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Paestum (SA), 10-14 settembre 2017

- Divisione di Chimica Industriale

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Programma Scientifico

Divisione di Chimica Industriale

Lunedì 11 Settembre 2017

	Sala Hera
Session I - Catalysis and Green Chemistry	
Chairperson Fabrizio Cavani	
9:00 – 9:20	IND-OR01: Elnaz Bahadori, Matteo Compagnoni, Antonio Tripodi, Laura Prati, Carlo Pirola, Gianguido Ramis, Ilenia Rossetti. *CO_2 photoreduction at high pressure to both gas and liquid products over titanium dioxide: the effect of unconventional reaction conditions.*
9:20 – 9:40	IND-OR02: Giuseppe Bonura, Catia Cannilla, Fabio Costa, Aldo Mezzapica, Francesco Frusteri. *How structural and surface properties affect stability of hybrid CuZnZr-zeolite catalysts during DME synthesis via CO_2 hydrogenation.*
9:40 – 10:00	IND-OR03: Filippo Bossola, Xavier Isidro Pereira-Hernández, Claudio Evangelisti, Yong Wang, Vladimiro Dal Santo. *Investigation of the promoting effect of Mn on a Pt/C catalyst for the steam and aqueous phase reforming of glycerol.*
10:00– 10:20	IND-OR04: Emilia Paone, Rosario Pietropaolo, Francesco Mauriello. *Selective arene production from aromatic ethers promoted by Pd/Fe_3O_4 catalyst under transfer hydrogenolysis conditions.*
10:20 – 10:40	IND-OR05: Riccardo Balzarotti, Matteo Ambrosetti, Gianpiero Groppi, Enrico Tronconi. *Investigation of coating deposition and catalytic activation of Periodic Open Cellular Structures (POCS) by spin-coating.*
10:40 – 11:00	Coffee Break
	Sala Hera
Session II - New Materials	
Chairperson Rinaldo Psaro	
11:00 – 11:20	IND-OR06: Pier Paolo Prosini, Mariasole Di Carli, Livia Della Seta, Maria Carewska, Ivan Fuso Nerini. *Ethylene vinyl acetate: a promising binding material for high power-high energy electrodes with a prolonged cycle life*
11:20 – 11:40	IND-OR07: Antonio Abbadessa, Antonio Rescifina, Angelo Nicosia, Andrea A. Scamporrino, Fabiola Spitaleri, Placido G. Mineo. *Synthesis and characterization of copolycarbonates having azobenzene units in the main chain as an active group for optical logic gate devices.*
11:40 – 12:00	IND-OR08: Vincenzo Villani, Vito Lavallata. *Unexpected viscoelasticity of Polydimethylsiloxane liquid blends.*
	Sala Hera
Flash Presentation Session 12:00-13:00	
Chairperson Martino Di Serio	
	IND-FC01: Francesca Coló, Federico Bella, Jijeesh R. Nair, Claudio Gerbaldi. *Polymer electrolytes prepared by industrially compatible processes for renewable energy storage in sodium batteries.*
	IND-FC02: Antonio De Luca, Emanuele Piciollo, Cluadio Picchi, Alessio Ceccarini, Emanuele Salvietti, Francesco Di Benedetto, Stefano Caporali, Stefano Martinuzzi, Massimo Innocenti. *Thin film of black-gold by electrodeposition, for jewellery making.*

	IND-FC03: Grazia Leonzio. *Study of Fenton reactor in a wastewater treatment plant.*
	IND-FC04: Giada Innocenti, Andrea Malmusi, Matteo Della Pasqua, J. Velasquez Ochoa, Fabrizio Cavani. *Isoprene production from methanol: an investigation on the reaction mechanism.*
	IND-FC05: David Hermann Lamparelli, Antonio Buonerba, Nunzia Galdi, Leone Oliva. *Diblock copolymer ethylene-syndiotactic styrene.*
	IND-FC06: Federica Leone, Andrea Gignone, Silvia Ronchetti, Roberta Cavalli, Luigi Manna, Mauro Banchero, Barbara Onida. *An organic-solvent-free route to obtain nanostructured zinc oxide-based reservoir of clotrimazole.*
	IND-FC07: Marino Malavolti, Antonietta Schirò, Marco Cerra. *Cool Roofing, where chemistry indirectly helps environment.*
	IND-FC08: Mattia Melloni, Fabrizio Cavani, Anna Maria Raspolli Galletti, Hilda Gomez Bernal, Claudia Antonetti. *Integrated catalytic process for biomass hydrolysis: a comparison of different pretreatments and catalysts.*
	IND-FC09: Wanda Navarra, Olga Sacco, Vincenzo Vaiano, Diana Sannino, Christophe Daniel, Vincenzo Venditto. *Removal of non-degradable organic compounds from water with nanocomposite aerogels.*
	IND-FC10: Veronica Pragli, Elnaz Bahadori, Matteo Compagnoni, Gianguido Ramis, Ilenia Rossetti. *Heterogeneous photocatalytic processes for the abatement of N-containing pollutants from wastewater.*
	IND-FC11: Francesco Puzzo, Giulia Pavarelli, Carlo Lucarelli, Fabrizio Cavani. *The upgrading of bio-alcohols: production of added-value chemicals by the gas-phase (oxi)dehydration of 1-butanol over V/P/O catalysts.*
	IND-FC12: Antonietta Cozzolino, Paola Rizzo, Gaetano Guerra. *Antimicrobial release from s-PS Active Packaging.*
	IND-FC13: Antonella Salvini, Arianna Bracciali, Bernardo Grossi, Donatella Giomi, Mario Tredici, Liliana Rodolfi, Massimo D'Ottavio, Luca Meschisi, Alberto Brandi. *Biorefinery from the marine microalga Nannochloropsisoceanica.*
	IND-FC14: Michela Signoretto, Alberto Olivo, Maela Manzoli, Ilenia Rossetti, Mercedes Maroto-Valer. *Lookingat the bigger picture in carbondioxidephotoreduction.*
	IND-FC15: Maria Ricciardi, Raffaele Cucciniello, Daniele Cespi, Carmine Capacchione, Ivano Vassura, Fabrizio Passarini, Antonio Proto. *Synthesis of monoalkylglyceryl ethers using glycidol as green starting material.*
13:00 – 14:00	Intervallo Pranzo – Lunch Break
	Sala Hera
14:00 – 15:00	***Riunione Gruppo Interdivisionale Catalisi*** ***Riunione Comitato Direttivo Divisione Chimica Industriale***
	Sala Paestum B
14:00 – 15:00	*Poster Session (IND-FC01 – IND-FC15)*
	Sala Hera
	Session III - Homogeneous Catalysis
	Chairperson Antonella Salvini
15:00 – 15:20	IND-OR09: Carlo Bravin, Donato M. Mancino, Giulia Licini, Cristiano Zonta. *Molecular recognition and catalysis within confined space.*
15:20 – 15:40	IND-OR10: Cristiano Bolchi, Francesco Bavo, Marco Pallavicini. *Producing amino acid benzyl esters under ecofriendly conditions and without racemization.*

15:40 – 16:00	IND-OR11: Alberto Villa, Ilenia Rossetti, Laura Prati, Aditya Savara. *Microkinetic modeling of benzyl alcohol oxidation on Pd and AuPd catalysts.*
16:00 – 16:20	IND-OR12: Federica Sabuzi, Pierluca Galloni, Valeria Conte. *Sustainable bromination of thymol: synthesis of new biologically active compounds.*
16:20 – 16:40	IND-OR13: Marco Zecca, Chiara Dalla Valle, Francesco Frison, Paolo Centomo. *New perspectives in the action of halide ions as promoter for the direct synthesis of hydrogen peroxide over palladium catalysts.*
16:40 – 17:00	Coffee Break
Sala Hera	
Session IV - Catalysis and Materials	
Chairperson Paolo Pollesel	
17:00 – 17:20	IND-OR14: Federico Bella, Anders Hagfeldt, Michael Grätzel, Claudio Gerbaldi. *Current efforts to make perovskite solar cells industrially viable*
17:20 – 17:40	IND-OR15: Silvia Bordiga, Elisa Borfecchia, A. Martini, Chiara Negri, Gloria Berlier, Pablo Beato, Kirill A. Lomachenko, Carlo Lamberti, Dimitrios K. Pappas, Michael Martin Dyballa, Stian Svelle, Unni Olsbye. *Composition and temperature dependent Cu-speciation in Cu-SSZ-13 catalysts: an in situ XAS and FTIR study.*
17:40 – 18:00	IND-OR16: Vito Di Noto, Keti Vezzù, Enrico Negro, Federico Bertasi, Giuseppe Pace. *Conductivity and relaxation phenomena in ion conducting materials by broadband electric spectroscopy.*
18:00– 18:20	IND-OR17: Galliano Simone, Bella Federico, Falco Marisa, Barolo Claudia, Giordano Fabrizio, Boschloo Gerrit, Grätzel Michael, Hagfeldt Anders, Gerbaldi Claudio, Viscardi Guido. *Biosourced polymers for aqueous solar cells: a possible breakthrough towards green photovoltaic commercialization.*
18:20 – 18:40	IND-OR18: Olga Sacco, Vincenzo Vaiano, Wanda Navarra, Christophe Daniela, Vincenzo Venditto. *Development of N-doped TiO_2 catalyst for the photocatalytic treatment of wastewater in presence of visible light irradiation*
18:40 – 19:00	IND-PZ01: Parmaliana Award Lecture by Matteo Monai *Nanostructured materials for environmental and energy-related applications*
Sala Hera	
19:00 – 20:00	***Assemblea dei Soci della Divisione di Chimica Industriale***

Martedì 12 Settembre 2017

Sala Hera	
Session V - Catalysis and Polymers	
Chairperson Vincenzo Venditto	
9:00 – 9:20	IND-OR19: Maria Michela Dell'Anna, Matilda Mali, Giuseppe Romanazzi, Antonino Rizzuti, Cristina Leonelli, Piero Mastrorilli. *Polymer supported palladium nanoparticles as catalyst for organic reactions in water.*
9:20 – 9:40	IND-OR20: Rosa Vitiello, Rosa Turco, Vincenzo Russo, Martino Di Serio, Riccardo Tesser. *Bromobutyl rubber synthesis: influence of the reaction temperature on product distribution.*
9:40 – 10:00	IND-OR21: Rosita Lapenta, Antonio Buonerba, Assunta De Nisi, Magda Monari, Alfonso Grassi, Stefano Milione, Carmine Capacchione. *Stereorigid OSSO-Type group 4 metal complexes in the polymerization of olefins and polar monomers.*

10:00 – 10:30	IND-IL01: Invited Lecture by Gaetano Iaquaniello *What role will chemistry and chemical engineering play in creating a sustainable and prosperous word*
10:30 – 10:50	Coffee Break
Sala Hera	
Session VI - Materials and Formulations I	
Chairperson Michela Signoretto	
10:50 – 11:20	IND-IL02: Invited Lecture by Amilcare Collina *Materials chemistry for sustainable buildings: a review of MAPEI technologies.*
11:20 – 11:40	IND-OR22: Elena Ghedini, Michela Signoretto, Alessia Costantin, Alessandria Semenzato, Giuseppina Cerrato. *Smart formulations for cosmetic industrial applications.*
11:40 – 12:00	IND-OR23: Matteo Guidotti, Rinaldo Psaro, Elisabetta Gargani, Alessandro Caselli, Enrico L. Appiani, C. Cattaneo, Roberto Rappuoli. *Inorganically and organically modified mineral clays: a sustainable approach in the control of the olive tree fly pest, Bactroceraoleae.*
12:00 – 12:20	IND-OR24: Mirco Nodari, Aldo Longo, Dino Ferri, Andrea Perolo. *Modeling approach for applied research: the case-study of PLA synthesis by ring-opening polymerization of lactide*
12:20 – 12:40	IND-OR25: Massimo Innocenti, Maurizio Passaponti, Emanuele Salvietti, Stefano Martinuzzi, Emanuele Piciollo, Stefano Mariottini, Luca Rosi, Stefano Caporali, Walter Giurlani, Francesco Di Benedetto. *Chemical research in the field of galvanic industries and fashion accessory.*
12:40 – 13:00	IND-OR26: Anna Malafronte, Claudio De Rosa, Finizia Auriemma, Carmen Sasso. *Manipulating the arrangement of arrays of nanoparticles on solid supports by using self-assembled block copolymers templates.*
13:00 – 14:00	Intervallo Pranzo – Lunch Break

Mercoledì 13 Settembre 2017

Sala Paestum B	
14:00 – 15:00	*Poster Session(IND PO01 – IND PO13)*
Sala Hera	
Sessione VII- MSc and PhD Thesis Awards	
Chairperson Federico Bella	
15:00 – 15:10	IND-PZ02: Best MSc Thesis Award, lecture by Massimo Christian D'Alterio. *DFT-D Study of crystal phase transitions in syndiotactic polypropylene*
15:10 – 15:20	IND-PZ03: Best MSc Thesis Award, lecture by Cristina Pizzolitto. *Development of nanostructured nickel based catalysts for hydrogen production*
15:20 – 15:35	IND-PZ04: Best PhD Thesis Award, lecture by Sebastiano Campisi. *Novel approaches towards the optimisation of metal nanoparticle based catalysts*
15:35 – 15:50	IND-PZ05: Best PhD Thesis Award, lecture by Tommaso Tabanelli. *Sustainable catalytic processes for the synthesis and use of organic carbonates*
Sala Hera	
Session VIII - Materials and Formulations II	
Chairperson Federico Bella	
15:50 – 16:10	IND-OR27: Giorgio Ferrari. *New Sustainable Technology to Recover Returned Concrete.*
16:10 – 16:30	IND-OR28: Raffaella Mancuso, Roberta Amuso, Biagio Armentano, Anna R. Cappello, Francesco Galiano, Alberto Figoli, Jan Hoinkisd, Bartolo Gabriele. *Acryloxyalkyltriethylammonium bromides: useful starting materials for the preparation of polymeric membrane coatings with anti-biofouling properties.*
16:30 – 16:50	**Coffee Break**

	Sala Hera
Session IX- Biochemicals	
Chairperson Francesco Pignataro	
16:50 – 17:10	IND-OR29: Paolo Centomo, Chiara Dalla Valle, Federico Rastrelli, Sandro Campestrini, Marco Zecca. *Novel ion-exchange catalysts for the esterification of vegetable oil solutions of fatty acids with methanol*
17:10 – 17:30	IND-OR30: Domenico Licursi, Claudia Antonetti, Sara Fulignati, Alessandro Corsini, Anna Maria Raspolli Galletti. *The hydrothermal conversion of cellulose-rich wastes deriving from the papermaking process to levulinic acid as smart opportunity for their re-use and valorization.*
17:30 – 17:50	IND-OR31: Vincenzo Russo, Rosa Vitiello, Rosa Turco, Riccardo Tesser, Martino Di Serio. *Levulinic acid esterification kinetics with ethanol in the presence of Amberlyst-15.*
17:50 – 18:10	IND-OR32: Nicola Scotti, Federica Zaccheria, Claudio Evangelisti, Rinaldo Psaro, Nicoletta Ravasio. *Dehydrogenative coupling promoted by copper catalysts: a way to upgrade bio-alcohols*
18:10 –18:30	IND-OR33: Rosa Turco, Martino Di Serio, Marcella Mazzocca, Vincenzo Russo, Riccardo Tesser, Rosa Vitiello, Donatella Cimini, Chiara Schiraldi. *Succinic acid Production from ArundoDonaxhydrolysate for bio-based poly(butylene succinate) synthesis.*
18:30 – 18:50	IND-PZ06: Mario Giacomo Levi Award Lecture by Fabrizio Cavani and Mario Novelli *n-Butane to Maleic anhydride: an impossible reaction and a catalyst which does miracles*
18:50 – 19:10	IND-OR34: Ferruccio Trifirò. *The history of the journal "La Chimica e l'Industria"*

Premi
della Divisione di Chimica Industriale

Premio Mario Giacomo Levi

Prof. Fabrizio Cavani, Università degli studi di Bologna

Dott. Ing. Mario Novelli, Polynt SpA

Premio Adolfo Parmaliana

Prof. Matteo Monai, Università degli Studi di Trieste

Premi Tesi di Laurea

Prof. Massimo C. D’Alterio, Università degli Studi di Napoli Federico II

Prof. Cristina Pizzolitto, Università degli Studi di Venezia

Premi Tesi di Dottorato

Prof. Sebastiano Campisi, Università degli Studi di Milano

Prof. Tommaso Tabanelli, C.I.R.I.-E.A.

Nanostructured materials for environmental and energy-related applications Premio Adolfo Parmaliana

Matteo Monai[a], *T. Montini*[a], *J. Luo*[b], *E. Fonda*[c], *T. Duchon*[d], *M.M. Khader*[e], *V. Matolin*[d], *C.B. Murray*[f], *R.J. Gorte*[b], *P. Fornasiero*[a]

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The world is facing an era of global environmental pollution, as a result of the tremendous population growth and the consequent massive fossil fuel-based energy consumption. A significant exploitation of renewable energies is needed to guarantee quality of human life and allow further sustainable growth, but this may take decades to happen. In order to mitigate the negative effect of human activities on the environment in the short- and mid-term, the development of more efficient technologies for emissions abatement and for renewable fuels production is imperative. Heterogeneous catalysis and photocatalysis are two key pillars of a multi-approach strategy to solve these issues. Exploiting the tools of nanotechnology, tailored nanostructured materials can now be produced, which show different properties in comparison to their bulky counterparts, often resulting in better catalytic performances. Combining the elements of the periodic table in nano-alloys allows to expand the possibility of catalyst generation. Consistently with these approaches, well-defined nanostructured materials were synthesized and characterized for environmental and energy-related applications, such as emissions control, biofuels synthesis and photocatalytic H_2 production. It is shown that structural control at the nanoscale is a great instrument for understanding reaction pathways, for studying the nature of catalytic active sites, and for synthesizing more selective, active and stable catalysts.Two synthetic strategies were followed to acquire nanostructural control: a self-assembly method was employed to prepare hierarchical materials starting from functional nanoparticles (1), and advanced solvothermal methods were used to prepare monodisperse nanocrystals having controlled size and composition (2-4). State-of-the-art hierarchical Pd-based catalysts embedded by metal oxide promoters were tested for methane catalytic oxidation in the presence of poisoning compounds typically found in real applications, such as H_2O, SO_2 and phosphates (5-7). Detailed surface studies allowed to propose deactivation mechanisms and strategies to improve catalysts resistance to deactivation. Well-controlled nanostructured Pt-based alloys and Ni-Cu alloys showed improved activity, stability and selectivity for hydrodeoxygenation reactions of biomass-derived feedstocks to produce biofuels (2-4).The control of nanostructure was pivotal to understand the reason for such enhanced performances.All these findings greatly contributed to the development of catalytic materials for energy-related applications.

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DFT-D study of crystal phase transitions in syndiotactic polypropylene
Premio Tesi di Laurea

Massimo C. D'Alterio[a], *Ana B. Muñoz-García*[a], *Finizia Auriemma*[a], *Claudio De Rosa*[a], *Michele Pavone*[a]

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Syndiotactic Polypropylene (sPP) is a semi-crystalline polymer, which exhibits an uncommon mechanical behaviour: after a mechanical stress, as an axial elongation, sPP recovers its initial length at the equilibrium. This elastic behaviour has an enthalpic driving-force, unlike common amorphous elastomers where driving-force is entropic. The reason behind this phenomenon is a first order transition between two different crystalline forms. In the unstrained phase (Form II), macromolecular chains of sPP are helices with **s**(2/1)2 symmetry, whereas by stretching the polymer they adopt a trans-planar conformation with **t***cm* symmetry, where they constitute a crystalline phase stable only under stress (Form III) (1). Much is known about these two forms, less about molecular mechanism of the transition from form II to III (Figure 1).

The main goal of this work is the characterization of the mechanism: we investigate the intermediates structures, the transition states and the related energetic barrier. For this purpose, the survey method is based on computational chemistry: in fact atomistic simulations provide a computationalmagnifying glass to follow atoms and chain movements along the transformation. In particular, we implemented an *ab initio* simulation strategy, based on density functional theory (2) (DFT-GGA) including a D3 correction to take into account dispersion forces among the sPP chains in the crystal (3). In order to confirm and examine in depth theoretical results, an experimental study of the morphology of stretched fibers after relaxations has been carried on.

In conclusion, by integrating theoretical and experimental results, we got proofs about the transition mechanism and we depicted new insights on structure-properties relationship in semi-crystalline polymers.

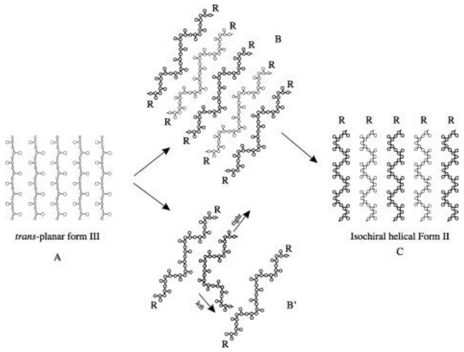

Figure 1. A possible transition pathway

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Development of nanostructured nickel based catalysts for hydrogen production
Premio Tesi di Laurea

Cristina Pizzolitto

Department of Molecular Sciences and Nanosystems, Ca' Foscari University Venice and INSTM RU of Venice, via Torino 155, I-30172 Venezia Mestre, Italy

Energy is world driving force because it controls every human activity and brings the population the possibility of a better future. Nowadays, most energy requirement relies on fossil sources like coal, oil and natural gas, that are still cost-effective (1). These sources, however, suffer environmental, social and economic issues. Hydrogen is the most promising fuel because it's a clean source, water is the only co-product of its combustion, it's nontoxic and it can be employed inside fuel cell enginesto obtain electrical energy directly from chemical bonds. One of the most promisingand efficient processesto produce hydrogen is ethanol steam reforming (ESR) for the high H/C ratio that makes ethanol a good feedstock. In particular, ethanol can be obtained from the fermentation of biomass,as clean and sustainable source,avoiding the use of fossil fuels. In addition to this, CO_2, a noxious by-product, finds application in other technologies. For example, another process that can be used to produce hydrogen, taking advantage of two of the main greenhouse gasses, is methane dry reforming (MDR).

The aim of this work is the development of heterogeneous nickel based catalytic systems that are active and versatile for both the reactions of ESR and MDR.

Nickel was chosen for its high activity to break carbon-carbon bond and for its inexpensiveness compared to noble metal but, due to its low thermal stability toward sintering and coke resistance, the role of support is crucial to minimize metal sintering and coke poisoning. Ceria was chosen for high redox properties, while zirconia for its elevated mechanical and thermal stability (2). Both have some limitations that can be overcome introducing lanthanum oxide. Indeed, this promoter could enhance redox ability of ceria and reduce acidity of zirconia (3). Aimed at optimizing support-promoter interaction and maximize their synergistic effect, the method of lanthanum oxide introduction was studied too. Lanthanum oxide was added to the support by two different synthetic approaches: via impregnation and co-precipitation.

It was found that lanthanum oxide is a good promoter both for ceria and zirconia catalysts because an increase in activity and stability was observed for both ESR and MDR. The introduction method was fundamental in order to achieve the maximum interaction between support and lanthana, in particular for ceria support. In fact, for this system, it was observed that co-precipitation method is the best technique to increase ceria redox properties, as confirmed by XRD analysis. On the contrary, for zirconia one, the introduction method has not been considered fundamental because the effect of lanthanum oxide is ascribed at its basic ability. In conclusion, with the addition of lanthanum oxide on nickel ceria and zirconia catalysts it was found a versatile catalytic system that works for both the different reactions of ethanol steam reforming and methane dry reforming.

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Novel approaches towards the optimisation of metal nanoparticle basedcatalysts
Premio Tesi di Dottorato

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Catalyst design requires an improved understanding of the chemistry on the surface, a clear disclosure of the mechanism of the process and the ability to probe active sites under reaction conditions. This is possible if a knowledge-based approach is shaped around three pillars: 1) the controlled synthesis of nanomaterials; 2) theoretical modelling of materials that enable experimental results to be understood; and 3) *ex situ* and *in situ*characterization. These aspects have been examined in my Ph.D. thesis, focused on the optimization of supported noble metal based catalysts for liquid-phase oxidation processes. Two possible strategies for tailoring the selectivity in the base-free glycerol oxidation have been extensively investigated, by exploring the ability to orientate the reaction pathway towards the selective oxidation either of the primary alcohol function or the secondary alcohol function. The selective oxidation of the primary hydroxyl group in the glycerol molecule results in the production of glyceric acid. AuPt bimetallic nanoparticles, when supported onacidic supports, have been shown to be active and durable catalysts for the selective glycerol oxidation to glyceric acid under neutral conditions. Starting from these considerations we studied more in the detail the effect of surface acidity, by comparing various metal oxides with different type, number and strength of acid sites. We observed that the acid properties, especially the strength of H-bonding, are the key factor in tuning the selectivity. In the past years many efforts were devoted to switch the reaction pathwaytowards the oxidation of the secondary alcohol function, to maximize the yield of dihydroxyacetone (DHA), a high value-added product. Until now, best results in terms of DHA yield have been obtained using Bi-Pt/AC catalysts. However these systems suffer from quick deactivation due to metal leaching. We then examined the possibility to improve the durability of BiPt based catalysts by tuning the metal composition. In particular BiAuPt nanoparticles were supported on activated carbon and tested in base free glycerol oxidation. By comparing the catalytic performances of trimetallic AuPtBi NPs with the ones of bimetallic AuPt and BiPt NPs, we concluded that:I)the addition of Bi promotes the oxidation of the secondary OH function;II)the addition of gold enhances the catalyst stability, thus resulting in a good selectivity to DHA even at high conversion. Beside the metal composition and the surface properties of supports, also the preparation route can influence the catalytic performances of supported noble metal nanoparticles. The sol immobilisation technique, in which a protective agent (such as polyvinylalcohol, PVA) is used to stabilize metal nanoparticles, possesses advantages like the control of the metal particle size. On the other hand, the presence of residual protective agent can affect the catalytic performances. Using operando ATR-IR spectroscopy we revealed that, in the liquid phase benzyl alcohol oxidation, PVA produces a selectivity enhancement to benzaldehyde limiting its decarbonylation. DRIFT experiments with CO as probe molecule allowed to relate this behavior to a specific blocking of Pd(111) facets which has been recognized to facilitate the decarbonylation step. In an ideal knowledge-based approach experimental evidences should be supported by theoretical results. For this reason, the last part of my Ph.D. was devoted to the application of Density Functional Theory modelling to the investigation of some of those features experimentally investigated. Promising preliminary results revealed that the local structure and composition of active site play a crucial role in affecting the reaction mechanism of ethanol oxidation. In particular the presence of oxygen and defects strongly modify the reaction mechanism from an energetic point of view. Concluding, the design of supported noble metal nanoparticle based catalysts can be optimized by using a novel approach, which takes into account and harmonizes all the different aspects involved in the process.

Sustainable catalytic processes for the synthesis and use of organic carbonates
Premio Tesi di Dottorato

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The present study is focused on the development and improvement of sustainable catalytic processes for the synthesis of organic carbonates (OCs). These compounds are among the most promising green alternatives for the replacement of conventional toxic solvents and fuel additives and for the development of innovative intermediates in the pharma and polymer industries(1,2). Thedirect condensation reaction between carbon dioxide and several alcohols and diols was investigated using a new generation of mesoporous nanosilicas functionalized by insertion of amino groups (3). Unfortunately, these reactionssuffer from strictly thermodynamic limitations and lead to very poor carbonates yields. Afterward, the carbonate interchange reaction (CIR) of the simplest linear organic carbonate, dimethyl carbonate (DMC), with several alcohols has been investigated in order to synthesize higher carbonates. Indeed, in the CIR one carbonate is converted into another one, because one or both of the acyl-oxygen moieties of the parent carbonate are displaced by an appropriate alkoxide/aryl oxide(4). However, these are equilibrium-limited reactions, often with low equilibrium constants, especially when used for the synthesis of aromatic carbonates. In order to solve this problem, complex reactive distillation systems (RDS) are usually applied for enhancing the removal of the lightest co-product of the reaction: methanol. Nevertheless, the formation of a complex azeotrope between methanol and DMC leads to important losses of this reagent during distillation, that finally are detrimental for the reaction. Therefore, the development of an innovative lab-scale implemented RDS, based on the selective adsorption of methanol from the distilled mixture inside appropriate molecular sieves was envisaged, accompanied by continuous recovery of DMC into the reaction mixture. In this way, a continuous and efficient in-situ removal of methanol (co-product of the reactions) with negligible losses of DMC was accomplished, shifting the reaction equilibriums and allowing to obtain yields considerably higher than the equilibrium values. The application of this method in the synthesis of catechol carbonate (CC), combined with the optimization of the isolation and purification steps, allowed us to obtain an isolated yield of 90% of this scarcely investigated compound. The obtained CC was investigated as an alternative, more efficient carbonate source for the selective synthesis of a wide plethora of both dialkyl and alkylene carbonates (e.g glycerol carbonate, GlyC), in the presence of a basic catalyst. Indeed, results obtained under very mild reaction conditions (40-80°C, ambient pressure) and low reaction time (30 to 60 min) proved the unprecedented outstanding potential of CC, that not only greatly enhanced the reaction kinetics, but also promoted the quantitative formation of symmetric carbonates ($ROCO_2R$), these products being elusive in the CIR of both EC and DMC(5). The obtained GlyC has been also used as innovative chemical intermediate, for the condensation reaction with catechol in order to obtain the efficient synthesis of 2-hydroxymethy-1,4-benzodioxane (HMB) an important intermediate for the pharma industry. Finally, some of the synthesized carbonates were tested for the gas-phase phenol alkylation showing an interesting reactivity that could be properly modulated by changing the reaction conditions and the catalyst acid-base properties.

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n-butane to maleic anhydride: an impossible reaction and a catalyst which does miracles
Premio Mario Giacomo Levi

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The production of maleic anhydride is carried out by means of the gas-phase selective oxidation of *n*-butane. This reaction still represents the most significant example of valorisation of a natural-gas component by transformation into an added-value intermediate chemical. It is carried out in industry by means of various technologies, amongst which one of the most advanced is the fluidized-bed process jointly developed by Lummus (today CBI) and Lonza (today Polynt) in the 80's (ALMA process). The catalyst is the key component of this technology; it allows the direct (one-pot) transformation of a saturated molecule, which is an unconventional reactant due to the absence of any functional moiety, into an unsaturated anhydride by means of a reaction which formally involves several steps with the exchange of 14 electrons in overall. Indeed, this reaction is regarded as "impossible to do" based on conventional reactions taken from Organic Chemistry textbooks. The catalyst which is able to perform this "miracle" is based on vanadyl pyrophosphate, $(VO)_2P_2O_7$; it was discovered in the 60's, and soon became a star in the field of catalytic selective oxidation.

Polynt SpA and the "Catalytic Processes Development Team", Bologna University, have been studying the vanadyl pyrophosphate catalyst since the 90's, with a twofold aim: (a) understand the key features of catalyst and the reaction mechanism, and (b) develop more efficient catalysts to implement for the ALMA process. The successful collaboration between Polynt SpA and Bologna University allowed the development of 4 generations of improved catalysts along the years, with an overall increase of MA yield of more than 10%, increased catalyst stability, and decreased catalyst consumption[1]. A detailed study of the nature of active sites, carried out by combining reactivity experiments with *in-situ* spectroscopic techniques, allowed us to develop an in-depth understanding of the characteristics of active sites in vanadyl pyrophosphate, which finally turned out to be the winning strategy for innovation from both a scientific and an industrial viewpoint[2].

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Conferenze su Invito

- INDIL01: Gaetano Iaquaniello, KT – Kinetics Technology SpA
- INDIL02: Amilcare Collina, MAPEI S.p.A.

What role will chemistry and chemical engineering play in creating a sustainable and prosperous word

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Cleaner water, fuels and energy; safer food; more consumer goods, effective medicines and medical devices; more efficient materials from automobiles to rocket ships. These are going to be global challenges which the chemical industry is going to face in the next 30-40 years.

How such issues could be addressed in a sustainable way? Without compromising the ability of future generation to meet their own needs. Society currently has a non-sustainable dependence on a finite supply of fossil-fuels-based hydrocarbons used in almost every synthetic material in our economy. The growth in energy demand is projected to continue and the cumulative impact of burning fossil fuel to meet this demand raises serious concerns (green house effect). In a transitional period the CO2 need to be recovered and reused. New and more efficient methods to activate inert molecules as H20 and CO2 are required to offset the conventional methanation process. CO2 conversion to olephines could be a valid alternative. With price of oil and gas at today levels the quest for renewable feedstocks, green products and processes is becoming harder and harder if we want to maintain a prosperous world. How in this contest we are going to face middle-class growth in the developing world which is going to spur massive demand?

My view point presentation will try to give a contribution by focusing on basic research in energy and energy conversion, green chemistry and processing, environment and last but not least education which will play a central role in the quest for sustainability. A waste-to-chemicals process will be illustrated as an example of how alternative feedstocks can be used to make bulk chemical productions as methanol or urea with fewer unwanted by-products.

Materials chemistry for sustainable buildings: a review of MAPEI technologies

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This lecture will refer to the contribution of materials chemistry to the sustainability of existing buildings, for which energy efficiency and seismic resistance are key factors.

1. Energy efficiency

In Italy at 2011, the date for the last ISTAT census, buildings for residential use amounted to 12.2 million, with more than 31 million homes. A large part of them, more than 45 years old, record annual consumption from a minimum of 160 kWh/m^2 to over 220 KWh/m^2.

Looking at nonresidential sector, the assets used by the Public Administration amount to approximately 420 million square meters, of which about 100 million m2 would require urgent renovation.

As far as the improvement of the energy efficiency is concerned, the most effective solutions proposed by chemical industry are the materials for thermal insulation, the phase change materials and the materials for window frames.

The External Thermal Insulation Composite System MAPETHERM®, proposed by MAPEI, will be described. The ETICS system, applied on the peripheral walls of the building, allows to reach significant energy savings, to improve the living comfort and to reduce the mechanical stress of the building structures.

2. Seismic risk

Almost half the Italian territory is at high risk of earthquakes. Three are the regions where the building heritage is exposed to greater seismic risk: Sicily (2.5 million homes), Campania (2.1 million homes), Calabria (1.2 million). Looking at nonresidential buildings, over 24,000 schools and 1,800 hospitals are located in highly seismic areas.

As far as the seismic risk mitigation is concerned, a number of technologies have been already developed by the chemical industry, both for structural reinforcement and nonstructural elements.

The technologies make use of fiber or tissue composite materials with polymeric matrix as well as cement based matrix.

The following technologies developed by MAPEI will be described:

- MAPEI FRP SYSTEM: Structural strengthening system comprising high strength and very high strength fibers (carbon, glass, steel or basalt) and epoxy matrixes specially formulated for the application to structures made from reinforced concrete, steel, masonry or wood.
- MAPEI FRG SYSTEM: A complete range of composites which, unlike traditional FRP, uses an inorganic, pozzolanic binder to guarantee excellent physicochemical and mechanical compatibility with masonry substrates (stone, bricks and tuff) as well as with reinforced concrete.
- MAPEI EQ SYSTEM: a protection system for internal and external secondary partition walls which stops walls collapsing or tipping over during seismic activity.
- PLANITOP HPC: High Performance Micro-Concrete, with extremely high compressive strength, characterized by its capability to absorb high fracture energy.

The already mentioned technologies give a significant contribution to the sustainability of the existing building heritage.

Comunicazioni Orali

CO_2 photoreduction at high pressure to both gas and liquid products over titanium dioxide: the effect of unconventional reaction conditions

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The photoreduction of CO_2 is an intriguing process, which allows the synthesis of fuels and chemicals. One of the limitations for CO_2 photoreduction in the liquid phase is its low solubility in water. Several studies have been proposed during the last years in order to enhance the photocatalysts performance and improve the phototreactors for this purpose (1, 2). This point has been here addressed by designing a fully innovative concept of pressurized photoreactor, allowing operation up to 20 bar and applied for the first time to improve the productivity of this very challenging process (3-5). The photoreduction of CO_2 in the liquid phase was performed using the commercial TiO_2 (Evonink P25) in the presence of Na_2SO_3 as a hole scavenger. The different reaction parameters (temperature, working pressure, pH) and various catalysts have been considered for investigation of productivity and selectivity in the gas and liquid phase. The expected and formed products in liquid phase in the constant pressure and temperature and in the course of reaction time were formic acid and formaldehyde, respectively. Moreover, for longer reaction time, gas phase products formed (H_2 and CO with no trace of methanol or methane) after accumulation of significant amount of organic compounds in the liquid phase. The formation of gas products takes place within two parallel reaction pathway: i) CO_2 photoreduction into formic acid which may further photoreduce to formaldehyde and finally evolve into CO/CO_2+H_2 (photoreforming), ii) enhancing the CO_2 dissolution in the water by addition of a base with formation of carbonates (pH= 12-14) resultedin the reduction of carbonates to formaldehyde and consequently formed CO/CO_2+H_2 in the gas phase through photoreforming. In order to improve visible light absorption and increase the lifetime of the photogenerated charges, Au was loaded on TiO_2 (0.1-0.5 wt%)by a deposition-precipitation method. Methanol and methane were the main products in liquid and gas phase, respectively, demonstrating the higher reactivity of catalyst in the present of Au. Increasing the Au loading from 0.1wt% to 0.2 wt% improved the productivity toward methanol and methane in liquid and gas phase, respectively. However, further increasing in metal loading negatively affected the Au dispersion and catalyst surface area and resulted in lower H_2 productivity. Furthermore, testing parameters, such as temperature and pressure directly affected the products formation. Increasing the pressure favored the liquid products accumulation was detrimental for H_2/CH_4 productivity. On the other hand, increasing the temperature, decreased the CO_2 solubility in the water, but enhanced the kinetics and mass transfer leading to the formation of H_2/CH_4.

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How structural and surface properties affect stability of hybrid CuZnZr-zeolite catalysts during DME synthesis via CO_2 hydrogenation

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The production of dimethyl ether (DME) by hydrogenation of CO_2 is an issue that recently is receiving a particular attention (1-6) As well known, in order to hydrogenate CO_2 it is necessary that catalyst possesses a multi-functionality suitable to activate both CO_2 and $H_2$and also to dehydrate methanol (MeOH) into DME (3,4,6). In general, MeOHis first generated by interaction of activated H_2 and CO_2 on metal and oxide sites respectively, while DME is then formed by MeOH dehydration on acid sites (1-6).
Recently, we paid attention on the preparationof novel hybrid CuZn-Zr–zeolite catalytic systems,so that the multi-functionality necessary for the reaction is grain-to-grain ensured. Catalytic results, in terms of CO_2 conversion and product distribution using a fixed bed reactor in several reaction conditions (T_R: 200-260 °C; P_R: 3.0 MPa, *GHSV*: 2,200-8,800 *N*L/kg$_{cat}$/h) allowed to ascertain asthe homogeneous distribution of neighbouring metal-oxide-acid sites significantly enhances the rate of mass transfer, sofavouring the achievement of high DME yield.
In the attempt to better assess the potential of such hybrid materials as very promising catalysts for the production of DME via CO_2 hydrogenation, in this work we performed several durability tests (tos, 30 h) at 260°C, 3.0 MPa and 2,200 *N*L/kg$_{cat}$/h of a mixture $CO_2/H_2/N_2$ (3/9/1), in presence of CuZnZr-FER systems containing home-made zeolites with a bidimensional framework (ferrierite topology) at variable acidity (Si/Al ratio: 8-60).
Catalytic data showed a not negligible decrease both in the CO_2 conversion and in the DME selectivity especially in the first 10 h of reaction, mostly evident on the systems containing a more acidiccharacter. Considering that no coke was detected on the "deactivated" catalysts, the plausible explanation about the observed trend was ascribed to the water formation that, absorbing on acid sites, inhibits the dehydration reaction, also leading to a rearrangement of oxide clusters with significant enlargement of metallic Cu particles, probed by N_2O chemisorption measurements that evidenced a considerable shrinkage in the copper surface area as a direct proof of metal sintering.

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Investigation of the promoting effect of Mn on a Pt/C catalyst for the steam and aqueous phase reforming of glycerol

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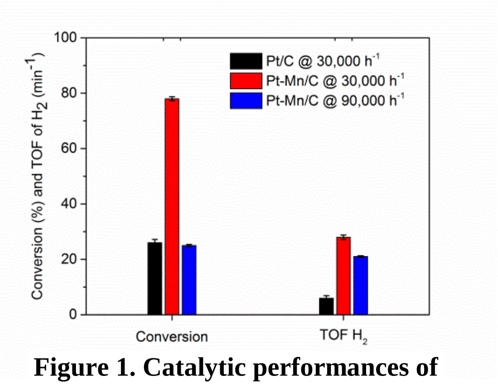

Figure 1. Catalytic performances of Pt/C and Pt-Mn/C in SR of glycerol.

Hydrogen is regarded as a clean energy vector suitable to replace the common fossil fuels. In order to achieve a production of fully green hydrogen, renewable feedstock, like biomass, should be used (1). Due to the complex nature of biomass, however, model molecules are mostly used in reforming reactions for hydrogen production. The addition of a promoter is often used to improve the performances of the catalyst (2). While the promoting effect of many noble metals has been elucidated, the precise impact on the surface features as well as on the reaction pathways of non-noble metals is still unclear. In this work, a Pt-based catalyst was modified by the addition of a Mn promoter, and tested in the steam (SR) and aqueous reforming (APR) of glycerol, which was chosen as model molecule of polyols and as by-product of the bio-diesel industry (3). The reactions were carried out at 225 °C with 10 wt.% glycerol aqueous solution. The presence of Mn had a major impact on the catalyst, mostly reflected in the SR reaction, with an increase in hydrogen productivity and total conversion of factors of 3 and 4, respectively. A weaker promoting effect was found in the APR reaction, with enhancements factors of 1.3 and 1.4. A thorough characterization of the catalysts was performed by mimicking the real working conditions, that is by treating the samples with steam at the reaction temperature. The addition of Mn introduced peculiar surface acidic sites in the form of few, strong Lewis acid sites, as detected by ammonia temperature programmed desorption experiments and attenuated total reflectance infrared analyses using pyridine as probe molecule. These sites, likely generated by exposed $Mn^{\delta+}$ sites in close proximity to Pt sites, contributed to the activation of the glycerol molecule. In fact, at comparable conversion levels, the hydrogen productivity of the bimetallic Pt-Mn/C catalyst outperformed the Pt/C catalyst (Figure 1). Under APR conditions, the promotion of Mn was exerted in a different way. Although the improvement in hydrogen productivity and conversion were lower than in SR, the selectivity toward hydrogen was increased. Moreover, most of the Mn leached out. These findings can be explained by the formation of an alloy between Mn and Pt, which prevented some of the Mn to be leached and promoted the CO spillover from the Pt sites (4). In fact, the C-O bond cleavage activity of the catalyst was not significantly altered, whereas under SR conditions was favoured at the expenses of the C-C cleavage. With this study, we made a significant step forward the comprehension of the actual promoting mechanism of non-noble metals on catalysts for reforming reactions, but much still needs to be done, especially when using harsh reaction conditions, like those of APR (5).

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Selective arene production from aromatic ethers promoted by Pd/Fe_3O_4 catalyst under transfer hydrogenolysis conditions

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The selective cleavage of C-O single bond preserving the aromatic nature represents one of the major challenges in the catalytic valorization of lignin [1].
In the last years, the co-precipitate Pd/Fe_3O_4 catalyst shown a powerful and efficient performance in the catalytic transfer hydrogenolysis (CTH) of lignocellulosic platform derived molecules. [2-4]
In this context, the selective cleavage of the C–O bond of benzyl phenyl ether (BPE), 2-phenethyl phenyl ether (PPE) and diphenyl ether (DPE) - as model compounds of lignin linkages – was investigated, under CTH conditions using 2-propanol as the H-donor and the Pd/Fe_3O_4 catalyst with a nominal palladium loading of 5 wt %.
The use of this catalyst, shown an appreciable BPE (0.1 M) conversion (19.7%) that increases by increasing the reaction temperature and, at 240°C, it is fully converted (100% conversion) into phenol and toluene as the only reaction products (100% aromatic yield) clearly indicating that the cleavage of the etheric C–O bond occurs as the primary reaction route under CTH conditions.
In the next step, the H-donor ability of simple primary (methanol, ethanol, 1-propanol, 1-butanol and 1-pentanol) and secondary (2-butanol, 2-pentanol and 3-pentanol) alcohols was tested and a tight relationship between the moles per l of aldehyde or ketone formed (H-donor ability) and the amount of BPE converted (moles per l) was observed. These results, coupled with the reactivity of the same pure alcohols in presence of the Pd/Fe_3O_4, suggest that the H-transfer from the alcohol and the hydrogen promoting the C-O bond breaking occur in a unique chemical process (Figure 1).
Reaction of PPE at 240 °C shows a lower conversion (22%) and 100% yield of aromatics. On the contrary, DPE was not converted at all. Interestingly, a linear correlation of the bond strength and the ability of the Pd/Fe_3O_4 catalyst in the CTH of aromatic ethers was found.
Therefore, the Pd/Fe_3O_4 catalyst is able to cleave the C–O bond of benzyl phenyl ether (BPE) and 2-phenethyl phenyl ether (PPE) under CTH conditions and, at the same time, avoid parallel hydrogenation reactions of the aromatic ring, being one of the most selective heterogeneous catalysts in the production of arene derivatives.

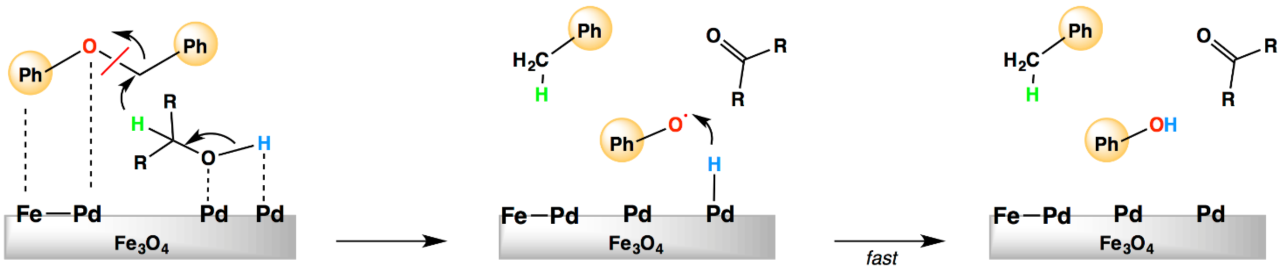

Figure 1. Pd/Fe_3O_4-catalyzed selective transfer hydrogenolysis of benzyl phenyl ether

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Investigation of coating deposition and catalytic activation of periodic open cellular structures (POCS) by spin-coating

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The development of structured catalysts for process intensification is a topic of high interest in industrial research. A large variety of supports have been reported in literature, such as honeycomb monoliths, open cell foams, wire mesh and felts (1). Nowadays, novel manufacturing techniques enable the production of open cellular structures with periodic ordered geometry (POCS). In comparison with open cell foams, the control of the geometrical properties allows optimizing the structure towards the enhancement of heat and mass transfer rates and the reduction of pressure drops (2). Despite the huge interest in these supports, at present time, a little information is present in literature regarding their catalytic activation; in particular, a detailed description of washcoating process to achieve catalytically active supports is missing. In this view, the aim of this work is to fill this gap by providing a complete overview of the application of spin coating technique for catalytic medium deposition on POCS.In this work, aluminum POCS of cylindrical shape (9 mm diameter and 15 mm length) were used. The internal structure of the POCS has ideal cubic cell geometry; samples with constant strut thickness of 0.5 mm and different open cell sizes, namely 1.5, 1.75 and 2.5 mm, were tested. In the first part of the work, basic knowledge concerning wet coating layer formation and management on POCS was achieved. In particular, the effect of spin speed, spin time, liquid media viscosity and support properties (i.e. cell size and support length) were investigated. Coating load was found to decrease with the increase of spin speed and time (Figure 1-a) and promising results were obtained in terms of control of wet coating thickness.On the basis of this preliminary investigation, POCS were made catalytically active by depositing Pd/CeO_2 catalyst by slurry coating (3) and tested for the CO oxidation process. Good results were obtained in terms of CO conversion despite the small volume of the catalyst (Figure 1-b).

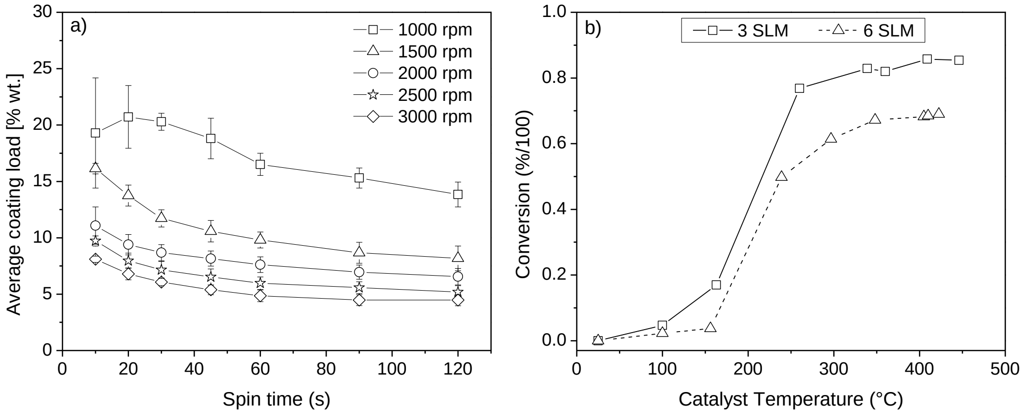

Figure 1. Coating dependence on spin speed and spin time for pure glycerol solution (a) and catalytic performance under CO oxidation process (b) for 1.75 mm cell size samples.

Thus, the use of spin-coating for washcoat deposition on POCS of different cell sizes was found to be a promising deposition technique, with remarkable advantages in washcoat layer management for the production of structured catalysts, enabling well adherent and catalytically active layers.

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Ethylene vinyl acetate: a promising binding material for high power-high energy electrodes with a prolonged cycle life

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The energy, the power, and the cycle life of a lithium-ion battery (LIB) are strictly related to the electrochemical characteristics of the active material. However, the binder used in the electrode formulation plays an important role since it influences the mechanical and electrical properties of the electrode (1). A suitable binder to be used in LIB technology must possess several characteristics such as high flexibility, good adhesion strength, and elevated electrochemical stability (2). In recent years there has been a gradual change in production technologies of electrodes moving from traditional electrodes based on fluorinated polymers (3) to new methods of preparation which employ water dispersible binder. The use of water-based emulsions, eliminating organic solvents necessary to dissolve the fluorinated polymers, makes the manufacturing of the electrodes an ecological process. Among the various polymers available on the market we selected ethylene vinyl acetatea hydro dispersible polymer largely used in the plastic industry, as a binder for the fabrication of the positive electrode of lithium-ion batteries. $LiNi_{0.5}Mn_{1.5}O_4$was used as the active material. The electrode was prepared by painting a thin aluminum sheet with a suspension obtained by mixing the carbon black, the active material, and the polymer in water. The electrode was first analyzed from a chemical-physical point of view. Thenthe anodic stability was examined versus a lithium anode. Finally the electrode was used to prepare a two electrodes lithium cell and the cell was tested to evaluate the electrode capacity retention as a function of the applied current and cycle number. The electrode has been found very promising for the realization of high energy, high power, long cycle life batteries being capable of cycling for hundreds of cycles with excellent performance and reduced loss of capacity.

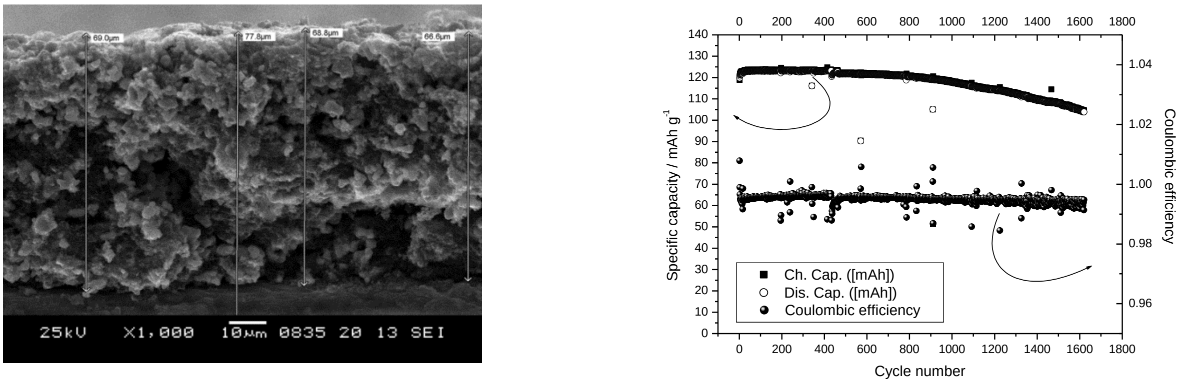

Figure 1. Left: high magnification SEM image of the cross section of the electrode. Right:Variation of the specific capacity and the Coulombic efficiency as a function of the cycle number

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Synthesis and characterization of copolycarbonates having azobenzene units in the main chain as an active group for optical logic gate devices

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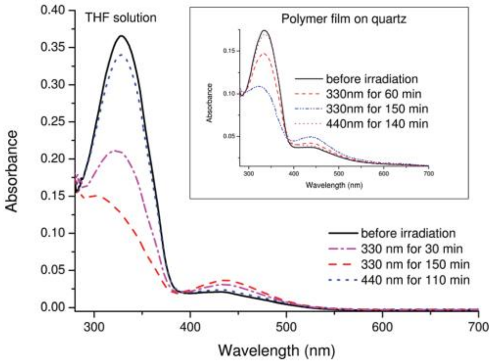
A photocromic compound stand out from its ability to change its absorption spectrum upon irradiation with a selective frequency light and to return to the initial state after the cessation of the light stimulation or upon irradiation with a different light. This phenomenon is due to a chemical reaction (usually an isomerization) which can be partially or wholly reversed by photochemical or thermal stimulations (1,2). The relative concentration of the two isomeric species,depending on the incident light wavelength, can generatephysicochemical properties changes such as the modification ofthe dipole moment and/or the geometrical structure of thechromophore (3). The same behavior is also observed when thechromophoric groups are contained in macromolecular structures both as side chain and as main chain units (4-6). In this context, in recent years both aliphatic and aromatic polymers containing azobenzene moiety (7), mainly as side groups (8), haveattracted considerable attention because of their uniquereversible photoisomerization and photo-induced anisotropicproperties.The present communication focuses on the synthesis of copolymers having photochromic azobenzene groups in the main chain,obtained by copolymerization between phosgene and suitable mixtures of azo-monomer and bisphenol-A (9).Moreover, we show the application of our novel copolymer as a potential logic gate. The chemical and physical properties of these statistical copolymers were investigated by means of MALDI-TOF mass spectrometry,gel permeation chromatography, thermo-analytic techniques and UV-vis and fluorescence spectroscopy.The structural analysis confirmed the formation of statistical copolymers. Furthermore, some of these copolymers exhibited a trans→cis reversible photoisomerization (***see figure***) not only in solution but also in the solid state onexposure to light of 330 or 440 nm. Finally, a discrete and unusual fluorescence was observed upon irradiation at 330 and 440 nm. An in silico TD-DFT calculation study was conducted to explain the observed fluorescence. Thanks to their spectroscopic features,these copolymers are suitable for use in photonic applications such as an optical logical gate.



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Unexpected viscoelasticity of Polydimethylsiloxane liquid blends

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Recently (1), we showed that lightly crosslinked networks based on vinyl-terminated Polydimethylsiloxane (PDMS) liquid rubbers, have unusual rheological properties. In fact, it is observed a decrease of zero-shear viscosity $\eta_0$and viscoelastic moduli $G(t), G'(\omega)$ and $G''(\omega)$ with respect to pure polymer. The Unentangled Crosslinked Nanodomains (UCN) model was proposed in order to explain the rheological behaviour. At low concentration of curing agent, the formation of isolated crosslinked nanodomains is determined. At the nanodomains surface, the dynamics of short chains determines an entanglement-free interface, which contribute to the drop of the rheological properties. The viscoelasticity was explained by means the tube model theory and an extension of Einstein viscosity equation proposed.
Now (2), the same elastomers based on vinyl-terminated PDMS were used (Fig. 1).

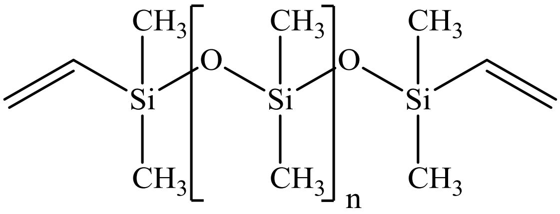

Figure 1. Liquid silicone rubber.

Liquid Silicone Rubbers (LSR, Dow Corning) at low, medium and high viscosity have been considered; low/high and medium/high viscous blends were prepared.
The rheometer DHR-2 (TA Instruments®) in a parallel plate configurationhas been used. To control the temperature from –15 to 150 °C, the instrument is equipped with a Peltier dispositive.
Pure components and their blends have been characterized in rotational and oscillating regime.Flow and viscosity curves, creep-and-recovery and stress-relaxationexperiments have been performed at 25 °C.
In oscillating regime, strain-frequency spectra have been carried out at 25 and 70 °C; dynamical-mechanical spectra from –15 to 150 °C performed, applying strain-frequency of 10 or 250 rad·s^{-1}.
The low/high blend exhibits an unexpected creep reduction and recovery increase with respect to high-viscous component.Surprisingly, the low-viscous component acts as a gelling-like agent reducing the compliance and enhancing the delayed elasticity (18% vs 7% for the high molecular weight precursor). Moreover, in the low frequency field, G'(ω) and G"(ω) increase with respect to the high-viscous component, corroborating the anomalous behaviour due to the low molecular weight component.
In order to explain the rheological behaviour, the tube model for the viscoelasticity of entangled polymer melts has been used.The viscosity decrease of the homopolymer blend should be ascribed to the reduction of the entanglement density, and the compliance drop and the increase of dynamic moduli due to the swelling of long chains by short ones, reducing the conformational flexibility.

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Molecular recognition and catalysis within confined space

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Biological containers and supramolecular cages have largely attracted the attention of scientists for their peculiar properties and applications.[1] These systems are characterized by defined internal cavities that have the fundamental functions to accelerate specific reactions with specific molecular targets, or as a transport containers. In particular we have recently reported a novel supramolecular cage built from the self-assembly of tris(2-pyridylmethyl)amine TPMA complexes that is able to perform molecular recognition of dicarboxylic acid.[2] The possibility to introduce multiple active metal sites having a non-saturated coordination sphere in the inner cavity of these objects open new frontiers in the field of molecular recognition and catalysis. In this communication we report the synthesis of an analogue cage synthesized from opportunely functionalized **TPMA** iron (II) complexes **1** that are already known to catalyze different oxidation reactions.[3] Initial attempts will show the efficiency of supramolecular cage 2 as catalyst respect to monomeric complex 1 in virtue of the confination of the reagents within the cavity.

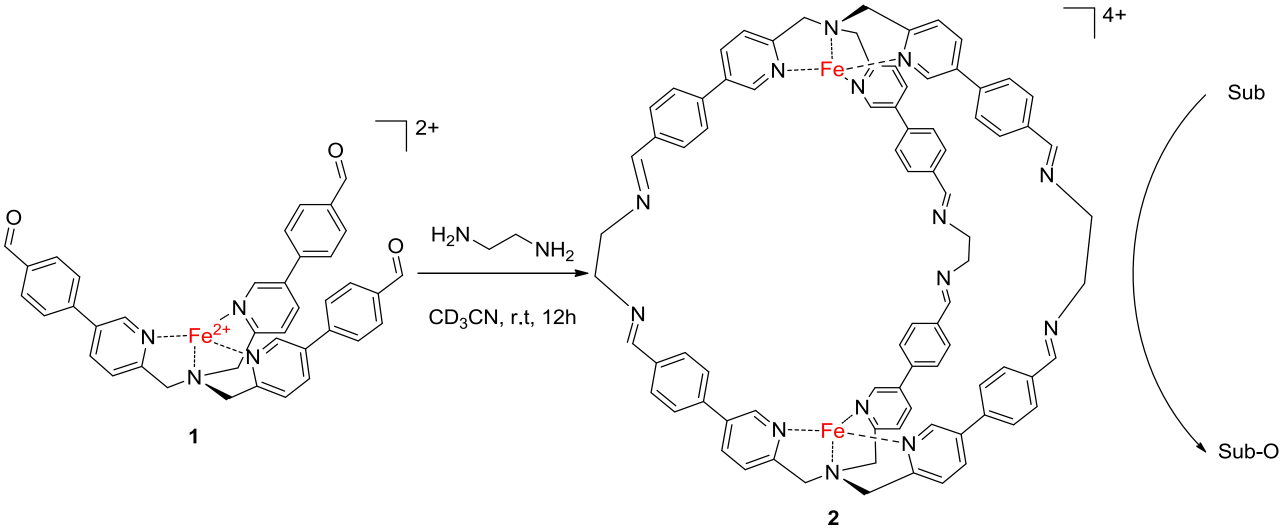

Figure 1. Synthesis of molecular cage 2 starting from complex 1. In all the structures, the counter anions are perchlorate.

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Producing amino acid benzyl esters under ecofriendly conditions and without racemization

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In the landscape of the constantly growing market of amino acids and derivatives, amino acid benzyl esters in unichiral form are high added value products of widespread use due to their multifaceted applications. Besides being starting materials for synthesis of unichiral active ingredients in pharmaceutical, cosmetic and food industry, they are important, often essential, intermediates in the chemical and chemoenzimatic synthesis of homo- and heteropolypeptides and, in particular, of dipeptides, a class of compounds having unique functions, unfindable in the constitutive amino acids.

Therefore, it is rather surprising that, within the abundant literature on any scale preparations of amino acid benzyl esters, little or no attention has been, to date, devoted to three key issues in their productions. These are:

(a) the use of green or at least acceptable solvents in place of banned benzene, carbon tetrachloride and chloroform to azeotropically remove water resulting from the acid-catalyzed reaction of the unprotected amino acid with benzyl alcohol;

(b) the enantiomeric excess of the formed amino acid benzyl esters, which should be punctually measured because of the well-known susceptibility of amino acids and even more of their esters to racemize also under mild reaction conditions;

(c) the nature of the enantiomeric systems formed by the amino acid benzyl esters salts, which cannot be ignored because crystallization is the large-scale process generally used to recover and to purify these products.

Starting with a selection of amino acids (1,2,3) and then including further substrates, we have undertaken a comprehensive investigation on how to efficiently prepare a wide number of enantiomerically pure amino acid benzyl esters under scalable and ecofriendly conditions, namely by replacing banned solvents with green solvents. Chiral HPC and DSC strictly supported our investigation in order to select and to develop the best procedures, to recognize the unsuitable ones, to cleverly accomplish the benzyl esters salts crystallization and, lastly, to rationalize the very different inclinations to racemize shown by the tested amino acids.

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Microkinetic modeling of benzyl alcohol oxidation on Pd and AuPd catalysts

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The liquid phase oxidation of alcohols over supported metal catalysts, using molecular oxygen as the oxidant, has been extensively studied in the last decade (1). In particular, benzyl alcohol oxidation to benzaldehyde is of practical use for pharmaceutical, perfume, dye, and agricultural industries (2). Many studies have been reported on the noble metal, in particular Pd, catalyzed benzyl alcohol oxidation in presence of molecular oxygen (1). However, a complete mechanism of Pd catalyzed benzyl alcohol oxidation has not yet been proposed. Detailed mechanistic and chemical kinetic information are necessary to understand the process and for an industrial application of these catalytic materials.In this study, we have performed experiments in which the temperature, gas-phase oxygen pressure, and initial concentration of the benzyl alcohol were varied to elucidate the mechanism (3). Furthermore microkinetic modeling (simulation and fitting) of the reaction were performed (4,5).

The liquid-phase oxidation of benzyl alcohol was performed over Pd and AuPd nanoparticles supported on activated carbon. Experiments were performed in a batch reactor with para-xylene as the solvent and continuous gas purging of the headspace. From trends in the concentration profiles and integrated production of each product, it was determined that there are two primary reaction paths: A) an alkoxy pathway leading to toluene, benzaldehyde, and benzyl ether, and B) a carbonyloxyl pathway ("neutral carboxylate") leading to benzoic acid, benzene, and benzyl benzoate (3).

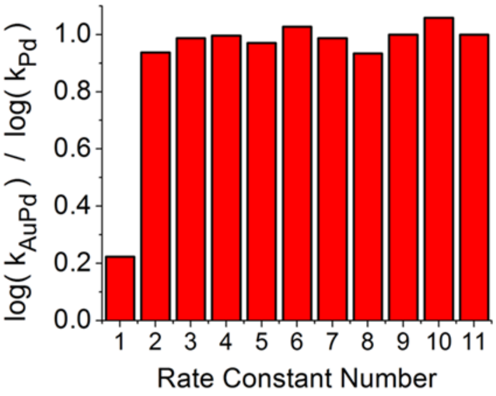

Figure 1. Ratios of the logs of the rate constants between AuPd/C and Pd/C, where the largest change on this scale was in k1 (5).

The microkinetic modeling in this work was able to reproduce the selectivities and trends observed for the production of both the main product (benzaldehyde) and the byproducts (benzene, toluene, benzoic acid, benzyl benzoate, and benzyl ether). The present study suggests that the most important activation energies are those of k2, k5, and k6 (Scheme 1), which we estimate as Ea_2=57.9 kJmol^{-1}, Ea_5=129 kJmol^{-1}, and Ea_6= 175 kJmol^{-1} corresponding to alcohol dissociation, alkyl hydrogenation, and reaction of alkyl species with alkoxy species. Under the same reaction conditions, AuPd/C has a lower activity compared to Pd/C and shows a different product distribution with less formation of products from the "carbonyloxyl" pathway (benzene, benzoic acid, benzoate). It was found that the selectivity changes can be explained by this change in k1, which corresponds to oxygen adsorption.

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Sustainable bromination of thymol: synthesis of new biologically active compounds

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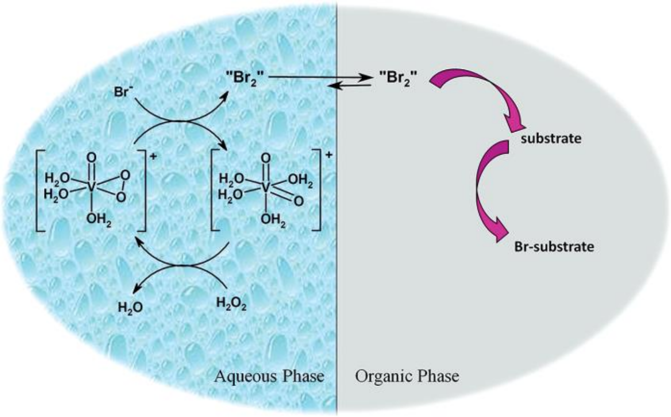
Vanadium peroxides, formed upon reaction between vanadium derivatives and hydrogen peroxide, are very effective oxidants of different substrates. Peroxido-vanadium complexes can oxide bromide ions to reactive species that can brominate organic substrates (1). This process mimics the activity of haloperoxidases enzymes (HalPO). Between them, vanadate dependent bromoperoxidase, a metal-enzyme containing vanadium (V) in the active site, catalyzes the oxidation of halide ions, such as bromide and iodide, by hydrogen peroxide (2). This activity is related to the formation of a peroxido vanadium species in the active site of the enzyme, which is a stronger oxidant than H_2O_2.

In this communication the oxidative bromination of thymol, a phenolic terpenoid compound main component of the *Thymus vulgaris* essential oilswill be presented. This "green" process occurs with no organic solvents, in very mild conditions and with sustainable reagents (3).



Importantly, biological tests showed that 4-bromothymol has a very high antimicrobial activity and low toxicity (4), so it can be used as a new active ingredient in several personal-care and home-care products.

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New perspectives in the action of halide ions as promoter for the direct synthesis of hydrogen peroxide over palladium catalysts.

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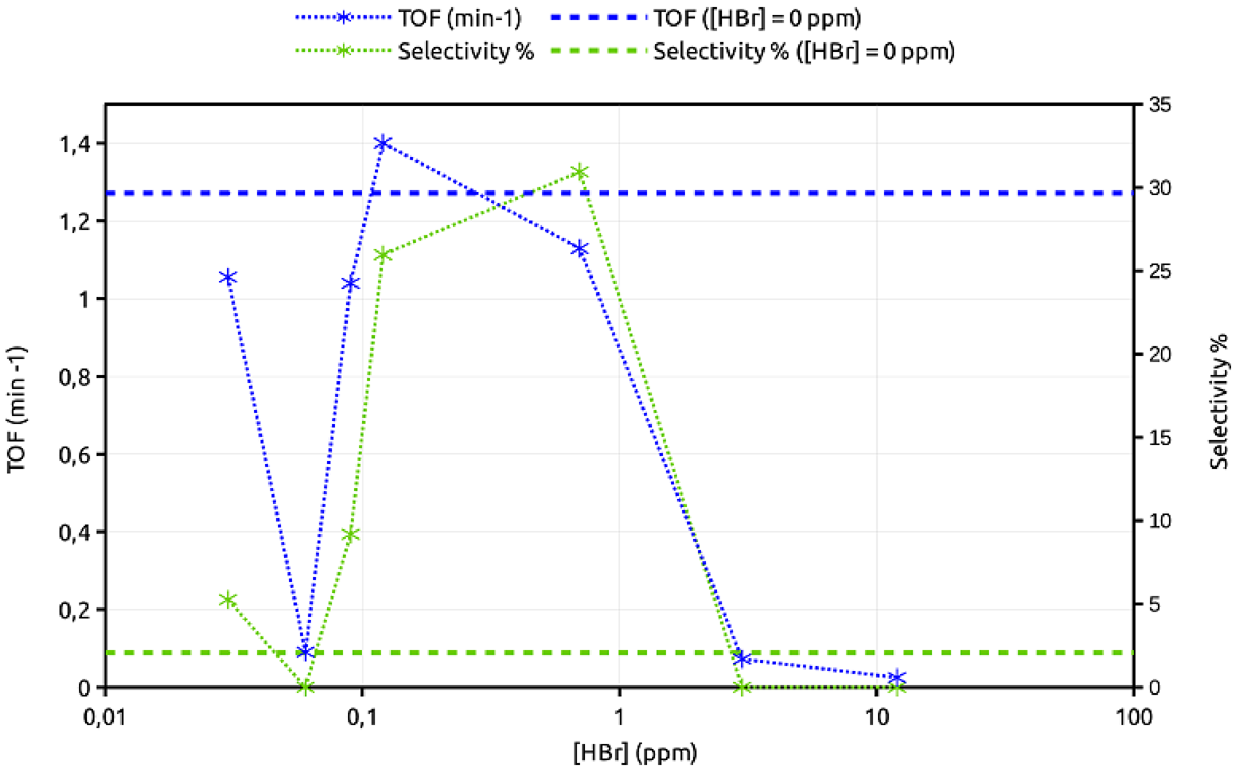
Cl^- and Br^- ions are well known promoters for the Pd catalysts of the direct synthesis of H_2O_2 (DS) (1). This is usually attributed to site blocking which prevents dissociative chemisorption of O_2 (2) or the formation of a surface layer of PdO (3). This form of selective poisoning should lead to the decrease of the catalytic activity. We have now found that under proper conditions Br^- ions increase the selectivity of a commercial Pd/C with no appreciable drop of its activity (Figure 1). This suggests that selective site blocking cannot be the cause of the observed effect of the promoter or the only one. As Br^- were found to be involved in Pd leaching (4) and metal phase reconstruction (5) these phenomena could provide a dynamic control of the surface coverage by atomic oxygen.



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Current efforts to make perovskite solar cells industrially viable

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Photovoltaic (PV) technology has evolved rapidly in the past few decades and now encompasses a large variety of materials and device structures. A perovskite solar cell (PSC) is a photovoltaic device which includes a perovskite-structured compound, most commonly a hybrid organic-inorganic leadhalide-based material, as the light-harvesting active layer. These devices are cheap to produce and simple to manufacture at a laboratory level.Solar cell efficiencies of devices using these materials have increased from 3.8% in 2009 to 22.1% in early 2016, making this the fastest-advancing solar technology to date.

Therefore, it is clear that – with the potential of achieving even higher efficiencies – PSCs have become commercially attractive, and a few issues should be fixed soon.

A key aspect to be taken into account in any PV technology is the operational durability of these systems in outdoor conditions. Clearly, loss of performance during operation represents a significant drawback and limitation for their commercialization. In this context, the large compositional flexibility of polymeric materials as well as their proven easy processability may be of great help in imparting improved durability to PV systems.We show that rapid light-induced free-radical polymerization at ambient temperature produces multifunctional fluorinated photopolymer coatings that confer luminescent and easy-cleaning features on the front-side of the devices, while concurrently forming a strongly hydrophobic barrier toward environmental moisture on the back contact side. The luminescent photopolymers re-emit ultraviolet light in the visible range, boosting perovskite solar cells efficiency to nearly 19% under standard illumination. Coated devices reproducibly retain their full functional performance during prolonged operation, even after a series of severe aging tests carried out for more than 6 months (1).

The industrialization of PSCs also requires the development of processes different with respect to those used in academic laboratories. For example, lab-scale PSC preparation is based on spin-coating technique, that is not transferable on a large scale. In this contribution we will also show the alternative strategies proposed by the scientific community to fabricatesolar cells components on large areas.

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Composition and temperature dependent Cu-speciation in Cu-SSZ-13 catalysts: an in situ XAS and FTIR study

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The small-pore Cu-SSZ-13 zeolite is attracting increasing attention as a versatile platform to design novel single-site catalysts for deNOx applications via NH_3-assisted Selective Catalytic Reduction (SCR) (1) and for the direct conversion of methane to methanol (MTM) (2). Cu is usually introduced into the zeolites *via* aqueous ion exchange, resulting in the formation of $[Cu(OH)]^+$ and/or Cu^{2+} counterions. Recent workspointed out that the relative abundance of $[Cu(OH)]^+$ and Cu^{2+} depends on the Cu/Al and Si/Al ratios, and proposed that only $[Cu(OH)]^+$ can be 'self-reduced' to Cu^+ sites during activation in inert atmosphere (3,4).To shed light on this aspect, which has important implications on the design and understanding of active catalysts for both SCR and MTM reactions, we prepared a large set of Cu-SSZ-13 samples with different Cu/Al and Si/Al ratios. These were characterized i*n situ* by X ray Absorption (XAS) and FTIR of adsorbed probe molecules (Figure 1), to follow Cu speciation and evolution during activation in inert conditions. Use of multivariate data-modelling allowed us to access an unprecedented level of understanding in a complex multi-component catalytic system, yielding novel insights into the birth of Cu-active sites in the cages of the SSZ-13 zeolite.

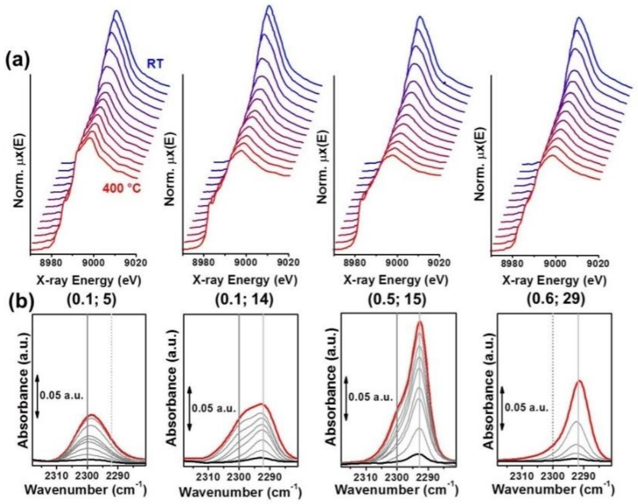

Figure 2. (a) *In situ* XANES collected on Cu-CHA at different catalyst composition (different samples are denoted with (Cu/Al; Si/Al) labels) during dehydration in He flow from 25 °C to 400 °C. (b) Low temperature normalized IR spectra of N_2 dosed at increasing equilibrium pressure on the same vacuum activated Cu-CHA catalysts.

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Conductivity and relaxation phenomena in ion conducting materials by roadband electric spectroscopy

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The charge transfer mechanisms of ion conducting polymer materials (ICPMs) is of crucial importance both for fundamental research and for a host of practical applications, including primary and secondary batteries, fuel cells, dye-sensitized solar cells, supercapacitors and sensors (1). A wide variety of ICPMs has been proposed, based on: (a) different families of polymer electrolytes; (b) ionic liquids (ILs); and (c) classical ion-conducting ceramics. In these materials, the long-range charge transfer events take place owing to complex processes, which involve several possible relaxation phenomena, such as: (a) ion hopping events between ion coordination sites; (b) relaxation modes of the host matrix; and (c) polarization effects occurring at the interfaces between the different domains characterizing the materials (2-5). Broadband electrical spectroscopy (BES) is a powerful tool for the accurate investigation of the roles played by electrical relaxation events in the charge transfer processes (6). Indeed, BES allows to carefully detect the fundamental relaxations governing the long-range charge transfer mechanisms and to correlate them to the morphology of ion-conducting materials. This presentation overviews results of the application of BES in the study of the charge transfer mechanisms of a variety of ICMs, including: (a) polymer electrolytes based on alkaline and alkaline-earth ions; (b) pristine and hybrid inorganic-organic proton-conducting and anion-conducting membranes. The general phenomena and the fundamental theory underlying the interpretation of the events characterizing the electric response of the materials is also described. Finally, the models adopted for the interpretation of conductivity mechanisms are described and a unified conductivity mechanism is proposed.

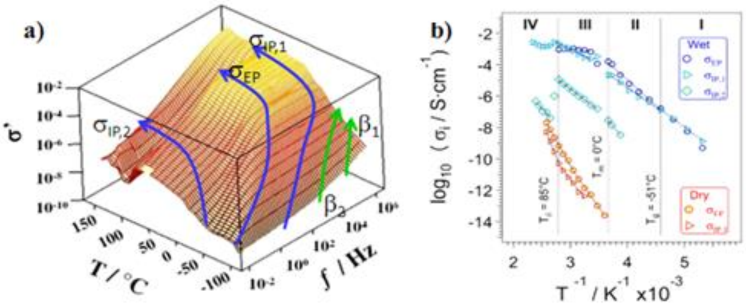

Figure 1. Three-dimensional σ' surface (a) and σ_i values vs 1/T curves of dry and wet samples in I, II, III and IV regions, delimited by thermal transitions T_g, T_m and T_δ, are fitted by Arrhenius-like behaviours (7)

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Biosourced polymers for aqueous solar cells: a possible breakthrough towards green photovoltaic commercialization

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In recent years, with the idea of creating efficient, safe, and low-cost DSSCs, the research moved the attention towards alternative solvent-based electrolytes. Above all, DSSCs with water-based electrolytes have been proposed as one of the possible solution providing reduced costs, non-flammability and environmental compatibility (1). Recently we demonstrated that stability issues can be properly addressed by choosing sensitizers with appropriate molecular structure (2). Moreover, the possibility of gelling the liquid solvent into a polymeric matrix can reduce the electrolyte leakage outside the device, increasing the long-term stability, without limiting the overall photovoltaic performances.

In this contribution, the investigation on a series of iodine and cobalt-based 100% aqueous electrolytes is presented. Thanks to our previous experience (3) and to a multivariate approach (Design of Experiment), the effects of the change in redox mediator concentrations and in photoanode preparation on DSSCs performances have been evaluated.

Finally, the gelation of the best aqueous electrolytes with low-cost, bio-derived polymers has been performed (4). Photovoltaic performances and stabilities will be discussed by comparing liquid and gel electrolytes. In lab-scale solar cells interesting photovoltaic efficiencies close to 4.5% were achieved.

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Development of N-doped TiO_2 catalyst for the photocatalytic treatment of wastewater in presence of visible light irradiation

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Traditional methods for wastewater treatment are usually based on physical and biological processes but unfortunately, some organic pollutants, classified as bio-recalcitrant, are not biodegradable. In this way heterogeneous photocatalysis may become an interesting water treatment technology to remove organic pollutants. The most common used photocatalyst is TiO_2. It is able to oxidize a wide range of toxic organic compounds into harmless compounds such as CO_2 and H_2O. Due to the value of TiO_2 band-gap energy, about 3.2 eV, it is effective only under irradiation of UV light. This is a technological limitation when aiming at implementation of large scale sustainable “green” technologies with renewable energy sources such as solar light. The main research objectives for the application of TiO_2 as a photocatalyst is the increase the photocatalytic performances of TiO_2 through the doping of its crystalline structure with non-metal ions (nitrogen) that reduce the band-gap making possible the absorption of the visible light. The results obtained from our research activity evidenced that the doping of TiO_2 with nitrogen (N-TiO_2) has led to an enhanced photocatalytic activity in presence of visible light irradiation. The optimized formulation of N-TiO_2 has shown very effective in the removal of organic dyes, such as methylene blue and methyl orange (1), antibiotics such as spyramicin (2) and in the inactivation of E.coli (3). However, one of the most important drawbacks of photocatalytic process is that photocatalysts are often used in slurry reactors. The limitation of slurry process is that the photocatalyst in powder form must be separated from the purified water after the treatment, and the cost of this separation stage may even invalidate economically this technique. With the aim to overcome this technical limitation, an innovative structured catalyst, in which N-TiO_2 is dispersed in transparent syndiotactic polystyrene monolithic aerogels (s-PS) has been developed (4). In particular, s-PS aerogels, due to their high specific surface area, present the possibility to disperse the catalysts in powder form, overcoming the aggregation phenomena that commonly happen when the catalyst is suspended in water solutions. These features allow not only to have a structured catalyst, but also to increase the photocatalytic activity of the N-TiO_2 under visible light in comparison with the powder sample dispersed in solution (4).

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Polymer supported palladium nanoparticles as catalyst for organic reactions in water

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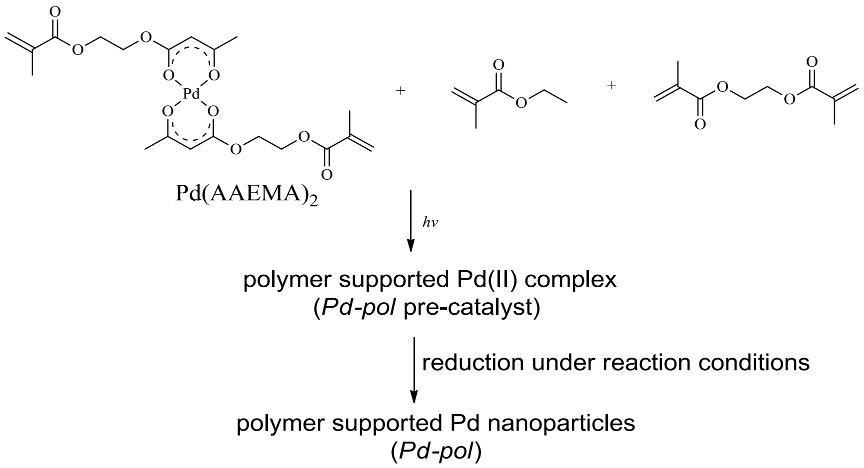
An insoluble palladium catalyst (*Pd-pol*) was obtained by copolymerization of the metal containing monomer $Pd(AAEMA)_2$ [$AAEMA^-$ = deprotonated form of 2-(acetoacetoxy)ethyl methacrylate] with ethyl methacrylate (co-monomer)and ethylene glycol dimethacrylate (cross-linker), followed by *in situ* reduction of Pd(II) to Pd(0), to give polymer stabilized metal nanoparticles (Scheme 1). The good swellability in water exhibited by *Pd-pol* rendered it an ideal potential catalyst for reactions carried out in a *green* solvent, such as water, since the migration of the reagents to the active sites would not be hampered by the solid support.



Scheme 1: synthesis of *Pd-pol*

With the aim to develop innovative catalytic processes that enable chemical transformations to be performed under mild and sustainable conditions with high efficiency, we decided to evaluate the catalytic activity of *Pd-pol* for several important organic reactions using water as solvent (1). *Pd-pol* resulted highly active and selective in catalyzing: the Suzuki-Miyaura coupling between aryl bromides or activated aryl chlorides and phenylboronic acid (2); the oxidation of benzyl alcohols to aldehydes (3); the reduction of quinolines (4,5) and nitroarenes (6) by H_2 or $NaBH_4$.

Pd-pol was recyclable for several consecutive runs (for example, at least twelve times in the nitroarene reduction). TEM analyses carried out on the catalyst showed that the active species were supported palladium nanoparticles having a mean size of 4 nm, which did not aggregate with the recycles.

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Bromobutyl rubber synthesis:
influence of the reaction temperature on product distribution

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Bromobutyl rubber is obtained by reacting butyl rubber with bromine. It has increased cure reactivity, higher compatibility with unsaturated polymers and enhanced adhesion compared to butyl rubber and higher thermal stability (1).

The bromobutyl rubbers are primarily used for the tires production, to produce tire inner liners and tire sidewalls, and are also used for tire treads. It is also suitable for pharmaceutical stoppers and rubber articles needing good resistance to chemicals, weathering, and ozone, such as tank linings, conveyor belts, and protective clothing. Vulcanizes have excellent resistance to weathering, ozone, and hot air; very good resistance to acidic and basic chemicals; very low permeability to gases and liquids; and good rheological properties (1).

Bromobutyl rubber is prepared by reacting bromine with a butyl rubber dissolved in n-hexane, at about 50°C (2). The reaction occurs involving the unsaturated isoprene units dispersed in the polymer.

The bromination reaction proceeds through a double bond shift and the formation of an exo-methylene allylic bromide.However, some allylic rearrangements and double bonds migration can follow. As a matter of fact,four different structures have been individuated in bromobutyl rubbers (BIIR) (3).

For example, HBr formed during bromination can react in a successive step by addition to the double bonds giving place to organic bromine but this structure is not active for the industrial purpose. It is possible to obtain also endo brominated structure but these structures are not important for the industrial purpose because they do not contribute to form the crosslinked networks.

In this work the screening of the operative conditions was performed in order to obtain the highest percentage of exo-methylene allylic bromide structure.

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Stereorigid OSSO-type group 4 metal complexes in the polymerization of olefins and polar monomers

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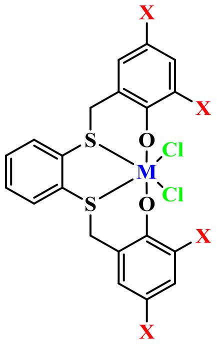
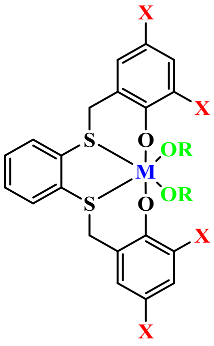
Among the post-metallocene catalysts active in the polymerization of unsaturated monomers, an interesting class of compounds is represented by group 4 complexes bearing thioetherphenolatechelating ligands, the (OSSO)-typeligands. These ligands are generally formed by two phenoxide groups linked to two donor sulfur atoms in the ortho or benzyl positions using nucleophilic substitution between the suitable phenols and dithiol. The resulting linear tetradentate OSSO ligands wrap around the group 4 metal center producing octahedral coordination geometries with special electronic and steric properties. The corresponding group IV metal complexes are known for the high performance in the α-olefin polymerization, yieldingstereoregular and high molecular weight polymers(1).Moreover, the alkoxide derivative of the [OSSO]-type group IV complexes are powerful initiators in the ring opening polymerization (ROP) of cyclic esters to obtained biodegradable and biocompatible materials, extremely interesting in biomedical fields thanks to the low toxicity of the catalytic ashes(2).In an effort tofurther examine the structure−activity relationships affectingthe reactivity and the stereoselectivity of this class of compounds, wehave prepared and structurally characterized anew series of group 4 metal complexessupported by*o*-phenylene-bridged bis(phenolato) ligands with general formula {OSSO$_X$}M(Cl)$_2$(X = tBu, M = Ti (**1**); X = cumyl, M = Ti, (**2**); X = tBu, M = Zr (**3**)) and {OSSO$_X$}M(OR)$_2$(X = tBu, M = Ti, R = iPr (**4**); X = R = tBu, M =Zr (**5**); X = cumyl, M = Zr, R = tBu (**6**); X= cumyl, M = Hf, R = tBu (**7**)).Compound**1**-**3**,combined with MAO, promote the reaction of ethylene and propeneyielding the corresponding polymers containing unsaturated end groups produced via aβ-hydrogen elimination reaction. Differently alkoxide derivatives **4**-**7** are active catalyst in the ring opening polymerization of *rac*-lactide.In the presence of exogenous alcohol, narrow molecular weight distributions and molecular weights of the resulting PLAs proportional to the equivalents of added isopropanol suggest that adequate conditions for effective "immortal" polymerizations are achieved (3).



(1) X = ^{t}Bu, M = Ti
(2) X = Cum, M = Ti
(3) X = ^{t}Bu, M = Zr



(4) X = ^{t}Bu, M = Ti, R = ^{i}Pr
(5) X = ^{t}Bu, M = Zr, R = ^{t}Bu
(6) X = Cum, M = Zr, R = ^{t}Bu
(7) X = ^{t}Bu, M = Hf, R = ^{t}Bu

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Smart formulations for cosmetic industrial applications

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Globally the cosmetic industry is a leading sector in the economy and the European cosmetics and personal care market is the largest in the world.

The largest national markets for cosmetics and personal care products within Europe are Germany (€13 billion), United Kingdom (€12.5 billion), France (€11.3 billion), and Italy (€9.7 billion)[1].The cosmetics industry is a science-driven and highly innovative sector which makes large investments in research and development in order to obtain increasingly performing and sustainable products.

The goal of this project was the formulation of innovative products for use in cosmetics through the development of a sustainable protocol aimed to the synthesis of high performant products but at the same time sustainable, in the maximum respect for the environment and for end users.

The attention was focused, in particular, on the development of gel for the body care (products to prevent skin aging, or designed to correct skin defects, such as blemishes and scars) choosing natural components whose efficiency will be maximized with the use of advanced technologies. For this purpose was used the Drug Delivery Systems technology (DDS, controlled release of an active molecule) already known and widely used in the pharmaceutical field but not effectively exploited in cosmetics. These systems help to optimize dosing, bioavailability and efficacy of active pharmaceutical ingredients already known and administered by traditional route[2,3]. This approach, when used in cosmetics allows to maximize the effectiveness of the active ingredients, overcoming the intrinsic limitations of the same (for example poor bioavailability) making the final products efficient and consequently more attractive to the consumer.

The gel was formulated by a sustainable "one-pot" sol-gel approach. A hybrid organic-inorganic material made of silica, chitosan, a polysaccharide derived from agri-food waste, and fatty acid such as azelaic and glycolic acids was used as matrix. Caffeine (with antioxidant properties) was selected as active molecules. The products features were analyzed in depth by FT-IR, Raman spectroscopy,by rheological tests and by microscopy analyses. The evaluation of the drug delivery properties of the gels was performed in vitro and ex vivo by using a vertical Franz diffusion cell. We have studied synthetic membranes (PVDF or Strat-M membranes formed from polyolefins in stratified polyether sulfone) and biologically derived membranes (ex vivo, for example pork membranes) in order to draw up a reproducible and reliable protocol for the release test capable of reproducing at best the real conditions of use of the formulated gel.

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Inorganically and organically modified mineral clays: a sustainable approach in the control of the olive tree fly pest, *Bactrocera oleae*

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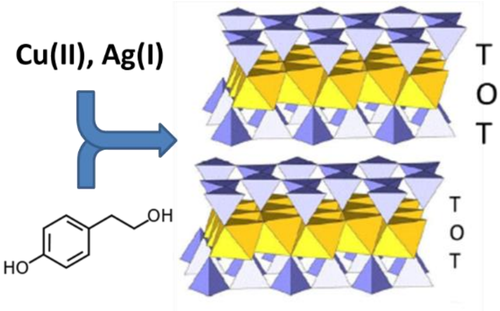
The most relevant phytophagous insect associated with olive tree plantations crops throughout the Mediterranean area is *Bactrocera oleae*, the olive tree fly. Innovative and environmentally-friendly methods for the mitigation of such pest have been attracting an ever-increasing attention, especially after 2014, when the whole Italian olive oil production suffered from dramatic losses. Novel prevention strategies should meet four main criteria: toxicologic safety, environmental selectivity and compatibility, pest-control efficiency and economic sustainability. In this aim, two series of solids showing a detrimental effect on the life cycle of *Bactrocera oleae* have been designed and prepared, *i.e.* montmorillonite-based clays from mineral origin containing: i) Group 11 transition metal cationic species, such as Cu(II) and Ag(I) or ii) polyphenolic organic compounds derived from olive mill waste waters. The bioactive solid materials have been prepared either by ionic exchange from aqueous solutions of sulfate or nitrate metal precursors at various concentrations or by impregnation of the polyphenol-containing effluents onto the clay support, respectively (Scheme 1). In the case of metal-based solids, by optimising the ion-exchange procedure, a fully adequate bioactive metal content was reached for practical purposes, although reducing by more than 80% the use of precursor salts with respect to the current state of the art (1). These materials contain approx. 5 wt.% of active metal and possess acid sites, which not only, when dispersed on the fruit surface, inhibit the egg-laying activity of flies into the olives, but also catalytically-active metal cation sites with enhanced biocide effect against parasites of several crops (2). In polyphenol-modified solids, on the other hand, amounts of organics in the range of 0.9-2.6 wt.% can be deposited. Thanks to the immobilisation within the interlayer spaces of the clay, lower concentrations of bioactive species may be applied onto the olive tree, thus reducing the potential undesired dispersal of the active molecules into the environment. In order to evaluate the performance of the most promising solids in open-field tests, two sets of experimental campaigns have been carried out on olive tree orchards in Southern Tuscany, in summer 2015 and 2016.

Preliminary promising results have been obtained with Cu(II) species and with aqueous-phase olive mill wastewaters deposited onto bentonite-like montmorillonite clays, in terms of reduction of both fly infestation and damages on the olive fruit. These materials have indeed proved to be easily prepared, cost effective, environmentally friendly, stable to rainwater leaching, toxicologically safe and led to a remarkable diminution in the use of bioactive species for on-field applications.



Scheme 1: inorganic or organically modified clays

CNR-ISTM and CREA-ABPDC gratefully acknowledge Podere Forte and Laviosa Chimica Mineraria.

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Modeling approach for applied research: the case-study of PLA synthesis by ring-opening polymerization of lactide

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The use of predictive models is a key tool for the comprehension and the development of chemical processes, especially for very complex systems like those in the field of materials science. Polymer Reaction Engineering (PRE) is a multidisciplinary approach that can be conveniently employed for the study of (novel) polymerization processes: in doing so, rationalization of the experimental trials, deeper understanding of the chemistry involved and certain predictive skill towards the process can be achieved. Such a result has useful implications also in terms of ability to control the physico-chemical properties of the product and process safety.

Many chemical companies use predictive models and Versalis, among these, adopted such tools in support of consolidated production processes as well as for the most recent R&D activities. Here the work done at the Versalis Research Centre of Mantova on the synthesis of PLA by Ring-Opening Polymerization (ROP) of lactide is presented. The production of PLA can be considered one of the most important processes for the synthesis of bio-based polymers to reach the commercial scale. Based on the kinetic scheme by Yu et al.[1], the process has been modeled for different reactor configurations by means of implementation and calculation with MathWorks® MATLAB® software, applying the method of moments. The results of the simulations have been compared with those obtained from a set of experimental trials, with the aim of studying the dependence of the polymeric mixtures properties on the reaction parameters (temperature, feed composition, catalytic system composition, reaction time, impurities) and validatingthe predictivity of the model in terms of conversion to polymer and molecular weight distributions.

In addition to the polymerization kinetics, some experiments were carried out in order to study transport phenomena of lactide/PLA mixtures, such as heat transfer and rheological properties[2], and their dependence on polymer content and molecular weight distribution.

In conclusion, provided that the models here discussed can be further developed in order to cover additional features like scale factors, fluid dynamics and non-ideality of real systems, the use of such an integrated approach has led to a deeper understanding of the process, giving key information and guidelines for a potential design on an industrial scale.

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Chemical research in the field of galvanic industries and fashion accessory

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The fashion market is by its very nature and requires continuous and innovative changes, but the galvanic industry has slower adaptation and response times.Galvanics are based on traditional knowledge that is sedimented over time, which is unlikely to be open to innovation and innovation.

As for the state of the art of technology, innovation lies in the goal of creating a modular and flexible galvanic that allows the study and creation of new production processes by varying the succession of layers of metals or alloys that normally settle in an attempt to increase the qualitative properties of the final accessory.In addition, in Galvanic Industries the problems associated with the analytical control of galvanic baths and the evaluation of the thicknesses of each single layer deposited that makes up the fashion accessory are the most felt demands of the companies.

In this presentation we show the results of an interesting collaboration born and consolidated in recent years between the Applied Electrochemistry Laboratory of the Department of Chemistry, University of Florence, and many companies related to the "fashion" world. The ability to know the demands of those who produce (galvanic industries) and who packs (YSL, Gucci, Prada etc) has made it possible to adapt their research to the industrial specificities of the territory by trying to produce products with low environmental impact and low energy demand.

Manipulating the arrangement of arrays of nanoparticles on solid supports by using self-assembled block copolymers templates

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Nanoparticles (NPs) exhibit a number of unique optical, electronic, and catalytic characteristics compared to those of bulk materials because of the small-size effect and extremelylarge specific surface area (1). Since the majority of unique properties of NPs is highly microstructure-dependent, forming arrays of NPs on solid supports with precisecontrol of the dimensions, spacingand morphology is animportant issuefor most scientific and technical applications.

We report the fabrication of two-dimensional arrays of different NPs (Pd, PdO, ZnO) on solid supports (glass, silicon, indium thin oxide (ITO)-coated slides) by exploiting the self-assembly of diblock copolymers (BCPs) to control the positioning of NPs, their characteristic sizes and lateral spacing.

BCPs consist of covalently linked distinct macromolecules that tend to segregate into different nanodomains due to their mutual repulsion, resulting in the spontaneous formation of periodic nanostructures by self-assembly (2).We have used nanodomains of self-assembled BCPs as hosts for sequestering NPs, producing nanocomposites with different morphologies (cylindrical andlamellar). The sizes and shapes of the arrays of NPs have been conveniently tuned by changing the molecular mass and compositions of the BCPs.

In particular, in the first part we present a systematic investigation of nanocomposite thin films based on polystyrene-*block*-poly(ethylene oxide) copolymers (PS-PEO), characterized by selective inclusion of palladium (Pd) species (Pd-acetate and Pd NPs) in the PEO domains (3). Cylindrical phase-separatedPS-PEO copolymers of different total molecular mass have been used to tune the characteristic sizes (diameter and lateral spacing) of the included Pd species. Arrays of palladium oxide (PdO) NPs, characterized by different particles diameters and gap distances, mirroring the pattern and the characteristic nanodimensions of the parent BCPs used as template, have been also obtained by treatment of the nanocomposites at elevated temperatures in air.

In the second part, the morphology and the electrical properties of hybrid nanocomposites characterized by the dispersion of ZnO NPs, a *n*-type semiconductor, within an organic nanostructured matrix of polystyrene-*b*-poly(methyl methacrylate) (PS-PMMA) copolymer are presented. A selective inclusion of NPs into the lamellar PS nanodomains of the BCP matrix has been achieved by synthetizing*ad hoc*organic-capped ZnO NPs and by thermal annealing the nanocomposites ZnO NPs/PS-PMMA. The study of the electrical proprieties of the nanocomposite confirms the key role of the nanostructured BCP for the obtainment of good conductive properties and make the BCP-based approach a promising strategy for the fabrication of materials for photovoltaic applications.

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New sustainable technology to recover returned concrete

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Concrete is the second most used material in the world, after water. More than 10,000 million cubic meters are globally produced every year, with the consumption of more than 19,000 million Tonnes of natural aggregates (coarse aggregates and sand) (1, 2). For different reasons, about 300 million cubic meters of concrete (3 per cent of the global production) are not placed at the jobsite and are returned to the ready-mixed production plant where, in most cases, are disposed to landfill as waste material. Recently, a new technology to treat returned concrete has been developed: one cubic meter of returned concrete is treated with non-dangerous additives and transformed, in few minutes, into 2.3 Tonnes of aggregates, without any waste production (3). The new aggregates can be used to produce new concrete materials, with excellent mechanical performance and environmental compatibility. The new method has many advantages because it allows to save virgin aggregates and to reduce the natural resource depletion. Furthermore, returned concrete is 100% recovered and no waste is produced, completely eliminating landfill disposal. For these reasons, the new technology has a positive effect on the environmental impact of returned concrete, with hundred-fold reductions of the main parameters characterizing the environment footprinting. Furthermore, the new technology allows a reduction of the costs for both waste disposal and aggregates supplying, representing an excellent example circular economy.

Figure 1. Example of newly formed aggregate from returned concrete

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Acryloxyalkyltriethylammonium bromides (AATEABs): useful starting materials for the preparation of polymeric membrane coatings with anti-biofouling properties

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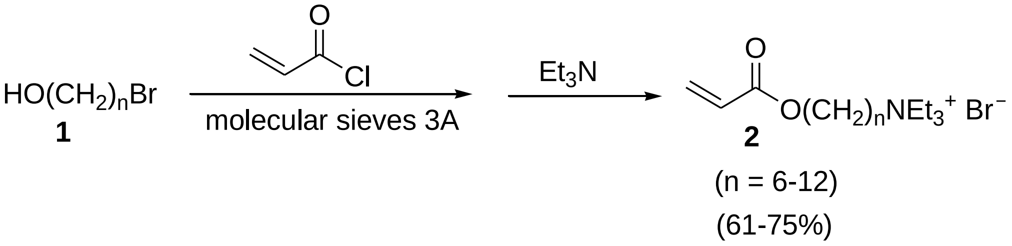
Polymerizable quaternary ammonium salts (PQASs) are important starting materials for the development of innovative polymers with antimicrobial activity. We report herean efficient synthetic approach for the preparation of a particularly important class of PQASs, that are, acryloxyalkyltriethylammonium bromides (AATEABs)**2**, which may find application for the development of antimicrobial coatings for commercial membranes with antifouling and anti-biofouling properties. The synthetic approach for the production of AATEABs**2** bearing an alkyl chain of 6, 9, 11, and 12 carbon atoms (Scheme 1) is based on a simple two-step procedure from commercially available substrates**1**, entirely carried out under air and without any need for chromatographic purification.



Scheme 1

All the newly synthesized AATEABs were tested for their antimicrobial activity, and the results evidenced that AATEABs bearing an alkyl chain of 11 and 12 carbon atoms (AUTEAB and ADTEAB, respectively) possessed significant activity against Gram +ve bacteria and yeast strains. Accordingly, these derivatives are excellent candidates for the industrial development of novel antimicrobial polymers and materials. In particular, we have efficiently employed AUTEAB and ADTEABfor the development of novel polymeric coatings for the surface functionalization of commercial membranes. The novel nanostructured membranes thus obtained are characterized by significant anti-fouling and anti-biofouling properties, and can be efficiently employed in industrial wastewater treatment.

Acknowledgment

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Novel ion-exchange catalysts for the esterification of vegetable oil solutions of fatty acids with methanol

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The acid catalyzed esterification (ACE) of fatty acids (FA) is a key process to upgrade oils with FA contents higher than 5% and make them available as raw materials for the production of biodiesel by the base catalyzed trans-esterification of natural triglycerides.

We show herein that a novel mesoporous form of sulfonated poly-divinylbenzene (pDVB_s) prepared by polymerization of DVB under high dilution condition (1) outperforms the conventional gel-type and macroreticular ion-exchange catalysts (IECs), and that its catalytic sites are almost as effective as those of p-toluenesulfonic acid in the model esterification of stearic acid (SA) with a large excess of methanol (2). Conventional gel-type IECs rely on full swelling, ensured by the relatively high amount of alcohol, to make their sulfonic groups accessible and achieve the highest activity (3). The activity of macroreticular IECs, which possess a permanent pore system, is less dependent on swelling, but not as high as that of gel-type catalyst under optimal conditions. In this respect, the mesoporous pDVB employed in this work is featured by the unusual combination of relatively large pore diameters, high pore volumes and permanent specific surface areas much higher than in macroreticular resins (4). As the consequence the surface of permanent pores can accomodate a large proportion of sulfuric groups, which are almost as efficient as those of a homogeneous catalyst and ensure a high catalytic activity.

The polar nature of the sulfuric groups make the micro-environment around he catalytic sites of IECs hydrophilic hence relatively little compatible with FA. The hydrophobic character of mesoporous pDVB was therefore enhanced by the introduction of fluorinated ponytails (C4F7O). This is expected to improve the catalytic performance of the IEC due to the assisted absorption of SA and the expulsion of water, a by-product of the reaction (5). For comparison we introduced the same kind of ponytails in a gel-type IEC, too. A measurable, albeit small, the improvement of the catalytic activity was observed only for the modified gel-type catalyst. For modified pDVB_s the effect of the functionalization was observed when the esterification was carried out in the presence of water (10% w, with respect methanol). Under these conditions the final conversions of SA were much lowered. However, the functionalized IEC was less affected by the addition of water and in particular the reaction rate was significantly higher. This suggests that the introduction of ponytails in pDVB_s

does not fully protect the catalysts from the action of water, but that limits its effect probably by facilitating the expulsion of its extra amount produced by the reaction.

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The hydrothermal conversion of cellulose-rich wastes deriving from the papermaking process to levulinic acid as smart opportunity for their re-use and valorization

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In recent years, the interest of industry has deeply increased towards the exploitation of any kind of waste biomass for the synthesis of new valuable biofuels and bioproducts, in place of the dwindling traditional fossil ones. This approach is strongly encouraged by the Waste Management Policy, which favors thewaste re-use rather than its immediate landfill disposal, by this way achieving significant environmental, social and economic benefits. In this context, the acid-catalysed hydrothermal route for the synthesis of levulinic acid (LA) represents a smart route for the sustainable exploitation of waste biomasses, fully meeting all of the above-mentioned advantages (1). This platformchemical has been classified by the United States Department of Energy as one of the top-12 promising building blocks, being a valuable intermediate for the synthesis of new fuel additives, fragrances, solvents, pharmaceuticals, and plasticizers. The hydrothermal process adopts water as a reaction solvent and very dilute mineral acid (generally H_2SO_4 or HCl) as a homogeneous catalyst for the hydrolysis/dehydration of the cellulose fraction to give LA. Certainly, the fundamental requirement for the choice of the starting feedstock is its high cellulose content, and wastes deriving from the papermaking process fully meet this specification. Most of the national papermaking production of cardboard and tissue paper takes place in the Lucchese territory (~70%). In particular, in the case of the cardboard production, the recycled paper is used as starting feedstock and it needs some preliminary mechanical/chemical treatments for its re-use within the papermaking process. Some of these ones produce considerable rejected waste fractions, such as ‘‘screen rejects”, which include both cellulose fibers and non-fibrous organic contaminants, or ‘‘stickies”, these last representing a shortcoming both for the papermaking process and for the quality of the final product. This waste, which still contains a cellulose fraction, has been hydrolyzed to LA by adopting a one-pot MW treatment, obtaining a LA yield amounting to about 7 wt% (on dry basis), under the best reaction conditions (2). The abundant presence of “sticky” and other impurities represents a strong limit for the optimal exploitation of the cellulose fraction, limiting the acid diffusion towards the cellulose and therefore the use of “cleaner” paper wastes represents a key point for the optimal production of LA, in high yield. Clean virgin cellulose is currently used as starting feedstock for the production of tissue paper, and a significant waste stream (~400-500 tons per year in the Lucchese area)is currently recovered as cellulose powder in the converting section, where the paper coil is unrolled and the sheet is subjected to mechanical operations (stripping, embossing, cutting, etc.) to give the final commercial product (toilet paper and handkerchiefs). The recovered powder is gathered by aspiration and sent to the landfill, because it is too fine to be used again within the same papermaking process. However, it is mainly composed of pure cellulose and, because it has been already mechanically “refined”, it should be more easily hydrolysable to LA, and therefore it represents an ideal feedstock for LA production. The optimization of the hydrolysis reaction of this waste has confirmed the above statements, allowing the LA recovery with very high yields, up to ~ 35 wt% (on dry basis), under the best reaction conditions.

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Levulinic acid esterification kinetics with ethanol in the presence of Amberlyst-15

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The esterification of carboxylic acid with alcohols is a very actual topic of the modern bio-refinery. It is normally performed to produce value-added products, such as solvents and plasticizers (1). This reaction is catalyzed by acid catalysts and occurs with the production of an ester (the main product) and water as by-product. Different catalysts have been already tested in the literature (1,2). Recent findings demonstrate that acid resins, such as Amberlyst-15, show good activity compared to zeolites, for example. This behavior is due to the nature of the catalyst itself. In fact, acid catalysts with high acidity, porosity and surface area are much more active in the reaction itself.

Ethyl levulinate shows promising applications in the field of inks and paints. It is synthetized from levulinic acid and ethanol in the presence of an acid catalyst, normally homogeneous (H_2SO_4).

In the present work, an effort was made to investigate the kinetics of the levulinic acid esterification with ethanol in the presence of Amberlyst-15. Experiments were performed by varying different operative conditions, i.e. stirring rate, temperature, catalyst loading and reactants ratio. As an example, see the effect of temperature in Figure 1.

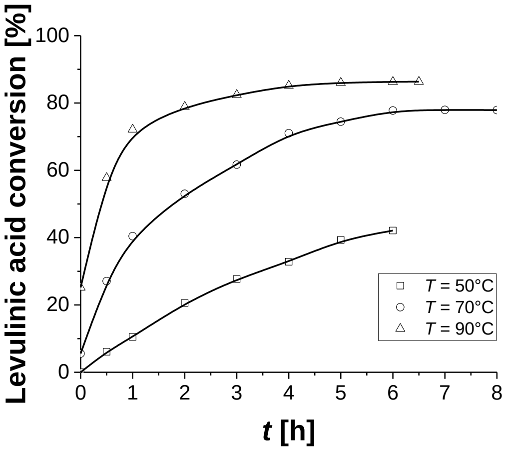

Figure 1. Temperature effect on the levulinic acid conversion. Experiments performed at 600rpm, levulinic acid/ethanol 5:1 mol/mol, 5bar N_2, 2.5wt.% Amberlyst-15.

The collected experimental data were interpreted with reliable models taking into account both the chemical and mass transfer phenomena involved in the reaction network, such as external and internal mass-transfer limitations. The mixed PDE/DAE systems given by the mass balance equations, Eq. 2 (3) were solved with advanced numerical techniques.

$$\frac{\partial C_{i,s}}{\partial t} = \frac{D_{eff,i}}{\varepsilon \cdot x^s} \cdot \frac{\partial}{\partial x}\left(x^s \cdot \frac{\partial C_{i,s}}{\partial x} \right) + \sum_{k=1}^{N} \frac{\rho}{\varepsilon} \cdot r_k \qquad (2)$$

The results can be considered as good starting point for continuous reactors optimization.

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Dehydrogenative coupling promoted by copper catalysts: a way to upgrade bio-alcohols

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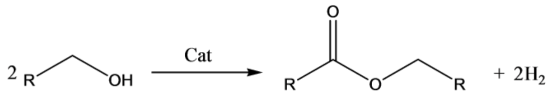
Alcohols represent very important molecules for the biomass transformation processes and biorefinery evolution. Taking into account their increasing availability, bio-alcohols are not only products but also represent new feedstock for the chemical industry, e.g. for the production of esters. In this regard, the DHC reaction is an attractive green strategy to directly transform alcohols into symmetrical esters. The process has a very high atom economy and with respect to the traditional esterification methods leads toboth waste reduction and process intensification.This reaction protocol has been mainly studied over expensive noble-metal (e.g. Ru, Os, Re, Pd and Ir) homogeneous complexes(1). Conversely, solid catalysts have been less investigated(2) and Cu heterogeneous systems have already been proposed for the gas-phase conversion of ethanol into ethyl acetate(3) but suffer from low yields (60-65%). Following the successful use of Cu catalysts prepared by Chemisorption-Hydrolysis method in alcohol dehydrogenation reactions(4), we tested a series of systems prepared with the same technique in the liquid phase DHC reaction, in order to develop a simple and robust catalyst able also to expand the substrate scope(5).



Scheme 1. General scheme of DHC reaction

A series of different Cu catalysts have been tested in the liquid phase DHC reaction of 1-butanol into a stainless steel autoclave (Table 1).CuO/ZrO_2 C shows the best performance in terms of activity, allowing one to reach 40% conversion after 3 hours with respect to 16% of CuO/ZrO_2 B and less than 10% of the others.The reaction produces H_2 as co-product thus generating an increase in pressure and freezing the equilibrium position as the substrate is converted (Scheme 1). Therefore by venting the reactor and removing the H_2 produced at regular lapses it is possible to reach 98% yield in 24 h. The activity of this catalyst is remarkable compared with homogeneous and heterogeneous literature on the same topic, considering also that the reaction is highly selective (≥99), carried out on gram-scale (12.6 g of 1-butanol, 170 mmol) and it is solvent- and additive-free. The deep characterization revealed that the high activity of CuO/ZrO_2 C is has to be ascribed to the intimate contact between copper phase and zirconia that form acid-base pairsbased on CuO Lewis acid sites and ZrO_2 strong basic sites. CuO will promote dehydrogenation of butanol and activate the aldehyde towards the attack of an alcohol molecule activated by the basic sites of ZrO_2.CuO/ZrO_2 C revealed to be also extremely robust and versatile. It is reusable up to four times without observing any Cu leaching and significant loss in activity. Moreover high conversions (93%) and selectivities (98-99%) in 24 h were obtained for C3-C8alcohols. Remarkable is also the yield of ethyl acetate (87%) obtained from ethanol, in particular if compared with the others catalytic systems reported in the literature.

Catalyst (400 mg)	**SSA (m^2/g)**	**C (%)**	**S (%)**	**Y (%)**
CuO/SiO_2	318	4	90	3
CuO/Al_2O_3	126	10	>99	10
CuO/ZrO_2 A	3	9	>99	9
CuO/ZrO_2 B	88	16	>99	16
CuO/ZrO_2 C	314	40	>99	40
CuO/ZrO_2 C*	314	98	>99	98

250 °C; N_2=1 bar; 1-butanol=170 mmol; t=3h; *t=24h

Table 1. DHC of 1-butanol to butyl butyrate

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Succinic acid production from arundo donax hydrolysate for bio-based poly(butylene succinate) synthesis

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The US Department of Energy (DOE) included succinic acid (SA) in the "Top 10" list of biomass-derived compounds, considering its high potential as building block in the field of the industrial chemistry (1). In fact, this dicarboxylic acid with four carbon atoms (1,4-butanedioic acid) represents an important precursor molecule for many chemical derivatives, used for food and pharmaceutical products, solvents, biodegradable polymers, surfactants and detergents (2). Nowadays SA is mainly produced by crude oil, starting from n-butane/butadiene via maleic anhydride. Due to its independence of petroleum, environmental benefit and reduction in CO_2 emissions, biotechnological production of SA from renewable feedstocks is gaining increasing attention in the last years. SA is an intermediate of the tricarboxylic acid cycle and one of the end products of the anaerobic metabolism. Extensive efforts have been made to optimize the SA biotechnological production, and they have principally concerned the development of biocatalysts to improve the productivity and the optimization of the downstream process to separate SA from the fermentation broths to minimize the process costs (3). The downstream purification costs affect about 60% of the total production costs. Furthermore, very high purity is often required in these cases. To this end, several methods of purification and separation, including electrodialysis, precipitation and extraction, have been studied and developed. Many companies such as Myriant, Everdia, BioAmber and Succinity established bio-based production platforms for the conversion of purified sugars to SA.

This work aims to provide an integrated process based on the biotechnological production of SA using a lignocellulose biomass (Arundo Donax) as raw material, for the synthesis of a biodegradable plastic, i.e. poly(butylene succinate) (PBS). The novelty lies in the type of raw material used, a harvested waste, to produce added value chemicals such as PBS. SA separation and purification procedure was developed and integrated to the fermentation process by a vacuum distillation at pH=4 to remove the volatile byproducts after a treatment with activated charcoal, followed by a final crystallization from mother solution. PBS was synthesized using SA, recovered and purified directly from its fermentation broth through the downstream protocol developed and optimized in this study. The synthesized polymers showed physical and mechanical properties comparable with a commercial PBS derived by crude oil, so highlighting the suitability of the proposed process.

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The history of the journal "La Chimica e l'Industria"

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The magazine "La Chimica e l'Industria", current official journal of the Italian Chemical Society (SCI), was created in 1919 with the name "Giornale di Chimica Industriale" with the aim of helping to let born also in Italy a significant chemical industry, as it had been in Germany over the decades before the First World War, trying to intensify the relationship between academia and industry. The journal wsas founded by the Society of Industrial Chemistry of Milano.

From March 1920 to December 1934, the magazine changed its name to "Giornale di Chimica Industriale e Applicata" and from 1935 until now the magazine changed its name in "La Chimica e l'Industria" The largest expansion of the magazine was in the years around 1963; this because in addition to the fact that Natta received that year the Nobel Prize for Chemistry, it was witnessed at that time to a large development of the Italian chemical industry. Since its birth until 1970, the magazine was the journal on which largely the industrial chemists of academia and of industry published essentially original articles and also reported informations on the Italian chemical industry. Natta from 1923 to 1954 on 207 published papers, wrote in La Chimica e l'Industria 42 original papers. It can certainly be said that if you want to have information about the Italian chemical industry and the innovations in the industrial chemistry of those times, you can read the magazine. For example, in Trincheri's book on the history of Italian chemical industry, there are many quotes of articles published in the magazine. After 1971, the magazine was opened not only to original scientific articles of industrial chemistry, but also to scientific reviews on other fields of chemistry. In 1994, with prof Ivano Bertini as director (president SCI), it was officially declared that the magazine did not more publish original scientific articles, but it had to be a review of all chemistry. With Trifirò, director from 1996 till now, the strategies of the previous directors have been confirmed, but the importance of having articles from the industrial world to foster innovation has also been emphasized. In 2000, a major revolution took place with the publication of the magazine on the site web. In 2014, there was a further change with the unification with the Order of Chemists and the publication of the two magazines together and then in 2015 with the publication of a single magazine. In 2017 the magazine returned to the Chemical Society and it is published only on the web. From 1967 to 1980 Trifirò on the journal published only 15 original works on a total of 91 published works, most in English, and he was one of the first to do it. From 1981 to 1990 he did not send more original articles, but only 6 scientific reviews of his work. From 1991 to 1995 began publishing 7 reviews of some sectors of Italian chemical industrie. Since 1996 when he became director of the journal till now he wrote 290 articles (as editorials and reviews of technologies of the chemical industry).

Comunicazioni Flash

Polymer Electrolytes Prepared by Industrially Compatible Processes for Renewable Energy Storage in Sodium Batteries

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With the fast development of renewable energy sources, such as wind and solar plant, large-scale and high energy storage system are becoming extremely important to realize the load leveling of these intermittent energies into the grid. The most promising technology for that are secondary batteries (rechargeable) because high energy conversion, simple design, flexibility, easy to maintain. In order to meet the low cost policy in the market, sodium based secondary batteries are the best deal actually.

However, the currently technology of batteries use liquid electrolytes as ion transport media, and these liquid electrolytes are based on organic solvents that are toxic and volatile, and the use of these flammable liquids in batteries raises safety concerns. The most powerful solution on it is switch on all solid state material such as polymer films, ceramics, etc…

Here, we offer an overview of our recent developments on polymer electrolytes for Sodium-ion batteries. Polymer electrolytes were prepared through different techniques, exploiting techniques very easily to applied on an industrial point of view, simple casting (1) and UV-curing (2). All samples were thoroughly characterized in the physico-chemical and electrochemical viewpoint. They exhibited excellent ionic conductivity and wide electrochemical stability window, which ensure safe operation at ambient conditions. Electrochemical performances in lab-scale devices are presented, evaluated by means of cycling voltammetry and galvanostatic charge/discharge cycling exploiting different electrode materials (prepared by water-based procedures with green carboxymethylcellulose as binder).

Work on Na-ion polymer batteries for moderate temperature application is at an early stage, only lab-scale cells were demonstrated so far. Nevertheless, with the appropriate choice and optimisation of electrode/electrolyte materials (and succesfull combination thereof), the intriguing characteristics of the newly developed SPEs here presented postulates the possibility of their effective implementation in safe, durable and high energy density secondary Na-based polymer devices conceived for green-grid storage and operating at ambient and/or sub-ambient temperatures.

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Thin film of Black-Gold by electrodeposition, for jewellery making

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In the making of jewellery the most common types of gold colours used are white gold and yellow gold. Anyway lots of other colours of gold are also possible to achieve by electroplating.

Nowadays purple gold, black gold and blue gold are the gold colors more interesting and researched by fashion market.

There are two electrochemical deposition processes used to obtain such colours: the first one is by forming a surface coating on gold, also referred to as Patination of Gold. The second process consists of the formation of gold metal alloys also referred to as Intermetallic Compounds.

The black gold thin films can be prepared by more methods, utilization of amorphous carbon during Plasma Assisted Chemical Vapour Deposition process, controlled oxidation of carat gold containing chromium or cobalt and electrodeposition processes.

We investigate mainly thin films obtained by electrodeposition processes.

Electrodeposition using black Rhodium or Ruthenium added to gold electroplating solution is one way. Electroplating solutions containing Ruthenium give a slightly harder black coating as compared to electroplating solutions containing Rhodium. We present some electrochemical results about the formation of thin films of black gold and their morphological characterizations by Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM).

We're going also to evaluate a correlation between films electrodeposited from different plating baths and corrosion resistance of the films themselves.

Study of Fenton reactor in a wastewater treatment plant

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Fenton technology is a promising and alternative method for wastewater treatment an environmental friendly method for pollutants treatment (1). In scientific literature, there are several applications of Fenton reactor for wastewater treatment, such as textile wastewater, laboratory wastewater, industrial effluents, cosmetic wastewater, dye wastewater, pesticides, fermentation brine from green olives, pharmaceutical wastewater, cork cooking wastewater, pulp mill effluents, and phenol degradation (2). In all cases, researcher's pin-point for a percentage of residual hydrogen peroxide remaining unreacted at the outlet of the oxidation reactor or at the exit of the treatment plant is analyzed. In this research, a study of Fenton reactor in a wastewater treatment plant is carried out. The plant processes hazardous liquid waste and not, and different treatments are present: biological, physical/chemical, distillation/evaporation. The most important treatment is the Fenton reactor used to reduce the odorigeno impact and to improve the operation of biological section. H_2SO_4 is added until a value of pH equal to 4 and then $Ca(OH)_2$ is added until a value of pH equal to 10.5. In the distillation/evaporation treatment, wastes with high concentrations of volatile solvents, salts, metals and organic substances not disposed in the biological section are treated. However, the feed of column distillation is excessively diluted, so another configuration of the plant is developed: all evaporated of concentrator, dryer and multiple effect (collected in D41 vessel) are sent to the Fenton reactor and not to the distillation. The response of Fenton reactor to this change is analyzed in this study, infect in the normal operation only the residue of column distillation is sent to the Fenton for the subsequent biological treatment. An ANOVA analysis is carried out to this purpose, using the Yates' algorithms for the estimation of main factors. Concentration of H_2O_2, concentration of FeSO4, evaporated of D41 vessel are considered as factors. The chosen responses are: values of chemical oxygen demand (COD) and oxygen uptake rate in the outlet of the Fenton. A 2^3 full factorial design with 8 tests is developed. The statistical significance is checked by the F-value and p-value at the 5% of significance level. In laboratory experiments, total COD concentration is analyzed using the Hach Lange test kit LCK (according to the standard method ISO 6060-1989). OURs measurements are carried out with a digital respirometer. Anova analysis is carried out in two different days and the effect of different days is confused with the effect of third order interaction. Four factorial experiments are carried out in order to evaluate the presence of similar results. Results show that for the values of COD the concentration of H_2O_2 has a negative effect, the vessel D41 does not modify the yield of the reactor and only in one case is reduced. The interactions of higher order produce a negative effect; different feeds are also significative. For the biodegradability of the sludge, the concentration of $FeSO_4$ has a positive effect only in one case. The evaporated of D41 vessel has manly a positive effect: the evaporated of the plant increase the biodegradability and different feeds have mainly a positive effect.

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Isoprene production from methanol: an investigation on the reaction mechanism.

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2-Methyl-1,3-butadiene, usuallycalled isoprene (IPE), is among the most important building blocks for the production of synthetic rubber. (1) One of the processes used for IPE production relies on the Prins reaction between isobutene and formaldehyde over acid catalysts (2,3). The main drawback of this process is the use of formaldehyde, which is carcinogenic and can be precursor of heavy compounds finally leading to catalyst deactivation.

In this work, IPE production through methanol-isobutene coupling is presented, opening the way for an alternative route to the nowadays-used industrial two-pot reaction. (4, 5)

The final aim of this study is to dig up into thecoupling reactionmechanism between methanol and isobutene over Al/P/O-based catalyst.

Amorphous Al/P/O catalystwas synthesized by a co-precipitation method followed by drying and calcination. (2) The catalysts were tested at 400 °C in gas-phase, using a continuous-flow glass reactor, feeding methanol and isobutene in ratio 1/6, at different contact times. Supplementary experiments, aimed at investigating the behaviour of the reaction products, were carried out feeding either dimethyl ether (DME) and isobutene or IPE only. Thanks to a comparative analysis of all the results, it was possible to hypothesize the reaction scheme reported in Figure 1. The reactivity tests have pointed out that IPE is produced along with 2-methylbutenes by methanol, as well as DME, and isobutene direct condensation. IPE might also undergo a consecutive decomposition to either retro-Prins products or 2-methylbutenes.

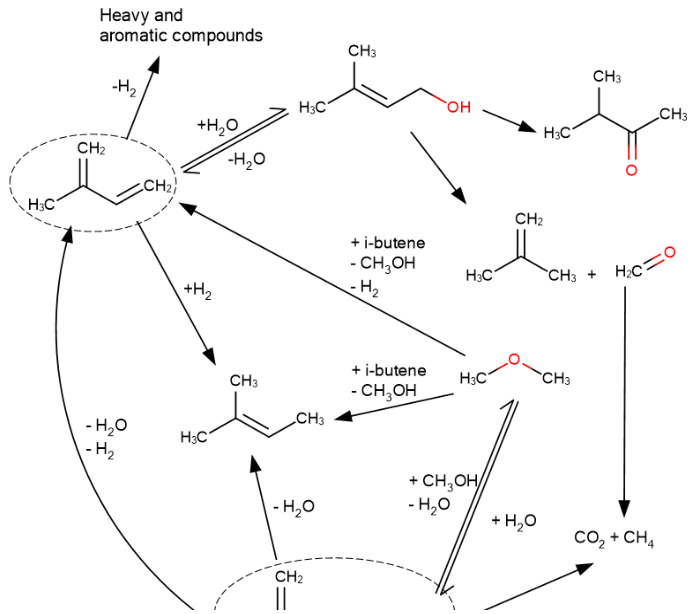

Figure 3. Simplified reaction scheme of isobutene-methanol coupling to isoprene.

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Diblock copolymer ethylene-syndiotactic styrene

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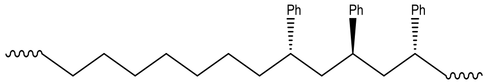
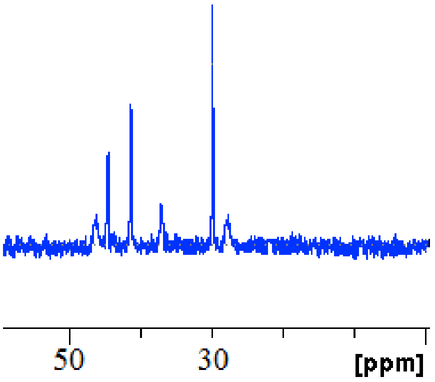
The one-pot synthesis of ethylene-styrene (ES) copolymers, where an isotactic polystyrene sequence is jointed to an alternating ES sequence, has been recently obtained by the quasi-living polymerization at low temperature using the catalyst zirconocene rac-methylenebis(1-indenyl)zirconium dichloride activated by methylaluminoxane (MAO) (1).

Keeping in the mind the idea of makingnew ES architectures copolymer, we have carry out the synthesis, through the living polymerization at low temperature, of a ethylene-styrenediblock copolymer with unprecedented structure, containingstereoregular polystyrene blocks.





Aliphatic regione of the^{13}C- NMR of the toluene soluble fraction

The key of the achievement is the homogenous polyinsertion catalysis by $CpTiCl_3$ at 0 °C combined with MAO and a judicious choice of monomers feed composition.

^{13}C nuclear magnetic resonance analysis of the boiling toluene soluble fraction (fig.) indicates the contemporarypresenceof syndiotacticstyrene sequence (**sPS**) andpolyethylene sequence.

The length of the ethylene sequence, estimated by the NMR resonances, increases with the growth of the ethylene concentration in the monomer feed composition.

The atomic force microscopy (**AFM**) techniques shows how these materials in the solid state organize themselves into nanostructures depending on the comonomers composition.

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An organic-solvent-free route to obtain nanostructured zinc oxide-based reservoir of clotrimazole.

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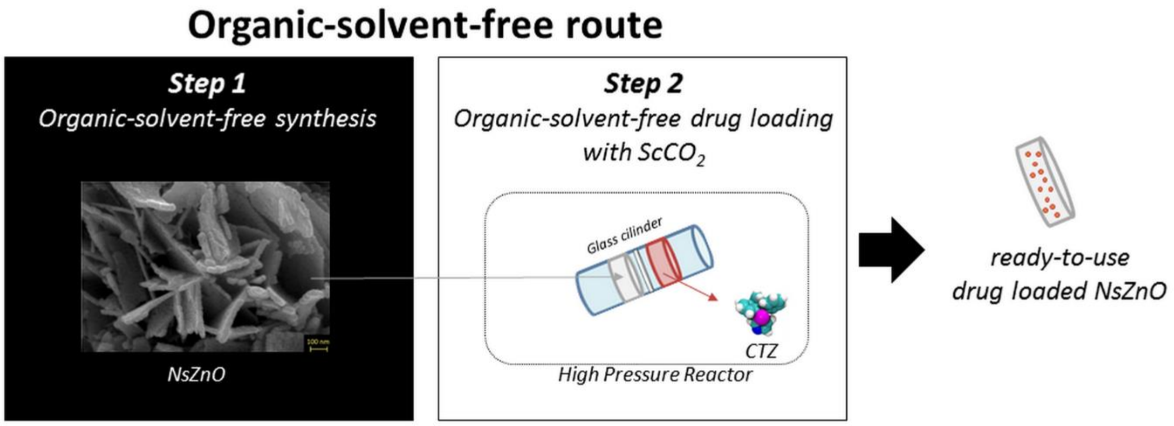
An organic-solvent-free route to obtain nanostructured zinc oxide (NsZnO) reservoir of clotrimazole was studied. Two different NsZnO materials were synthesized, selecting wet chemical approaches without any organic solvents: chemical bath deposition and a soft-template sol-gel method.

For the first time, loading of clotrimazole (CTZ) in a ZnO carrier by impregnation using supercritical CO_2 as solvent was studied. The NsZnO materials were characterized, before and after drug loading, by FESEM, XRD, nitrogen adsorption isotherms, TGA, DSC, in order to elucidate their morphological and physico-chemical properties.

CTZ was dispersed in the NsZnO carrier in amorphous form, with a maximum loading of 17 % w/w. *In vitro* drug-release was investigated, revealing that the NsZnO carriers can deliver clotrimazole, ensuring a fast release of a larger drug amount when compared to the solid crystalline drug. This might play a key role in several biological applications where the bioavailability of poorly-water-soluble drugs is still a challenging issue.



Cool Roofing, where chemistry indirectly helps environment

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In the inhabited part of planet where the ambient temperatures are high, a lot of energy is spent for air conditioning the houses, the figures are striking, thus a way to reduce this energy was found.

As in these areas the roofs are not made by tiles but they are flat or in general with a cement finish like the external walls, the idea was to cover the upper part of the houses with a white highly reflecting paint in order to reduce the absorption of the sun rays

The elastomeric roof covering has very similar characteristics to a mural painting. They are applied by spraying or roller on newly installed roofs or on existing surfaces.

The properties and performance of the elastomeric roof covering have a very similar appearance and viscosity to mural paintings, but a major difference is that the elastomeric "Roof Coating" coatings are, as the name suggests, more elastic and give the ability to expand and contract. This versatility can make the film very tough during temperature changes because it expands with heat and contracts to cool, reducing the likelihood of breaking.

Another big difference is the application thickness, mural paintings usually have a dry film thickness around 70-100 microns, while the elastomeric roofing applications have a dry film thickness of about 450-500 microns.

For this kind of very demanding application a special type of polymers have been designed: the most important requirements is to have a high durability on the outside for long exposure periods,. in addition due to temperature variations and natural elements such as snow and rain, the roofs are subject to humidity fluctuations, seismic expansion, wind and building vibration lifting then a very high flexibility is required.

Another feature requested is to withstand with occasional pedestrian traffic so the polymer for elastomeric roofing coatings must be flexible but at the same time resistant to static and dynamic pressures

Another important requirement is the reflectivity of infrared and ultraviolet rays. These coatings are mainly pigmented in white or light colors to maximize the amount of solar radiation to reflect. A high-performance coating can reflect 80% of solar radiation. The reflection of the liner helps keep the building cooler and reduce energy costs. To maintain this requirement, they must also have excellent resistance to dirt, to keep the coating always white and reflectant.

In this presentation we will describe the characteristics of elastomeric coatings for roofs formulated with acrylic or styrene acrylic emulsion polymers, which have many advantages and high performance. Emulsion polymers are able to provide better adhesion to a variety of substrates, low temperature low water absorption and very low dirt pick-up.

Integrated catalytic process for biomass hydrolysis: a comparison of different pretreatments and catalysts

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The conversion of lignocellulose biomass into valuable chemicals is one of the pillars of the biorefinery, the aim of which is to develop integrated processes for the transformation of renewables collected from agricultural, forestry and urban waste into “bio-platform molecules”. For these reasons, there is a great interest in developing reusable solid acid catalysts, which are effective in cellulose transformation, in place of the traditional processes that make use of mineral acids.

The starting point of the transformation chain is the deconstruction of the lignocellulose and depolymerization of the hemicellulose and cellulose to give monosaccharides, or even transform sugars into other valuable bio-based building blocks. Difficulties derive from both the resistant lignin sheath and the tight packing of cellulose chains. This implies the need for pretreatments procedures, aimed at improving the accessibility of catalytic acid sites.

The aim of this work is to compare the performance of metal phosphates catalysts in cellulose and lignocellulose (conifer wood sawdust) hydrolysis, after pretreatment of the biomass with different procedures.The catalysts tested in hydrolysis reaction were based on Zr/P/O and Nb/P/O systems, previously tested in other hydrolysis reaction(1) and showing interesting and diversified performances, thanks to their peculiar acidic properties. We compared two different types of pretreatment: a mechanical pretreatment, in which the substrate was subjected to a 48-hours treatment in a high-energy ball mill, and a thermal pretreatment, in which biomass was autohydrolyzed at 180°C for 1 hour in a monomodal microwave reactor. Results of tests conducted with metal phosphate catalysts on cellulose and lignocellulose, either as such or after the two different treatments, showed that pretreatments were effective in facilitating the hydrolysis: in particular, with pretreated substrates, we observed an important improvement of catalytic performance. However, autohydrolysis in microwave reactor permitted to obtain better conversion and yields to monosaccharides and successive decomposition products, compared to the ball-milled substrate.

As regards catalytic behaviors, the differences of performances between the two metal phosphates can be explained by invoking both the different total concentration and type of acid sites: we evaluated the total concentration of acid sites by means of ammonia TPD and the type of acidity (Brønsted/Lewis acid site ratio) by means of FT-IR adsorption of pyridine.It is possible to conclude that: the Zr/P/O system has a higher concentration of total acid sites, that results into a higher conversion of the biomass, in particular of the cellulosic fraction; instead, the Nb/P/O system presents a higher Brønsted/Lewis acid sites ratio, that reduces the production of monosaccharides in favor of successive decomposition products.

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Removal of non-degradable organic compounds from water with nanocomposite aerogels

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To remove the non-degradable organic compounds from wastewater several methods like adsorption, filtration and chemical oxidation, are used. These common treatment processes have the disadvantage of not degrading but only capturing contaminants, often creating secondary pollution. A possible alternative is to use heterogeneous photocatalysis which are able to degrade these soluble organic contaminants. The photocatalyst, in form of nanopowder or nanocomposite, is generally dispersed in a slurry reactor as suspended powder. This process has the following drawbacks, the separation of nanopowders from purified water is very expensive and the use of powder photocatalysts in slurry reactors damages reactor recirculation pumps. A possible solution to overcome this technical limitation is to fix the photocatalyst nanopowder on bulky organic or inorganic support materials.

Highly attractive support materials for photocatalysts are high porosity monolithic aerogels which can be easily obtained by drying of physical gels with supercritical CO2. The preparation of physically cross-linked aerogels has been reported for different thermoplastic polymers such as polyethylene, syndiotactic polystyrene (s-PS), poly(2,6-dimethyl-1,4-phenylene oxide) (PPO), poly(ether-ether-ketone) or poly(lactic acid). A particular class of monolithic physically cross-linked aerogels, having the peculiarity that the crystallites forming the aerogel physical knots are nanoporous crystal phase, can be achieved by using PPO and s-PS. The PPO and s-PS crystalline nanoporous aerogels are able to rapidly absorb volatile organic compounds (VOCs), mainly halogenated or aromatic hydrocarbons, from water and air, also when present at very low concentrations (2).

This contribution will focus on the preparation and characterization of composite monolithic aerogels based on s-PS and N-doped TiO2 (NdT) photocatalyst. In detail the photocatalyst activity of well dispersed NdT nanoparticles in s-PS crystalline nanoporous (NdT/s-PS) aerogels will be compared with that of the pure NdT powder. The higher photocatalyst activity of NdT/s-PS aerogles will presented and discussed (3).

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Heterogeneous photocatalytic processes for the abatement of N-containing pollutants from waste water

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Since the last four decades, the viability of photocatalytic degradation of organic compounds in water streams has been demonstrated. Nitrogen containing compounds, such as dyes, pesticides, drugs, etc. as well as inorganic ammonia (1), nitrites and nitrates (2), are harmful contaminants for drinking water and ground water (3). These compounds are particularly relevant in agriculturally intensive zones and in the case of some industrial processes involving e.g. nitration reactions. Therefore, the development of effective methods for the abatement of these harmful pollutants from waste waters and from hydric resources is a challenging task. Different configurations for solar TiO_2 photocatalytic reactors have been used (4), however pilot and demonstration plants are still countable.

This work represents the photocatalytic processes for the abatement of N-containing compounds focusing mainly on the photoreduction of nitrate ions and the photooxidation of ammonia in semibatch mode, aiming at maximum selectivity towards N_2(5). Innovative photoreactors were specifically designed and optimized for this application.

Different photocatalysts have been prepared with two different methods and their photocatalytic performance has been compared with commercial nanostructured TiO_2 (P25). TiO_2 has been prepared in nanosized form by using an innovative flame pyrolysis (FP) approach, and mesoporous $TiO_2$was prepared by sol-gel method. Pd has been in case added TiO_2 by post synthesis impregnation. The physical/chemical properties of the photocatalysts were studied by means of XRD, BET and UV-Vis spectroscopy.

The results of both photooxidaton and photoreduction of photocatalysts imply that the flame pyrolysis procedure is a viable technique for the preparation of nanosized $TiO_2$for this application, leading to ca. double conversion with respect to commercial samples. Furthermore, the addition of a small amount of Pd (0.1 wt%), likely enhanced the lifetime of the photoproduced charges by electron trapping and resulted in higher conversion in almost all photocatalysts. However, the best performance was obtained by Pd doped on TiO_2 (FP) especially in the photooxidation process with conversion up to 31% after 5h and selectivity up to 100%.

The specific configuration of designed photoreactor, enhanced the uniform mixture of catalyst and light distribution and opens possibility for further optimization for scale up in order to be used with direct sunlight.

Keywords:
Photoreduction, Photooxidation,N-containing compounds, Waste water treatment, TiO_2, Flame pyrolysis

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The upgrading of bio-alcohols: Production of added-value chemicals by the gas-phase (oxi)dehydration of 1-butanol over V/P/O catalysts

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During latest years bio-alcohols, such as 1-butanol, are being studied as platform molecules alternative to the fossil-based building blocks. This alcohol can be used as the reactant for the production of butenes(1) and maleic anhydride (MA)(2), as illustrated in figure 1.

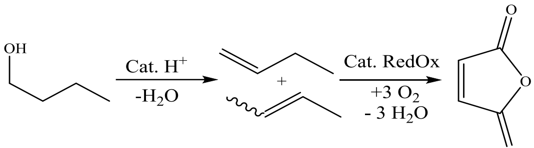

Figure 4: Oxidehydration of 1-butanol to maleic anhydride via butenes.

In this work, we report about the catalytic performance of vanadyl phosphate, α$_1$-VOPO$_4$ (VPD),for the synthesis of butenes and MA from 1-butanol. The presence of acid and redox sites on the surface of VPD [3] allowedus to use it as a multifunctional catalyst for the dehydration and oxidation steps.By varying catalyst textural properties and reaction conditions, it was possible to modify the catalytic behavior, thus the selectivity into olefinsand MA. The catalytic performances were tested by feeding 1 mol% of 1-butanol either in helium or in air, at different temperatures. Under anaerobic conditions the formation of 1- and 2-butenes and a non-negligible amount of butyraldehydewas observed. However, C balance was poor, because of the formation of heavy compounds on catalyst surface, which also were responsible for VPD deactivation at high temperature. The performance of VPD catalyst in the presence of air, summarized in figure 2; at low temperature, the catalytic behavior was similar to that one observed in absence of air. However, in this case, complete conversion was achieved already at 260°C, with 97% selectivity to butenes, no lack in C balance and no deactivation. At temperatures higher than 330°C, wenoticed the formation of CO, CO$_2$, maleic anhydride (MA), other oxygenated compounds such as acrylic and acetic acid, furan and phthalic anhydride. At 440 °C, the highest selectivity into MA (36%) and CO$_x$ (38%) were achieved.

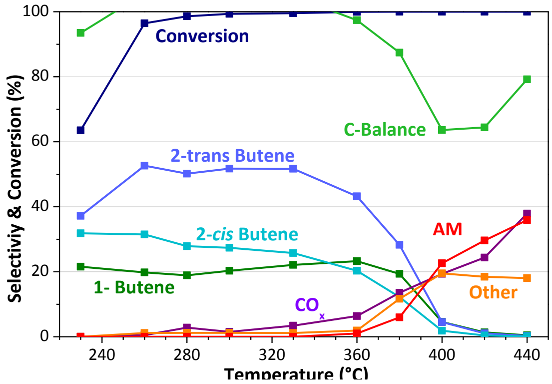

Figure 5: Effect of temperature on 1-butanol conversion and selectivity to products with the VPD catalyst. Feed composition: 1% butanol in air.

The characterization of the spent catalysts by Raman spectroscopy showed the presence of carbonaceous compounds, especially in the case of tests carried out without oxygenin feed, and both α$_1$ VOPO$_4$ and (VO)$_2$P$_2$O$_7$ (VPP) compounds. The formation of the VPP during reaction in air can be attributed to the strong interaction of 1-butanol with the catalyst surface and the development of a redox equilibrium between the gas-phase and the V ions involved in the reaction. In conclusion, by varying temperature and reaction environment, it is possible to modify the catalytic behavior of α$_1$-VOPO$_4$in order to address the transformation of the alcohol into olefins and/orMA. Oxygen plays a fundamental role for the entire process, because it disfavors the formation of heavy compounds on the catalytic surface and also supports the oxidation reactions.

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Antimicrobial release from s-PS Active Packaging

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Active packaging is used successfully for improvement of shelf-life and nutritional quality of fresh food, especially processed ones, consumers need more and more high quality products that are also fresh and safe (1). Active packing is an innovative concept that can be defined as a packaging mode in which the bag, product and environment interact with each other in a synergistic way to extend shelf-life or enhance safety and sensory properties, while maintaining the quality of the product. This is particularly important in the fresh food sector, such as cut fruit (2). Semicrystalline s-PS samples, exhibiting thenanoporous δ and ε crystalline phases, can rapidly andselectively absorb volatile organic compounds as well as gasmolecules, even when present at very low concentrations (3).These s-PS films, mainly for low guest content(possibly <1 wt %) can be useful for packaging of fruits andvegetables, due to the combination of ethylene and carbondioxide removal from the empty cavities of the δ nanoporouscrystalline phase (4-6) and the slow release of a scented naturalantimicrobial guest from the filled cavities of the same crystallinephase (7).This slow release assures and hence long-term antimicrobialproperties (7).

Fig. 1. Orange fridge storage in BOPP film (left) and in sPS Activepackaging film (right) after 30 days.

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Biorefinery from the marine microalga Nannochloropsis oceanica

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The exploitation of renewable materials coming from biomass is a strategic objective for the chemical industry in order to reduce the consumption of fossil resources resolving, at the same time, the problem of agricultural and other wastes disposal.The sustainability of a process is strongly dependent on the choice of raw materials able to produce high value derivatives or common productspreserving the availability of natural resources (especially for food supply) for the future generations. In this context, the valorization of biomass which production does not compete with food (wastes or microalgae) is an importantgoal. In this research project, extraction processes from algal biomass were studied for the optimization of biofuels production as well as the recovery of biomolecules to exploit in the pharmaceutical and nutraceutical domains or to develop high value products such as solvents, chemical industry intermediates and biopolymers.

Nannochloropsisoceanica biomass was provided by Fotosintetica & Microbiologica Srl (F&M), spin-off company of the University of Florence, within the activities of VALORE (Centro di Competenza *Gino Florenzano*of the University of Florence for the valorization of algal and residual biomasses). Improvement of extraction processes was studied in order to recover high value molecules for their industrial exploitation. In particular, the extraction process aimed at obtaining products with different applications: oils to obtain biodiesel and omega-3 fatty acids, carbohydrates or their derivativesable to be converted into other compounds of industrial interest and finally proteins for use in nutraceuticals.The main components extracted were characterized by NMR, FT-IR, GC-MS and CHN elemental analysis and synthetic processes were studied to transform some of these products in high value-added derivatives.

A combined microwave (MW)/Soxhlet method was chosen to extract high purity oil from *Nannochloropsis* biomass. In the Soxhlet extraction,petroleum ether was used as solvent with both oil poor and oil rich biomasses, with or without preliminary MW treatment. The best result in oil extraction (30% as w/w yield on a 55% total lipid content) was obtained using a lipid-rich biomass and MW/Soxhlet combined protocol. The ^{1}H-NMR analysis of the extracted oil revealed the presence of triglycerides with high purity and low amounts of other fatty acid derivatives. Polyunsaturated fatty acids (omega-3) were also detected and recovered as methyl esters by distillation in the biodiesel (BD) production. In fact, a mixture of fatty acid methyl esters was obtainedusing MeOH and TMSCl as a recyclable acidic mediator (8h, 60°C) and a conversion of 95% was evaluated via ^{1}H-NMR. This synthetic procedure was already applied for BD production from other biomasses (1-3).

Methyl-D-glucoside and cellulose derivatives were synthesized from the carbohydrate components and a protein enriched fraction was also recovered.

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Looking at the bigger picture in carbon dioxide photoreduction

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CO_2 photocatalytic reduction, a growing field in green catalysis, shows great potentialities to avoid fossil fuels exploitation and to obtain C-based solar fuels through a sustainable process using water as a reductant and light irradiation as only energy input (1). Despite the simplicity of this reaction on paper, actually, there are several physical phaenomena and chemical side-reactions to be dealt with (2), but the two most critical are still carbon dioxide compatibility in reaction medium and light harvesting. In fact, reactants, catalyst (usually a TiO_2 based material) and light must all come together in order to successfully achieve effectiveness in carbon dioxide photoreduction. In this contribution, these parameters effects are considered carefully through a "catalysis by design" approach.Carbon dioxide compatibility toward water is extremely low and this issue still represents a challenge. To overcome this drawback, in this work the authors considered carbon dioxide photoreduction in different media, namely aqueous liquid phase and gas phase. It was observed that in liquid phase, where CO_2 absorption in water is less likely to happen, reaction occurs with a good yield only when reactor temperature and pressure are increased. Whereas, working in gas phase allows to perform the reaction at room temperature and atmospheric pressure and to modify products distribution to more reduced C-based products. CO_2 adsorption on the catalyst could be also tuned through catalyst modification, i.e. the introduction of basic components (such as CaO or MgO) on the catalytic surface, though these promoters modify the chemical properties of adsorbed carboxyl-species with different reducibilities, as indicated by physicochemical characterisations.

Carbon dioxide adsorption aside, light harvesting on photocatalyst can be increased by materials modification. Enhanced electronic circulation on semiconductive materials by metal doping boosts the effectiveness of incident photons. In this work, the effects of CuO (a co-catalyst) and Au (an electron trap) is carefully considered to reduce electron-hole recombination in titanium dioxide. While CuO increased both activity and selectivity to methane, surprisingly gold suppressed methane formation in favour of hydrogen due to water splitting side-reaction. A deep physicochemical characterisation allowed to correlate this experimental data to materials' properties: in fact, from FTIR data, it was possible to observe that gold nanoparticles acts as a too strong trap for electrons preventing them from remaining in titanium dioxide's conduction band and being photocatalytically active. Finally, CO_2photoreduction to methane in both photons-rich and photons-poor conditions, in order to assess the effect of the promoters on light harvesting in different experimental regimes. In all conditions CuO and Au modified TiO_2 photoactivity, but this difference was more evident in low irradiance conditions, where light harvesting takes on great importance. From all the experimental evidences and considerations, there is a wide variety of pursuable strategies to increase carbon dioxide photoreduction efficiency, but they must be carefully considered by an in-depth consideration of physical and chemical phenomena involved in the process.

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Synthesis of monoalkyl glyceryl ethers using glycidol as green starting material

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The present work deals with the selective preparation of monoalkyl glyceryl ethers (MAGEs) starting from glycidol (2,3-epoxy-1-propanol) by ring opening reaction with alcohols.

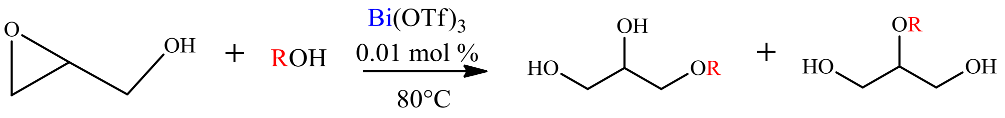
MAGEs are a versatile class of chemical compoundswith several industrial applications, in particular theyare used as the building blocks for the production of additives (for fuels,lubricants, printing inks etc.), detergents, polymers, pharmaceutical and cosmetic products.(1)

One of the most investigated pathway to synthesize MAGEs is represented by the direct etherification of glycerol,thanks to thegreat abundance of this feedstock on the market (2.3 Mt in 2013).

The use of glycidolas starting material to produce such valuable chemicals appears to be very promising if we considerthat it can be obtainedthrough the conversion of 2-chloro-1,3-propanediol, a by-product in the epichlorohydrin production plant. (2)

We have studied the catalytic etherification of glycidol with alcohols in the presence of Lewis acids and we have obtained the best results by using metal triflates as catalysts. (3)

In this work, we explore the synthesis of MAGEs catalyzed by an environmental friendly Lewis acidscatalyst, such as $Bi(OTf)_3$ (Scheme 1), which is recognized asthe best catalyst for the synthesis of monobutoxy glyceryl ethers starting from glycerol.



R= CH_3, CH_2CH_3, $CH(CH_3)_2$, $(CH_2)_3CH_3$, $(CH_2)_4CH_3$, $(CH_2)_7CH_3$, CH_2Ph.

Scheme 1. Glycidol etherification with alcohols in the presence of bismuth triflate.

Under the investigated reaction conditions, $Bi(OTf)_3$ was shown to promote the total conversion of glycidol with high selectivity (90%) to monobutoxy glyceryl ethers in only 2 h.

A simplified life cycle approach was followed by comparing thesustainabilityof the proposed route with that of the most investigated pathway from glycerol, in order to evaluate the green potentialof MAGEs synthesis from glycidol.The results showa considerable reduction of all the impact categories considered, suggesting that the glycidol-to-MAGEs route can be a valuable integration to the glycerol-to-MAGEs chain. (4)

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Comunicazioni Poster

Titanium grids and polymer electrolytes for flexible dye-sensitized solar cells

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Dye-sensitized solar cells (DSSCs) gather great interest for the possibility of different applications such as architectural integration, wearable photovoltaics and supply systems for low power electronics. For the development of flexible devices some critical issues still have to be solved, such as the use of solid or quasi-solid electrolytes and convenient sealing materials for the packaging, able to provide satisfactory duration in time.

This work presents the results obtained on a flexible DSSC, fabricated in our lab using UV-crosslinked polymeric membrane as electrolyte and titanium grids both as the anode andas the cathode substrate. The Ti grid was vertically dipped into a diluted TiO_2 paste (18NR-AO ActiveOpaque, Dyesol), in order to obtain a suitable mesoporous semiconductive layer, which was subsequently annealed at 525 °C. The photoanode was then incubated into a 0.3 mM N719 dye solution (Ruthenizer535bis-TBA, Solaronix) for 15 h. The cathode was obtained depositing a 5 nm layer of platinum by means of sputtering (1). Regarding the polymeric membrane, this was prepared UV-irradiating a solution of two oligomers (bisphenol A ethoxylate dimethacrylate, BEMA and poly(ethylene glycol) methyl ether methacrylate, PEGMA) and a free-radical photoinitiator (2). The packaging was made with two 75μm-thick PET foils and each layer of the cell was spaced by a thermoplastic foil. The sealing was performed using a hot press set at 85 °C.

Both rigid and flexible DSSC configurations have been tested by a careful characterization of their electrical performances. The small decrease in the overall efficiency of the flexibleDSSC configuration with respect to the rigid one is related to the different quality of the electrodes/electrolyte interface contacts.

In conclusion, the simplicity of fabrication and the relatively low cost employed materials pave the way for an industrial scale-up and a possible future commercialization.

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Bioadditives from waste materials

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Recycling and reprocessing of waste materials to obtain bioadditives, biopolymers or biodiesel (BD) is becoming a primary topic for biorefinery productions. In fact, in a world wide scale production, with different economic, political, environmental and ethical issues, many efforts have been made to convert non-ediblefeedstocksuch as non-edible oils, exhausted fried oils, oils from microalgae, animal fats and other waste materials into chemicals or biofuels. A preliminary study has been performed in order to obtain bioadditives with different reagents potentially achievable from a biorefinery, with the aim to identify the major transformation products and their industrial applications. In particular, due to the complexity of the mixtures obtained from substrate as glycerol or sugars, ethylene glycol was used as a model compound to optimize selectivity and conversions in the esterification with oleic acid usingchlorotrimethylsilane (TMSCl) as a recyclable acidic mediator. In fact, this compound was already applied for the transesterification of triglycerides to obtain BD (1-3) and also for the chlorination of glycerol to obtain mono and dichlorohydrins (4). The use of ethylene glycol is interesting for the valorization of this product after its recovery from waste materials coming from the demolition of cars.Three products were obtained from the reaction between oleic acid and ethylene glycol(Figure 1).

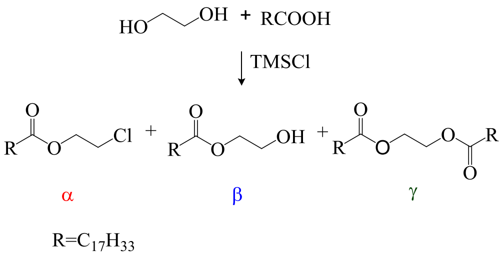

Figure 1. Synthesis of oleic acid derivatives

The selectivity can be changed modifying the molar ratio between the reagents or the temperature and in particular compound αor β were obtained with high selectivity using different reaction conditions. Product α could be used for the synthesis of a cationic biosurfactant, while β and γ could be used as surfactant and as plasticizer, respectively. Work up procedure was optimized to recover and recycle unconverted ethylene glycol and oleic acid.

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The reactivity of metal phosphate catalysts in the synthesis of methyl methacrylate from bio-based propionic acid and methanol

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Poly(methyl methacrylate) (PMMA) is a plastic material widely used by automotive, construction, electronics and display industries. Most methyl methacrylate (MMA) produced globally is employed in the manufacturing of PMMA, but so far MMA synthesis almost relies on oil-derived chemicals such as acetone, ethylene, propylene and isobutene (1). Among the renewable resources available for MMA synthesis, an interesting option would be propionic acid (PA), which can be produced either by sugars or by glycerol fermentations (2), or by dehydration and oxidation of 1,2-propanediol. Here we report a study on the direct synthesis of MMA and methacrylic acid (MA) in the gas phase in a fixed-bed continuous-flow reactor, by means of esterification of PA with MeOH and aldol condensation between PA and formaldehyde (the latter produced in-situ by MeOH dehydrogenation). Amorphous Al phosphate proved to be effective in the esterification of PA giving good selectivities in methyl propionate (MP), namely 72%, with a time factor of 1 s*g/mL. However,in the range of temperature investigated (300-350-400°C), this catalyst yielded MMA and MA with overall selectivity no higher than 8%, because of the expected poor catalyst activity in methanol dehydrogenation to formaldehyde, and the need for a dehydrogenating element such as Cu or Ag.Surprisingly, at high temperatures (400°C), 3-pentanone (3-P) became a major product of the reaction with a selectivity of 20%. The ketonic decarboxylation of carboxylic acids has been studied extensively on basic and transition metals oxides (3) but, to the best of our knowledge, there are very few literature references on the use of metal phosphates as catalysts for ketonization of carboxylic acids.Since bio-oil produced from ligno-cellulose pyrolysis contains carboxylic acids and this leads to low pH, instability and corrosiveness, ketonization would be a viable option to remove contaminants and enhance the quality of bio-fuels (3). For these reasons, the self-ketonization of PA over amorphous Al phosphate and Zr phosphate has been investigated as well. When PA was fed over $AlPO_4$ in the range of temperatures 300-375 °C, the conversion rose from 12% to 83% and the major products was 3-P, with selectivity around 70%, the remaining however being mainly due to the CO_2 co-produced. Selectivity of 3-P was lower than that which would occur in the absence of consecutive reactions (83%) due to self-condensation, which formed heavy products on catalyst and reactor's walls. Rising temperatures to 400°C enhanced this side reaction lowering 3P selectivity down to 55%. The activity of Zr phosphate was lower than that of Al phosphate: the conversion of PA at 350 °C was 19% and rose to 53% when temperature was increased until 425 °C, while the trend of 3-P selectivity was similar to that obtained with Al phosphate.

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Alumina-supported niobia catalystsfor methylesters epoxidation reaction

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Epoxidized soybean oil and epoxidized methylesters derived by oils play an important role as building blocks for the preparation of a wide variety of consumer products, such as plasticizers and stabilizers for PVC, and components of lubricants. On the industrial scale, the epoxidation reaction is currently carried out with peroxocarboxylic acids, obtained in situ by using mineral acids as catalysts according with the Prileshajew method. However, several drawbacks of this method have been recognized over the years, such as the occurring of side reactions (ring opening and polymerization) caused by the presence of homogeneous acids in the reaction system, and the environmental pollution of the waste acids [1]. New efficient and environmentally friendly systems, such as the use of alternative oxidants and heterogeneous catalysts, may overcome these limitations. In particular, the use of hydrogen peroxide as oxidant is very attractive because the only one by-product of the reaction is water.

Recently, many niobium oxide (niobia) based materials (Nb_2O_5/SiO_2) were proposed for the epoxidation reaction with hydrogen peroxide, due to the high leaching stability and good water tolerance. In particular, it was demonstrated that the niobia–silica based materials, containing the same amount of Nb_2O_5 and prepared by different synthesis methods, have different catalytic activity in methyloleate epoxidation with H_2O_2 [2,3]. This singular behavior was ascribed to the presence of different species of niobium (isolated or bulk) depending on the nature of the niobium precursor and the synthesis method. Different methods of synthesis lead to the presence of different structures and surface distribution of active sites (Brønsted and Lewis sites), influencing in this way the activity and selectivity in the epoxidation reaction. Commercial alumina was reported as an efficient catalyst for the epoxidation of methyloleate with hydrogen peroxide, also in the presence of a large substrate like soybean oil [4] moreover it has recently been demonstrated that catalysts obtained supporting Nb_2O_5on alumina are very good catalyst with high activity and selectivity [5].

The aim of this work is to study deeper the catalytic system (Nb_2O_5/Al_2O_3). In particular, the influence of the preparation conditions on catalyst structure and on catalytic performance will be examined.

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Epoxidation of methyl oleate with hydrogen peroxide as oxidizing agent over niobium and titanium oxide-based catalysts

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Epoxidised vegetable oil fatty acid methyl esters (FAMEs) are considered among the most versatile intermediate materials for oleochemistry, as they may give rise to a broad palette of valuable derivatives via epoxide ring opening (1). Niobium- and titanium-based silica catalysts proved to be promising heterogeneous catalysts able to promote the use of aqueous hydrogen peroxide as an eco-friendly oxidant in epoxidation reactions (2,3). Since several literature reports rely on the use of chemically complex, non-commercial solid catalysts, that are scarcely suitable for a large-scale application, the present study aimed at investigating the performance of conceptually simple, cost effective inorganic oxides to be used in the liquid-phase epoxidation of methyl oleate (Me-OLE), as a model substrate, in the presence of aqueous (30 wt.%) hydrogen peroxide.

Commercially-available samples of nanometric-sized $Nb_2O_5\cdot5H_2O$, anatase $TiO_2$and SiO_2-TiO_2 mixed oxides (with TiO_2 content spanning from 0.3 to 2.3 wt.%) were chosen as catalysts. The materials underwent a thorough physico-chemical characterization (XRD, DRS-UV-vis and SEM). Only the SiO_2-TiO_2 0.3% sample displayed a major fraction of isolated Ti(IV), whereas in the rest of the materials the presence of bulky aggregates of TiO_2 or Nb_2O_5 species was clearly evident.

In batch epoxidation tests (Fig. 1), under non-optimized conditions, $Nb_2O_5\cdot5H_2O$ showed the highest performance in terms of Me-OLE conversion (43%) and epoxide selectivity (54%) and yield (23%). A TS-1 zeotype (Ti content 1.7%), taken as a benchmark catalyst, was more selective (71%), albeit at the cost of lower conversion values (down to 14%) due to its narrow and poorly accessible micropore network. The encouraging results obtained on $Nb_2O_5\cdot5H_2O$ and its intrinsic structural robustness in water-containing media are feature worth studying in deeper detail.

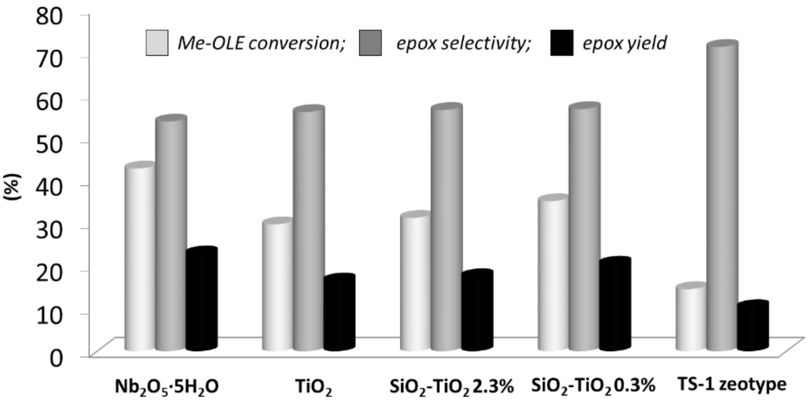

Fig. 1. Catalytic performance of the oxidic heterogeneous catalysts in the batch liquid-phase epoxidation of methyl oleate. Reaction conditions: H_2O_2:Me-OLE 4:1 mol/mol; 0.7g solid; 3 g CH_3CN; 90°C; 4h.

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Copolymerization of Propylene Oxide with Succinic Anhydride using Dinuclear Zinc-*N*-heterocyclic carbene complexes

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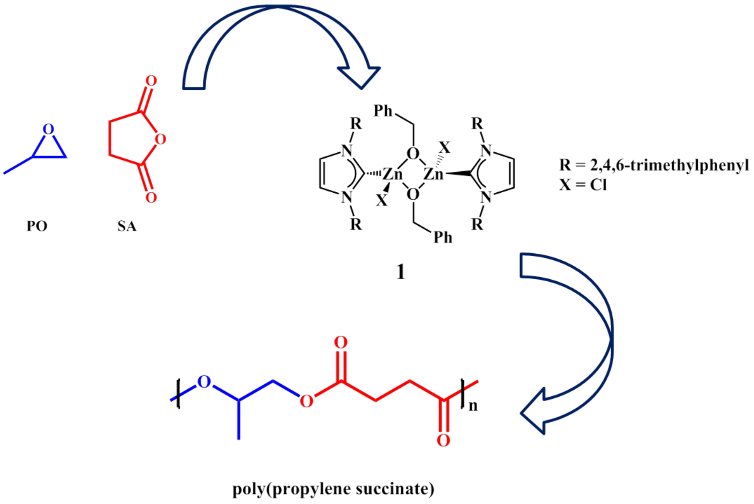
The growing demand for biodegradable polymers as alternative materials to conventional polyolefins requires the sustainable production of new materials, preferentially using monomers from renewable resources (1). In recent years, much attention has been being paid to aliphatic polyesters due to their biodegradability and biocompatibility (2): the latter include materials such as polylactide (PLA), poly(ε-caprolactone) (PCL) and, more recently, copolymers like poly(propylene succinate) (PPSu) and poly(cyclohexene succinate) (PCSu). PPSu and PCSu are polyesters of potential interest for application in the drug delivery agents, as fibers and medical sutures/stents (3). These copolymers can be produced in a controlled manner by ring-opening copolymerization (ROCOP) of epoxides and cyclic anhydrides, typically mediated by complexes of oxophilic metals, such as group 13 M(III) and Zn (II) (4). Zn(II)–alkoxide species are particularly attractive metal-based ROP initiators because of the low cost and low toxicity of Zn. Besides, Zn(II) species are well-established catalysts for the effective and controlled homo-polymerization of various cyclic esters/carbonates. However, the use of Zn-based initiators for the epoxide/anhydride ROCOP remain little studied so far. Herein a series of robust zinc complexes bearing monodentate N-heterocyclic carbenes (NHCs), synthetized according to a literature procedure (5), were investigated as initiators of the copolymerization of propylene oxide (PO) with succinic anhydride (SA). The present contribution describesour preliminary results in the area under different reaction conditions. Complex **1** was found to be an active ROCOP catalyst leading to good polymerization control and activity.



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Hydrogen production by ethanol steam reforming on Ni-based catalysts: effects of the support and of CaO and Au doping

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Energy is everywhere. Energy is the base for social and economic development, and it represents a necessity for everyday life.One of the main challenge for scientists today is to reduce the dependence from fossil fuels. However, how can we meet the ever-growing world energy demand in a sustainable way?Renewables can be the answer (1). Hydrogen and renewables-derived hydrogen in particular, is the ideal candidate for both energy and transport sectors. It is a high-density energy vector; it is clean and carbon-free, so its sole combustion product is water. Ethanol emerged as a good candidate for hydrogen production because it is renewable, easy to store, handle and transport because of its low volatility and non-toxicity and has a high hydrogen content. Therefore, ethanol steam reforming (ESR) is promising to produce hydrogen in a sustainable way.

The aim of the present work is the development of Ni based catalysts for hydrogen production by ESR. As the choice of the support plays a vital role in determining the activity, selectivity and stability of a catalyst, we have studied three different metal oxides: titania, zirconia and ceria. In particular, we have investigated 10 wt% supported Ni samples with the addition of calcium oxide (9 wt%) by incipient wetness impregnation and of a small amount of gold (1wt%) by deposition precipitation. As regard as the active phase, nickel is extremely attractive to upscale the process for one reason: the price. Nickel showed a high activity and efficiency in breaking the C-C bond but its use is limited by coking and sintering phenomena. Noble metals are known for their ability to break the C-C bond and it is known that gold nanoparticles favor the water gas-shift reaction as well. Moreover, calcium oxide was added to the supports in order to reduce the acidity of the catalysts and prevent coke formation (2).

Both fresh and used samples were properly characterized to understand the influence of the dopants on morphological, textural and surface properties by N_2-physisorption, XRD, TPR, TPO, CO_2-TPD, SEM, AAS and IC. The evaluation of the catalytic performances in the ESR were proved in a plug-flow reactor PID (Process Integral Development Eng&Tech) coupled to a gas-chromatograph and to quadrupole mass analyzer.

It was found that the support plays a very important role on nickel activity in ESR.Zirconium and cerium oxides proved to be suitable supports, even if both still suffer from coking phenomena.

Doping by calcium oxide prevented deactivation and highly increased the hydrogen yield and productivity. The resistance towards coking increased due to the formation of oxygen vacancies, that can activate CO_2 and H_2O, thus favouring the gasification of coke.

Addition of gold nanoparticles greatly improved the hydrogen yield.

The combination of the two dopants resulted in the best performing catalyst: the basic doping by CaO and the promotion of the WGS by gold nanoparticles contributed to the highest hydrogen production.

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A new Material for Digital Doming: Preparation of Polyurethanes based on Soybean Oil

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Most of the worldwide market plastics derive from fossil fuels such as oil, coal and natural gas, accounting for about 7% of world consumption of these resources. Considering the continuous depletion of fossil raw materials, the oil price fluctuations and environmental problems, in the last decade a wide-ranging research started on the production of "bio-based" polymeric materials coming directly or indirectly from renewable raw materials such as starch, cellulose, sugars, lignin, etc. (1) In this context, vegetable oils, such as castor, linseed, and soybean oils, have been regarded as a convenient renewable feedstock for developing bio-based polyurethanes. (2) In our previous work, we reported an efficient, cost-effective, and environmentally-safer conversion of soybean oil (SO) into soy-based PU, (fig. 1A) (3).A special application of PU is the digital doming, a process which adds value to any shape or size non porous material by coating the surface with a thick layer of resin (up to 5 mm) having a dome shape, that is due to the high surface tension of the liquid polymer during solidification. This technique gives to the surface a three-dimensional effect (fig.1B).

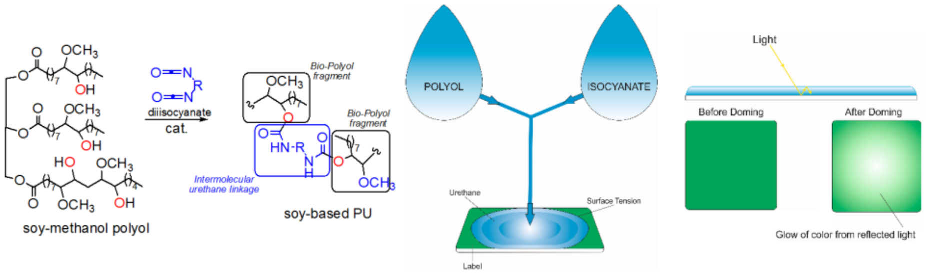

Figure 1. (A)Soy-methanol polyol and PUs, (B) Example of Doming Effect

We now report a new formulation to obtain e Bio-based Polyurethane for innovative application in Digital Mosaics. (fig. 2)

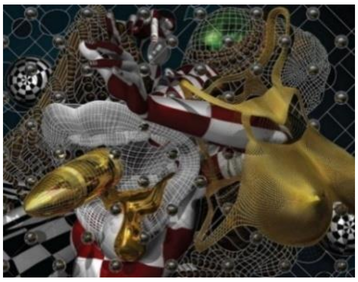

Figure 2. An example of Digital Mosaic in Erarta Museum

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Methane dry reforming: effects of lanthanum oxide in Ni/CeO_2 catalyst

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Nowadays the world is facing a big issue regarding the environmental problems represented by the use of fossil fuels as energy source. In fact, great emissions of CO_2, derived from fossil fuels combustion, and uncombusted methane have been responsible for the steep growth of the global mean temperatures, i.e. the so-called greenhouse effect.

In this work, methane dry reforming (MDR) is investigated in order to valorise methane and carbon dioxide, two of the greatest greenhouse gasses. *Syngas* in a low H_2/CO ratio is the product of this reaction and it's possible to exploit it in Fisher-Tropsh liquid hydrocarbons synthesis. The goal of the work is the formulation of a heterogeneous nanostructured catalyst based on nickel for MDR. Nickel is very active for this reaction but it suffers from deactivation caused by sintering and coke deposition (1). For this reason, it's necessary to increase its stability and resistance using supports with high surface area and thermal stability. Ceria was selected for its redox properties(2) that allow the storage and delivery of oxygen thanks to the reversible change of oxidation state from 3+ to 4+. Conversely, it has limited mechanical strength. For this reason, it was used lanthanum oxide as a promoter, in order to enhance the stability and the redox properties of this system. Aimed at optimising support-promoter interaction and maximise their synergistic effect, the synthetic method has been studied. Lanthanum oxide (6 wt %), was introduced on ceria support by two different methods: incipient wetness impregnation into the support and co-precipitation with the support. Reactivity tests were performed in a lab made reactor rig(3), controlling the products by an online mass spectrometer. Different techniques were used to characterise the samples: temperature programmed reduction (TPR), temperature programmed oxidation (TPO), X-Ray diffraction (XRD) and physisorption. In this way, it was seen how the support influences nickel particles size and interactions with the active phase, and the direct effect of these properties on the activity and stability of the catalyst for *syngas* production. It was observed an increase in hydrogen production after lanthanum oxide addition, but at the same time the activity was strongly affected by the promoter introduction method. XRD analysis have been essential in order to understand the reason of this behaviour. It has been observed an increment in lattice parameter with the addition of the promoter. In particular, co-precipitation method provides materials characterised by larger lattice parameter cell than impregnation method, proving former method's greater effectiveness in entering ceria lattice; in fact, La^{3+} and Ce^{4+} have similar -ionic radii. This feature therefore has a direct effect on catalytic performances. It is possible to suppose that the substitution of Ce^{4+} with La^{3+} in ceria lattice leads to a higher redox ability that decreased catalytic deactivation due to carbon deposition, and brought higher methane conversion.

Therefore, a proper lanthanum oxide modification on Ni/CeO_2 catalyst represents an efficient and innovative method to increase both activity and stability for MDR.

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Photonic Crystal Sensors based on Poly(p-Phenylene Oxide)

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1D polymer photonic crystals, based on of poly(phenylene-oxide)(PPO), both in amorphous and clathrate crystalline phases, have been prepared.

The diffusion of certain molecules (VOC vapors) within amorphous PPO induces the formation of cocrystalline phases where guest molecules are included within the polymer lattice (1-6).

During exposure to the different VOCs, the DBRs (distributed Bragg reflectors) show a very dissimilar optical behavior, also detectable by naked eye. We have demonstrated a proof-of-concept all-polymer DBR sensor able to distinguishing benzene, 1,2-dichlorobenzene, carbon tetrachloride and toluene via colorimetric detection (7).

The visual colorimetric response of the sensor, which does not require any signal transduction, could potentially make these systems effective safety devices suitable for untrained end-users for monitoring of air quality and of VOCs leakages, also allowing constant and extensive pollution monitoring in industrial and urban areas

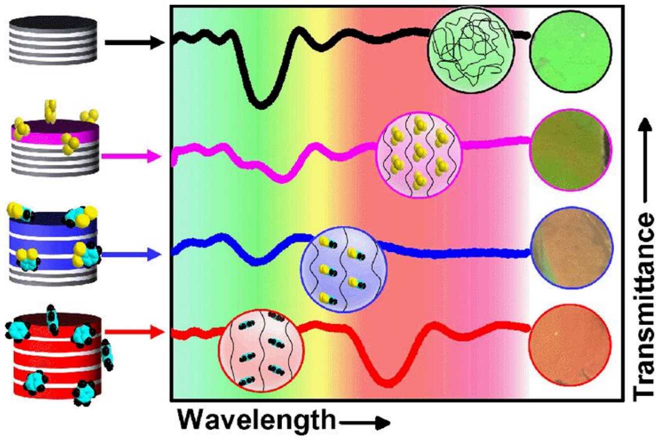

Fig. 1. A visual colorimetric response of a Photonic Crystal Sensors based on Poly(p-Phenylene Oxide) during exposure to VOC vapours

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Crystalline orientation in poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) cast films

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The properties of polymeric films largely depend on the type and degree of molecular orientation developed during the processing or during the crystallization process, therefore it is very important to study and control the molecular orientations that can be generated in polymeric films (1).

It was found that polymers, which are able to form co-crystalline phases with low molecular mass molecules, can lead *without any stretching procedure* to high degrees of different kinds of uniplanar orientations of the crystalline phases, i.e., a high degree of parallelism of well defined crystal planes with respect to the film plane (2-12).

In particular, for s-PS films, three different kinds of uniplanar orientations can be achieved by simple procedures involving co-crystallization in the presence of suitable guest molecules (solution crystallization (2-4)solvent-induced crystallization in amorphous samples (5-7) or solvent-induced recrystallizations of suitable crystalline films (8)). The three observed uniplanar orientations correspond to the three simplest orientations of a high planar-density layer (formed by close-packed alternated enantiomorphous s-PS helices) with respect to the film plane (9-10). As for PPO, two different kinds of uniplanar orientations have been obtained by co-crystallization, as induced by different guests in amorphous films (11).Recently it was found that suitable guest molecules that are able to co-crystallize with poly(L-lactic acid) (PLLA) canalso generate uniplanar orientations of co-crystalline phases, by low-temperature sorption inamorphous unoriented PLLA films (12).

As for PPO it is worth underlining that due to the absence of fiber spectra, the occurrence of uniplanar orientation may be particularly useful to solve the PPO co-crystal structure as well as the related nanoporous-crystalline modification.

In this communication we will present a new kind of crystalline phase orientation developed on PPO polymeric films by casting procedures.

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Sustainable biochemicals production by esterification reaction using heterogeneous catalysts

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Waste raw materials obtained by several sources of both food and agro industries could be considered for biomaterials production. In the last years, this topic was growing in interest, in particular considering oleins, mixtures of free fatty acids (FFAs) and glycerides. The purpose of this study is related the investigation of the performances of synthetic acid resin (sPSB-SA) as a new heterogeneous catalyst characterized by a high stability at high temperatures (180°C). This catalytic system was tested in esterification reaction in order to obtain bio-chemicals (such as plasticizers or surfactants) and bio-lubricants (an alternative to the petrochemical lubricants).

Typical catalysts used for the esterification reaction are acid homogeneous catalysts such as p-toluen-sulfonic acid, phosphoric acid, sulfuric acid [1]. The use of classic heterogeneous catalysts such as acid resins is instead limited by the fact that they are not stable at temperatures higher than 120°C [2]. For the esterification of FFAs, for different applications such as bio-lubricants synthesis or bio-chemicals synthesis the temperature must be higher than 180°C to favor the elimination of water from the reaction environment because the reaction is limited by chemical equilibrium.

For these reasons the objective of this study has been the investigation of the performances of synthetic acid resin (sPSB-SA) as a heterogeneous catalyst characterized by a high stability at high temperatures (180°C) [3]. This catalytic system has been successfully tested in the above mentioned esterification reaction and compared to classic commercial strong acid catalysts like Amberlyst®, Nafion® and sulfuric acid. The catalytic system was tested in a batch reactor and a loop reactor, in order to verify the catalyst stability. The esterification reaction was performed using different polyalcohols with saturated monocarboxylic acids.

In particular, the reaction was performed using oleic acid, as references of fatty acid from biomasses, and 1,3-propanediol, pentaerythritol, trimethylolpropane as alcohols, in order to obtain different bio-lubricants bases. The second reactive system, instead, used oleic acid and glycerol in order to obtain bio-chemicals.The typical reaction conditions were chosen as follows: the temperature was 180°C, the molar ratio (considering the function groups) was 1:1, the catalyst was variable.

Acid resin (reticulated and not-reticulated) has shown high activity in esterification reaction and a good resistance to the deactivation. The specific activity of the sPSB-SA resins (referred to the acid equivalent) is similar than that of sulfuric acid in the conversions of FFA. The introduction of crosslinks in the resin reduces the overall acidity of the resin and, consequently, its activity but sPSB-SA2 is more stable and it can easily be separated from the reaction products. The results showed that the synthetic resins sPSB-SA1 and sPSB-SA2 (reticulated) had similar activity of sulfuric acid, in particular the resin showed higher activity than all catalysts tested.

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Flagship demonstration of an integrated biorefinery for dry crops sustainable exploitation towards biobased materials production

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The role of University of Bologna team, a partner of the Flagship First2Run project, is focused on the study of the catalytic process for the transformation of fatty esters (triglycerides) and fatty acids into shorter dicarboxylic acids, more specifically the oxidative cleavage of oleic acid (or the corresponding triglyceride), from cardoon flower, into Pelargonic acid and Azelaic acid (or the corresponding ester). These acids are industrially used as component in a series of applications such as polyamides, polyesters, cosmetics, pharmaceuticals, plasticizers, lubricants, or hydraulic fluids (1).

This process is currently carried out in industry with ozone as the oxidant, which however implies the use of dangerous process conditions. Matrìca, a joint venture between Versalis and Novamont, has developed a process for the oxidative cleavage in two-steps, consisting first in an hydroperoxidation of the triglyceride to the corresponding glycol and then in the oxidative cleavage of the glycol into the shorter chain acids (2) (Figure 1). Aim of my research work will be to investigate various options for the catalytic oxidation of fatty acids and esters, by means of more sustainable oxidants and catalysts. For example, one option will be the design and implementation of a heterogeneous catalyst for the oxidative cleavage step.

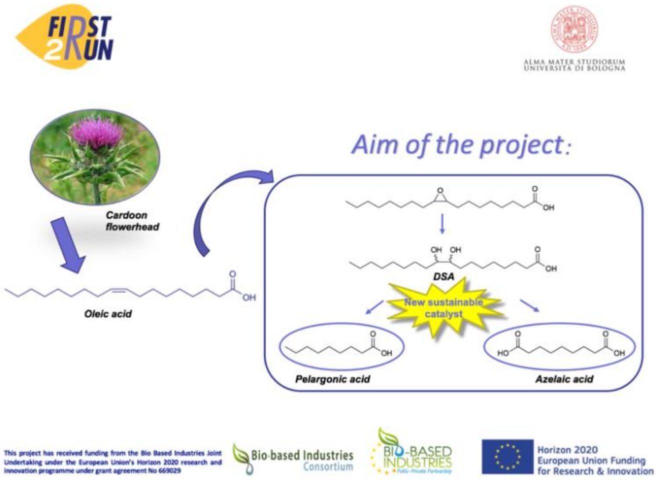

Figure 6: Main reaction pathways for the cleavage of oleic acid to Azelaic acid and Pelargonic acid.

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