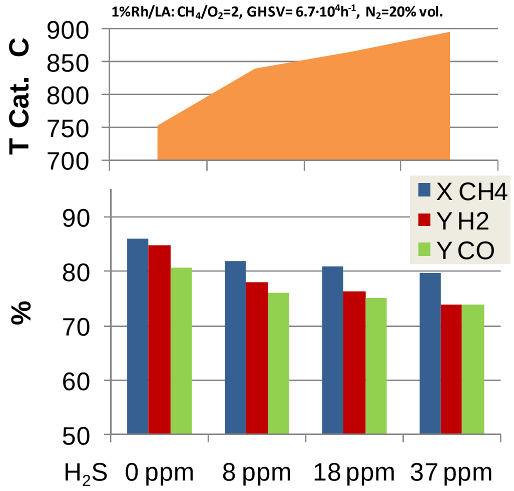
The production of syngas via the catalytic partial oxidation (CPO) of methane is an attractive and feasible alternative to steam reforming reaction in the utilisation of the world's abundant natural gas reserves. [1-2]. Rh-based catalysts have shown the highest activity and selectivity to syngas in the CPO of several hydrocarbons from methane up to diesel [1]. However, the presence of sulphur bearing compounds naturally occurring in the fuel, or added as odorants to pipe-line natural gas (~up to 10 ppm), can have a detrimental effect on the CPO activity.

Accordingly, we set out to investigate the effects of sulphur addition during the CPO of methane at short contact times and self sustained high temperatures over Rh catalysts supported on stabilized aluminas (by La, Si, P) and coated on honeycomb monoliths. Furthermore we studied the enhancement of the sulphur tolerance of Rh-based catalyst by partially substituting Rh with either Pt or Pd, which will be highly economical due to high cost of Rh metal.

The catalysts were fully characterized by BET, SEM-EDS, H_2-TPR, SO_2-TPD and in situ DRIFTS of adsorbed CO, which was used to study changes on the surface state of Rh before and after exposures to sulphur at conditions representative of actual CPO operation.

Results of CPO light-off, steady state and transient operation confirmed that Rh is always the most active and selective element for syngas production from methane in sulphur free conditions, due to its unique ability to catalyze the steam reforming reaction. However, sulphur reversibly inhibits the steam reforming, reducing methane conversion and yields to syngas (mainly H_2), whilst increasing the catalyst operating temperature (Fig.1). Sulphur inhibition occurs by preferential adsorption on smaller, well dispersed Rh crystallites whilst the larger metallic Rh aggregates are mostly unaffected.



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IND-OR-29 Biogas dry reforming over bimetallic Ni-Cu/CGO catalysts suitable for SOFCs applications

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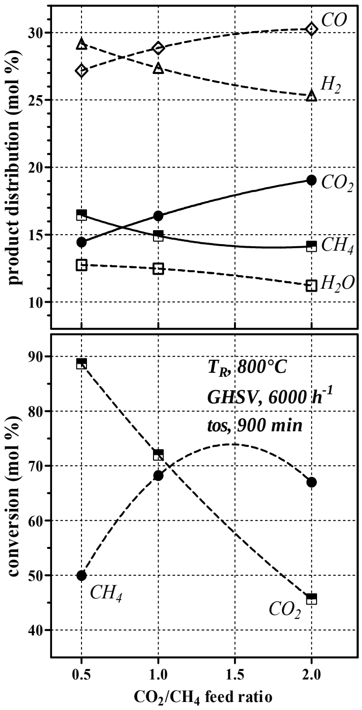
Biogas represents an attractive fuel for fuel cells applications. Compared to natural gas, it is considered a renewable source containing a large fraction of CO_2. It could be directly fed into SOFCs under internal reforming conditions to produce H_2-rich fuel for the electrochemical reaction at the anode side [1], but, in presence of a typical biogas composition (CH_4:CO_2=6:4), conventional Ni-based anode materials are deactivated by coke formation [2]. On this account, due to the poor catalytic activity of Cu towards the C-C bond formation, the development of effective and stable bimetallic Ni-Cu catalysts should mitigate the carbon deposition [3].

In this work, several NiCu alloy (70wt.%)/CGO ($Ce_{0.8}Gd_{0.2}O_{1.9}$) (30 wt.%) catalysts have been investigated in terms of activity and stability in dry reforming of a simulated biogas mixture at temperature lower than 800°C. The reaction was carried out in a fixed bed reactor operating at atmospheric pressure. The effects of preparation method, calcination and reduction temperature on the Ni-Cu alloy formation have been probed. Besides catalysts activity, product distribution and coke formation have been also evaluated as a function of fed mixture composition. Irrespective of the preparation route, NiCu/CGO catalysts are active in dry reforming at T_R as low as 650°C. As the temperature increases, CO_2 and CH_4 conversion increases up to ~70% at 800°C (*GHSV, 6000* h^{-1}; $CO_2/CH_4=1$). CO_2/CH_4 ratio strongly affects the conversion rate (Fig. 1); by increasing CO_2 content in biogas, H_2/CO ratio slightly decreases but carbon doesn’t form. This is an interesting result which will be adequately discussed.



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IND-OR-30 The reactivity of spinel ferrites in the two-step methanol reforming

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Catalytic steam-reforming (SR) is an option that can be used for the transformation of hydrocarbons and bioalcohols into hydrogen. Because of the fascinating challenge of obtaining an inherent separation of hydrogen from the C-containing products, during last years various alternative approaches to conventional SR + WGS have been investigated. In the so-called chemical-loop approach, the SR reaction is decoupled into two spatially and temporarily separated steps: during the first step a reductant (usually methane) is first contacted with a metal oxide, which oxidizes the former into carbon oxides and water [1]. The reduced metal oxide is then reoxidized with water, to produce hydrogen and restore the original oxidation state and the O^{2-} content of the metal oxide.

We investigated the feasibility of a two-step cycle approach for the catalytic production of hydrogen from methanol and water, using different ferrite-type oxide as the electrons/O^{2-} carrier. Motivation for this research was the development of a process aimed at the production of hydrogen starting from alcohols (in the present case methanol, in perspective bioethanol), and to investigate the structural changes occurring in the spinel mixed oxide during the reduction and oxidation steps.

The study was focused on the characterization of the solid material and the interpretation of the mechanism of the reduction step both from the result of the catalytic tests and from characterization of the used materials (Mossbauer, XRD, XPS). Finally the attention was focused on the reproducibility of the cycle: for this purpose multiple cycles were performed on the different ferrites.

Sperimentally, the fresh spinel was firstly reduced with methanol at different temperatures (first step of the cycle); products were CO, CO_2, CH_4, H_2O, and H_2. The relative amount of each product continuously changed because the reduction grade of the solid material is continuously growing up (from the oxidized fresh material to the completely reduced one). An important aspect of this study is the accumulation of coke, which was formed from the very beginning of the reaction time. The activity and the distribution of products, especially during the initial period of the reaction time, were affected by the morphologic and the chemical features of the spinel.

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IND-OR-31 Catalysts for H_2S abatement from biogas to feed MCFC

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One of the most interesting application of biogas is linked to the energy production by MCFC.

The main problem of biogas application in energy production by fuel cells is due to the presence of the sulphur compounds, usually at level of hundred of ppm, that represents a serious poisoning problem of the cells anode and electrolyte.

For this reasons, it is very important to reduce the H_2S concentrations at values about 1-5 ppm.

In this regard, a very effective and promising solution is represented by the catalytic reaction of the selective partial oxidation of H_2S to sulphur and water performed at very low temperatures (50-250°C), where, any significant thermodynamic limitations are showed. This problem maybe solved if an active and selective catalyst is allowable.

The aim of this work is to prepare and characterize new catalysts, for the selective for the low temperature H_2S oxidation to sulphur.

In a previous work different catalysts[1] (activated carbon, mixed metal oxides) were investigated in the reaction of H_2S oxidation to sulphur. Preliminary results showed that the mixed metal oxide performs better than activated carbon in terms of both catalytic activity and selectivity.

In this work vanadium based catalysts supported on ceria, titania, alumina and copper ferrite was prepared by wet impregnation method. The samples were compared in terms of H_2S and O_2 conversion, SO_2 selectivity and durability in the range of temperature of 50-250°C.

The most interesting catalysts were V_2O_5/CeO_2 and $V_2O_5/CuFe_2O_4$ that showed very high H_2S conversion, higher than 95% and respectively a SO_2 selectivity of 4% and 20%.

On this promising samples a deeper study of catalytic performances were performed by investigating the influence of the O_2/H_2S molar feed ratio, H_2S concentrations, and space velocity, in order to obtain preliminary kinetic data that are fundamental importance to the correct design of a catalytic reactor for the biogas clean-up to feed MCFC.

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IND-OR-32 Propene epoxidation on heterogeneous copper catalysts

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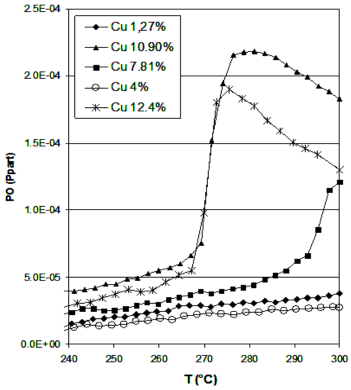
The industrial synthesis of propylene epoxide (PO) is one of the most demanding processes in term of energy requirement. Very high selectivity was observed in the direct epoxidation of propene over Au/TiO_2 and Cu/SiO_2 catalysts and pure Cu (111) facets were found to be very active in epoxidation of styrene [1,2,3]. Here we report our results on the epoxidation of propene on supported Cu catalysts (Cu/SiO_2-Al_2O_3, Cu/SiO_2) prepared by chemisorption-hydrolysis method (CH). The reaction was carried out in fixed-bed reactor with He, C_3H_6 and O_2 and products were analyzed by mass spectroscopy.

In our work we observed a significant activity only on reduced catalysts with high metallic surface area, in contrast with the unreduced ones. This is particularly evident on Cu/SiO_2-Al_2O_3 catalysts (Fig. 1). Only unreducible Cu(I) is formed on for 1-5 wt% of Cu, but to higher loading also a well reducible CuO phase is obtained[4], leading to high catalytic activity. Best activity is showed by reduced Cu/SiO_2: on SiO_2 only reducible Cu is formed as shown by EXAFS-XANES analysis. The FT-IR spectra of CO on reduced Cu/SiO_2 B shows the presence of several bands attributed to a well formed Cu crystallite: the catalyst with high Cu content (15 wt%) exposes in particular (111), unlike 9 wt% Cu catalyst. As a matter of fact 15 wt% Cu/SiO_2 B achieves higher partial pressure of PO. From our results we can say that CH method enables to obtain very small Cu particles also with higher loading compared with other preparation methods, allowing one to increase productivity of the catalysts.



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IND-OR-33 A Biphasic Kinetic Approach to Biodiesel Production

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Biodiesel is normally obtained by transesterification reaction of tri-glycerides (vegetable oils) with methanol in the presence of KOH, NaOH or related alkoxides as catalysts. The reaction is normally performed in stirred tank reactors requiring at least 1-2 hours of reaction time. As the reactants are immiscible the reaction rate, in these types of reactors, is strongly affected by mass transfer limitation. In order to intensify the transesterification process (PI) and to project opportunely a continuous reactor, a detailed study on both kinetics and mass transfer of the reaction still needs to be deepened. Although a lot of studies have been performed about the kinetics of this reaction [1-3], no publication can be found in the literature about a biphasic kinetic approach. Moreover, all the kinetic models developed till now are pseudo-monophasic, i.e., consider the reaction occurring in one phase, catalyzed directly by KOH. In these models, some aspects have been neglected: for example, Aracil et. al [2-3] have experimentally found that by increasing the catalyst concentration, the obtainable methylesters plateau, at long reaction time, strongly changes. This fact can be observed also in the continuous runs performed by using both microreactors and static mixers, where a different maximum in methylesters yield is obtained at different catalyst concentrations. This fact cannot be properly explained simply by imposing the occurrence of a chemical equilibrium. In a recent paper [4], this problem has been theoretically investigated by adopting a via enotales mechanism. In fact, initially the reaction is characterized by the presence of two reacting phases: a polar phase, containing methanol and methoxide anions obtained from KOH by an exchange reaction with OH^- and an apolar phase containing triglycerides and dissolved methanol. Then, methoxide anions promptly react, at the interphase, with triglycerides giving place to methyl ester and diglyceroxide anions [4], that are soluble in the apolar phase and promote the further transesterification steps. As suggested by Dijkstra et al. [4], digliceroxide anions react with triglyceride molecules giving an enolate intermediate and a molecule of diglyceride; then the enolate reacts with methanol dissolved in the apolar phase to give methylester and a new digliceroxide anion. In conclusion the catalyst is transferred from the polar phase to the apolar one. With the same mechanism both the monoglyceroxide anion, glycerol and glyceroxide are formed in successive steps. Glyceroxide is not soluble in the apolar phase and the catalyst return to the polar phase but in a less active form. As a consequence, an increase of the catalyst concentration strongly affects the equilibrium of the anions population and the methylesters yield changes with the amount of used catalyst. For this reason, a more reliable biphasic kinetic model, based on Dijkstra et al. mechanism [4] has been developed in this work with the aim of properly describe both batch and continuous experimental runs, in both static mixers and microreactors. At last, it will be demonstrated that the increase in the interphase area is a crucial aspect in determining the transesterification reaction rate for two reasons: the reaction of CH_3O^- with triglycerides occurring at the interphase and the methanol supply by mass transfer for feeding the reaction occurring in the oil phase. As a matter of fact, by using reactor favouring the local micromixing (microwave assisted reactors, ultrasounds assisted reactors, micromixers, microreactors, static mixers etc.) the activity increases so much that cannot be described with a pseudo-monophasic model.

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IND-OR-34 H_2 production by catalytic dehydrogenation of fuels.

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The study of catalytic dehydrogenation of liquid hydrocarbons is addressing one of the key problems for fuel cell application. The conversion of hydrocarbon mixtures into H_2 can be performed on-site, avoiding the difficulties involved in hydrogen storage; therefore the interest in the application of this technology is getting an increasing interest [1-3].

The dehydrogenation of kerosene surrogate and low sulphur Jet A fuel was investigated for the production of H_2. A complete study on catalytic activity of prepared catalysts has been carried out. The role of acidity has been carried out with the aim of finding a good compromise with dehydrogenation and condensation-polymerization properties of catalysts. Pt/Sn-Al_2O_3 catalysts showed good activity (Figure 1) but a loss of activity with time of stream was evident. Raman and TPO analysis of spent samples confirm that the deactivation was caused by coke deposition. Decreasing catalysts acidity by potassium impregnation leads to small loss of activity but strongly increases catalysts stability. All studied catalysts can be regenerate by thermal treatment.

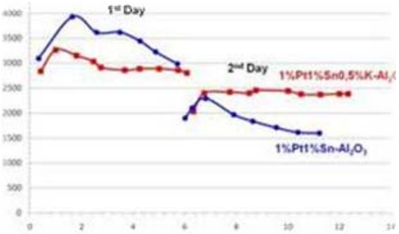

Figure 1: H_2 productivity over 1%Pt-1%Sn/Al_2O_3(■) and K doped 1%Pt-1%Sn/Al_2O_3 (•)

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IND-OR-35 Epoxidation of soybean oil: kinetic study and modeling in continuous reactors.

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Epoxidized vegetal oils are important industrial products nowadays used as plasticizers and stabilizers for polymeric resins, mainly as substitutes of phthalates that have been banned for their toxicity. In our study we have focused on the epoxidation of soybean oil for a detailed investigation on the reaction kinetics in order to acquire sufficient data to develop a suitable mathematical model.
The epoxidation reaction of soybean oil is characterized by an extremely high exothermicity and is a biphasic reaction occurring between the double bonds of soybean oil (oil phase) and an oxidant mixture (acqueous phase) containing hydrogen peroxide, formic acid and a mineral acid like sulphuric or phosphoric acid. These last, act as catalysts for the reaction of formic to performic acid that is the actual epoxidizing agent. Performic acid reacts promptly with double bonds and gives place to the desired product, that is, the epoxidised oil.
The reaction is normally performed industrially by using pulse-fed-batch reactors strategy, according to which the catalyst is initially added to the oil and then only limited amounts of oxidizing mixture are pulsed to the reactor to avoid runaway. The temperature moderately increases and the reaction mixture is cooled by an external or internal heat exchanger until the initial temperature is restored to the desired value. The reactants adding operation is repeated different times and after each addition a more or less prolonged cooling operation is required. This procedure requires many hours of reaction time (5-8 hours) and the conversion from fed-batch to continuous operation represents the key point to increase the productivity of the process. Such shift can be obtained only by acquiring sufficient insight on the reaction kinetics and by developing a reliable physical model able to describe the evolution of all the components involved, considering in particular the secondary reactions that decrease the selectivity.
In an our recent paper we have developed a kinetic model that contains the main physico-chemical peculiarities of the considered reacting system [1]: components partition between the two liquid phases, mass transfer limitation across liquid-liquid interface, heat transfer between the reacting mixture and reactor jacket, different reactivity in epoxidation and oxirane ring opening (degradation).The model has been successfully applied, in a first step, to a set of experimental fed-batch runs performed in controlled isothermal conditions with the scope of evaluating the kinetic parameters at a reference temperature. Subsequently, a group of pulse fed-batch runs with variable temperature has been used to evaluate activation energies and thermal parameters such as the global heat transfer coefficient. The very good agreement between the experimental data and the model prediction has given the confirmation that the model was able to describe the behavior of the fed-batch reactor in different conditions [1].
With the aim to further validate the model, new experiments have been performed in a conventional continuous tubular reactor, filled with glass or stainless steel (AISI 316) spheres. We have found that also for continuous runs the performances of the model are satisfactory.
In conclusion we have now demonstrated that the proposed model and the related kinetic parameters could be useful to design a continuous epoxidation operation in safe conditions and could be the basis for the process intensification in microreactors or static mixer reactors.

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MS-IL-01 Shaping the Beating Heart of Artificial Photosynthesis: Oxygenic Nano-Hybrid Interfaces

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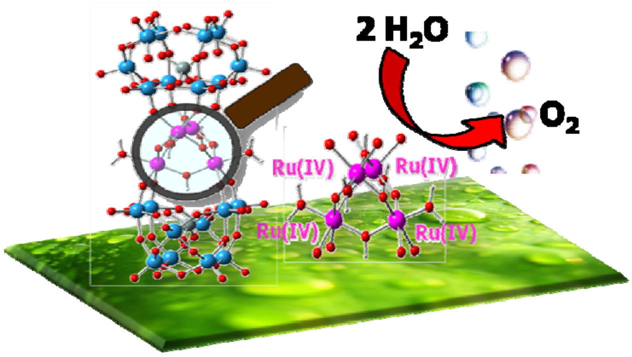
Water oxidation is the crucial stage in the chemical and molecular sequence of photosynthesis, designed by Nature to convert solar light into chemical energy. The artificial "off-leaf" transposition is a major goal of energy research, aiming at the continuous production of hydrogen as solar fuel, through the photo-catalytic splitting of H_2O.[1] Success in this task primarily depends on the interplay of light-activated multi-electron oxidation and reduction routines and on the invention of stable and robust water oxidation catalysts, liberating oxygen with fast rates, high quantum yield, and long-term activity. Indeed, the Achilles' heel of the chloroplast assembled architecture stems from the intrinsic weakness of the functional components chosen by Nature. The artificial perspective should find its roots on more solid materials. The vision here is to transcend the natural wonder, while being inspired by its key guidelines along the design of a functional system/device, with superior operation stability. We will highlight a recently discovered pathway carved within the class of inorganic metal-oxides displaying a unique mimicry of the PSII enzyme.[2] Furthermore, the shaping of their functions at the interface of specifically tailored carbon nano-structures and/or polymeric scaffolds opens a vast scenario for tuning electron/proton transfer mechanisms in term of rates, distance, geometries and communication between donor/acceptor centers.[3]



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MS-IL-02 Supramolecular Ligands in Transition metal catalysis, evolutionary ligand screening and a first approach to catalyst selection

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The interface between supramolecular chemistry and transition metal catalysis has received surprisingly little attention in contrast to the individual disciplines. It provides, however, novel and elegant strategies that lead to new tools for the search of effective catalysts, [1] and as such this has been an important research theme in our laboratories. In this presentation I will focus on supramolecular strategies to make bidentate ligands and compare that to traditional catalyst development. Supramolecular approaches appear ideally suited for the creation of large ligand libraries. The large number of catalyst that become available in this manner, asks for screening strategies and evolutionary approaches. A first academic example of catalyst selection from a mixture will be discussed. In addition, the application of a cofactor strategy will be presented, which is also ideally suited for selection procedures.

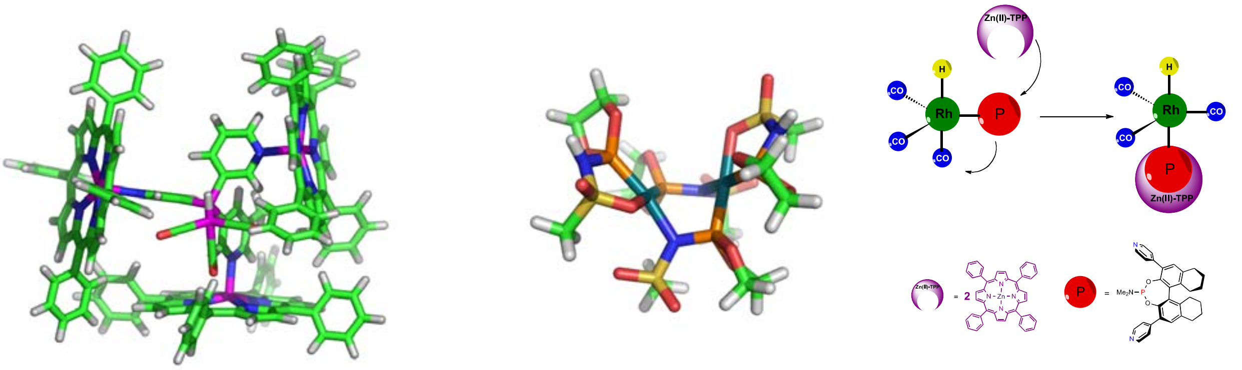

Figure 1: New concepts in TM catalysis: Left) a ligand-template approach to porphyrin encapsulated rhodium catalyst. Middle) dinuclear complexes based on METAMORPhos ligand Right) coordination chemistry steered by supramolecular chemistry.

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MS-01 Supramolecural Control on Product and Substrate Selectivity via Encapsulation within a Hydrogen Bonded Self-assembled Hexameric Capsule

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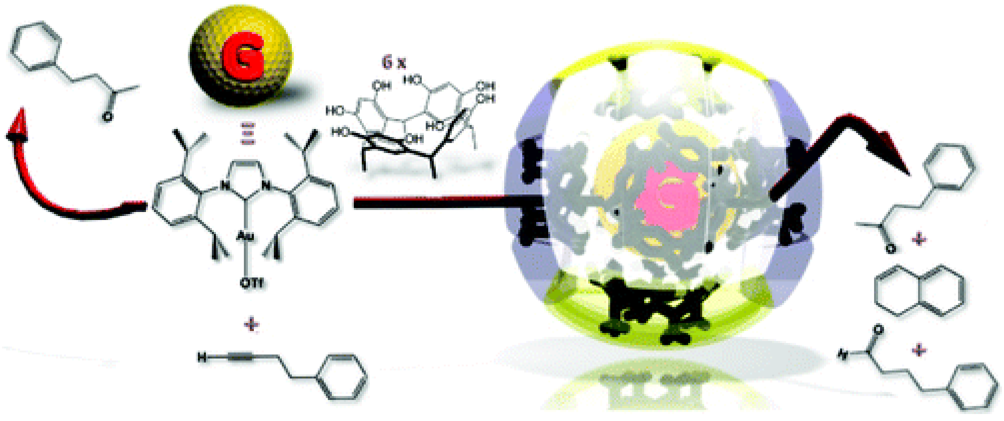
The impressive chemo, regio and stereoselectivity displayed by enzymes are the result of a large number of weak attractive intermolecular interactions as well as repulsive steric requirements operating between the substrate and the catalytic site. In the latter, recognition phenomena allow also the selective picking of the substrate among a series of similar reagents bearing same functional groups but different size. Overall enzymes control both sides of a chemical transformation, while common organometallic catalysis usually puts its effort prevalently on the right side of the catalytic reaction. Hosting of organometallic catalysts within well defined porous supports led to enhancement of enantioselectivitywhile for catalytic systems working under homogeneous conditions, encapsulation within rigid metal-ligand tetrahedral or square bi-pyramidal assemblies allowed rate acceleration and substrate selective reactions for a series of small reagents.
Herein we report about the simple modification of the product and substrate selectivity properties of an organometallic catalyst via encapsulation in a spherical hexameric self-assembled capsule held together by a seam of sixty hydrogen bonds. The steric requirements imparted by the capsule modify product distribution in the alkyne hydration reaction towards uncommon species and, at the same time, steer substrate selectivity in parallel competitive experiments towards the substrate that better fit the residual space available in the cavity.



MS-02 Rhodium-Catalyzed Asymmetric Hydrogenation of Olefins with PhthalaPhos, a New Class of Chiral Supramolecular Ligands

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Nature makes wide use of non-covalent interactions to build its complex supramolecular architectures and to achieve efficient and selective transformations. In recent years, supramolecular approaches to the development of new enantioselective catalysts have gained momentum [1]. Herein we report the design and synthesis of a novel class of chiral monodentate phosphite ligands, named PhthalaPhos [2], which contain a phthalic acid diamide moiety (Figure 1). Such phthalamide group displays both donor and acceptor hydrogen bonding properties that can give rise to supramolecular interactions both between the ligands and with the substrate. The modular nature of the PhthalaPhos ligands allows to tune their properties by simply varying structural elements such as the linker, the BINOL unit and the ancillary amide group (i.e. the amide not connected to the phosphite group), thus allowing a parallel-combinatorial ligand optimization.

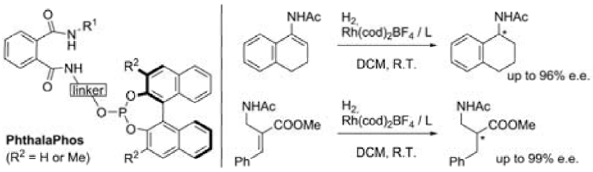

Figure 1

The catalytic properties of the PhthalaPhos library (19 representatives) were tested in the rhodium-catalyzed enantioselective hydrogenation of dehydro aminoesters and *N*-acyl enamides. Excellent results in terms of catalytic activity and stereocontrol were obtained with both benchmark substrates and 'challenging', industrially relevant olefins (Figure 1). Spectroscopic and computational studies, together with control experiments, suggest that the role of the phthalamide group consists in binding and orientating (by hydrogen bonding) the substrate during the catalytic cycle of the hydrogenation process [2b].

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MS-03 Covalent Nano-Clip and Nano-Box Compounds Based on Free Base Porphyrins

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There is an increasing interest in developing smart nanostructures for applications in many different fields, from environmental monitoring to biological, medical and industrial chemistry. For some specific properties (e.g. strong molar absorption, bound metal atoms in pyrrolic cores, extensive aromatic structures, peculiar affinity for neoplastic cells, etc.), porphyrin-derivatives are among the most studied compounds and some applications like chemical and/or biological receptors, artificial sensors for drug determinations, mimesis of biological systems, etc., are already well-defined. Recently, several 3D cyclic oligo-porphyrins with different architectures [e.g. spheres, prisms, regular polyhedra (with a varying number of faces), etc.] have been studied[1]. The properties of these molecules may depend on the size and hydrophobic nature of the cavities inside their 3D structure (for example, suitable to accommodate hydrophobic chemicals).

In the present paper, as the first step in the preparation of water soluble Nano-Clip and Nano-Box compounds, the synthesis and characterization of some novel macromolecular cyclic ethers, constituted by two (Nano-clip, fig. 1) or four (Nano-box, fig. 2) porphyrin units and spaced with methylene bridges, are reported. These compounds, obtained by the reaction between dibromomethane and 5,15-di[p-(9-methoxytriethylenenoxy)phenyl]-10,20-di[p-hydroxyphenyl] porphyrin, have a co-facial (nano-clip) or a four wall-box (nano-box) architecture. The aim of these syntheses was to obtain molecular systems for the recognition and/or the carriage of bio-molecules. Spectroscopic data of the Nano-clip showed modified Soret and Q-bands, with respect to the monomer and cyclic tetramer, as a probable consequence of a hybrid orbital deformation (HOD) phenomenon involving the two porphyrin π rings forced to a closer co-facial spatial arrangement [2].

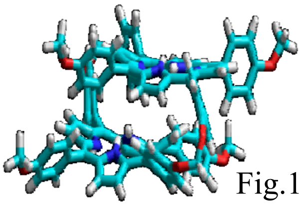
Fig.1

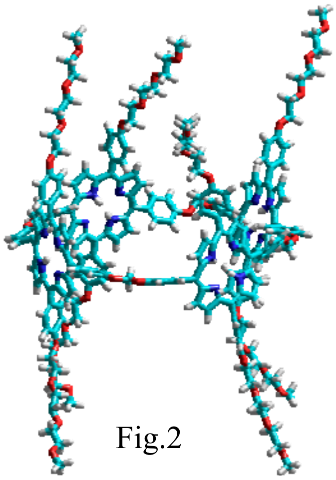
Fig.2

A UV-vis titration allowed verification of the easy and reversible protonation of the pyrrolic cores which, by electrostatic repulsion, modifies the spatial distance between the two co-facial porphyrins and, therefore, the cavity size. This reversible modification could be used to change the dimer molecule status from Open to Closed, and facilitate the accommodation or release of suitable chemical species, acting then as a drug carrier. The tetrameric porphyrin molecule (Nano-box) could also be used as a drug-carrier, forming an inclusion complex with macromolecular drugs, or as a nano-reactor, for the peculiar nano-space conditions inside the box. In this case, ^{1}H-NMR spectroscopic analysis showed a high-field shift of the aromatic and ether protons present in the upper and lower box rims as a specific characteristic of this molecular structure[2]. These compounds differ from previous analogous porphyrinic systems in that their totally covalent structure makes them more versatile potential macromolecular tools.

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MS-04 Novel functionalized PTA ligands, their coordination complexes and use in catalysis

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PTA (1,3,5-triaza-7-phosphaadamantane), the neutral water-soluble and air-stable monodentate phosphine firstly reported by Daigle et al. in 1974 [1], has been used by us and other groups to obtain water-soluble transition metal complexes which have been applied as homogeneous catalysts in aqueous or biphasic systems [2].

The largest part of modifications of PTA has so far involved the P or N atoms, so we focused on the functionalization at one carbon of the upper rim [3]. The optimized derivatization reaction is based on the isolation of the pyrophoric PTA-Li salt, which was then reacted with electrophiles such as aromatic aldehydes and ketones [4]. Thus, new chiral ligands were obtained and used to bind Ir(I) and Ru(II) organometallic moieties. The corresponding complexes were tested as catalysts for hydrogenation reactions under mild conditions. In parallel, modifications of the lower rim of PTA, i.e. alkylations at N atom, were also carried out and the new N-alkylated PTA derivatives so obtained were used as water soluble ligands in biphasic Rh-catalyzed hydroformylations of long-chain olefins in the presence of randomly methylated □-cyclodextrins.[5].

We thank financial contributions from MATTM (PIRODE project), CNR for bilateral CNR-CNRS project, COST Action CM0802 "PhoSciNet", MAE for JRP Cooperation Italy-USA (2008-2010).

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IND-PO-01 Synthesis and Characterization of New Copolyacrylates Containing Porphyrin Units as Pendant Groups and Their Use as Sensors.

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Porphyrins are highly-conjugated organic molecules having useful properties for some functional devices as photodiodes, catalysts, artificial solar energy conversion systems and, particularly, for sensor devices. [1]

Obviously, their use as sensing of specific analytes (as acid vapours or NO_2) requires a direct contact, so that only chromophore units present on sensor surfaces are active. In previous works [2], good results were obtained assembling porphyrin monolayer on a quartz surface, but both materials and synthetic procedure were expensive.

The present work regards the construction of an inexpensive sensor device obtained depositing a thin layer of a MMA/porphyrin copolymer on PMMA plates, with the hope of reducing both the amount of sensitive material and the cost of the support. By reaction between MMA and an acrylic comonomer, obtained by condensation of a porphyrin derivative (having three triethylene glycol mono methyl ether branches and a free-hydroxyl group) and acryloil chloride, copoly-porphyrin-acrylates of different compositions were prepared. Sensor devices were then assembled stratifying very thin layers of these materials on transparent commercial PMMA plates by immersion of these last in very diluted solutions of copolymers.

The efficiency of the devices was tested by exposition to trifluoroacetic and hydrochloric acid vapours or NO_2 gas. Under exposition, as expected, the Soret porphyrin band (at 424 nm) rapidly and totally disappears (substituted, in both cases, by a new band at about 450 nm) to be quickly recovered by treatment of the devices with ammonia or hot air, respectively.

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IND-PO-02 What a chemical industry from biomass?

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The biomass to use to produce chemicals can be of three types: 1) wastes (manly lignocelluloses ones) from agriculture, from forests, form food and papers industries, wastes from municipalities ,from wood transformation , sludges from depuration of water , sewages from animals; 2) food and feeds crops, and in this case we have triglycerides carbohydrates and proteins ;
crops dedicated only to energy and chemistry produced from marginal lands. From biomass we can produce chemicals in several stages: the first one is always a physical extraction of active principles, after having reduced in small dimensions and isolated the single components, leaving unchanged the original structure. Further steps are chemical or biological transformations to produce several products that are called **platform molecules** which are called in petrochemistry building blocks. A further strategy is to arrive to the final product in several steps without separations of intermediates (one pot synthesis) . Some platform molecules are succinic acid, ethanol, fumaric acid, glycerine, butanol, levulinic acid, itaconic acid, glutammic acid, and 3 hydroxipropionic acid. From cellulosic raw materials via gasification or reforming it is possible to obtain syngas. and from syngas is possible through methanol to obtain olefins or paraffins via Fischer Tropsch reaction. With pyrolisis or hydroliquefaction of lignocellulosic materials is possible to obtain aromatics (benzene phenol, toluene and xylens). Triglycerides C12-C18 can be transformed by transesterification with methanol to methyl esters and glycerin and after hydrolyzed to acid and hydrogenated to alcohols. From the single aminoacids isolated from proteins or obtained by fermentation of carbohydrates in presence of ammonia or nitric acid after their isolation and purification with reactions of decarboxilation and deamination is possible to obtain several functionalized molecule . From protein is possible to obtain several intermediates as acrylamide from asparagines, 1,2-etanediamine from serine, ε-caprolactame from l-lisine, styrene from fenilalanine, ethylamine from serine, isobutirraldheyde from valine, isoprene from leucine. By anaerobic fermentation of wastes it is possible to obtain methane and from ethane to create all C1 chemistry .There are four strategies to develop a chemical industry from biomass and from all these strategies the advantages are the reduction of CO_2 emission, the use of rinnovable raw materials , the independence from fossil fuel and further going from the first to the last one there are additional advantages. These strategies are:1) to produce the some building blocks of petrochemistry starting from platform molecules from biomass (ethylene from ethanol etc) 2) to use platform molecules to produce the first building blocks of petrochemistry 3) to use the platform molecules to produce the second or successive intermediate to obtain the some product of petrochemistry 4) to synthesizes new products alternative to the petrochemistry starting from platform molecules or through several steps without separation of intermediates. The advantages of second strategy and third strategy is the simplification of the process to produce the intermediate. Example of first strategy is the production of polyethylene by first dehydratation of ethanol to ethylene. Examples of second strategy is the alkylation of benzene to ethyl benzene with ethanol or the production of phenol from lignin. or synthesis of terephthalic acid starting 5-hydrossimethylfurfurole and glycerin. l'1,2-propandiole can be obtained by hydrogenolysis of the glycerin l'1,3-propandiole can be obtained from glycerin. It is possible to use directly succinct acid for the synthesis of 1,4- butandiole, γ-butyrolactone and tetrahydrofurane, insteas from maleic anhydride from n-butane . The advantages of fourth strategy is the production of bioproducts which can be biodegradable and can us the prefix bio These product are biosolvents, biolubrificants, biopolymers, biofuels, bioadhesives, bionks, biocosmetics, biodetergents and biofarmaceuticals.

IND-PO-03 Reductive mono-alkylation of nitro aryls in one-pot and Suzuki-Miyaura coupling in water: catalysis by polymer-stabilized palladium nanoparticles.

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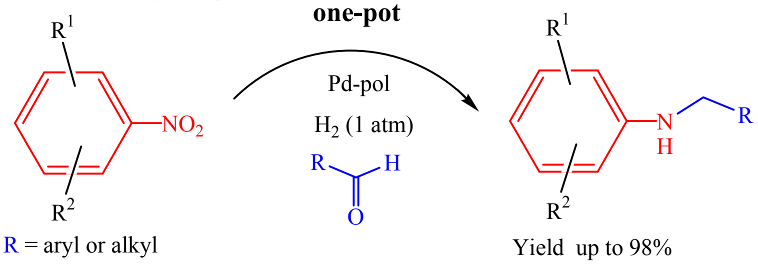
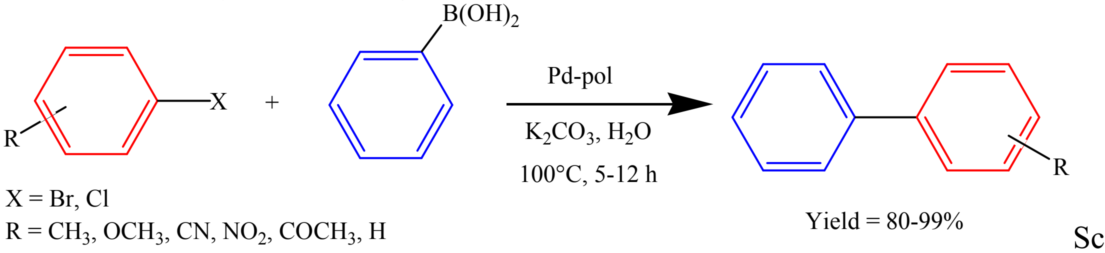
This presentation deals with the use of polymer supported palladium nanoparticles (Pd-pol[1]) in:

i) the direct reductive amination of carbonyl compounds with nitroarenes in the presence of molecular hydrogen as the reductant (scheme 1).



Scheme 1

ii) the Suzuki-Miyaura coupling of aryl bromides and chlorides in water (scheme 2).



Scheme 2

In both the reported reactions, Pd-pol catalyst is recyclable and can be reused without significant loss of catalytic activity for several times.
Chemical and TEM analyses showed that the catalytically active species are supported Pd nanoparticles with a primary particles' size distribution centered around 5 nm formed under reaction conditions.

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IND-PO-04 Surface Properties of a Series of Monodisperse Perfluoroalkylated Polyoxyethylene Glycols

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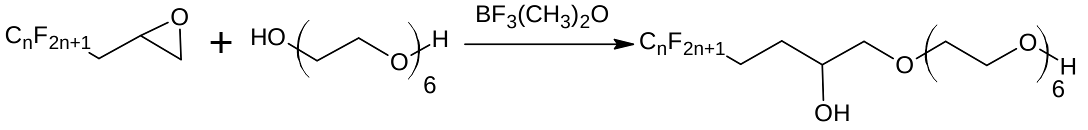
Three monodisperse perfluoroalkylated polyoxyethylene glycols were synthesized by direct addition of a poly(ethylene glycol) having an average molecular weight of 300 (PEG-6) to 2-(perfluoroalkylmethyl) oxiranes having a general formula $C_nF_{2n+1}CH_2CH(O)CH_2$ (n = 4, 6, 8):



Critical micelle concentrations (c.m.c.'s), surface and interface tensions, cloud-point curves, surface-pressure vs. area (π, A) diagrams and micelle hydrodynamic diameters were determined in order to correlate surface properties of surfactant-water systems and the length of the fluorinated chain.

The lengthening of the fluorinated chain was found to induce a strong hydrophobic effect resulting in a abrupt decrease in surface tension, interfacial tension, critical micelle concentration, cloud point and surface area occupied by a surfactant molecule.

Further, the effects of inorganic and organic anions on cloud points and c.m.c.'s of aqueous solution of monodisperse perfluoroalkylated polyoxyethylene glycols were studied. Salt constants k_s were determined for 8 inorganic and 3 organic salts. The magnitude of k_s varied as follows: $P_3O_{10}^{5-} > PO_4^{3-} > SO_4^{2-} > Cl^- > Br^- > NO_3^- > I^- > SCN^-$ for inorganic anions and Ethylenediaminetetraacetic acid tetravalent anion ($EDTA^{4-}$)> 2-hydroxypropane-1,2,3-tricarboxylic acid trivalent anion ($CITRATE^{3-}$) > 1-Hydroxyethylidene-1,1-diphosphonic acid divalent anion ($HEDP^{2-}$) for organic anions.

The salting effect of a specific anion was found to be strongly influenced by the length of the fluorinated tail: the higher the number n of fluorinated carbon atoms, the stronger the salting effect of a specific salt.

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IND-PO-05 Mg/Al Hydrotalcite catalyst for Biodiesel production.

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In the classical biodiesel production technology, the triglycerides (vegetal oils) are transesterified with methanol at 60-80°C, using basic homogeneous catalysts (alkaline metal hydroxides or methoxides), achieving high yields of a mixture of fatty acid methyl esters (FAME). Together with biodiesel, glycerol is also produced (10% by wt of biodiesel). However in this process the use of an homogenous catalyst is a drawback, requiring for product purification, the use of an acid neutralizing agent producing salts which remain dissolved in the glycerol. The obtained crude glycerol have a very lower price than the higher grade product, but to achieve the purity requested by the market, the glycerol distillation is necessary, with a consequent increase of the total energy duty of the process. This problem can be solved using an heterogeneous catalyst as it was demonstrated by the technology Esterfip-H developed by IFP [1]. Despite many catalysts studied in laboratory have shown better performance than the catalyst developed by IFP (zinc aluminates), no other catalyst among the dozens in the literature has been developed up to the construction of an industrial plant.

The principal problem linked with the use of an heterogeneous catalyst, in biodiesel production, is the stability of the catalyst, although in many papers reported by the literature this aspect is often completely neglected [2]. However the only way to reliably establish the stability of a catalyst is to conduct tests in packed bed reactors for long periods [3].

The Mg/Al Hydrotalcites have been proposed as catalysts for biodiesel production in many papers [2] but no one have reported data about the performance of Mg/Al hydrotalcites in a continuous packed bed reactor for a long time working. In this paper, the performances of a commercial Mg/Al hydrotalcite (PURAL® MG 76) have been tested before in an autoclave and then in a continuous packed bed reactor.

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IND-PO-06 Photodegradation of 4-chlorophenol sensitized by waste derived soluble organic substances using experimental design

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Advanced Oxidation Techniques represent an alternative to more traditional water treatments since they are able to promote the degradation of organic substrates, leading to their complete mineralization. These processes are based on the production of highly reactive species (mainly radicals) and are often light assisted. Among the compounds able to photogenerate reactive species, humic and fulvic acids (HS) have been widely studied in order to understand the water auto-purification mechanisms. It is thus in principle possible to propose the use of HS in wastewater photodegradation treatments; however neither waters nor soils can be considered as exploitable source of HS. The organic fraction of urban wastes has been demonstrated to be an interesting source of soluble organic substances (SOS), structurally similar to HS and exhibiting good photosensitizing properties [1].

In the present research the photodegradation of 4-chlorophenol (4-CP), a toxic and hardly biodegradable pollutant, has been studied in the presence of one type of SOS. In order to optimize experimental conditions and to evaluate possible synergistic effects with other photoactive compounds (TiO_2 and H_2O_2) a chemometric approach has been chosen. Two designs of experiments (D-Optimal, DoE) have been planned and the following parameters have been considered: 4-CP concentration (from 10 to 100 mg L^{-1}), SOS concentration (from 0 to 1000 mg L^{-1}), TiO_2 concentration (from 0 to 500 mg L^{-1}) or H_2O_2 concentration (from 0 to 10^{-2} M), cut-off filter for the light source (340 nm, 400 nm and without filter). By mean of the Modde software, 39 experiments were selected for the TiO_2-DoE and 25 experiments for the H_2O_2-DoE. The resulting response surfaces evidenced that, in the presence of TiO_2, a competition for the active photogenerated species seems to take place between 4-CP and SOS, since also SOS can be in turn photodegraded.

On the contrary, a synergistic effect between SOS and H_2O_2 occurs, when the 400 nm cut-off filter is used. After three hours of irradiation 25% of 4-CP abatement was achieved in the presence of 500 mg L^{-1} of SOS, 35 % was achieved in the presence of 5 mM of H_2O_2, whereas 45% of 4-CP abatement was obtained in the presence of both SOS and H_2O_2 at the above mentioned concentrations.

These results encourage the use of chemometric tools and give useful information for a possible scale-up of the process in pilot plants exploiting the solar light as radiation source.

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IND-PO-07 Hydrogen production through $NaBH_4$ hydrolysis over activated carbon supported Ru and Co catalysts

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Nowadays chemical hydrides represent an ideal source of pure hydrogen for fuel cells application. Sodium borohydride ($NaBH_4$) is the preferred hydride due to its high gravimetric and volumetric hydrogen density [1, 2]. The aim of this work was to investigate the $NaBH_4$ hydrolysis ($NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2$) over mono and bimetallic Ru and Co catalysts supported on different activated carbons.

Catalysts were prepared by incipient wet (co)impregnation of the support with aqueous solutions of the precursors ($RuCl_3$, $Ru(NO)(NO_3)_3$, $Co(NO_3)_2$, coded respectively C, NN and N). Three activated carbons, two minerals with surface of area 1059 and 650 m^2 g^{-1} (coded respectively D and E) and one vegetable from exhausted olive husks (coded H, with 1200 m^2 g^{-1}) were used as support. Catalysts were named MeX(Y)/Z, where Me is the metal, X the precursor, Y the metal charge and Z the support used. Catalytic tests were carried out at atmospheric pressure in isothermal conditions. Catalysts were characterized by TEM, EDX and BET surface area.

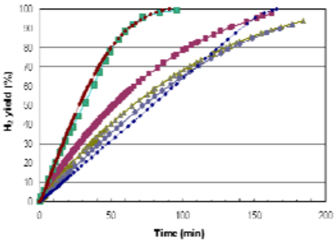

Fig. 1 H_2 yield (T=25°C) over Ru catalysts.
(●)RuNN(2)/H; (■)RuC(2)/D; (■)RuC(2)/E; (▲)RuNN(2)/E; (●)RuNN(2)/D; (♦)RuC(2)/H.

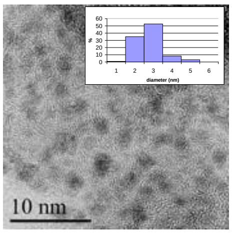

Fig. 2 TEM microphotograph of the most active catalyst, RuNN(2)/H.

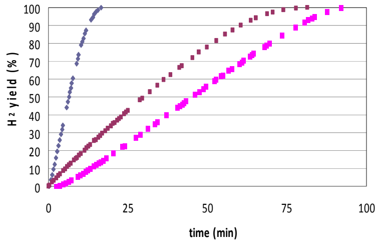

Fig. 3 H_2 yield (T=25°C) over Ru and Co catalysts.
(■)RuNN(0.5)/H; (■)RuNN(0.5),CoN(10)/H; (■)CoN(10)/H.

The activity tests of Ru catalysts (Fig. 1), showed that the H_2 yields are in the order: RuN(2)/H≈RuC(2)/D>RuC(2)/E>RuN(2)/E>RuN(2)/D>RuC(2)/H. On the basis of TEM and EDX analyses, it was suggested that this trend is related to the Ru particle size, which depends both on the support and Ru precursor used. The use of an activated carbon from a vegetable source, as the H support, results in bigger Ru particles, probably due to the higher amount of calcium and potassium present on the H support. $RuCl_3$ leads to bigger particles than $Ru(NO)(NO_3)_3$. It was proposed that there is an optimum Ru diameter (2-3 nm, Fig.2) for the hydrolysis reaction. On the most active carbon (H) it was found that Co, even if present at higher amount than Ru (10 wt% vs 0.5 wt%), shows a very low activity (Fig.3). The bimetallic Ru-Co catalysts exhibit a H_2 yield much higher than the sum of the corresponding monometallic Co and Ru samples (Fig. 3). This was attributed to an increase of the Co dispersion caused by the presence of Ru.

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IND-PO-08 $CuFe_2O_4$ catalyzed SiC WFF as MW susceptible catalytic trap for Diesel soot abatement

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The diesel engine emissions control is one of the most important aspects of modern air quality management [1]: the EURO 5/6 standards impose the development of both new engines and more effective exhaust gas after treatment devices. The Wall-Flow Diesel Particulate Filters (DPFs) represent the best technology available to reduce soot emissions under EU standards [2]; they consist of alternately plugged parallel channels, so forcing the exhaust gases through their porous walls, where the PM is collected. When the accumulated PM reaches a certain level, DPF must be regenerated to maintain efficient engine operation; but all the actually used strategies (heating of the exhaust gases or reduction of the soot burning temperature using a fuel borne catalyst) require an extra energy consumption. An appealing technological proposal to perform active DPF regeneration is the combined use of MW energy and of a catalyst for the soot oxidation that is simultaneously MW sensible: so, due to the instantaneous and selective heating process, one can reduce the soot burning temperature and the overall energy employed for the complete regeneration. In this work we studied the MW assisted regeneration of a specifically catalyzed Pirelli Ecotechnology SiC Wall-Flow monolith Filter with 200 cpsi. The selected catalyst is based on the $CuFe_2O_4$, due to its good dielectric properties and oxidation activity [3]. The preliminary results of soot loading and on-line regeneration tests showed that the system realized is able to achieve the complete filter MW assisted regeneration, and monitoring continuously the applied power, to evaluate the overall energy employed in the regeneration phases: in particular the tests showed that using both the MW and the catalysed filter, the energy supplied and the regeneration time are about 50% lower than that necessary for the uncatalysed filter. Further researches are still in progress to study the influence of the operating parameters (i.e. exhaust gas flow rate), in order to find the optimal regeneration conditions allowing further energy saving.

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IND-PO-09 On the regeneration of gold nanoparticles for the selective oxidation of furfural

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Innovative transformations of furfural are highly desired: among these, the synthesis of alkyl furoates can open very interesting perspectives for the use of xyloses, because they can be used either as solvent or extracting agents in many different industrial plants if produced in larger amounts and at low price. Currently we are studying the oxidative esterification of furfural on Au/ZrO_2 samples without the addition of $NaCH_3O$, a base that would make the process less green and more expensive. The goal of the work herein presented is to investigate the stability and the reusability of our best Au/ZrO_2 samples.

Catalysts were prepared by deposition-precipitation (dp) on calcined support. The oxidative esterification of furfural with oxygen and methanol, without $NaCH_3O$ addition, was investigated at 120°C and 12 bar. After the first catalytic run the sample was filtered off, washed with methanol, dried and used again, obtaining very low selectivity in the subsequent runs. As the reason for catalysts deactivation we have excluded gold leaching in the discharged samples. In order to investigate catalyst poisoning, by TPO analyses we have verified on exhausted catalysts the presence of an organic residue. According to TPO profiles, we have decided to heat the catalyst until 450°C in oxygen atmosphere, in order to eliminate organic poisons. The deactivation in this case is reversible and by thermal calcination at a proper temperature it is possible to restore almost fully the initial selectivity. In fact, by pulse-flow CO chemisorptions [1] we have found for the regenerated samples a mol_{CO}/mol_{Au} ratio comparable to the value of the fresh samples, meaning the absence of gold sintering during the catalytic reaction.

FTIR spectroscopy demonstrated that the organic residue can be removed starting from 350°C in O_2. At the same time, CO adsorption reveals that the Au phase is quite stable, even after repeated thermal treatments in O_2 at increasing temperature up to 6 hours.

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IND-PO-10 Catalytic multifuel ATR reformer for distributed H2 production

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Hydrogen fuel cells seem to be the most viable solution to the antithetic problems of pollution reduction and growing energy demand. Distributed production overcomes the difficulties in H2 transport and storage, therefore very compact and flexible plants are required: AutoThermal Reforming (ATR) of hydrocarbons assures self-sustainable operation and high reaction system compactness [1]. Fossil fuels still remain the favorite choice due to the widespread existing delivery pipelines of natural gas and the high energy density of liquid fuels such as gasoline and diesel. Very different characteristics of liquid and gaseous hydrocarbons make it very difficult to realize a multifuel reformer, and to achieve high performances in terms of thermal efficiency and H_2 yield.

A catalytic multifuel autothermal reformer thermally integrated was developed, able to process both methane (as natural gas) and dodecane (as diesel-like hydrocarbon). Great attention was paid to the development of a feed system for liquid fuel. In order to avoid fuel preheating, an alternate high pressure spray system, based on the common-rail technology, was adopted, allowing the formation of micro-droplets that assure a very quick liquid vaporization and an optimal mixing with other reactants, avoiding coke formation and improving hydrogen yield and thermal efficiency. Catalytic region was designed for use structured catalysts such as honeycomb monoliths and foams, according to literature experiences [2, 3]. In order to realize a full self-sustained system, without any external heat sources, great attention was focused to the system thermal integration. An heat exchanger system integrated into the reactor was able to preheat water and air streams by cooling products stream to a temperature consistent with a further water-gas shift stage.

In order to have a very comprehensive process control, temperature and composition was monitored in 6 points of catalytic bed. Preliminary tests showed low start-up times, and a very quick response of the system to the operating conditions changes, with a good hydrocarbon conversion. During whole tests, high thermal efficiency and good fuel conversion was observed.

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IND-PO-11 La/Mn Perovskite catalysts for Biodiesel production.

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Biodiesel (a mixture of Fatty Acid Methyl Esters, FAME) is the second biofuel produced in the world and the first in Europe. Nowadays the major part of biodiesel is produced by transesterification with methanol of refined edible oils such as rapeseed, sunflower, palm, soybean, etc. However, the majority of this raw materials do not fulfill the sustainability criteria indicated by the UE Directive 2009/28/EC, and so they shall not be taken into account for measuring compliance with the requirements of this Directive concerning national targets. Instead, the waste vegetable or animal oils widely fulfill the sustainability criteria and so are more convenient by an ecological point of view. Moreover the use of waste oil is also economically of great interest. Actually more than 85% of the cost of biodiesel obtained from edible vegetable oils is the cost of raw materials.

Biodiesel is produced today by the transesterification of triglycerides of refined/edible type oils using methanol and an alkaline homogeneous catalyst (NaOH, NaOMe): The reaction is normally performed at 60–80 °C. The glycerol and FAME are separated by settling after catalyst neutralization. The crude glycerol and biodiesel obtained are then purified. However, homogeneous alkaline catalysts cannot directly be used with waste oils due to the presence of large amounts of free fatty acids (FFA) [1].

Recently Russubueldt et al [2] found that La_2O_3 leads to an excellent activity for transesterification of refined palm oil. However, the pure oxide shows an insufficient catalytic stability and a partial homogeneous catalysis by the formation of soaps in the reaction with crude palm oil (FFA 5%). Moreover, although La mixed oxides with a perovskite structure are lower active than the pure oxide, they supposed a much better resistance towards free fatty acids.

In this paper we will report the performances of mixed oxide La/Mn with a perovskite structure prepared by flame pyrolysis technique [3] in the transesterification of refined and acid soybean oil.

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IND-PO-12 Chlorohydrins Production by Glycerol Chlorination

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The growing availability of glycerol, obtained as a co-product in biodiesel production, has determined a great interest in the development of new processes using glycerol as feedstock, also with the aim of reducing biodiesel production costs. A promising choice should be the glycerol chlorination reaction, in order to produce chlorohydrins (both mono- and dichlorohydrins). For example, dichlorohydrins can be easily converted into epychlorohydrin, that represents an important intermediate in the production of epoxy resins [1,2]. Moreover, in this process both monochlorohydrins and glycidol can be obtained: these last products could represent a possible intermediate in different industrial syntheses.

The first literature studies and patents on the reaction between glycerol and hydrochloric acid are rather old (about 1940) and are based on the use of aqueous HCl solutions in the presence of acetic acid as catalyst, in a temperature range of 80-100°C. Therefore, these processes have some drawbacks, such as the slow rates for the diluted mixture, the loss of catalyst by evaporation and several difficulties in the separation of the products, as investigated in more recent studies [3-5].

In the present work, the glycerol chlorination reaction has been studied by using a pressurized reactor made in hastelloy, operating in fed-batch conditions by feeding gaseous hydrochloric acid to glycerol in order to maintain the reaction system at a constant pressure. The reactor temperature was kept at 100°C and the total reaction time was of 4 h. Some effects have been investigated, such as the catalyst concentration (2-8 mole %) and reaction pressure (1-8 bar). With the scope to evaluating the mechanistic aspects, in this study different catalysts have been tested, for example, the homologue series of acetic, mono-, di- and trichloroacetic acid, that gave interesting results in terms of selectivity. In particular, acetic acid resulted selective in the production of 1,3-dichlorohydrin, while chloro-substituted acids have produced a mixture of mono- and dichlorohydrins. A decreasing activity has been observed in the order: acetic > monochloro > dichloro > trichloro acetic and a suitable reaction mechanism has been proposed for interpreting the collected results. At last, a reliable kinetic model has been developed for the description of the experimental data collected in the fed-batch reactor, allowing a comparison between different catalysts in terms of kinetic constants.

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IND-PO-13 Gas Phase Photocatalytic Selective Oxidation of Ethanol to Acetaldehyde on $VO_x/TiO_2/SiO_2$ Catalysts

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Aldehydes are important products and intermediates in the field of fine chemicals. A commonly used method for their preparation is the oxidation of alcohols. From an environmental and economic standpoint, the use of heterogeneous photocatalysis is particularly attractive. In this work the gas-solid photocatalytic partial oxidation of ethanol to acetaldehyde on $VO_x/TiO_2/SiO_2$ was studied. The catalysts were prepared by sequential grafting of vanadyl triisopropoxide onto a support of silica coated with TiO_2 by a mono- or multi-step grafting procedure. The obtained samples were characterized by N_2 adsorption-desorption at -196°C, X-ray diffraction, Raman and UV-Vis spectroscopy.

Photocatalytic tests were carried out at 60°C and atmospheric pressure, feeding 30 (stp)L/h He stream containing 0.2 vol. % ethanol, with oxygen/ethanol ratio of 2. The catalyst weight was chosen on the basis of nominal content of TiO_2 and it was equal to 1.2 g. The fluidized bed photoreactor was illuminated by two UVA-LEDs (emitting at 365 nm) modules of 40 pieces each (light intensity: $90mW/cm^2$). The outlet gas composition was continuously measured by an on-line quadrupole mass detector and a continuous $CO-CO_2$ NDIR analyser.

For TiO_2/SiO_2, ethanol conversion passed from 53 to 46% for SiO_2 loaded with a monolayer of TiO_2 ($TiSi_1$) and three layer of TiO_2 ($TiSi_3$), respectively.

The presence of VO_x species anchored on $TiSi_1$ enhanced photocatalytic activity up to 66 %, with acetaldehyde selectivity higher than 99%. On the contrary, vanadium on $TiSi_3$ inhibited photoreactivity decreasing ethanol conversion from 46 to 37%, although acetaldehyde selectivity was higher than 98%.

IND-PO-14 The Baeyer-Villiger oxidation of cyclohexanone to ε-caprolactone with hydrogen peroxide: the role of radicalic reactions

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The Baeyer-Villiger (BV) reaction has aroused great interest as a powerful tool for the preparation of pharmaceuticals (e.g., antibiotics, steroids) and compounds for the fine chemicals and intermediates industry [1]. Within this context, in recent years many efforts have been spent in the study of new catalysts that may allow the selective transformation of cycloalkanones into the corresponding lactones with hydrogen peroxide, the ideal oxidant for developing a cleaner process. In general, it is believed that the electrophilic attack of (activated) hydrogen peroxide generates the Criegee intermediate, which then rearranges into the lactone; the latter may undergo hydrolysis and ring opening to form hydroxyacids.

During our investigation aimed at studying the activity of heterogeneous and easily recyclable catalysts for the BV oxidation of cyclohexanone into ε-caprolactone, we realized that indeed thermally-activated radicalic reactions control the mechanism, and that the lactone may very rapidly react to yield dicarboxylic acids, even when a stoichiometric amount of the oxidant is used [2]. ε-Caprolactone is the primary reaction product, but it is more reactive than cyclohexanone, and quickly undergoes consecutive transformations by means of two different reaction pathways, (a) an hydrolythic pathway to 6-hydroxyhexanoic acid, which also is oxidized to adipic acid, this reaction being however slower than the concurrent ones, and (b) a direct oxidative scission to adipic acid.

The relevant reaction rates are modified when titanium-silicalite-1 (TS-1) is used as catalyst. In this case, in fact, the high concentration of hydroxy radicals within pores accelerates the reaction rates, especially the consecutive formation of adipic acid and of lighter diacids. The proper choice of the solvent, which also may act as a radical scavenger, both without catalyst and with TS-1, is a powerful tool for controlling the rates of the various reactions involved. With either *t*-butanol or dioxane - efficient radical scavengers - all the reaction rates are slowed down, in special mode the consecutive oxidation of the very reactive ε-caprolactone into diacids.

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IND-PO-15 Low molecular phenols: useful starting materials for the production of fine chemicals. Toward the valorisation of active compounds and agro-industrial fractions from vegetal waste.

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In this communication we report our recent results on the preparation of new biologically active compounds from commercially available low molecular phenols by using ecofriendly chemical procedures. As example, flavonoids were converted into new derivatives showing apoptotic activities against tumoral cell lines, antifungal and antioxidant properties [1]; cinnamic acids were converted into the corresponding 4-vinyl phenols, flavoring compounds useful for perfumery, food, and beverage industries [2]; tyrosol into biologically active hydroxytyrosol and its lipophilic derivatives [3].

More recently, our efforts have been turned on the utilization of low molecular phenols which are selectively extracted from agro-industrial wastes by using innovative technologies, in particular, new biophenolic fractions from different waste and tissues of *Olea europaea* L.[4]. Further investigation are in progress to obtain biologically active compounds useful for industrial applications such as food, cosmetic and pharmaceutical fields.

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IND-PO-16 Synthesis and characterization of hydroxylated oligoamides obtained from renewable resources

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Several hydroxylated oligoamides have been synthesized and characterized in order to obtain water soluble compounds with a high affinity for polar materials as wood, paper and natural fibres. The interest for the synthetic procedures is the use of renewable resources as starting compounds. In fact natural compounds or their derivatives, as tartaric acid, *D(+)*-glucaric acid and α,α-trehaluronic acid, have been used as diacids in the polycondensation reactions.

In order to activate the acids, the dimethyl esters have been obtained using modified versions of the procedures reported in literature [1, 2]. The polycondensation reactions between different dimethyl esters and different diamines have been performed in order to obtain oligoamides with different behavior. In fact products with different molecular weight and different hydrophilic/hydrofobic ratio have been obtained using diamines as 1,2-ethylenediamine, 1,6-hexamethylenediamine, 1,12-diaminododecane, 2,2’-(ethylenedioxy)bis(ethylamine), p-xylylenediamine and several polyamines.

Several attempts have been made by changing the reaction parameters (time, temperature, solvent, catalyst). Generally the best conditions for the synthesis have been found using methanol or DMSO as a solvent and triethylamine as a catalyst. All the compounds obtained in this study have been characterized through FT-IR, ^{1}H, ^{13}C NMR spectroscopy and through 2D NMR techniques (gCOSY, gHSQC) .

The oligoamides with low molecular weights have been employed in wood consolidation. Other different applications for example as additives in the commercial formulations of polymers have been studied.

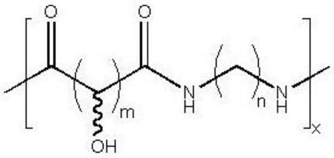

Figure 1

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IND-PO-17 Ethanol Dehydrogenation to Ethyl Acetate: a Kinetic Study

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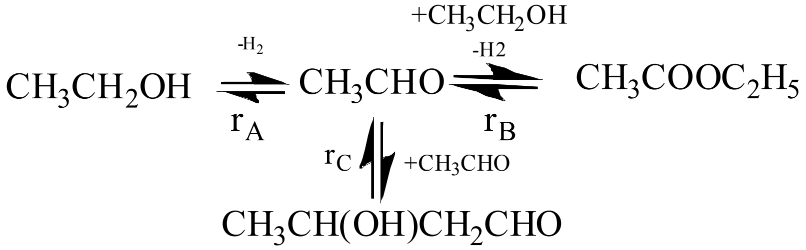
A one step reaction of ethanol dehydrogenation to ethyl acetate, promoted by a copper/copper chromite catalysts, has been studied. The reaction has been performed in a stainless steel fixed bed reactor under pressure (10-30 bar), in a temperature range of 200-260°C and with contact time values, W/F_{EtOH}^{0}, ranging from 30 to 100 $ghmol^{-1}$. In the best operative conditions: T= 220°, P= 20 bars and W/F_{EtOH}^{0}= 100 $ghmol^{-1}$ a conversion of 70% with a selectivity of 98% to ethyl acetate have been obtained. These values are very promising for the industrial development of the process because have never obtained before. Therefore, it is important to study the kinetic behavior of the catalyst that has given the best performances. At this purpose, a depth study of the mechanism and reaction kinetic has been performed. According to the literature, the mechanism of ethanol dehydrogenation to ethyl acetate is not well defined yet, but most authors agree that the first elementary step would be the molecular adsorption of ethanol on the active site to give ethoxide and adsorbed hydrogen [1,2]. The ethoxide species are subsequently dehydrogenated to adsorbed acetaldehyde that can further reacts with an adsorbed ethoxy group to give ethyl acetate. As it was shown [3], the use of optimal operating conditions favor the selectivity to ethyl acetate with respect to acetaldehyde. From the analysis of the reaction products, we have deduced that ethyl acetate is produced in two different steps, as reported in the following scheme:



As reported in the same scheme different by-products can be obtained via aldol condensation as a consequence of the reaction between two acetaldehyde molecules.

A preliminary evaluation of the eventual external and internal mass transport limitations has been made by applying Weisz-Prater and Mears criteria [4], respectively valid for intra-particles diffusion and inter-phase transport. From this analysis we concluded that in our experiments a chemical regime was operative. On the basis of the assumed mechanism, different kinetic models were used for interpreting kinetic data. The obtained results in simulating experimental data have been compared with the aim to individuate the best kinetic model and related parameters.

Moreover, starting from a reliable reaction mechanism, different possible rate-determining steps have been hypothesized, deriving, in each case, the related expressions of the reactions rate laws to be used for describing the collected experimental runs. In alternative also other kinetic models have been considered in the comparison, such as, for example a Langmuir-Hinshelwood-Hougen-Watson model and other different empirical models (power law). The knowledge of the kinetics and the reaction mechanism is of fundamental importance for the scale-up to the industrial process. The best kinetic model has been applied to create a flow-sheet of a continuous industrial plant with ChemCAD 6.2 process simulator.

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IND-PO-18 Experimental and numerical study on methane combustion in a catalytic monolith at elevated pressures

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In view of its capability of burning fuels with high efficiency and at a relatively low temperatures, thus reducing the formation of NO_x and unburned hydrocarbons, catalytic combustion (CC) has been identified as a promising technique for clean and efficient combustion. Despite of this interest, CC suffers from several limitations due to the high cost of materials (catalysts are based on noble metals) and their low thermal resistance (substrates can achieve 1200 °C). These limitations could be partially overcome using low-cost catalysts, such as perovskite oxides that show good activity and high thermal stability [1]. Up to now, CC has been predominantly studied at atmospheric pressure. The extension of these results to higher pressure is not trivial [2]. In this study, combustion of methane in a $LaMnO_3$/La-γAl_2O_3-coated monolithic reactor is studied under conditions relevant to gas turbine applications (temperature up to 800 °C and pressure up to 11 bar). A two-dimensional CFD model is developed to simulate steady and unsteady behaviors of the high-pressure catalytic combustor and its bifurcational features.

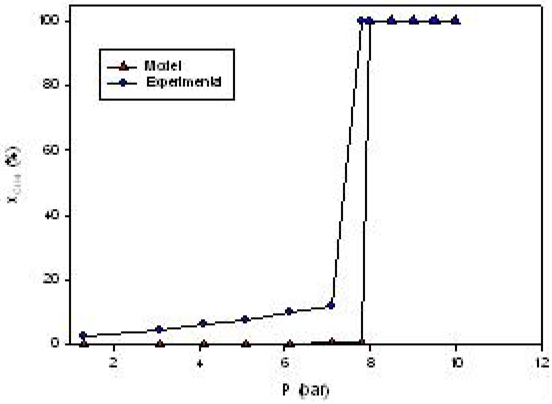

Figure 1.

In the figure 1, the experimental and numerical bifurcation plots are shown in terms of methane conversion as a function of the combustor pressure. At about P =8 bar, a passage from the non ignited solution to a ignited solution occurs accompanied by a rapid increase in methane conversion (from 15 % to 100 %). The experimental trend is well reproduced by the CFD model which can then be used as a tool for simulating the effect of operating conditions and parameters.

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IND-PO-19 POLYMER SUPPORTED HETEROGENEOUS CATALYSTS FOR THE FORMATION OF HYDROGEN PEROXIDE FROM THE ELEMENTS

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The formation of hydrogen peroxide from the elements (direct synthesis, DS) has been investigated for years as an alternative to the antraquinone process for the production of low concentrated solutions.[1] Heterogeneous catalysts supported on inorganic solids have been mainly investigated so far.[2] However, organic polymers are suitable candidates as catalytic materials for this reaction in view of the low temperature applied. In particular, strongly acidic ion-exchange resins have been already proposed for this reaction, either as carriers of Pd^{2+} ions [3] or Pd^0 nanoparticles,[4] but not for bimetallic Pd/Pt catalysts, which are also active in the DS,[5] yet. Commercial ion-exchange resins (Lewatit K2621 and K2629) were ion-exchanged with suitable Pd^{II} and Pt^{II} complexes and subsequently treated with different reducing agents ($H_2C{=}O$; H_2; aqueous $NaBH_4$) to afford bimetallic Pd/Pt catalysts (1%/0% to 1%/1%, w/w). The catalysts were tested in the DS at 2°C in MeOH, at 3.8 MPa (76% inert gas, 21% O_2, 1% H_2). Preliminary results showed a productivity of 43 $mol(H_2O_2)\cdot h^{-1}\cdot kg_{cat}^{-1}$, with a 0,24 % final concentration of H_2O_2.

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IND-PO-20 Emerging materials for dye sensitized solar cells

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Dye-sensitized solar cells (DSSCs) represent a promising, low cost alternative to silicon photovoltaic devices and are a particular type of photo-electrochemical cell.[1]

Because of low fabrication costs, simple manufacturing process and using no toxic materials, a DSSC is expected to be a large-scale prevalent device and a source of clean renewable energy.

A DSSC consists of a thin mesoporous film (10-15 μm thick) of nanocrystals of a metal oxide, often TiO_2, which is sensitized to visible light with a metallorganic or organic light absorber. The so formed photo-electrode is combined with an electrolyte (based on I^-/I_3^- redox couple) and a counter electrode (covered by a thin catalytically active platinum layer), thus obtaining the photo-electrochemical device.

Daunia's activities on materials development focuse above all on the preparation and optimization of performing, low cost and environmentally friendly materials, whose scale-up process is easy and industrially applicable.

In particular, a screen printing paste based on crystalline anatase nano-rods was developed. NanoTiO_2 for DSSC anode was synthesized by adopting a non-aqueous, solvothermal method, involving the use of a high boiling organic solvent and $Ti(^iPrO)_4$ as precursor.[2] A significant dimensional and morphological control over the resulting TiO_2 nanostructures was obtained and an easily scalable (up to 100 liters) synthetic protocol was developed.

On the other hand, another fundamental component of dye sensitized device is represented by the active redox electrolyte. By using the traditional liquid electrolyte good performances could be reached, but a long-term stability cannot be guaranteed. Therefore, our studies focused on the realization of new quasi-solid polymer gel electrolytes, able to improve cell stability preventing electrolyte leakage. The home-made gel electrolytes have been obtained by adding to the electrolyte solution (molecular solvents containing redox couple) a polyiodide (a methacrylate based polymer containing cationic unities, iodide is the counter ion),[3] that works as gelator for the liquid solution and at the same time enhances a coordination-decoordination of iodide ions mechanism, while ion migration occurs inside liquid phase.

Figure 2. A picture of a DSSC module

Finally, cell long-term stability could be reached thanks to the use of an efficient sealant. It should have the following characteristics: representing a protecting barrier from external agents (such as water, humidity and other impurities), be inert towards electrolyte's chemical aggressivity and resist to photo-degradation and temperature variations. Our studies showed that an inorganic glassy sealant could satisfy the aforementioned requirements.

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IND-PO-21 Synthesis of Titanium Dioxide/PS-b-PEO BCPs Nanocomposites and Inorganic Nanoscopic Materials by Sol–gel Synthesis

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The nano-composites formed by inorganic and polymeric materials have large potential to be the candidates for the next-generation materials owing to their excellent optical, electrical, optoelectronic, mechanical and magnetic properties. We have studied the possibility of obtaining smart hybrid nano-composites combining the techniques of Sol-Gel synthesis for the preparation of inorganic metal oxides and the self-assembly of block copolymers (BCPs) to form periodic nanostructures ordered over large areas. Starting from the hybrid nanocomposites, the possibility to prepare metal oxide nanoparticles of well defined shape and geometry arranged in ordered arrays with periodicities dictated by those of BCP nanostructures [1,2], has also been explored.

The concept of using nanostructured thin films of poly(styrene-*b*-ethyleneoxide) (PS-*b*-PEO) BCP of different morphologies as a "structure guiding host" matrix to drive the selective inclusion of titanium dioxide precursor in the PEO domains, has been exploited. A high molecular mass sample of PS-*b*-PEO with volume fraction of the PEO block of ≈0.20, showing a phase separated nanostructure with cylindrical microdomains of PEO in a PS matrix, and a low molecular mass sample of PS-*b*-PEO with volume fraction of the PEO block of ≈0.50 and characterized by a lamellar morphology, have been employed. The TiO_2 precursor has been selectively included in the hexagonally packed PEO cylinders and in the PEO lamellae of the two PS-*b*-PEO samples. Thin films of these hybrid nanocomposites have been subjected to proper heat treatments to obtain TiO_2 crystals and remove the polymeric matrix.

We show that hybrid nanostructured thin films with high degree of orientational and positional order of PEO cylinders filled with the TiO_2 precursor can be easily obtained. We also show that these hybrid thin films give rise upon heat treatments to TiO_2 nanoparticles of elongated shape, standing up on the surface of the substrate according to a pseudo-hexagonal geometry reminiscent of the hexagonal morphology of the hybrid nanostructure.

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IND-PO-22 RUTHENIUM SUPPORTED ON HYDROPHILIC ALKYLSULFONIC RESINS AS BIFUNCTIONAL CATALYSTS FOR THE HYDROGENOLYSIS OF GLYCEROL TO 1,2-PROPANEDIOL

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The replacement of fossil fuels with renewable energy sources is a challenging goal and in this connection biodiesel could help in reducing the dependence on oil. This fuel is obtained upon transesterification of triglicerides with methanol and glycerol is the main coproduct (10 % w/w). [1] To make the biodiesel production affordable glycerol has to be transformed into valuable products. Its hydrogenolysis to 1,2-propanediol (1,2PD) has been under scrutiny. [2] It entails the dehydratation of glycerol to acetol and its subsequent hydrogenation to 1,2PD; hence it is catalyzed in water either by bifunctional catalysts (e.g. $CuCr_2O_4$) [2] or by a physical mixture of a sulfonic polymeric catalyst (sulfonated polystyrene-divinylbenzene resins) and Ru/C. [3] No bifunctional catalysts based on metals supported on acidic organic resins has been employed yet.

Although the sulfonated polystyrene-divinylbenzene resins are hydrophilic materials, compatible with the aqueous reaction medium often employed for the reaction, in the presence of water their arylsulhonic moieties generally undergo C-S bond cleavage (desulfonation) at $T > 120$-130 °C. Under this respect, alkylsulfonic resins are much more stable and should withstand the usually higher temperatures employed in the glycerol hydrogenolysis. We report herein on the preparation and catalytic performance of bifunctional catalysts, comprised of ruthenium supported on alkylsulfonic resins. The latter ones are extremely hydrophilic [4] copolymers of N,N-dimethylacrylamide, 2-acrylamido-2-methyl propane sulfonic acid and ethylenedimethacrylate.

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IND-PO-23 *Ab-initio* single crystal structure solution of dihydrodibenzoazepines

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X-ray diffraction represents the most direct non-invasive technique to investigate the structure of crystalline material in terms of atom positions in the crystalline cell. The availability of a single crystal of appropriate size and quality is required. X-ray diffraction is based on constructive interference occurring when Bragg's Law ($2d \sin\theta = n\lambda$) is satisfied. Crystal structure solution needs to know the structure factor moduli and their phases. Unfortunately the diffraction experiment provides the moduli and not the phases. Therefore, the phase problem must be solved in order to find the unique set of phases that, combined with moduli, permits to calculate the electron density map from which an approximate structure model is derived. In a final step a reliable model may be carried out by structure refinement.

Direct Methods (DM) are able to estimate the phases and solving *ab-initio* crystal structures. In this work, the structure determination process of two dihydrodibenzoazepines (Figure 1) is performed by means the software Sir2011[1]. This is an automatic program supported by a very user friendly graphic interface. Several new algorithms have been implemented in Sir2011, making the program very efficient: it is able to solve both small/medium-sized structures as well as macromolecules. Details about synthesis and theoretical calculations of these molecules can be found in a companion paper [2].

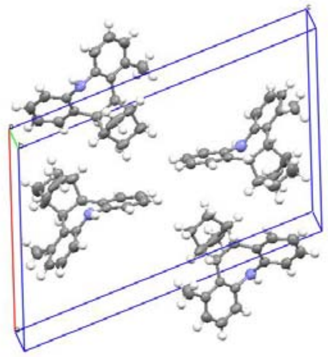

Figure 3. Crystal structure of a dihydrodibenzoazepine molecule.

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IND-PO-24 Experimental and modelling study of the impact of interphase and intraphase diffusional limitations on the deNOx efficiency of V-based catalyst for NH_3-SCR Diesel exhausts aftertreatment.

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In order to control the emissions of NO_X from Diesel and other lean burn engines, the Selective Catalytic Reduction of NOx by ammonia/urea has been applied in recent years to HD and LD Diesel vehicles with excellent results. In this context, the application of numerical simulations has been found a valuable and important tool to support development and practical applications of SCR sytems. In the present contribution, an evaluation of the impact of mass transport effects on the performances of an extruded SCR monolith catalysts made of V_2O_5-WO_3/TiO_2 is presented, based on both experimental and modelling work.

Intrinsic kinetic data were collected over the catalyst in the form of powder to study the typical SCR reacting systems, covering the effects of temperature and of NO_2/NO_x feed content. These data were used to estimate the rate parameters of the reactions included in a suitable kinetic model. Intrinsic rate equations were afterwards incorporated into a 1D + 1D dynamic mathematical model of SCR monolithic converters which accounts for both gas/solid and intraporous mass-transfer resistances [1]. Simulations were carried out for different feed conditions and temperature variations and then compared to experimental data collected on a 5 cm^3 monolithic catalyst sample. The model predictions were found in good agreement with experimental results: negative deviations for the $deNO_x$ efficiency of the monolith configuration with respect to that of the powdered catalyst were observed at T > 250 -300°C. Comparison between data collected in the kinetic regime over the powdered catalyst and data obtained over the lab scale monolith points out the role of mass transfer in determining the activity of SCR catalytic converters. Numerical simulations by means of the 1D+1D monolith channel model allowed decoupling the effects of intra- and inter-phase mass transfer limitations, emphasizing their impact on the performances of extruded SCR monolith converters: their effect on NO_x conversion was found to be significant, depending on temperature and NO_2/NO_x feed content, in line with recent reports for wash-coated systems [2].

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