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PLENARY ABSTRACTS

Itelyum: Open Technology Platform for Used Oil Regeneration

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Itelyum is the new Italian player with more than half a century of history, internationally recognized for its technology, expertise and quality in the regeneration of lube oils, purification of solvents and chemical streams, and environmental services for the industrial sector. Itelyum provides a growing integrated and sustainable offer of products, solutions and services, adopting a model of circular economy that extends the life cycle of products and creates partnerships in the market segments served.

As an example, regeneration of used base oil lays on a technological improvement path, combining sustainability drivers with innovation. This evolution ensures products with high technical and environmental performances. LCA approach proves the advantages of regeneration compared to the virgin production and versus the treatment to fuel.

Regeneration remains an open technology platform, allowing for innovative growth and scientific cooperation. In fact, the sector still deploys great R&D efforts and process upgrading, exploring further improvement margins, in both short and long term.

Used oil composition is variable depending on commercial formulations, applications and degradation paths. Process needs continuous improvements to maintain industrial yields and final products with performance and environmental requirements, matching growing market expectations. Methane supports the energy demand for heating and hydrogen production via steam reforming. Alternate bio-sources for methane and hydrogen are feasible. Recovery of byproducts of hydrofinishing can be further enhanced, also testing new type of catalysts to improve products performances. New type of catalysts regenerable can be testing and on site new catalyst regeneration process can be applied. Steam reforming syngas before purification is rich in CO₂, allowing for CO₂ capture options. Bitumen obtained from the thermal deasphalting column can be used to produce rubberized asphalt.

In a longer term, other paths deserve attention: re-refining of biotechnological mineral used oil via bioreactors, biofractionation of used oil to obtain lube bases and other products, biohydrofinishing of lube bases or other intermediates to improve saturation and desulphurization, full recovery and reuse of water, thermodynamic solar plants as energy sources, and new pollutants abatement system focusing on biotechnologies.

Keywords: *used oil, re-refining, performance, innovation, sustainability.*

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References

Francois Audibert, *Elsevier*, **41400** (1994)

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When physical-chemistry meets catalysis: stories around the active site

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Heterogeneous catalysis significantly shapes society, as it plays a fundamental role in the production of chemicals and pharmaceuticals, in the petrol industry and even for the environmental protection. In this field, the knowledge of the nature and structure of active sites, also when dispersed and/or embedded on solid (eventually porous) supports, represents a fundamental task for the optimization of the catalytic performances¹. Nevertheless, the intrinsic complexity of heterogeneous catalysts, often prepared through multistep reactions, requires the use of a multidisciplinary approach to have information on the nature and structure of both active sites and solids surface, as well as on the active phase-support interactions and on the effects on the catalytic reaction pathway. The tailoring approach for the design of high-performance catalysts relies on the definition of preparation procedures guided by a step-by-step multi-technique characterization approach based on a synergic use of advanced investigation methods. In this contribution, several examples of the physico-chemical approach for the characterization and optimization of different classes of heterogeneous catalysts will be given. This will cover case studies spanning from a fine tuning of surface acidity of catalysts for the production of fine chemicals to the optimization of metal supported catalysts for oxidation reactions^{2,3}. The importance of the fine control of the acid-base properties of both porous and layered supports for the optimization/stabilization of particle dispersion in metal-supported catalysts will be then described⁴. Moreover, recent results related to the optimization of single-site based catalysts able to promote selective oxidation reactions of toxic chemicals in non-noxious species will be described together with the physico-chemical and catalytic properties of novel multifunctional materials for environmental purposes⁵.

Keywords: *heterogeneous catalysts, nanosized materials, metal-support interactions*

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References

- [1] J. Vadrine, *Applied Catalysis A: General*, **474** (2014) 40
- [2] M. Guidotti, R. Psaro, N. Ravasio, M. Sgobba, F. Carniato, C. Bisio, G. Gatti and L. Marchese, *Green Chemistry*, **11** (2009) 1173
- [3] C. Bisio, K. Fajerweg, G. Martra, P. Massiani, *Catal. Today* **36** (2007) 124
- [4] F. Carniato, C. Bisio, G. Gatti, E. Boccaleri, L. Bertinetti, S. Coluccia, O. Monticelli, L. Marchese, *Angew. Chem. Int. Ed.* **48** (2009) 6059; C. Tiozzo, C. Bisio, F. Carniato, M. Guidotti *Catalysis Today* **235** (2014) 49
- [5] F. Carniato, C. Bisio, R. Psaro, L. Marchese and M. Guidotti, *Angew. Chem. Int. Ed.* **53** (38) (2014) 10095

MASTER THESIS AWARDS

MSc-01: Chemicals production from biosuccinic acid

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Succinic acid is a dicarboxylic acid having the molecular formula C₄H₆O₄ which represents an important feedstock for chemical industries, finding several applications in the cosmetic, pharmaceutical, food industry and in the polyesters synthesis. Nowadays, succinic acid is predominantly produced via petrochemical processes, considered harmful to the environment, so the biological production of succinic acid via fermentation was considered as an attractive alternative [1]. After fermentation, downstream processes are needed. These processes usually include three main steps: (i) the removal of microbial cells, (ii) the removal of impurities and primary separation of succinic acid from the fermentation broth, (iii) final purification of succinic acid [2]. The aim of this work is the recovery of succinic acid produced from biomasses, using *Arundo donax* as raw material and the subsequent production of chemicals, lubricants or precursors for polymers. At this purpose, an operative protocol of recovery and purification of succinic acid has been developed and applied to obtain succinic acid with a high purity. This procedure consisted in: (i) a preliminary treatment of fermentation broth with activated carbons to remove the coloured impurities, (ii) vacuum distillation to concentrate the broth, (iii) crystallization of succinic acid. A pilot plant has been used to conduct this procedure. Moreover, an alkaline treatment has been developed to increase further the purity of succinic acid. Then the recovered succinic acid has been used in esterification reaction to produce biochemicals. In fact, esters are very important among the products derived from succinic acid because they are used to obtain resins, plastics and other industrial commodities [3]. At this purpose, a reaction system consisting in a loop reactor has been built, where a commercial heterogeneous acid catalyst, Amberlyst - 15, is used in preliminary tests.

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Keywords: *bio-chemicals, green chemistry, succinic acid*

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References

- [1] M.J. Van De Graaf, F. Vallianpoer, G. Fiey, L. Delattre, E.A.M. Schulten, US 2012/0238722 A1 (2012)
- [2] K.K. Cheng, X.B. Zhao, J. Zeng, R.C. Wu, Y.Z. Xu, D.H. Liu, J.A. Zhang, *Applied Microbiology Biotechnology* **95** (2012) 841
- [3] J.G. Zeikus, M.K. Jain, P. Elankovan, *Applied Microbiology Biotechnology* **51** (1999) 545

MSc-02: Crosslinkers for polyvinyl alcohol based formulations

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In recent years, environmental regulations require the research of new adhesives formulations with high safety and low environmental impact, maintaining high performance. In particular, polyvinyl acetate formulations without NMA (N-methylolacrylamide) were studied in order to eliminate formaldehyde emissions while maintaining high performance in the presence of humidity or contact with cold water. In addition, the use of appropriate crosslinkers is essential to obtain high performance in extreme conditions. In this work different commercial crosslinkers based on polyisocyanate were compared analyzing their role in the variation of the application properties of polyvinyl adhesives. This research was promoted by Vinavil company to obtain information on the different behavior observed in the use of analogous crosslinkers with different formulations of commercial polyvinyl adhesives. In fact, the tested commercial crosslinkers (DESMODUR[®] DA-L and EASAQUA[™] WAT-4) showed different behavior with different adhesive formulations, despite the presence in both of hexamethylenediisocyanate trimers. Both products are suitable for use with water-based adhesive formulations but they are differentiated by the strategy with which the molecules have been made hydrophilic: in DA-L a hydrophilic group is inserted on an isocyanate group, while in WAT-4 free ionic groups are present. At first, the crosslinkers formulations were evaluated in presence of water. Moreover, the reactions in the presence of polyvinyl adhesives were studied, analyzing the residual solubility of the components such as PVAc and PVOH, the latter used as colloid protector. With this purpose, the films obtained from the mixing between adhesive and crosslinker were extracted with solvents of different polarity and analyzed by NMR and FT-IR spectroscopy. In agreement with the literature (1), it has been observed that the presence of NMA with the concomitant presence of AlCl₃ is sufficient to obtain low solubility for PVOH but also for PVAc; the use of crosslinkers has not shown any further reductions. Instead, for polyvinyl adhesives lacking NMA and/or AlCl₃, the actual role of the crosslinkers in terms of solubility reduction was observed. By comparing these data with the performance it is possible to highlight the importance of the hydrophilic system used in the crosslinker to facilitate its dispersion in the water-based formulation but also of the final hydrophobicity of the adhesive film to make it more resistant to water penetration. In fact, in the presence of polymeric diphenylmethane diisocyanate (PMDI), as hydrophobic crosslinkers, performance results are much better. Another fundamental factor is the interaction that is created between the wood and the adhesive formulation. At the end, the gelling capacity of the systems was also studied evaluating their potential use in the conservation of cultural heritage for the cleaning of artistic surfaces of various kinds.

Keywords: *crosslinker, adhesive, polyvinyl alcohol.*

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References

[1] Salvini, A.; Saija, L. M.; Finocchiaro, S.; Gianni, G.; Giannelli C. and Tondi, G.; J. Appl. Polym. Sci. **114** (2009) 3841

PhD THESIS AWARD

PhD-01: Electrode and Electrolyte Materials for the Development of Advanced Lithium and Magnesium Secondary Batteries

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This work has been focused on the development and study of novel electrolyte and electrode materials for application in Lithium and Magnesium secondary batteries. The proposed materials belong to the “*beyond Li-ion*” class of compounds, where systems exceeding the energy density values of Li-ion batteries or completely innovative chemistries are presented.

A solid polymer electrolyte is obtained by lithium functionalization of a poly(vinyl alcohol-co-vinyl acetate), forming lithium alkoxide functional groups [1]. In this material, the counter anion of Li⁺ is the overall polymer chain, giving rise to a single lithium ion conductivity. A further doping with an ionic liquid gives rise to a solid polymer electrolyte with a room temperature conductivity of $1.3 \cdot 10^{-5} \text{ S} \cdot \text{cm}^{-1}$. A second single lithium-ion conducting electrolyte is prepared by reacting glycerol with different quantities of lithium hydride. Here the lithium glycerolate component acts as a large and flexible macro-anion which is able to provide a conductivity of $2.0 \cdot 10^{-4} \text{ S} \cdot \text{cm}^{-1}$ [2]. In the last class of electrolytes, the ionic liquid's cation and anion replacement effects on the structure, conductivity mechanism, and electrochemical performances are studied. The proposed materials exhibit a magnesium conductivity value comprised between 10^{-4} and $10^{-3} \text{ S} \cdot \text{cm}^{-1}$, an overpotential in the magnesium deposition $< 50 \text{ mV vs. Mg/Mg}^{2+}$, and a coulombic efficiency up to 99.94 % [3].

In the second part of this work, the improvement of the electrochemical features of various cathode materials has been studied. In the first case, the formation of CuO-rich regions on olivine nanoparticles is able to improve the charge-transfer kinetics during the charge/discharge processes of the cathode for Li batteries. At the same time, the structural flexibility of the olivine crystal can be enhanced by adding graphite during the pyrolysis of the material [4]. Improvements of the rate capability and specific energy of a high-voltage olivine cathode are gauged by V, Nb, or Ta insertion within the structure. A specific energy of $650 \text{ mWh} \cdot \text{g}^{-1}$ is demonstrated. Finally, a cathode material for magnesium secondary battery which consists of a graphene oxide surface functionalization of vanadium-based nanoparticles is proposed. This functionalization allows for the obtaining of a material able to: a) sustain extremely high current rates ($1000 \text{ mA} \cdot \text{g}^{-1}$, $1700 \text{ mW} \cdot \text{g}^{-1}$ of specific power); and b) give specific capacity values up to $72 \text{ mAh} \cdot \text{g}^{-1}$.

A brief summary of the main outcomes achieved in this project will be discussed.

Keywords: *Beyond Li-ion, Magnesium, Electrolyte, High-voltage cathode*

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References

- [1] G. Pagot, V. Di Noto *et al.*, *Solid State Ion.*, **320** (2018) 177
- [2] G. Pagot, V. Di Noto *et al.*, *Batteries*, **4** (2018) 41
- [3] G. Pagot, V. Di Noto *et al.*, *Electrochim. Acta*, **246** (2017) 914
- [4] G. Pagot, V. Di Noto *et al.*, *Electrochim. Acta*, **225** (2017) 533

ORAL COMMUNICATIONS ABSTRACTS

O-01: Types of microreactors to study in laboratory oxidation catalysts

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In order to study oxidations catalysts and to avoid explosion reaction, lost on selectivity, strong increase of local temperature and deactivation of catalysts along the years and to avoid influence of mass transfer. I have used the following special types of micro reactors; puls microreactor [1-2] differential flow recirculating reactor [3], fluid bed [4-5], stacked pellet reactor [6], continuous stirred tank reactor [7], batch stirred tank reactor [8], monolithic type reactor [9].

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References

- [1] I.Pasquon, F.Trifirò, P. Centola, *La Chimica e l'Industria* **49(11)** (1967) 1151
- [2] D.Brkcic, F.Trifiro, H. Hofmann, *Chemiker Zeitung* **100(12)** (1976) 529
- [3] Trifirò and.I Pasquon, *La Chimica e l'Industria* **52(1)** (1970) 228
- [4] L.Cairati, L.Di Fiore, P.Forzatti, I.Pasquon, F.Trifirò, *Industrial & Engineering Chemistry Process Design and Development* **19(4)** (1980) 561
- [5] S.Masetti, F.Trifirò, G.Blanchard, *Applied Catalysis, A: General* **217(1-2)** (2001) 119
- [6] G. Centi, G Fornasari, F. Trifirò, *Industrial engineering chemistry product reasearch and development* **24(1)** (1985) 32
- [7] F.Trifirò, C.Banfi, G.Caputo, P.Forzatti, I.Pasquon, *Journal of Catalysis.*, **30(3)** (1973)393
- [8] F Trifirò P.L. Villa I Pasquon, *La Chimica e L'Industria*,**32(9)** (1970) 853
- [9] E.Cristallo, A. Roncari, A.Rinaldo, F.Trifirò, *Applied CatalysisA:General* **209(1,2)**, (2001), 249

O-02: A New Calcium Aluminate Phase in Hydrated Portland Cement

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Modern concrete technology makes extensive use of chemicals to improve the characteristics of the final hardened structures and to reduce the complexity and the impact of the labor of construction. Accelerating additives are added during mixing to increase the rate of cement hydration and improve the early strength development of the hardening cementitious materials. They are widely used at low temperatures and/or to speed up the construction activity. Known accelerators include calcium nitrate, calcium thiosulphate, calcium chlorides and several organic compounds. Among these calcium formate (CF) acts as accelerator for the hydration of the main phases of Portland cement: tri-calcium silicate C_3S , di-calcium silicate β - C_2S and tri-calcium aluminate C_3A [1]. The mechanism of action of CF on the cement hydration process has been debated for a long time and it is generally attributed to the diffusion rate of formate anions through the hydrated layers covering the C_3S and β - C_2S grains [2]. The influence of CF on the strength development of cement may also depend on the C_3A content, with a marked acceleration of strength development at low C_3A content [3].

A novel C_3A -CF hybrid phase has been discovered and isolated from hydrating Portland cement in the presence of calcium formate. Its crystal structure was fully elucidated by single crystal synchrotron X-ray diffraction data (ESRF, beamline ID11). The formation of the new phase has been confirmed by reacting pure cubic C_3A with CF in water. The new phase consists of very small needle-like crystals with composition $Ca_3Al(CHOO)_3(OH)_6$; the structure is trigonal R $\bar{3}$, unit cell $a=13.740$ $c=10.640$ Å. It is thought that the precipitation of the new phase depletes formate anions from the pore water solution of the cement paste, so that they are no longer available to exert the accelerating effect to the other cement silicate phases C_3S and β - C_2S .

Keywords: *accelerators, calcium formate, Portland cement,*

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References

- [1] M. Heikal, *Cement and Concrete Research*, **34** (2004) 1051
- [2] R. Kondo, M. Daimon, E. Sakai, H. Ushiyama, *J. Appl. Chem. Biotechnol.* **27** (1977) 191
- [3] M. Levitt, *Precast Concrete*, Applied Science Publishers, London (1982)

O-03: The circular economy in the tanning industry

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The Italian tanning industry is traditionally organized in industrial districts, each of them with its own production specialization: Arzignano, Zermeghedo and Montebello in Veneto; S. Croce sull'Arno and Ponte a Egola in Tuscany, Solofra in Campania and Turbigo and Castano Primo in Lombardy. The main productive specialization of the Venetian tanning pole concerns the processing of large bovine leathers that are destined for upholstery customers (furniture and car interiors) to footwear and leather goods. The Tuscan district is characterized by a high degree of craftsmanship and flexibility of the productions, primarily intended for high fashion; processing mainly concerns calf skins and medium-large cows, some of which are used for the production of sole leather. In Campania, on the other hand, there is a tanning area specialized in the tanning of sheep and goat leathers for clothing, footwear and leather goods. Finally, a significant tanning presence remains in Lombardy, in the Magenta area, whose industrial specialization concerns the production of sheep and goat skins for high fashion. The tanning industry is essentially concerned with the transformation of a waste from the meat and / or milk industry into an industrial product suitable for use in the production of leather and / or leather articles. Therefore, leather can be considered as an environmentally sustainable solution to a real problem of disposal of large quantities of animal remains that originate from the meat industry. In fact, the availability of raw hides on the market depends on the amount of slaughtering for food purposes and is in no way influenced by the needs of the leather manufacturing industry; in essence, the number of animals reared and slaughtered at the end of their life is functional to the needs of other industries (meat, milk, wool, etc.). With reference to the environmental impact of the tanning production process, the type of centralization in production districts makes it possible to deal rationally and in a targeted manner with some of the environmental problems linked to leather processing, such as wastewater purification and waste treatment. Concerning waste, such as fleshings, shaving and leather clippings (specific solid residues of tanning), they are adequately managed and enhanced for the production of fertilizers, soil improvers, etc., particularly in the industrial districts of Tuscany and of Veneto. Furthermore, in the Tuscan tanning district the recovery of trivalent chromium is carried out through a centralized system; in fact, suitable treatments of exhausted chrome-tanning liquids allow the recycling of this tanning agent in the production process. In the present work, the industrial processes that allow the valorisation of the main waste, typical of tanning process will be illustrated.

Keywords: *circular economy, tanning industry, tanning waste*

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References

[1] B. Naviglio, T. Gambicorti, D. Caracciolo, G. Calvanese, R. Aveta, Caratteristiche dei residui solidi da conce wet-white/metal free, 46°Convegno Nazionale AICC

O-04: Valorization of Papermill Wastes for the Production of Levulinic Acid and Butyl Levulinate

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The waste management policy strongly encourages the valorization of waste biomass to give strategic biochemicals, instead of their traditional combustion for energy recovery or, even worse, of their landfill disposal. In this context, the acid-catalysed hydrothermal conversion of negative-value bio-wastes into levulinic acid (LA) and butyl levulinate (BL) represents a smart exploitation widely adaptable to different kinds of waste feedstocks. Now LA and BL production was investigated starting from different cellulosic wastes. Particular attention was devoted to the powder which derives from the cutting operations occurring during the tissue paper production and represents a waste for paper mill processes. It is mainly composed of pure short-fibers of cellulose and, because it has been already mechanically reprocessed, it should be more reactive in acid-catalyzed conversion. LA is obtained by acid hydrolysis of biomass cellulose fraction and was classified 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 [1]. BL has been identified as important versatile biomolecules employed for the preparation of fuel additives, polymers and flavoring formulations. Due to its high boiling properties, it finds advantageous applications for blends in diesel-type combustion systems, allowing a reduction of soot particle emissions.

In this research, these cellulose-rich feedstocks were used for the production of levulinic acid in water and butyl levulinate in *n*-butanol, adopting in both cases a dilute acid and/or inorganic salts as catalysts. The effects of the main reaction parameters (biomass loading, temperature, duration) on the catalytic performances to the target products were investigated and optimized. Traditional heating and microwave-irradiation effects were also compared. The highest LA mass yield was obtained in the presence of very diluted HCl at 180 °C under MW-heating, corresponding to about 45 wt%. On the other hand, under the best reaction conditions, working in *n*-butanol, at 190°C in the presence of diluted H₂SO₄, adopting traditional heating or MW irradiation, butyl levulinate yield over 40 mol% respect to glucan content was reached. The obtained results were compared with those previously obtained on wood and herbaceous biomass.

Keywords: *waste cellulosic biomass, levulinic acid, butyl levulinate*

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References

[1] C. Antonetti, D. Licursi, S. Fulignati, G. Valentini, A.M. Raspolli Galletti, *Catalysts*, **6** (2016) 196

O-05: Development of high capacity lithium sulphur batteries

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In a rapidly changing electrical system scenario, where the energy mix sees an increasingly massive penetration of energy from renewable sources, technological solutions for the accumulation of electrical energy will progressively acquire a fundamental role. Recently, innovative storage systems have been developed, in particular lithium-ion batteries, with a double or triple energy density compared to other previous technologies [1,2]. Nevertheless further technological progress and greater cost competitiveness are required for the development of storage systems for electro-mobility or stationary energy storage. To increase the energy density of the energy storage systems, it is necessary to use innovative electrochemical materials and systems. Lithium sulfur batteries (Li-S) are promising candidates to replace lithium ion batteries because they are cheaper, lighter and, for the same weight, can store almost twice as much energy [3,4]. In this presentation we want to show some of the most recent results obtained in our laboratory concerning the fabrication of lithium sulphur batteries [5]. For their construction we used two different binders and two carbons with different surface area, deposited directly on the separator. Sulphur was introduced mixed with the electrolyte in the form of polysulphide. The particular cell configuration has allowed to obtain stable specific capacities after numerous charge and discharge cycles of more than 800 and 1200 mAh g⁻¹ and low cell resistances.

Keywords: *electrochemical energy storage, lithium-sulfur battery polymer binder, carbon*

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References

- [1] P.G. Bruce, B. Scrosati, J.M. Tarascon, *Angew. Chem., Int. Ed.* **47** (2008) 2930
- [2] R. Van Noorden, *Nature* **507** (2014) 26
- [3] N. Moreno, A. Caballero, J. Morales, E. Rodriguez-Castellon, *J. Power Sources*, **313** (2016) 21
- [4] M. Wei, P. Yuan, W. Chen, J. Hu, J. Mao, G. Shao, *Electrochim. Acta*, **178** (2015) 564
- [5] G. Tarquini, M. Di Carli, L. Della Seta, M. Moreno, P. P. Prosini, *Solid State Ionics*, **317** (2018) 170

O-06: Glycerol carbonate as an innovative alkylating agent for phenolics**T. Tabanelli**^{1*}, **C. Giliberti**¹, **Rita Mazzoni**¹, **R. Cucciniello**², **F. Cavani**¹*1 - Industrial Chemistry Department "Toso Montanari", Università di Bologna, Viale Risorgimento 4, 40136 Bologna, Italy**2 - "Adolfo Zambelli" Department of Chemistry and Biology, University of Salerno, Via Giovanni Paolo II 132, 84084 Fisciano (SA), Italy*

Organic carbonates (OCs) are an important class of molecules with a wide range of applications.(1) Nowadays, cyclic OCs are synthesized from the corresponding epoxides and CO₂ by a cycloaddition reaction.(2) On the other hand, the utilisation of glycidol, a toxic and carcinogenic compound, as a starting material for the synthesis of glycerol carbonate (GlyC), is not desirable. For this reason, we have recently proposed the utilisation of catechol carbonate (CC) as an alternative, extremely efficient carbonate source for the selective synthesis of a wide plethora of both symmetric dialkyl and cyclic alkylene OCs, including GlyC. Indeed, starting from a stoichiometric amount of glycerol and CC, in the presence of a basic catalyst at very mild reaction conditions (60°C, ambient pressure, 30 minutes) the quantitative, selective, formation of GlyC was achieved with only catechol as the co-product of the reaction.(3) For this reason, the so-formed GlyC was tested as a pioneering alkylating agent for catechol, by only increasing the temperature from the previous step, in a one-pot strategy. In this way, 2-hydroxymethyl-1,4-benzodioxane (HMB), an important intermediate for pharmaceutical industries, has been selectively synthesized in the presence of both homogeneous (NaOCH₃) or heterogeneous (MgO, Na-Mordenite) basic catalysts. Currently, HMB is synthesised by a multistep sequence of reactions and the use of toxic solvents (DCM and DMF) and reagents (glycidol derivatives, pyridine etc.).(4) In our optimized conditions, a slight excess of GlyC has been reacted with catechol in the presence of a homogeneous basic catalyst (NaOCH₃) at 170°C for just one hour; both reagents have been quantitatively converted with a HMB yield up to 88%. Moreover, a detailed mechanistic study, supported by kinetics, GC-MS, and HMBC NMR, have underscored the unique behaviour of GlyC compared to other OCs. Indeed, the multifunctional structure of GlyC, in particular of the free aliphatic OH group, plays a fundamental role in obtaining the reactive carbonate intermediate responsible for the intramolecular cyclization aimed at the selective formation of HMB, with only water and carbon dioxide as benign coproducts. The reported results represent a completely innovative and greener synthesis pathway to benzodioxanes which was patented (5).

Keywords: *glycerol carbonate, catechol, alkylation, 2-hydroxymethyl-1,4-benzodioxane*

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References

- [1] B. Schaffner, F. Schaffner, S. P. Verevkin and A. Borner. *Chem. Rev.* **110** (2010), 4554
- [2] M. North, R. Pasquale and C. Young. *Green Chem.* **12** (2010), 1514.
- [3] T. Tabanelli, E. Monti, F. Cavani and M. Selva. *Green Chem.* **19** (2017), 1519.
- [4] M. Ilic, P. Dunkel, J. Ilaš, and D. Kikelj, *Eur. J. Med. Chem.* **62** (2013), 329.
- [5] T. Tabanelli, C. Giliberti, R. Mazzoni, R. Cucciniello, and F. Cavani, *Green Chem.* **21** (2019), 329

O-07: DME production by one-pot CO₂ hydrogenation: key factors affecting the behaviour of CuZnZr/zeolite catalysts

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In the future energy scenario, DME is considered a very promising energetic vector able to directly introduce renewables in the chemical production chain [1, 2]. The production of DME from CO₂ hydrogenation is a way of recycling CO₂ and it requires the use of a hybrid multifunctional catalyst to efficiently catalyse the two consecutive reaction paths of methanol synthesis and methanol dehydration directly in one single step [3]. The aim of this work was to investigate the main features of a zeolite architecture affecting activity, selectivity and lifetime of catalytic systems prepared by gel oxalate co-precipitation of Cu-Zn-Zr precursors in a slurry solution of different home-made FER- and MFI-type zeolites.

Catalytic tests showed that not only the zeolite topology, but also the interaction of the metallic phase with the zeolite, act as determinant factors in terms of activity and stability. If on one hand the "construction" of a suitable metal-oxide interfacial area is fundamental for the activation of CO₂, on the other hand the "ensemble" of neighboring metal-oxide-acid sites significantly determines the DME productivity. Obviously, nature and strength of the acid site control the rate of methanol dehydration to DME, so affecting the final value of DME productivity. In this context, the Cu-Zn-Zr methanol phase carried on bi-dimensional ferrierite (FER) resulted to be an excellent hybrid system, allowing to reach CO₂ conversion of 25% and DME/CH₃OH selectivity close to 75%, which is the best result up to now published, without exhibiting a significant loss of performance during operation owing to a better resistance both to the copper particle sintering and to the loss of acidity typically induced by H⁺/Cu²⁺ ion exchange.

Keywords: CO₂ recycling, dimethyl ether, heterogeneous catalysis, zeolites

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References

- [1] G. Olah, *Angew. Chem. Int. Ed.* **52** (2013) 104
- [2] S. Perathoner, G. Centi, *ChemSusChem* **7** (2014) 1274
- [3] E. Catizzone, G. Bonura, M. Migliori, F. Frusteri, G. Giordano, *Molecules* **23** (2018) 31

O-08: Iron functionalized hydroxyapatite: effect of iron speciation on the catalytic performances in the NH₃-SCR reaction

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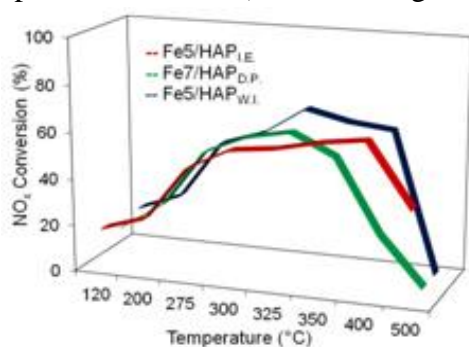
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Nitrogen oxides (NO_x) are known to have a harmful impact on the environment and human health. Selective Catalytic Reduction by ammonia (NH₃-SCR) is one among the most performant technologies for NO_x emission abatement [1]. In view of ever more stringent regulations for NO_x emission, the development of new friendly catalysts represents an unavoidable challenge.

Stoichiometric calcium hydroxyapatite (Ca₁₀(PO₄)₆(OH)₂, HAP), is an inorganic material, bioavailable, of low cost, easily modulable for the number of acid-base sites, and capable to exchange the calcium atoms with some other metal ions of catalytic interest and allocate them into its lattice.

A preliminary comparative study between several copper- and iron-modified HAP catalysts prepared by ion exchange procedure revealed that both the catalyst series are active and selective in NH₃-SCR reaction, even if in different temperature interval [2]. Moreover, iron-based HAP catalysts could have high potentiality, if suitably developed, because of their low cost.

In this work, we examined in depth the introduction of iron onto a synthetic HAP framework in different amount (ca. 2-7 wt.%), using iron(III) nitrate as precursor and by three different preparative methods (ionic exchange, deposition-precipitation and impregnation). The catalytic



performances of iron functionalized hydroxyapatite catalysts have been evaluated in the NH₃-SCR reaction in the 120-500°C interval with different NH₃/NO ratios and at fixed contact time. XRPD, UV-vis-DRS, Mössbauer spectroscopy, ammonia adsorption, and H₂-TPR provided fundamental details on catalyst properties and Fe sitting on HAP surface.

As a general trend, all Fe/HAP samples were active and selective in the NH₃-SCR reaction starting from ca. 350°C. The better performances (Figure) have been observed on catalysts containing ca. 6 wt.% of Fe prepared by deposition-precipitation and impregnation (ca. 70% of NO_x conversion and selectivity to N₂ higher than 95% at 350°C), where α-Fe₂O₃ and 3D-Fe₂O₃ nanoclusters were present, as indicated by Mössbauer and UV-vis-DR spectroscopies.

Keywords: *Iron functionalized hydroxyapatite; Iron speciation; de-NO_x catalysts; NH₃-SCR.*

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References

- [1] W.Wardencki, J.Curylo, J.Namiesnik, *Pol. J. of Environ.Stud.* **14** (2005) 389-395;
 [2] S.Campisi, M.G.Galloni, F.Bossola, A.Gervasini, *Catal. Comm.* **123** (2019) 79-85.

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O-09: Carbonaceous materials for the selective hydrogenation of HMF

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Biomass has recently attracted much attention as renewable carbon feedstock since it is abundant, widespread and inexpensive [1]. One of the most important products directly derived from lignocellulosic biomass, and particularly from fructose and cellulose, is 5-hydroxymethylfurfural (HMF). Currently, a wide range of HMF derivatives are reported to be potentially suitable to use in several sector of chemical industries and as biofuels [2]. Among all these, the HMF hydrogenation products are of particular interest.

In this work, HMF hydrogenation was carried out with Ru nanoparticles supported on carbonaceous materials, specifically activated carbon (AC) and a wide range of functionalised carbon nanofibers (CNFs). The goal was to study the influence of the support on the reaction activity and selectivity. Special attention was given to three hydrogenation products (Figure 1a), namely 2,5-dimethylfuran (DMF), 2,5-dihydroxymethylfuran (DHMF) and alkoxyethyl furfurals (AMF). The results show a strong influence of the nature of the support, particularly on the selectivity (Figure 1b). High amount of DMF was produced with AC as support, while DHMF was the main product when CNFs were used. Moreover, different functionalities on the CNFs supports led to changes in the DHMF/AMF ratio. All the catalysts were characterised with HRTEM, in order to obtain information on the Ru particle size and dispersion, and with XPS, in order to identify and quantify the surface functionalisation of each of the catalyst used, the degree of graphitisation of the carbon and the oxidation state of the Ru nanoparticles.

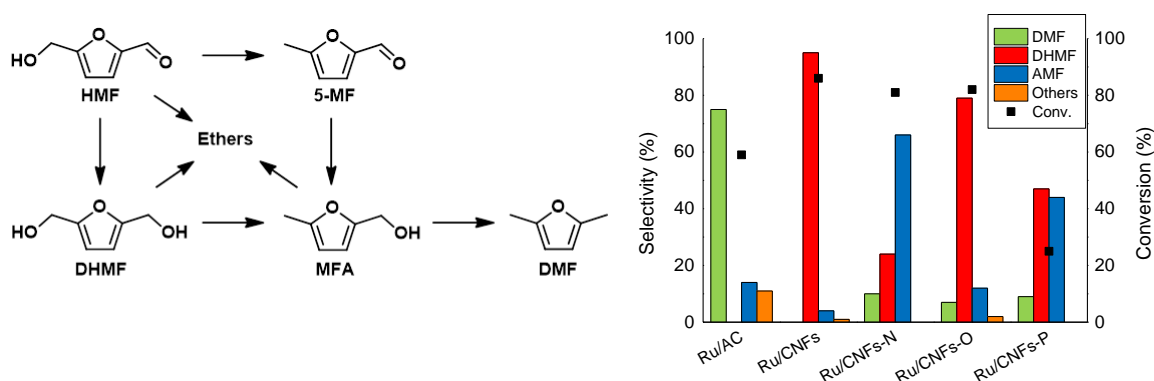


Fig 1. a) Scheme of the HMF hydrogenation and b) catalytic results at 150 °C and 20 bar of H₂.

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References

- [1] J. B. Binder et al., *J. Am. Chem. Soc.* **131** (2009) 1879
 [2] Y. Romàn-Leshkov et al., *Nature* **447** (2007) 982

O-10: Biogas purification process by adsorption on activated carbon

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The adsorption of hydrogen sulphide is one of the most widely used treatment technologies in various industrial sectors, such as the refining of refinery gas, the standardization of natural gas and, in recent years, the desulphurisation of biogas produced from biomass. In this last application, adsorption plays an important role as it allows a high removal efficiency even for very low hydrogen sulfide concentrations.

The adsorption operation is based on the transfer of the target compound from a gaseous stream to a suitable solid phase in contact. For H₂S removal typically a chemical adsorption process is used which allows to selectively remove this compound by virtue of a reaction with the solid phase surface. However, physical processes can benefit of a more effective regeneration of the exhaust material [1].

The present work is focused on both physical and chemical adsorption of low H₂S concentrations in the feed on microporous activated carbon sorbent and it was carried out on model gas mixtures, containing in addition N₂, O₂ and H₂O [2].

The microporous carbon was characterized in terms of granulometry, specific surface area and pore size distribution.

The study of the adsorption process was carried out in a fixed bed reactor under different operating conditions, and the effect of gas flow rate, the mass of adsorbent, the composition of the gaseous mixture, humidity of the gaseous mixture and pre-adsorbed moisture was studied and some optimal conditions were identified. The removal efficiency was evaluated by monitoring over time the concentration of hydrogen sulfide at the outlet of the packed column. The experimental activity has been supported by the identification and application of the most appropriate theoretical models, in order to understand the various phenomena involved in a separation process that is on the whole rather complex.

Reactive adsorption tests have shown that the adsorbing capacity of activated carbon is increased by the presence of water, the presence of oxygen and their combined effect. In particular, in the latter case, the adsorbing capacity is more than tripled compared to that typical of purely physical adsorption.

Keywords: *adsorption, hydrogen sulfide, activated carbon.*

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References

- [1] D. M. Ruthven. *John Wiley & Sons, New York* (1984)
- [2] Bandosz, T. J. *J. Colloid Interface Sci.* **246** 1 (2002)

O-11: Synthesis of Defective TiO₂ Materials for Hydrogen Production

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Titanium dioxide is a semiconducting oxide employed in several fields. Photocatalytic water splitting for hydrogen production is one of its most relevant energy applications. In order to enhance specific functional properties of TiO₂ different strategies are investigated, including the introduction of dopants or structural defects (Ti³⁺, oxygen vacancies) [1, 2].

The present work is addressed to synthesize stable TiO_{2-x} materials with a controlled population of defects, starting from hybrid chemical gels in which titanium is involved in a charge transfer complexation equilibrium with an organic compound [3]. The hydrolytic sol-gel procedure and the following thermal treatments of the gel in mild conditions have synergistic effects in determining the characteristics of the final product. Gel-derived TiO₂ samples annealed in different atmospheres have a defective structure without evidence of surface Ti³⁺, as verified by XPS spectroscopy, but featuring carbon species derived from the organic component. Graphitic carbon appears to form a heterostructure with TiO₂, affecting its electronic properties and electronic structure, investigated by XPS, EPR and THz spectroscopy. The materials exhibit a grey or black color, associated with a wide visible light absorption.

Their photocatalytic activity was tested in hydrogen generation using glycerol as electron donor (photoreforming), without the addition of noble metals or other co-catalysts. They show highly significant H₂ evolution rates under both UV irradiation (up to about 400 μmol h⁻¹ g⁻¹) and visible light (200 μmol h⁻¹ g⁻¹). Recuse tests indicate an almost unchanged H₂ production after 4 h of UV irradiation in 5 reaction cycles, attesting the stability of the photocatalyst activity.

Keywords: *titania, sol-gel, photocatalysis, photoreforming*

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References

- [1] S. Bai, N. Zhang, C. Gao, Y. Xiong, *Nano Energy* **53** (2018) 296
- [2] X. Liu, G. Zhu, X. Wang, X. Yuan, T. Lin, F. Huang, *Adv. Energy Mater.* **6** (2016) 1
- [3] A. Aronne, M. Fantauzzi, C. Imperato, D. Atzei, L. De Stefano, G. D'Errico, F. Sannino, I. Rea, D. Pirozzi, B. Elsener, P. Pernice, A. Rossi. *RCS Adv.* **7** (2017) 2373

O-12: Rheology of PDMS liquid or rubber blends

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In the last years, we have investigated the rheology of liquid or rubber blends of vinyl terminated PDMS. The parallel plate rheometer in rotational or oscillating regime, and the dynamic-mechanical analyzer in compression mode were used and interpretative models proposed. The high molecular weight PDMS lightly crosslinked (well below the gelation point) exhibit an anomalous reduction of zero-shear rate viscosity η_0 and a drop of rheological properties. This was interpreted by means of the formation of isolated crosslinked nanodomains with a free-volume interface due to the short dangling ends [1].

Thereafter, we have shown that a homologous PDMS liquid blend consisting of unentangled short chains in long entangled ones presents an enhancement in rheological properties: increase in viscosity η_0 , relaxation modulus G_0 , dynamic moduli G' and G'' and decrease in compliance $J(t)$. The rheological increase was interpreted by the absorption of short chains at entanglements [2].

The rheology of liquid blends based on PDMS was studied by varying the components molecular weight, the temperature and the concentration of the curing agent. The formulated lightly-cured blends showed interesting unusual behaviors and an interpretative model based on the nanocomposite polymer, the relaxation of dangling chains and the free-volume variation has been proposed [3].

The stress-strain curves, the creep and step-strain, and dynamic-mechanical experiments showed a complex behavior of the PDMS rubber blend formulations. In the dynamic-mechanical experiments, the behavior at small strain can be interpreted on the basis of the classical rubber theory taking into account the increase of the density of the active chains. At higher concentrations of blending agent, we have the adsorption of short chains on entanglement sites involving long dangling chains. In this way, the locking entanglements give rise to the formation of effective crosslinks.

Experimental outcome and proposed mechanisms confirm the interest of rheology behavior of liquid or rubber silicone blends both from an applicative and scientific point of view and stimulate other characterizations (as FTIR, NMR, non-linear rheology measurements) and the development of a theory for nanocomposite liquid polymer blends.

Keywords: Polymer viscoelasticity, rubber blends, polydimethylsiloxane

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References

- [1] V. Villani, V. Lavallata, *Macromol. Chem. Phys.* **218** (2017) 1700037
- [2] V. Villani, V. Lavallata, *Macromol. Chem. Phys.* **219** (2018) 1700623
- [3] V. Villani, V. Lavallata, *European Polymer Journal* **117** (2019) 434

O-13: Azo-based functional polymers for 3D printing

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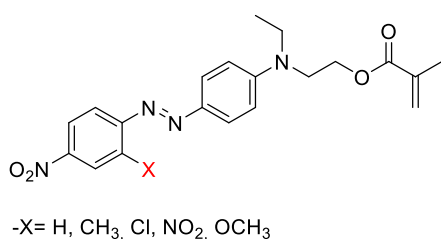
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Additive Manufacturing (AM), which also includes 3D printing, has become increasingly popular^[1], and it can be used into the production processes, as well as in the prototyping. Among the various classes of materials that could be formed through 3D printing techniques, polymers plays a leading role^[2]. The considerable saving of raw materials, the progressive reduction of costs and the high versatility are only some advantages of this new technology. Temperature-, light-, pH-responsive and mechanochromic smart polymers are deeply investigated to this end.

a)



b)

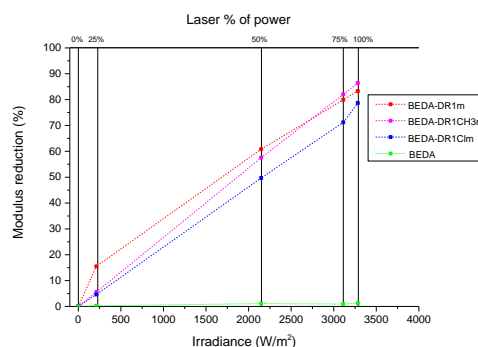


Figure a) Molecular scaffold of the azo monomers; b) Elastic modulus reduction as a function of laser irradiance

In the present work we designed and synthesized different azo compounds to be functionalized with a methacrylate group for Digital Light Processing (DLP). Our attention is focused on these dyes because they give mechanical responses upon irradiation, probably due to the *cis/trans* isomerization. Various substituents (Figure 1a) have been introduced, in *ortho* position to the azo moiety, to tune the monomer/polymer properties, both by steric and electronic effects. We have noticed that the polymers glass-transition temperature (T_g) and the elastic modulus have shown remarkable variations, as a function of the laser power at 532 nm (Figure 1b)

Keywords: 3D printing, azodyes, DLP, smart polymers

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References

- [1] Q. Mu, L. Wang, C. K. Dunn, X. Kuang, F. Duan, Z. Zhang, H. J. Qi, T. Wang, *Additive Manufacturing* **18** (2017) 74-83
- [2] G. Gonzalez, A. Chiappone, I. Roppolo, E. Fantino, V. Bertana, F. Perrucci, L. Scaltrito, F. Pirri, M. Sangermano, *Polymer* **109** (2017) 246-253

O-14: Photocatalyst/polymer aerogels for the removal of water organic pollutants

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At present, the water pollution is the most important problem for the environment sustainability. Some of the recalcitrant pollutants (POPs) and Contaminants of Emerging Concern (CECs) are partially removed from wastewater conventional physical and biological wastewater treatment. Over the last two decades, an intensive research activity has focused on the study and development of semiconductor photocatalyst nanoparticles (NPs) for the removal of non-biodegradable toxic organic compounds from wastewaters (1). Photocatalyst NPs are particularly efficient for the degradation and mineralization of many recalcitrant organic compounds but their real effectiveness can suffer from particles aggregation in water. Moreover post-treatment recovery from the treated water is a main issue since common photocatalysts such as TiO₂ and ZnO present toxicity both to human and aquatic lives. A possible solution could be to fix the catalyst on supporting organic or inorganic materials (2).

These monolithic aerogels are appealing thanks to their high surface area and high macroscopic operability and recoverability. In addition to these characteristics the photocatalyst aerogels should also maintain high photocatalytic performances associated with high absorption capability for organic compounds as well as good chemical and mechanical stability for a potential large-scale use (3).

In this contribution, the photocatalytic activity of different nanocomposites photocatalyst/aerogel based on N-doped TiO₂ and ZnO as catalysts and sPS as polymeric matrix, in the degradation of target water pollutants, such as phenol and toluene is reported and compared with that of the catalysts in powder form (4).

Keywords: *Photocatalysts, polymer aerogels, recalcitrant pollutants, water treatments*

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References

- [1] B.D. Miklos, C. Remy, M. Jekel, G.K. Linden, E.J. Drewes, *Water Research* **139** (2018) 118
- [2] C. Daniel, S. Longo, R. Ricciardi, E. Reverchon, G. Guerra, *Macromol Rapid Commun* **34** (2013) 1194
- [3] C. Daniel, D. Sannino, G Guerra, *Chem Mater* **20** (2008) 577
- [4] V. Vaiano, O. Sacco, D. Sannino, P. Ciambelli, S. Longo, V. Venditto, G. Guerra, *Journal of Chemical Technology and Biotechnology*, 89(8) (2014) 1175

O-15: The periodic table of elements turns 150 years old: how metals have marked and still mark today the civilization of man

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The succession of the various ages, from those of copper to that of bronze, then iron and so on, is dictated by the chemical properties of the various metals and, ultimately, by the periodic table of the elements. The ability expressed by Homo Faber to extract and work the various metals has marked such radical technological evolutions as to be chosen by historians to designate real civilizations. Gold was the first metal used by man, although it could not be used either as a tool or as a weapon. More than any other ancient element, gold has always been associated with a timeless charm. None of the chemical elements discovered by modern science has been able to overcome its supremacy.

Since the time of its discovery, gold has been used for ornamental purposes and only with technological development has it been used also for technical and scientific purposes. For titanium, however, the reverse path was verified, from its essentially technological use it then passed to the aesthetic one. Starting in the 1960s, when titanium became available even for non-military uses, its applications have done nothing but grow and diversify. His fame in architecture is unquestionably linked to the Guggenheim Museum in Bilbao created by the architect Frank Gehry in 1997, while in the titanocromie of Pedefferri we have the combination of art and technology.

Keywords: *homo faber, metals, art*

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POSTER ABSTRACTS

P-01: Study of the catalytic hydrogenation of 5-(hydroxymethyl)furfural

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The production of biomass-derived fuels and chemicals is of great importance for the transition to a more sustainable future. In this context, 5-(hydroxymethyl)furfural (HMF) has been identified as a key precursor for the production of biofuels and high added value chemicals. Indeed, the products obtained by hydrogenation of HMF are potential sustainable substitutes for petroleum-based building blocks used in the production of chemicals. (1,2) Among them, the product of the selective reduction of the formyl group of HMF, the 2,5-bis(hydroxymethyl)furan (BHMF), is widely used as an intermediate for the synthesis of resins, fibers, foams, drugs, polymers and crown ethers. The further reduction of the furan ring leads to the formation of 2,5-bis(hydroxymethyl)tetrahydrofuran (BHMTHF), which can be used as green solvent and monomer. (2) In this work, the catalytic hydrogenation of HMF has been investigated over three supported Pd heterogeneous catalysts. Two of them were made of palladium supported on carbon with different metal loadings, 1 and 10 wt%, both being commercial samples. The catalyst consisting of palladium supported on γ -alumina, Pd/ γ -Al₂O₃ 1 wt%, was prepared in the lab through the so-called "sol-immobilization" method (3). The reactions were performed in liquid phase using water as the solvent, working in both batch (stainless steel autoclave) and continuous-flow (H-Cube Mini, developed by ThalesNano Inc.) reactors. The effect of the main reaction parameters, such as temperature, hydrogen pressure and reaction time/contact time has been investigated in detail. The obtained results clearly show the importance of the reaction set-up in order to enhance the selectivity toward an intermediate product such as BHMF. Indeed, by working at 90°C and 50 bar of hydrogen over the Pd/C 10 wt% catalysts, the selectivity of BHMF achieved was up to 77% by choosing the optimal contact time in the flow reactor. Some by-products given by the subsequent hydrogenolysis, hydrogenation and ring opening reactions of the main products were identified in the reaction mixture by GC-MS. According to the results obtained, a reaction pathway that needs future investigation has been proposed.

Keywords: *HMF, palladium catalyst, hydrogenation, continuous-flow reactor*

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References

- [1] Li, H., Fang, Z., Smith, R.L., Yang, S. Prog. Energy Combust. Sci **55** (2016) 98
- [2] L. Hu, L. Lin, Z. Wu, S. Zhou and S. Liu, Renew. Sustain. Energy Rev **74** (2017) 230
- [3] Villa, A., Campione, C. & Prati, L., Catal. Lett. **115** (2007) 133

P-02: Biosourced Polymers and Lignocellulosic Materials for Eco-Friendly Electrochemical Energy Conversion and Storage Devices

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In the last 10 years, applied research on electrochemical energy conversion and storage devices market has rapidly grown. In order to lower the cost and reduce the environmental impact of these systems, efforts must be devoted to reduce the amount of inactive components in the cell, to substitute synthetic polymer binders/separators and organic solvents with low-cost and biosourced materials and to develop new eco-friendly processes for the manufacture of cell components (both electrodes and electrolyte). Here we review the use of paper-making technique and selection of biosourced polymers for manufacturing:

- Bio-inspired all-paper Li-ion polymer cells, constituted by nanoscale-microfibrillated cellulose (NMFC)-bonded paper-electrodes, and NMFC-reinforced polymer electrolytes. The use of NMFC as filler/binder leads to produce high performing, safe and extremely flexible electrolytes for LiBs. No organic solvents or synthetic polymer binders are used during the entire electrode/electrolyte/cell preparation process (1).
- Cellulosic membranes as separators/electrolytes for post-lithium technologies, such as Na-ion and Li-S (2), thus demonstrating the possibility of obtaining “truly green” energy storage devices in the near future.
- Paper-based flexible electrodes and electrolytes for third generation solar cells (3), useful to lower oil-derived components and typical temperatures used to electrodes processing.
- Aqueous solar cells, where biosourced polymeric matrices are used for the preparation of hydrogel electrolytes (4).

This materials platform is promising not only for the sustainable manufacture of energy devices components, but also for their processability at the end of life.

Keywords: *biosourced, battery, solar cell, sustainability, cellulose*

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[1] L. Zolin, J.R. Nair, D. Beneventi, F. Bella, M. Destro, P. Jagdale, I. Cannavaro, A. Tagliaferro, D. Chaussy, F. Geobaldo, C. Gerbaldi, *Carbon* **107** (2016) 811

[2] F. Colò, F. Bella, J.R. Nair, M. Destro, C. Gerbaldi, *Electrochim. Acta* **174** (2015) 185

[3] F. Bella, D. Pugliese, L. Zolin, C. Gerbaldi, *Electrochim. Acta* **237** (2017) 87

[4] F. Bella, S. Galliano, M. Falco, G. Viscardi, C. Barolo, M. Grätzel, C. Gerbaldi, *Green Chem.* **19** (2017) 1043

P-03: Au/Pd-DECORATED ELECTROSPUN MEMBRANES AS CATALYTIC SYSTEMS FOR SELECTIVE HMF OXIDATION

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The need to decrease the dependence on fossil resources has led researchers to look for bio-derived chemicals to replace the already existing ones. For instance, 2,5-furandicarboxylic acid (FDCA) has been pointed out as the bioderived counterpart of terephthalic acid for the synthesis of polyesters, since FDCA could be obtained by means of selective oxidation of the bio-derived 5-hydroxymethylfurfural (HMF). HMF oxidation to FDCA is generally performed under batch conditions, being supported metal nanoparticles (NPs), such as alloyed Au/Pd NPs, the most studied catalysts [1]. On the other hand, the possibility to perform such reaction under continuous conditions has not yet been extensively studied. Recently, polymer/inorganic composites have been demonstrated to be useful tools in several industrial fields, such as catalysis, considering their low cost and tunable hydrophobic/hydrophilic properties. Among all the paths to produce such composites, electrospinning represents a useful strategy to prepare catalytic membranes which can be used in continuous processes for biomass valorization. In this work, the production of Au/Pd NPs decorated polymeric/inorganic membranes have been studied. Preformed NPs were directly electrospun using stable suspension containing the metals, TiO₂ and the polymer. Two polymers were utilized in the process, polyacrylonitrile (PAN) [2] and nylon 6,6 [3]. Both suspensions were successfully electrospun and the obtained membranes have been fully characterized and tested as catalyst in the batch HMF oxidation under aqueous conditions. Smooth filaments containing agglomerates were detected in all samples by SEM, while TEM images seem to suggest that the inorganic components are coated by a polymer layer. Catalyst screening showed that both membranes are active in HMF oxidation, and among them, the Nylon-based one leads to higher FDCA yield. This difference in activity has been ascribed to the different glass transition temperature (T_g) of the two polymers: indeed, Nylon T_g (around 62°C) is lower than the reaction temperatures, thus tentatively leading to an improved accessibility of the catalytic active sites with respect to PAN, whose T_g (around 100°C) is higher or at least close to the testing conditions.

In conclusion, this work showed that electrospinning is a suitable technique to obtain catalytically active membranes, whose activity, being dependent on the active site exposure, is strictly correlated to the possibility of operating at temperature above the T_g of the polymeric component.

Keywords: *HMF conversion, Catalytic membranes, Electrospinning, Nanoparticles*

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References

- [1] A. Lolli, et al., *Appl. Catal. A Gen.* **504** (2015) 408
- [2] C. Gualandi, et al., *Adv. Polym. Sci.* **267** (2015) 87
- [3] E. Maccaferri, et al., *Composites Part B*, **166** (2019), 120

P-04: Dextrin-based nanosponges for environmental applications

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Pollution poses a serious threat to the future of the environment. The spreading of contaminants, such as heavy metals and several toxic organic compounds, through the ecosystem exposes all living beings to a multitude of deadly diseases. At the same time, the increase of the environmental concentration of naturally occurring compounds can irreversibly damage the delicate ecosystem balance. Starting from the 20th century, anthropogenic activities have significantly changed the global nitrogen cycle, causing an environmental increase of nitrate levels. Excessive nitrate concentrations have been found to be toxic in human, cattle, marine animals, and causing eutrophication, generating a growing concern. For this reason, several regulations and guidelines have been developed in advanced countries, regarding the treatment of municipal and industrial wastewater before their disposal [1]. Among the treatments reported, the use of ion exchange resins is a simple, effective, and low cost method. However, despite the possibility to regenerate the resin after the treatment, being the resin made of synthetic polymers, it represents a waste after its life cycle [2]. The possibility to synthesize a performing ion exchange polymer starting from green sources would be beneficial for the disposal of the exhausted material.

Cyclodextrins and linear dextrins are well known for their outstanding ability to form inclusion complexes with a wide series of organic compounds, including organic pollutants. Crosslinked dextrin polymers, commonly referred to as “Nanosponges” [3], show even higher adsorption performances. In addition to organic pollutants, nanosponges can bind either positively or negatively charged chemical species, depending on the nature of the crosslinker.

In this study, novel dextrin-based nanosponges bearing negatively charged citric acid crosslinking units for the retention of heavy metal cations and maltodextrin-based positively charged ether nanosponges for the removal of nitrate contaminants are presented and discussed.

Keywords: *cyclodextrin nanosponge, maltodextrin nanosponge, heavy metal adsorption, nitrate adsorption*

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References

- [1] D. E. Canfield, A. N. Glazer and P. G. Falkowski, *Science* **330** (2010) 2
- [2] S. Samatya, N. Kabay, Ü. Yüksel, M. Arda and M. Yüksel, *React. Funct. Polym.* **66** (2006) 1206
- [3] F. Trotta and A. Mele, *Nanosponges: Synthesis and Applications*, Wiley-VCH (2019)

P-05: Bio adipic acid production from sodium muconate and muconic acid

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The limited fossil resources availability and the climate change are raising wide interest between the scientific researchers and the civil community. Among the several subjects, the production of bulk chemicals from renewable sources is one of the great challenges that researchers are facing. Concerning this theme, adipic acid (AdA) production from wood biomass is one of the most important topics due to the large amount of AdA consumed and the market growth, in particular for the production of polyamides (Nylon 6,6). Bio-AdA can be produced from t,t-muconic acid (t,t-MA), a metabolic intermediate of the catechol ortho-cleavage pathway.^[1] In nature, microorganisms displaying this pathway are quite common and they can accumulate at least 13.5 g/l of MA as sodium muconate.^[2] The so produced sodium muconate is then converted to AdA with a heterogeneous hydrogenation chemical reaction. MA coming from the fermenter needs a purification step due to the high purity grade required for the market. The purification process consists in an acidification and crystallization steps, that transform sodium muconate into muconic acid, separating this chemical from all the compounds used in the fermenter. Considering water as hydrogenation reaction media, unfortunately MA is less soluble than sodium muconate. On the basis of these considerations different hydrogenation reactions were performed varying the operating conditions both on muconic acid and sodium muconate. The reaction was performed using mild operating conditions (T= 50°C, P(H₂)=1 bar and metal to substrate ratio=1/200) and home-made catalysts (Pd/AC 1%) prepared by sol-immobilization method^[3] in which the stabilizer (polyvinyl alcohol, PVA) to metal ratio was varied from 0 to 1.2. t,t-MA was fully hydrogenated to AdA in 90 min while for Na-Muc hydrogenation only 1.2PVA catalyst gave 100% yield of sodium adipate. All the home-made catalysts showed an initial activity higher than the commercial Pd/AC 5%. Initial activity was evaluated considering the conversion per unit of time divided by the moles of active metal. Catalyst characterization revealed the presence of higher amount of Pd in 0.65PVA and 1.2PVA samples, sign of a possible higher activity.

Keywords: *adipic acid, heterogeneous catalyst, Pd/AC*

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References

- [1] Kaneko, Y. Ishii, K. Kirimura, *Chem. Lett.* 40 (2011) 381
- [2] D.R. Vardon, M.A. Franden, C.W. Johnson, E.M. Karp, M.T. Guarnieri, J.G. Linger, M. J. Salm, T. J. Strathmann, G. T. Beckham, *Energy Environ. Sci.* 8 (2015) 617
- [3] R. Arrigo, S. Wrabetz, M.E. Schuster, D. Wang, A. Villa, D. Rosenthal, F. Girsgdies, G. Weinberg, L. Prati, R. Schlögl, *Phys. Chem. Chem. Phys.* **14** (2012) 10523

P-06: Synthesis and characterization of innovative materials from renewable resources

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The interest of academia and industry for the use of renewable resources, in particular lignocellulosic biomasses, as an alternative to oil for the production of energy, fuels but also of new chemicals, has grown in recent years.

In this research new biopolymers and nanocomposites were synthesized using saccharides as feedstocks and their application in the conservation of cellulosic artefacts was studied. Saccharides were chosen as starting materials in order to introduce in the final products units with a structure similar to that of the cellulosic substrate and the synthetic methodologies were selected taking into account the principles of the Green Chemistry and the future application in the preservation of the cultural heritage.

Allyl saccharide monomers were synthesized using allyl bromide to functionalize trehalose, obtaining products whose degree of functionalization varies according to the molar ratio between the reagents [1].

These bio-based monomers were used for the synthesis of vinyl acetate copolymers and three different molar ratios between the two monomer units were selected to evaluate the influence of the composition on the chemical and consolidating properties.

At the end, the vinyl acetate copolymers were hydrolysed to the corresponding vinyl alcohol copolymers in order to obtain water soluble products suitable to be used in the treatment of wood and paper and to prevent the hydrolysis of the vinyl acetate groups after the application on the degraded material.

New nanocomposites based on TiO₂ (in the anatase form) and allyl saccharide/vinyl acetate copolymers were also synthesized by grafting the copolymers on properly functionalized nanoparticles. The nanocomposites were designed in order to study new products capable to performing an antifungal action towards cellulosic substrates.

All the products obtained after polymerization and after hydrolysis were characterized using FT-IR and ¹H-NMR spectroscopy and preliminary tests were carried out to evaluate the performance of the products as consolidants for cellulosic artefacts.

Keywords: *biopolymers, renewable resources, consolidants*

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References

[1] A. Papacchini, M. R. Telaretti Leggieri, L. Zucchini, M. A. Ortenzi, F. Ridi, D. Giomi, A. Salvini, *Royal Society Open Science* **5** (2018) 171313

P-07: New Synthesis of Benzothiophene Derivatives by Pd-Catalyzed Oxidative Carbonylation of (2-Alkynyl)(methylthio)benzenes

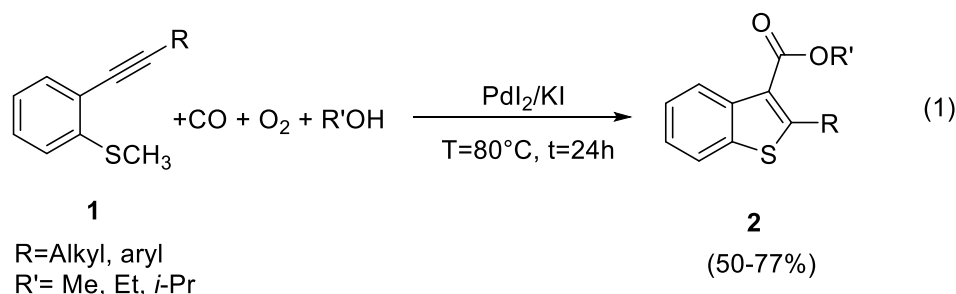
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It is known that carbonylation reactions are particularly efficient and convenient processes for the direct synthesis of carbonylated heterocycles^[1].

In the present communication we report that benzothiophene derivatives **2** can be conveniently synthesized by palladium-catalyzed intramolecular carbonylative heterocyclization of (2-alkynyl)(methylthio)benzenes **1** (Eq.1).

Benzothiophenes are an important classes of *S*-heterocycles in pharmaceutical science. They are used in a variety of drugs, pesticides and biologically active compounds^[2].



Reactions are carried out at 80 ° C, in alcoholic solvents (R'=Me, Et, *i*-Pr.), in the presence of PdI₂ (1 mol%) in conjunction with KI (20 mol%) and under 40 atm of a 1: 4 mixture of CO / air. Benzothiophene derivatives **2** are obtained in good yields (50-77%).

Keywords: *benzothiophenes, carbonylation, cyclization, palladium.*

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References

- [1] B. Gabriele, R. Mancuso, G. Salerno, *Eur. J. Org. Chem.* (2012) 6825
 [2] (a) L. Berrade, B. Aisa, M. J. Ramirez, S. Galiano, *J. Med. Chem.* **54** (2011) 3086
 (b) H. F. Guo, H. Y. Shao, Z. Y. Yang, S. T. Xue, *J. Med. Chem.* **53** (2010) 1819
 (c) I. Jarak, M. Kralj, L. Suman, *J. Med. Chem.* **48** (2005) 2346
 (d) D. H. Boschelli, J. B. Kramer, S. S. Khatana, *J. Med. Chem.* **38** (1995) 4597

P-08: Innovative bifunctional catalytic system for methyl methacrylate synthesis: the peculiar role of gallium

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Methyl methacrylate (MMA) is the monomer for polymethyl methacrylate manufacture. The state of art in MMA production is the Alpha process (1) which use formaldehyde (FA) for the hydroxy-methylation/dehydration of methyl propionate (MP), the latter produced by ethylene hydroformylation. In order to achieve a more sustainable MMA manufacture, MP should be produced from bio-based molecules such as 1,2-propanediol (2) avoiding the utilization of FA (known carcinogen) in favor of a one-pot approach which consists in its in-situ production by methanol (MeOH) dehydrogenation. Basic catalysts are known to catalyze MeOH dehydration at high temperatures (3) therefore preliminary studies have been conducted with MgO: the main reaction in the temperature range 350-450°C is ketonization, which produces 3-pentanone (3-P), CO₂ and MeOH. At 500°C MgO become much more active for MeOH dehydrogenation and hydroxy-methylation, but the desired product is never obtained with satisfying yield due to consecutive H-transfer reactions which transform MMA into methyl isobutyrate (MIB), methacrolein (MA), isobutyraldehyde (IBA), 2-methylpropanol (2-MP) and isobutylene (the latter is formed from 2-MP dehydration). The results obtained over MgO suggest that an effective catalyst should possess a strong dehydrogenating activity at low temperatures in order to produce a large excess of FA to minimize parasitic reactions. Starting from this hypothesis we investigated the catalytic activity of β -Ga₂O₃ and found that is much more selective than MgO for the desired reaction. Since Ga is a rare and expensive element, we investigated its role as promoter for MgO and prepared two bifunctional systems with Mg-to-Ga ratio equal to 20 and 10. On the basis of our results so far, the best one is the Mg/Ga/O mixed oxide with a Mg/Ga atomic ratio of 10 (X = 34%, MMA Sel.=24%). The presence of Ga not only enhances the dehydrogenating properties at 300-350°C leading to more FA and H₂ but also reduces ketonization to an extent that makes it almost negligible. Indeed, in this case the reaction by-products are mainly those deriving from H-transfer reactions. Finally, combining characterization technics and catalytic results we were able to determine the reaction scheme and minor/major reaction pathways, and assess structure-activity relationships.

Keywords: *methyl-methacrylate, gallium, methanol*

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References

- [1] W. Bauer JR, Methacrylic Acid and Derivatives, Ullmann's Encyclopedia of Industrial Chemistry **23** (2012) 1
- [2] M. Pagliaro, R. Ciriminna, H. Kimura, M. Rossi, C. Della Pina, Angew. Chem. Int. ed. **46** (2007) 4434
- [3] N. Ballarini, F. Cavani, L. Maselli, A. Montaletti, S. Passeri, D. Scagliarini, C. Flego, C. Perego, J. of Cat. **251** (2007) 423

P-09: Ceria-Zirconia as an Effective Support to Stabilize Catalytically Active and Stable Molybdenum Species in the Epoxidation Reaction

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“Molybdenum oxide was dispersed onto the ceria-zirconia support by co-precipitation or wet impregnation, using ammonium eptamolybdate tetrahydrate as precursor. The Ce to Zr molar ratio was fixed equal to 3, the nominal Mo content of 6.6 wt.% was selected to be under the value of the reported monolayer capacity for molybdenum oxide. The effect of the synthesis route on the activity of the MoOx was assessed by using either urea or ammonia as precipitating agent. The activity and reusability of MoOx/Ce_{0.75}Zr_{0.25}O₂ catalysts were assessed in cyclooctene epoxidation with *cumene hydroperoxide* to investigate the differences that arise from the preparation route and from specific Mo-support interactions. X-ray powder diffraction patterns revealed that urea promotes the formation of hydrated ceria oxycarbonate, which can compromise the attainment of the ceria-zirconia solid solution and the homogeneous distribution of active MoOx species. Surface acidic properties, as studied by IR spectroscopy using NH₃ as probe molecule, revealed that the strength and type of Lewis acid sites are also influenced by the synthesis route. Larger amount of surface isolated molybdenyl species acting as Lewis acid sites is likely the crucial feature shown by samples prepared using ammonia and positively affecting their catalytic activity in the cyclooctene epoxidation reaction. A very strong evidence that these materials act as real heterogeneous catalysts was obtained by analysis of reaction solution and leaching test.

Keywords: *molybdenum-containing catalysts; epoxidation; ceria-zirconia solid solution*

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P-10: Realization of a pilot plant for the on-line monitoring of a water network that focuses on the disinfection product (DBP) for human consumption.

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Chlorination is the most cheap and widespread water purification treatment in Italy. This treatment produces some toxic by-products (DBP). The predominant chlorine disinfection by-products are the trihalomethanes (THMs) whose limits are imposed by law. This work describes the realization of a pilot implant for continuous qualitative and quantitative monitoring, in situ, remotized, for the analysis of the main chemical and chemical-physical parameters of drinking water (pH, conductivity, total organic carbon and etc.) with particular focus on by-products that form during the process of sanitation of the water that is destined to human consumption.

The pilot plant project includes:

- three units that measure the main parameters: turbidity, conductivity, free residual chlorine, pH and temperature;
- a gas chromatograph that measures the concentration of THMs and other volatile organic compounds (VOC);
- an ion chromatograph that measures the concentration of ions precursors of THMs (halides) and other ionic by-products of disinfection;
- a NDIR based system to estimate the content of Total Organic Carbon (TOC);
- a potentiometric system to determine fluoride concentrations.

Keywords: *DBP, drinking water, pilot plant*

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References

- [1] Black and Veatch Corporation, *White's Handbook of Chlorination and Alternative Disinfectants*, 5th ed., Wiley, New Jersey, USA (2011)
- [2] Minear R.A. e Amy G.L., *Disinfection by-products in water treatment*, Lewis, Boca Raton, Florida (1995)
- [3] Sarno V. e Federiconi L., *Il trattamento delle acque per usi vari*, Hoepli, Milano (2012)

P-11: Synthesis platinum containing PLLA macrocomplex and catalytic performances in hydrogenation of α,β -unsaturated carbonyl compounds

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Development of heterogenous catalyst is one of the breakthroughs of industrial chemistry. In this concise study, we described the synthesis of poly(lactide) carboxylic end-capped macroligand functionalized with a bipyridine system¹⁻⁴ bonded to a platinum center.

Platinum based macrocomplex was used to perform a selective catalytic hydrogenation of α - β unsaturated carbonyl compounds⁵. Catalytic system studied has proved a high selectivity for double bond hydrogenation of 2-Cyclohexen-1-one (up to 99%) and for the production of 1-butanol from But-2-enal. This catalysts showed a high solubility in reaction media using reaction condition but a total insolubility at room temperature. This behavior is ascribed to the polymeric tailoring and induced the same activity of an homogenous system together with the high recyclability of a heterogenous one.

Keywords: *PLLA, heterogenous catalysis, platinum*

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References

- [1] Giachi, G.; Frediani, M.; Oberhauser, W.; Passaglia, E. *Journal of Polymer Science Part A: Polymer Chemistry* **49** (2011) 4708
- [2] Oberhauser, W.; Evangelisti, C.; Jumde, R.; Petrucci, G.; Bartoli, M.; Frediani, M.; Mannini, M.; Capozzoli, L.; Passaglia, E.; Rosi, L. *Journal of Catalysis* **330** (2015) 187
- [3] Oberhauser, W.; Evangelisti, C.; Jumde, R. P.; Psaro, R.; Vizza, F.; Bevilacqua, M.; Filippi, J.; Machado, B. F.; Serp, P. *Journal of Catalysis* **325** (2015) 111
- [4] Petrucci, G.; Oberhauser, W.; Bartoli, M.; Giachi, G.; Frediani, M.; Passaglia, E.; Capozzoli, L.; Rosi, L. *Applied Catalysis A: General* **469** (2014) 132
- [5] Bartoli, M.; Rosi, L.; Petrucci, G.; Armelao, L.; Oberhauser, W.; Frediani, M.; Piccolo, O.; Rathod, V. D.; Paganelli, S. *Catalysis Communications* **69** (2015) 228
- [6] Bartoli M., Rosi L., Mini B., Petrucci G., Passaglia E., Frediani M., *Applied Science*, (2019) submitted

P-12: Microwave-assisted catalytic conversion of cellulose: synergistic effect of sulfated zirconia and zeolites

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The demand for renewable sources has steadily increased over the last two decades, though chemical industry still runs mainly with fossil feedstocks. Biomass has been recognized as a worldwide renewable source of fixed carbon for the production of platform chemicals. In this context, residual lignocellulosic material could be used as the substrate for zero-waste cascade protocols into valuable chemicals, one of the hottest goals of current research. 5-hydroxymethylfurfural (HMF), derives from the conversion of cellulose through the dehydration of fructose. HMF is a key intermediate for the production of fine chemicals, such as 2,5-furandicarboxylic acid (polyester precursor), 2,5-dimethylfuran, (potential biofuel), and gamma-valerolactone, used as fuel additive and green solvent. [1]

Usually, the synthesis of HMF is performed in strong acidic media (as sulphuric acid) starting from fructose, glucose or, less approached, from cellulose. [2]

Herein we report a sustainable HMF synthesis mediated by microwave (MW) irradiation, starting from microcrystalline cellulose, in the presence of heterogeneous acid catalysts. The focus of the work is the removal of organic solvents and strong acids by means of synergistic effects of sulfated zirconia (ZS from 2 wt% to 8 wt%) and zeolites (Y or β). In order to better understand the correlation activity/acidity, different conditions (time, temperature and catalyst loading) were screened, optimizing the composition of the mechanical mixture. Furthermore, the effects of planetary ball-milling were investigated on either the formation of a more reactive catalytic system or the amorphisation of cellulose.

The optimized protocol improved the overall reaction (hydrolysis, isomerization and dehydration) leading to nearly complete conversion and high selectivity and yield in HMF in only one hour. XRD characterization was performed on both the substrate and the catalysts, pre- and after-reaction. Complete characterization of the products was performed by GC-MS analysis.

Keywords: *cellulose conversion, HMF, microwave, heterogeneous catalysis.*

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References

- [1] S.S. Chen, T. Maneerung, D.C.W. Tsang, Y. Sik, C. Wang. *Chem Eng J.* **328** (2017) 246
 [2] X. Tong, Y. Ma, Y. Li. *Appl. Catal. A* **385** (2010) 1

P-13: Eco-design for photovoltaic materials

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Nowadays an industrial process must be planned taking into account not only its efficiency and its cost but also its environmental impacts.

The industrial chemist in addition to process optimization, safety evaluation, product and efficiency development and improvement is progressively more involved in the eco-design of a product and more in general in environmental and sustainability issues.

Solar power is one of the fastest growing industries in the world but although it is referred as a green energy source, it causes its own negative externalities. The technology behind solar energy production is not yet sustainable for different reasons: (i) critical raw materials exploited into the device are threatened by low availability and supply shortage; (ii) the synthesis of photovoltaic materials have to be optimized in order to reduce solvent volumes and waste production; (iii) the waste management, in particular for emerging PV technologies, is not mature yet.

My PhD project, Applying Circular Economy to Innovative Materials for Energy, is intended to design materials for photovoltaic applications exploiting waste materials and/or green chemistry guidelines. The final goal of my project is to contribute to have a more sustainable renewable energy.

Keywords: *solar energy, sustainability, critical raw materials, green chemistry*

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References

- [1] C.R. Clemmer, T.P. Beebe Jr., *Science* **251** (1991) 640
- [2] J. Xhie, K. Sattler, M. Ge, N. Venkateswaran, *Phys. Rev. B* **47** (1993) 15835
- [3] R. Hentschke, B. Schurmann, J. Rabe, *J. Chem. Phys.* **96** (1992) 6213

P-14: 3D printing of Photoresponsive Polymers for Microrobotics

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Manipulating objects at the micro- and nano-scale is an open fascinating challenge that scientists are addressing by proposing different approaches, obtaining machines with basic or complex functions. Combining shape-changing polymers that respond to optical stimuli with 3D structuration at the microscale, we demonstrated synthetic microrobots entirely powered by light with a non-invasive and remote control. The arbitrary design allows to reproduce diverse animal and even humanoid tasks as walking and swimming but also the ability to grab and manipulate objects - overcoming natural limitations present at such small scale.

The devices have been realized by Liquid Crystalline Networks (LCNs) which allow to perform different movements depending on their molecular alignment and, controlling their elastic deformation by light, wireless activation of the micro-machines obtained. A micro walker was demonstrated to advance on different substrates; [1] a micro swimmer to be prompted in liquids by structured light; a micro hand to catch micro objects by external light control and even autonomously, depending on the target optical properties. [2]

All the aspect related to the material characterization, starting from the liquid crystalline properties of the monomeric mixtures to the mechanical behaviour of polymeric materials will be presented to demonstrate how, starting from simple mesogenic monomers, it is possible to create polymeric microrobots with different abilities.

Acknowledgements: The research leading to these results has received funding from Ente Cassa di Risparmio di Firenze (2017/0713) and “Network Italiano di ricerca Extreme Light Infrastructure ELI- Italy”

Keywords: *Liquid Crystalline Polymers, Soft Robotics, 3D structuration, Photolithography*

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References

[1] H. Zeng *et al.*, *Adv. Mater.* **27** (2015) 3883

[2] D. Martella *et al.* *Adv. Mater.* **29** (2017) 1704047

P-15: Chemical and Morphological Identification of Microplastics in the Marine Environment

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The plastics industry generates roughly 400 million tons of virgin plastic each year, part ending-up in nature due to production, consumption, recycling and disposal of plastic processes. In recent years, a growing environmental concern regarding microplastics emerged, i.e. small fragment of plastic materials. It was shown that these contaminants are widespread and ubiquitous within the marine environment, showing high damage potential to the biota. Their small dimensions make them bioavailable to organisms throughout the food chain. Microplastics also behave as substrates on which the organic pollutants present in the water adhere, thus conveyed and ingested, introducing these substances at the base of the food chain: high potential for bioaccumulation [1]. The European Chemical Agency (ECHA) has adopted a working definition for microplastics as *Any polymer, or polymer-containing, solid or semi-solid particle having a size of 5mm or less in at least one external dimension.*

The present research is part of the monitoring program of the Marine Strategy Directive 2008/56/CE, implemented in Italy with the legislative decree n. 190/2010, for the analysis of microplastics. Water samples were taken from Arpa Campania (ARPAC) for the analysis of microplastics in four stations of the Campania coast and specifically in: Gulf of Naples, Cilento, Volturno river and Gulf of Salerno. For the determination of the microplastics, the legislation provides only the sampling of the screen of a manta net and a visual analysis to the stereomicroscope, this method according to data of scientific literature has the disadvantage of identifying being positive in a percentage that varies between 20% and 70% [2]. A chemical characterization of microplastics samples was conducted, to verify the presence of false positives and optimizing the procedure for identifying ARPAC microplastics samples. This characterization is carried out by RAMAN spectroscopy analysis and aims to identify the polymeric matrix of the collected fragments. The determination of the polymer, to which the fragments belong, is fundamental to evaluate the preponderance of some classes of polymers to identify and manage both the health risks associated with the ingestion and the impact the microplastics have on the marine environment.

Keywords: *Microplastics, Marine Strategy, Raman, health risks*

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References

- [1] C. Cole, P. Lindeque, C. Halsband, T. S. Galloway, *Marine Pollution Bulletin* **62** (2011) 2588
- [2] L. Frère, I. Paul-Pont, J. Moreau, P. Soudant, C. Lambert, A. Huvet, E. Rinnert, *Marine Pollution Bulletin* **113** (2016) 461

P-16: Effects of supports for Nickel based catalysts in Methane Dry Reforming

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Methane dry reforming (MDR) is a promising process for syngas production through the valorisation of two of the main Greenhouse gases. The catalyst plays a key role in this process, as it must encourage syngas formation by limiting coke deactivation [1, 2].

This work focusses on the effect of different supports in the activity and stability of nickel-based catalysts. In particular, MDR has been studied at relatively low temperature, 500 °C, to deeply investigate how the support influences the reaction pathway.

Ceria, zirconia, alumina, silica and titania were considered and the morphological and structural features of the materials were analysed via N₂-physisorption, AAS, TPR, XRD, CO₂-TPD, and SEM techniques. Moreover, by analysing the spent catalysts, it was possible to identify the causes of catalysts deactivation.

It was found that support has a strong effect on the activity and stability of the nickel-based catalyst. Titania based catalyst didn't show any activity for MDR due to the low surface area and the irregular dispersion of Ni nanoparticles, as demonstrated by SEM analysis.

In the case of silica, despite the initial activity, the collapse of the structure and the presence of a strong basic site had caused the formation of carbon nanotubes that deactivate the catalyst. Zirconia based catalyst, as well, deactivated in time but in this case, nickel sintering was the cause. On the contrary, ceria and alumina catalysts remain stable for the 18 hours of reaction; analysing the spent catalyst via SEM and Raman spectroscopy, two different behaviours were observed. NiCe was completely free from carbon deposits due to its strong redox ability, meanwhile NiAl was covered by carbon nanotubes. Nevertheless, conducting the reaction for 70 hours, NiAl remained stable while NiCe gradually deactivated. Concluding, NiAl was the most stable catalyst. The catalyst is not as active as the metallic form, but it keeps stability in time. This effect relates to the strong interaction between nickel and alumina.

Keywords: *Ni catalysts; methane dry reforming; catalysts' deactivation; support effect*

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References

[1] C Abdulrasheed A, Jalil AA, Gambo Y, Ibrahim M, Hambali HU, Hamid MYS. A review on catalyst development for dry reforming of methane to syngas: Recent advances. *Renew Sust Energ Rev* **108** (2019) 175

[2] Zhang G, Liu J, Xu Y, Su Y. A review of CH₄CO₂ reforming to synthesis gas over Ni-based catalysts in recent years (2010–2017). *Int J Hydrogen Energy* **43** (2018) 15030

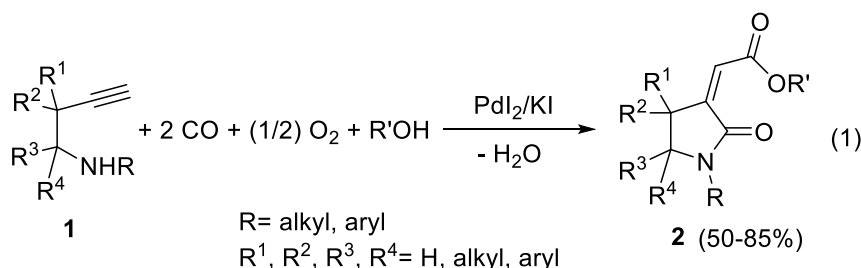
P-17: Carbonylative Regio- and Stereoselective Synthesis of (Z)-2-(2-Oxopyrrolidin-3-ylidene)acetates

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The γ -lactam core is an important structural motif in a large number of biologically active natural products and synthetic small pharmaceutical molecules for the potential treatment of cancer, cardiac arrhythmia, hypertension and disorders of the central nervous system.¹

In this contribution, we report a new synthesis of (Z)-2-(2-oxopyrrolidin-3-ylidene) acetates **2** by regio- and stereoselective PdI₂-catalyzed oxidative cyclocarbonylation-alkoxycarbonylation of N-substituted-3-yn-1-amines **1**, according to Equation 1. The structure of a representative product (R¹ = R² = R³ = R⁴ = H, R⁵ = Ph, R' = Me) has been confirmed by XRD analysis



Reactions are carried out in alcoholic solvents (R'=Me, Et, *i*-Pr, *t*-Bu), under relatively mild conditions (100°C under 40 atm of a 4:1 mixture of CO-air for 2 h) using 2 mol% of PdI₂, in conjunction with 20 mol% of KI, to give **2** in satisfactory good yields (50-85%)

Keywords: *carbonylation, γ -lactam, palladium, regioselective synthesis, stereoselective synthesis.*

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References

[] (a) G. F. Vafina, R. V. Kuz'mich, F. Z. Galin, M. S. Yunusov, *Chemistry of Natural Compounds* **49** (2013) 4; (b) S. Rachid, L. Huo, J. Herrmann, M. Stadler, B. Köpcke, J. Bitzer, R. Müller, *ChemBioChem* **12** (2011) 922; (c) R. R. Manam, S. Teisan, D. J. White, B. Nicholson, J. Grodberg, *J. Nat. Prod.* **68** (2005) 240

P-18: Effect of the dopants on the α -Fe₂O₃/rGO nanocomposites as anode materials for sodium-ion batteries

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Relying on the great abundance of sodium, its low cost and similar chemistry to lithium, sodium-ion batteries (SIBs) represent a potential alternative to lithium-ion batteries (LIBs) in the field of grid-scale energy storage. However, producing sustainable and high-performance anode materials with suitably tailored physical properties is the crucial factor for the industrialization of SIBs. Good results have been obtained by using composite electrode materials based on graphene and transition metal oxides (TMOs). Among TMOs, which store Na⁺ ions via conversion reactions, iron oxides are promising candidates thanks to chemical stability, high theoretical specific capacity, easy synthesis, low cost and non-toxicity.

This contribution reports the synthesis of novel composites via a one-step solvothermal approach, a very easy and scalable preparation method. The composites consist of hematite (α -Fe₂O₃) nanoparticles, doped with alio-valent elements, anchored on reduced graphene oxide (rGO). In order to improve the electrochemical performance of the α -Fe₂O₃/rGO composites, both tetravalent and bivalent dopants, such as Ti⁴⁺ and Mn²⁺, are evaluated. Textural, structural and morphological properties of the easily synthesized nanostructures are studied by several complementary analyses to investigate how the presence of the dopant influences the nanostructure, the crystalline phase and the electrochemical activity of the resulting oxide.

The composites are obtained by solvothermal reaction of ferrous acetate, a proper amount of titanium (IV) isopropoxide or manganese (II) acetate tetrahydrate and graphene oxide (GO), prepared by a slightly modified Hummers method. Reaction is carried out in a stainless steel autoclave at 170 °C. It leads to simultaneous deposition of iron oxide nanoparticles and *in situ* transformation of GO to rGO.

The results of the physico-chemical characterization prove the successful incorporation of dopant in the α -Fe₂O₃ lattice. The results of the electro-chemical tests show that both dopants modify the properties of hematite enhancing its electrochemical properties.

Keywords: *doped-Fe₂O₃, reduced graphene oxide, sodium-ion batteries*

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P-19: Transfer hydrogenolysis of aromatic ethers and lignin promoted by the bimetallic Pd/Co catalyst

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One of the major challenges in the catalytic valorization of lignin is the selective cleavage of the C–O bond [1]. Therefore, in order to develop selective catalytic processes for the production of aromatics from lignin, a complete understanding of the molecular aspects of the basic chemistry and reactivity of aromatic ethers is still crucial. A lot of research efforts have been directed to the study of the catalytic hydrogenolysis of benzyl phenyl ether (BPE), phenethyl phenyl ether (PPE) and diphenyl ether (DPE) that are the simplest model molecules of α -O-4, β -O-4 and 4-O-5 lignin linkages.

CTH reactions have recently gained increased attention as an efficient alternative to the direct use of molecular hydrogen by improving the sustainability and economics of hydrogenation reactions [2,3].

In this context, to further explore the enhancement of the palladium activity promoted by other transition metals, the Pd/Co bimetallic catalyst was prepared by using the coprecipitation method and fully characterized by TEM, XRD, H₂-TPR, XPS and EXAFS.

By using Pd/Co as the catalyst and 2-propanol as the H- source, under batch conditions, an appreciable BPE (0.1 M) conversion was achieved after 90 minutes at 210 °C. The conversion of BPE increased by increasing the reaction temperature and it was fully converted at 240 °C. Transfer hydrogenolysis reactions over 2-phenethylphenylether (PPE) and diphenyl ether (DPE) were also investigated. Catalytic tests show that the cleavage of C-O bond of PPE and DPE is less efficient due to the higher bond dissociation energies (β -O-4 = 289 kJ/mol and 4-O-5 = 314 kJ/mol) involved.

Reactions carried out with the analogous Pd/Co catalysts prepared by using the impregnation method are by far less efficient. Therefore, the enhanced catalytic performance shown by Pd/Co catalyst can be related to the coprecipitation method that allows the formation of bimetallic PdCo ensembles that positively promote the C-O bond cleavage of aromatic ethers.

The last part is dedicated to the investigation of the transfer hydrogenolysis reaction of lignin, obtained by organosolv processes, studying the relative conversion by means of 2D HSQC NMR, using the Pd/Co catalyst, in order to investigate the potential applicability in the direct valorization of lignocellulosic biomasses.

Keywords: *biomass, lignin, transfer hydrogenolysis, heterogeneous catalysis, bimetallic, bimetallic Pd-based catalysts*

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References

- [1] M. Besson, P. Gallezot, C. Pinel, *Chem. Rev.* **114** (2014) 1827
- [2] D. Wang, D. Astruc, *Chem. Rev.* **115** (2015) 6621
- [3] M. J. Gilkey, B. Xu, *ACS Catal.* **6** (2016) 1420

P-20: Surfactant assisted sol-gel synthesis of silica supported cobalt catalysts for ethanol steam reforming

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The steam reforming of biofuels, such as ethanol, represents a hot research topic of the last few years where cobalt has always played a primarily role as an active non-precious metal catalyst for C-C bond scission. The overall ethanol steam reforming (ESR) reaction can be represented by Eq. (1)



but this process involves several steps and reactions leading to the formation of by-products, such as carbon monoxide, methane, acetaldehyde or ethylene, which are also coke precursors. A suitable catalyst of ESR should then respond to severe requirements, not only to speed up this process and allows achieving higher ethanol conversion to hydrogen at lower temperatures, but also to overcome the possible undesired reactions. From one side the formation of Co_3O_4 species are considered the precursors of metal cobalt in name of their low reducibility; on the other hand, the formation of segregated Co_3O_4 is symptomatic of a low dispersion of the cobalt species, detrimental for the catalytic activity.

With the intent to tailor the materials features through the variation of the synthesis parameters, two different synthesis procedures were adopted to prepare Co-SiO₂ catalysts: a conventional hydrolytic alkoxide sol-gel route (I) and a surfactant assisted sol-gel route (II). All the catalysts were characterized by various techniques, including X-ray powder diffraction (XRPD), N₂ physisorption, scanning electron or transmission microscopy (SEM-TEM-EDX) and temperature-programmed reduction (TPR). The activity testing was done in a home-made micro-pilot plant for ethanol steam reforming under different process conditions.

The use of non-ionic surfactants was able to act as porogen template and chelating agent of cobalt ions during the sol-gel synthesis prevents the formation of the cobalt oxide phase, Co_3O_4 for all composition, leading to high dispersion but lower reducibility.

Keywords: *cobalt catalysts, sol-gel, ethanol steam reforming, surfactant templating*

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References

[1] Esposito, S., *Materials* **12** (2019) 668

P-21: Kinetics of the levulinic acid esterification with ethanol in the presence of Amberlyst-15

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Levulinic acid (LA) has been recognized by the U.S. Department of Energy as one of the top biomass-derived platform molecules, due to its reactivity and because it can be produced at relatively low cost from lignocellulose waste. Levulinic acid esters may find an application as alternative green solvent, polymer plasticizers and fragrances [1]. LA esterification with alcohols is typically acid-catalyzed by homogeneous catalysts (i.e. sulfuric acid, phosphoric acid). Although this approach remains the most frequently utilized, a variety of heterogeneous acid catalysts have been used since recent times (i.e. zeolites, sulfated metal oxides, silica) [2]. Among the catalyst mentioned, Amberlyst-15 showed a remarkable high yield of ethyl levulinate. This behavior is due to the acidity provided by SO₃H functional groups. In the present work, the kinetics of the levulinic acid esterification with ethanol in the presence of Amberlyst-15 was investigated. Experiments were performed by varying different operative conditions, i.e. stirring rate, temperature, catalyst loading and reactants ratio. 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. 1 were solved with advanced numerical techniques.

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

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

Keywords: *kinetic, ethyl levulinate, ionic-exchange resin*

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References:

- [1] V. Trombettoni, L. Bianchi, A. Zupanic, A. Porciello, M. Cuomo, O. Piermatti, A. Marrocchi, L. Vaccaro. *Catalyst* **7** (2017) 235
 [2] N.A.S. Ramli, N. H. Zaharudin, N.A.S. Amin. *Journal Teknologi* **79:1** (2017) 137

P-22: Catalytic hydrogenations to high value-added products

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Biomass represents the main source to produce renewable fuels and high-value industrial chemicals by means of some main chemical routes among them the hydrogenation. Starting from platform molecules such as levulinic acid and glucose, γ -valerolactone (GVL) and sorbitol can be obtained by hydrogenation. Ru/C catalysts are normally employed, showing deactivation. Novel sol-gel Ru-based catalysts were synthesized and tested. We demonstrated that Ru-Nb-SiO₂ catalysts is an active catalyst for GVL synthesis, combining the synergic effect of Ru (hydrogenation agent) and Nb (acid site) [1], Figure 1A. Ru-SiO₂ catalyst showed high activity in sorbitol synthesis. Further reduction of these species in the reaction environment was observed due to the synergic effect of both H₂ and glucose which act as in situ reducing agents for the Ru-SiO₂, that ultimately proved to be a self-activating catalyst (Figure 1B) [2].

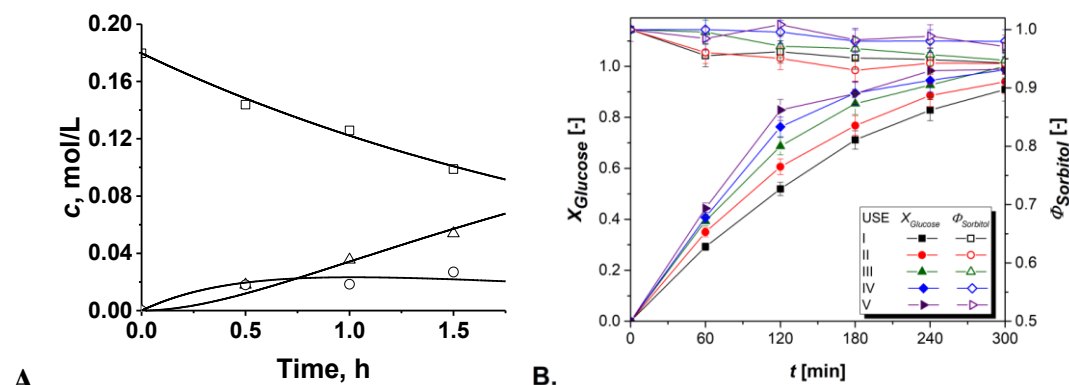


Figure 1. A. Concentration profiles obtained using Ru-Nb-SiO₂ catalysts. Reaction condition: $T=70^{\circ}\text{C}$; catalyst loading = 0.5 g; LA= 4.0 g; water 200.0 g; $p_{\text{H}_2}=2.0$ MPa. B. Glucose conversion (X_{glucose}) and sorbitol selectivity (Φ_{sorbitol}) reuse trends using Ru-SiO₂. Reaction conditions: $p_{\text{H}_2}=2.0$ MPa, $c_{\text{Glucose}}(t=0)=0.1$ mol/L, catalyst load=0.25wt.%, $T=120^{\circ}\text{C}$.

The obtained results are of high impact, as these catalysts could be tested in continuous device, leading to the optimization of the overall process.

Keywords: *hydrogenation, sol-gel catalysts, sugar, levulinic acid, γ -valerolactone*

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References

- [1] L. Minieri, S. Esposito, V. Russo, B. Bonelli, M. Di Serio, B. Silvestri, A. Vergara, A. Aronne, *CHEMCATCHEM* **9** (2017) 1
- [2] S. Esposito, B. Silvestri, V. Russo, B. Bonelli, M. Manzoli, F. Deorsola, A. Vergara, A. Aronne, M. Di Serio, M., *ACS Catalysis* **9** (2019) 3426

P-23: Fluoride adsorption for wastewater treatment

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Fluoride toxicity is characterized by a variety of signs and symptoms. Poisoning most commonly occurs immediately after ingestion (accidental or intentional) of fluoride containing products. Fluoride has several mechanisms of toxicity. Ingested fluoride initially acts locally on the intestinal mucosa [1]. It can form hydrofluoric acid in the stomach, which leads to gastrointestinal irritation or corrosive effects. Fluoride has two sources. It can appear “naturally” in water or it can appear as a toxic waste. Adsorption has been found to be superior to other techniques for fluoride removal based on initial cost, flexibility and simplicity of design, and ease of operation and maintenance. Hydroxyl apatite show good performances in fluoride removal. In the present work, detailed kinetic and equilibrium investigation was conducted using a commercial Hydroxyl Apatite (Fluor-Andel). The results are promising in terms of fluoride removal compare to classical sorbents (Figure 1).

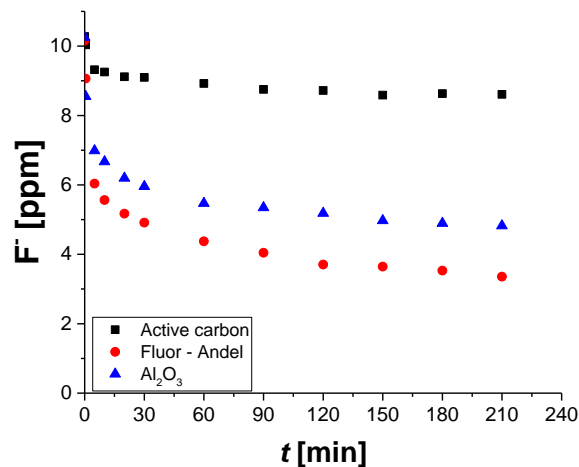


Figure 1. Adsorption kinetic experiments conducted with different sorbents. $T=30^{\circ}\text{C}$, $\rho_B=0.67\text{g/L}$.

The obtained results are of high impact and can be considered as a starting point for a continuous plant design.

Keywords: *fluoride removal, Hydroxyl Apatite, adsorption, kinetics, equilibrium*

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References

[1] M. Islam, P.C. Mishra, R. Patel, *Chemical Engineering Journal* **166** (2011) 978

P-24: Effect of mesoporous zeolites for the selective conversion of carbohydrates into methyl lactate.

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The depletion of fossil fuels and the need to find eco-friendly alternative resources has pushed the academic and industrial research to find renewable and more sustainable alternatives for every-day use goods like plastics. A well-known example is given by lactic acid (LA) and its esters (e.g. methyl lactate, ML) which represent promising bio-building blocks: they derive from renewable biomass like sugarcane and corn, and are used for the production of polylactic acid (PLA). PLA is a biodegradable thermoplastic polyester, it is mainly produced with a solvent-free process in combination with a distillation which involve a first cyclic intermediate (lactide) and its subsequent opening with polymerization. With an industrial production of 206 Ktons ^[1] per year, PLA finds a wide range of applications ranging from plastic bottles, textiles and food packages. The production of ML from glucose had already shown great efficiency when using a Sn-beta zeolite as catalyst due to the synergistic effect of Lewis acid sites and crystalline structure ^[2]. However, the microcrystalline structure present in the zeolite can lead to some limitations when dealing with bulky substrates, inducing to a limited choice of substrate. Considering that biomasses hydrolysis processes often lead to complex mixture of products, finding a catalyst able to deal efficiently with complex molecules is convenient both in terms of valorization of the starting material and from an energetic point of view, avoiding different step of preparation of the substrate.

Therefore, different synthetic routes for the formation of mesopores have been performed on BEA and FAU frameworks and tested with inulin and sucrose as model bulky substrates since they are oligomers made up of glucose and fructose units. This allowed the investigation of the effect of mesopores on the reaction pathway and their influence on the formation of products and intermediates. The full substrate conversion and unaffected yield into methyl lactate confirmed the selectivity of the new synthesized catalysts. A faster formation of the intermediate methyl-fructosides and the product methyl lactate showed that the presence of mesopores aid the entrance of bulky molecules into the active site, due to lower diffusional limitations, speeding up the reaction rate ^[3].

Keywords: biomass conversion, methyl lactate, mesoporous zeolites, inulin, Sn-BEA.

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References

- [1] European Bioplastics, nova-Institute (2017)
- [2] Holm, M.S., S. Saravanamurugan, and E. Taarning, *Science*, **328** (2010) 602
- [3] I. Tosi, A. Sacchetti, J. S. Martinez-Espin, S. Meier and A. Riisager, *Topics in catalysis* (2019) doi.org/10.1007/s11244-019-01135-8

P-25: Biorefinery from *Nannochloropsis oceanica***Antonella Salvini**^{1,3*}, **Donatella Giomi**^{1,3}, **Mario Tredici**^{2,3}, **Liliana Rodolfi**^{2,3}, **Alberto Brandi**^{1,3}

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The sustainability of a biorefinery is strongly dependent on the choice of raw materials to produce high value derivatives or commodities. The valorization of biomass which production does not compete with food (wastes or microalgae) is an important goal. In this research project, extraction processes from algal biomass were studied for the optimization of biofuel production as well as for the recovery of biomolecules or to develop high value products such as chemical industry intermediates and biopolymers for the pharmaceutical and nutraceutical sectors. Nitrogen starved and nitrogen replete *Nannochloropsis oceanica* biomasses were 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). In this work, a quantitative and qualitative comparison between the lipid fractions of the nitrogen starved and nutrient replete *Nannochloropsis oceanica* has been performed. In fact, the lipid content of biomasses can be increased by decreasing nitrogen availability during the cultivation of lipogenic microalgae (starvation process) [1]. 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. Methyl-D-glucoside and cellulose derivatives were synthesized from the carbohydrate components and a protein enriched fraction was also recovered. The triglyceride fraction has been subjected to transesterification reaction with TMSCl for biodiesel production using synthetic procedure already applied for BD production from other biomasses [2-4].

Keywords: *Biorefinery, microalga, biomasses valorization*

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References

- [1] N. Biondi, N. Bassi, G.C. Zittelli, D. De Faveri, A. Giovannini, L. Rodolfi, C. Allevi, C. Macrì and M. R. Tredici, *Environ. Prog. Sustain. Energy*, **32** (2013) 846
- [2] A. Brandi, A. Salvini, G. Cipriani, D. Giomi and G. Bartolozzi WO 2011023712 A1 (2011)
- [3] A. Salvini, D. Giomi, G. Cipriani, G. Bartolozzi, R. Alfini and A. Brandi *RSC Adv.* **2** (2012) 4864
- [4] M. Malavolti, A. Brandi, A. Salvini, D. Giomi, *RSC Adv.* **5**, 2015, 77341

P-26: Materials for CO₂-to-valuable-products photoconversion: efficiency optimization in mild reaction conditions.

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One of the actual challenges consists in both reducing CO₂ emissions and to provide CO₂ valorisation, together with gas capture. Photocatalysis represents a promising alternative technology for CO₂ conversion in mild reaction conditions, despite the low activity represents the current main limiting factor. Additionally, experiments usually employ concentrated CO₂ stocks when compared to environmental or industrial sources, which are conversely much more diluted. For this reason, the development of a polyfunctional material both able of CO₂ capture and photoconversion is currently indeed attractive. Zinc oxide (ZnO) is recently emerging as an appealing wide bandgap semiconductor with suitable band-edges position and higher carrier mobility compared to other metal oxides (e. g. TiO₂), accounting for an increased activity, despite its lower photochemical stability. Moreover, ZnO reported¹ ability to adsorb CO₂ also suggest a potential application for effective capture from diluted streams and subsequent photoconversion into re-usable chemicals. The research focused on material identification for the efficient UV-light-mediated reduction of CO₂ into methane (CH₄), in mild temperature and irradiating conditions. ZnO-based materials were employed for CO₂ photoconversion in CH₄ and compared to TiO₂ and TiO₂/SiO₂ systems. Lab-made ZnO materials were synthesized by either hydrothermal and aqueous precipitation method, followed by air annealing. A micro-sized benchmark material was also taken as ZnO reference. A benchmark TiO₂ (P25, Evonik) was chosen and a 10% in weight was supported by either SBA-15 or commercial SiO₂. ZnO-based materials were analysed by XRD analysis, showing zincite crystallites of smaller dimensions for the synthesized material, with respect to the benchmark. TiO₂/SiO₂ composites were mainly investigated by SEM, whereas BET specific surface area of commercial SiO₂ resulted to be very low. Both ZnO and TiO₂ were tested for CH₄ production in a lab-made reaction setup using a CO₂/H₂O gas mixture under a 60 W/m² (345 nm) UV-light irradiation. Synthesized ZnO-based materials were found to be less photostable than the benchmark and yet less effective in CH₄ production than P25. Nevertheless, the latter's activity was further increased in presence of SiO₂, especially with mesoporous SBA-15, possibly due to enhanced light scattering and reagent adsorption. Therefore, light-mediated CO₂ reduction has been proved more effective in optimal enlightening conditions, despite the catalyst binding ability, whereas still further advances are expected concerning ZnO photoprotection, to fully exploit its already proven promising potential.

Keywords: *photocatalysis, alternative fuels source, heterogeneous catalysis, CO₂ uptake*

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References

[1] B. Feng, H. An, E. Tan, *Energy & Fuels* **21** (2007) 426

P-27: Hydrodeoxygenation of isoeugenol over Ni-SBA-15: Kinetics and modelling

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Hydrodeoxygenation (HDO) of lignin derived bio-oils is currently an important research area due to depleting fossil fuel resources. Due to complicated analytics and complex composition of bio-oils, different model compounds have been used including guaiacol [1], vanillin [2], isoeugenol [3]. In this work hydrodeoxygenation (HDO) of isoeugenol has been investigated over Ni-SBA-15 and Ni-SZ-SBA-15 containing sulfated ZrO₂ with Si/Zr molar ratio of 8.4. Sulfated zirconia (SZ) supported on SBA-15 promoted with nickel is a potential catalyst for HDO reaction due to its acidic nature, high surface area and large pores coupled to the presence of the metal component. The catalysts were characterized by N₂ adsorption, AAS, TPR, X-ray diffraction (XRD), thermal gravimetric/differential thermal analyses (TG-DTA), organic elemental analysis, pyridine adsorption-desorption with Fourier-transform infrared spectroscopy (FTIR) and transmission electron microscopy (TEM).

The results revealed that 75% yield of propylcyclohexane was obtained over a non acidic Ni-SBA-15 in isoeugenol HDO at 300 °C under 3 MPa H₂, while Ni-SZ-SBA-15 gave only very low HDO activity [4]. This was explained by location of the acid sites both inside and outside SBA-15, whereas nickel particles were partially located inside the SBA-15 structure. On the other hand Ni particles in Ni-SBA-15 with the size of 20 nm were located outside SBA-15 promoting HDO.

The kinetic model was developed for HDO of isoeugenol based on the proposed reaction network, which took into account formation of intermediate products as well as oligomers. The activation energy for hydrogenation of propylcyclohexene and for demethoxylation of dihydroeugenol to 4-propylphenol are equal to 92 kJ/mol and 62 kJ/mol, respectively.

Keywords: *Isoeugenol, Hydrodeoxygenation, sulfated zirconia, SBA-15, Ni catalysts*

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References

- [1] X. Zhang, W. Tang, Q. Zhang, T. Wang, L. Ma, *Energy Procedia* **105** (2017) 518
- [2] J.L. Santos, M. Alda-Onggar, V. Fedorov, M. Puerla, K. Eränen, P. Mäki-Arvela, M.Á. Centeno, D. Yu Murzin, *Appl. Catal. A Gen.* **56** (2018) 137
- [3] M. Alda-Onggar, P. Mäki-Arvela, A. Aho, I.L. Simakova, D. Yu. Murzin, *React. Kinet. Mech. Catal.* **126** (2019) 737
- [4] S. Tieuli, P. Mäki-Arvela, M. Puerla, K. Eränen, J. Wärnå, G. Cruciani, F. Menegazzo, D. Yu. Murzin, M. Signoretto, *Appl. Catal. A Gen.* **580** (2019) 1

P-28: Alternative approach in the filler recovery from recycled paper waste stream

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Paper & Pulp industry is one of the main industrial activities in the world. Around 400 million tons of paper and paperboard are globally produced each year (1). In this field, recycling is a fundamental aspect to reduce consumption of virgin fibres from wood and, therefore, prevent deforestation. However, used paper products contain materials in addition to the fibres such as fillers and inks (2). From the chemical point of view, these materials are calcium carbonate, kaolin, inorganic pigments (e.g. iron compounds) and organic components such as polyvinyl acetate. Paper of newspapers and magazine need the removal of these materials because they cause problems in papermaking and for optical properties of the final products. The brightness cannot be realised. The removal of these contaminants is obtained through a process called deinking that consists in a flotation to remove the hydrophobic components (contaminants) from the hydrophilic materials (fibres). This process causes the formation of a waste defined as “Deinking Sludge”. Around 180 kg of waste is formed to produce 1 ton of newspaper (1). A recovery of that waste is necessary to avoid the use of landfills to get rid of the them. The main method is the incineration of the “Deinking Sludge” at temperatures around 900 °C to remove the carbonate and produce oxides (3). The ashes are then used in the construction industry.

The target of our study is to propose a different valorisation path of the inorganic components of the “Deinking Sludge” of newspaper and/or magazine production. The calcium carbonate structure can be preserved by incineration at 575 °C (4). The obtained ashes have a brightness value suitable to be used as filler for newspaper production (ISO brightness >55). In addition, by applying a bleaching step with dithionite, the ashes can be used for magazine production (ISO brightness >66). So, a low-grade waste can be transformed in valuable material. It was also noticed that the brightness of dry ashes did not decrease by time.

In the final step of the project, paper sheets were made from recycled pulp of newspaper in presence of bleached ashes from paper sludge and their physical properties were studied. An increase of brightness and opacity was found but with a small quality reduction in terms of porosity and breaking length. In conclusion, application of this method could be an alternative for the inorganic material recovery and its use as filler. Further studies in terms of process optimization and economic analysis will be necessary for a decision to go for scaling-up.

Keywords: *paper sludge, ashes, incineration, dithionite*

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References

- [1] P. Bajpai, Eds. Springer, *Management of Pulp and Paper Mill Waste* (2015) 2
- [2] P. Bajpai, Eds. Elsevier, *Recycling and Deinking of Recovered Paper* (2014)
- [3] Wong, H.S., Barakat, R., Alhilali, A., et al., *Cement and Concrete Research* **70** (2015)
- [4] Halikia, I., Zoumpoulakis, L., Christodoulou, E., Prattis, D., *The European Journal of Mineral Processing and Environmental Protection* **1** (2001)

P-29: Mechanistic insights into the Pd-catalyzed intermolecular alkyne hydroarylation reaction: the role of the ligand on activity and selectivity unveiled.

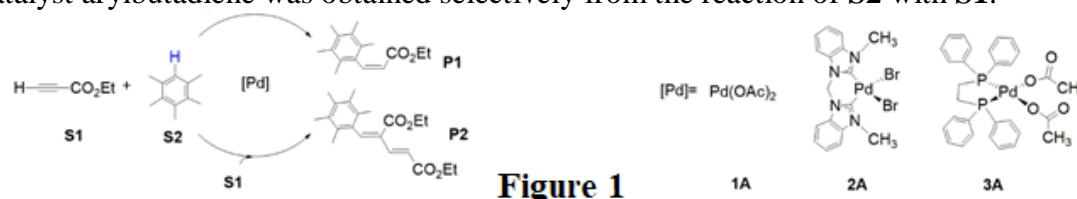
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Catalytic activation of aromatic C-H bonds leading to the formation of C-C linkage between molecular fragments is of considerable interest to chemical industries. Recently, cationic Pd(II) complexes generated *in situ* by Pd(OAc)₂ (OAc=acetate, **1A**) or (di-NHC)PdX₂ (X=halide and NHC=methylenebis(N-methylbenzimidazol-2-ylidene), **2A**) or (dppe)Pd(OAc)₂ (dppe=1,2-bis(diphenylphosphino)ethane, **3A**) and trifluoroacetic acid HTFA, showed to be promising candidates for the synthesis of *cis*-aryl alkenes by addition of aromatic C-H bonds to alkynes, Figure 1.¹ These Pd(II) catalysts steer the reaction selectivity towards the two main products of single or double alkyne insertion into the aromatic C-H bond. The **1A** and **2A** complexes catalyzed hydroarylation of ethyl propiolate **S1** with pentamethylbenzene **S2**, proceeded in regio- and stereoselective manner to afford ethyl *cis*-cinnamate **P1** as major product and arylbutadiene derivate **P2** as minor product.^{1a, b} At contrary, when the **3A** complex was used as a catalyst arylbutadiene was obtained selectively from the reaction of **S2** with **S1**.^{1c}



The mechanistic features of the reaction have been discussed but no systematic study has been reported so far, particularly for what concerns the role of the ligands.² In this work, we performed a detailed theoretical study on the three different systems in order to provide conclusive results.³ Remarkably, the use of tetrafluoroboric acid HBF₄ together with the **2A** complex catalyst provides a dramatic change in the selectivity of the reaction, with the prevalent formation of the product **P2**.⁴ Encouraged by these results we decided to elaborate the study considering the acid media in order to rationalize the effect of the acid nature on the obtained products.³ All the results obtained, in agreement with experiments, lead to the same conclusions strengthening our new mechanistic hypothesis and paving the way for the scientific community to exploit this novel concept of design new catalysts tuning opportunely both the Pd-ligand and Pd-acid interaction on the base of the desired product.

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References

- [1] a) C. Jia, D. Dongguo, J. Oyamada, W. Lu, T. Kitamura, Y. Fujiwara, *Science* **287** (2000) 1992-1995; b) A. Biffis, C. Tubaro, M. Baron, *Chem. Rec.* **16** (2016) 1742; c) J. Oyamada, T. Kitamura, *Chem. Commun.* (2008) 4992.
- [2] a) J. A. Tunge, L. N. Foresee, *Organometallics* **24** (2005) 6440–6444. b) E. Soriano, J. M. Contelles *Organometallics* **25** (2006) 4542.
- [3] M. Voccia, L. Falivene, L. Cavallo, C. Tubaro, A. Biffis, and L. Caporaso *ACS catalysis* submitted.
- [4] A. Biffis, L. Gazzola, P. Gobbo, G. Buscemi, C. Tubaro, M. Basato, *Eur. J. Org. Chem.* **2009** (2009) 3189

P-30: Study of polymeric formulations for gels and adhesives

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A new methodology was used to study several crosslinkers reactions for their use in gel production or in adhesives formulations.

In particular, polyisocyanates with different hydrophobic or hydrophilic behavior were compared as crosslinkers with polyvinyl alcohol (PVOH) or other polymeric material containing hydroxyl groups. Oligosaccharides obtained from renewable sources were also used to obtain greener formulations.

In fact, the exploitation of biomass, obtained from renewable material, has taken on an increasingly important role in the chemical industry, due to the fact that their use has a dual aim: the consumption reduction of fossil resources and the waste disposal. Although it is important to consider that the use of these resources doesn't have to modify the availability of natural resources.

Several commercial crosslinkers containing hexamethylenediisocyanate trimers with different formulations showed different solubility or dispersion ability and different performance as crosslinkers agents. The reactions of each polyisocyanate with water or DMSO solution of hydroxyl polymeric chains have been studied, also evaluating the possible use of these systems to produce chemical gels. All reactions were studied by NMR and FT-IR spectroscopy using a suitable protocol with selective extractions in solvents with different polarity (acetone and DMSO) [1].

The production of polyurea or polyurethane three-dimensional structures was evaluated and correlated with different performance of each formulation. The role of crosslinkers in reducing the solubility of the components of adhesive formulations was studied. The gels have been characterized by the calculation of the gel fraction (G%), in order to calculate the yield of the gelation process. The EWC (equilibrium water content) parameter allowed us to know how much the gel is hydrophilic, through the calculation of the water contained in the system.

The images acquired with SEM (Scanning Electron Microscope) allowed to obtain information on morphology and structure of the gels and in particular to study the presence or absence of porosity inside.

Keywords: *crosslinker, adhesive, gel*

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References

[1] A. Salvini, L. M. Saija, S. Finocchiaro, G. Gianni, C. Giannelli, G. Tondi, *J. Appl. Polym. Sci.* **114** (2009) 3841

P 31: Kinetic study of solketal formation from glycerol and acetone

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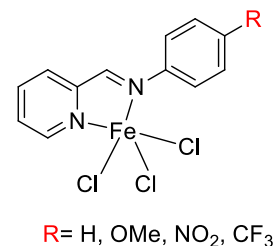
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The world economy is based on petrochemical processes for the production of fine chemicals, polymers and fuels. Efforts have been focused on the development of renewable feedstocks that are able to satisfy the production of chemicals minimizing the negative impact on the environment [1]. Many processes are based on the use of glycerol as a starting material for the production of solvents, chemicals and intermediates. Ketals are a class of products that can be used as nontoxic solvents and fuel additives. The formation of glycerol-based ketals is an equilibrium reaction and is typically acid-catalyzed [2]. Most of the catalysts used in this reaction are solid heterogeneous acids, such as Amberlyst, Zr- and Sn-mesoporous substituted silicates, zeolites [2]. In these cases, complete conversion of glycerol is rarely achieved, and a substantial amount of solid catalyst is generally required.

Instead, homogeneous catalysts require milder reaction conditions and they have high efficiency; however, their use is limited by the difficult separation from the product. They are both Brønsted and Lewis acids, such as *p*-toluenesulfonic acid or metal complexes [2]. Within this context, Esposito et al. [2,3] have recently conducted the screening of simple iron (III) complexes (in Figure) in the synthesis of glycerol ketals, demonstrating their high efficiency (TOFs up to 10⁵ h⁻¹) at very low catalysts loading (up to 10 ppm).

This work presents a detailed kinetic study for the synthesis of the acetone ketal of glycerol (solketal) using the homogeneous catalyst with R= NO₂ in a batch reactor.



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Keywords: *bio-chemicals, solketal, glycerol, acetone*

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References

- [1] L. Li, T.I. Korányi, B.F. Sels, P.P. Pescarmona, *Green Chem.* **14** (2012) 1611
- [2] R. Esposito, U. Raucci, M.E. Cucciolito, R. Di Guida, C. Scamardella, N. Rega, F. Ruffo, *ACS Omega* **4** (2019) 688
- [3] R. Esposito, M.E. Cucciolito, A. D’Amora, R. Di Guida, F. Montagnaro, F. Ruffo, *Fuel Processing Technology* **167** (2017) 670

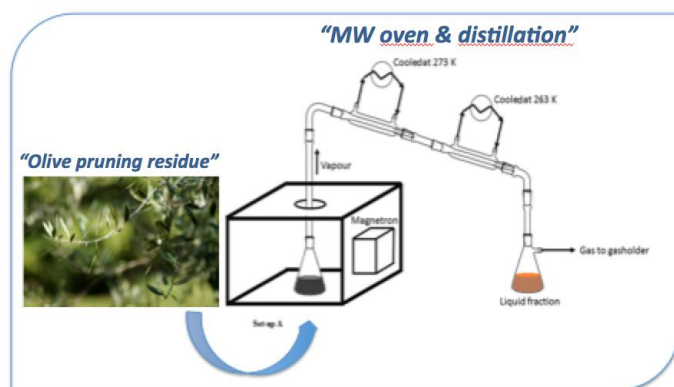
P-32: Low temperature microwave assisted pyrolysis of olive pruning residue

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In this work, we reported the low temperature Microwave Assisted Pyrolysis (MAP) treatment of the olive pruning residue. Pyrolytic experiments have been performed using different absorbers (carbon from MAP of waste tires¹, silica, silicon carbide, sodium hydroxide and Irons) evaluating the different interactions with the feedstock. We processed hundreds grams of olive residue with short process time using ranging from 15 min to 36 min. We reported the massively production of bio-char (up to 61.2 %), bio-oils (56.2 %) or gas (41.7 %) changing the adsorbers. Particularly, recovered liquids were characterized using different techniques: FT-IR ATR, ¹H-NMR and a quantitative GC-MS analysis using a consolidate



GC-MS analysis using a consolidate qualitative/quantitative methodology based on the calculation of response factor (RRF) for unknown compounds^{2,3}. We proved that MAP of olive pruning residue was a sound way to obtain useful chemicals (mainly bio char, acetic acid, aromatics, and furans) avoiding olive residue inceneration.

Keywords: *pyrolysis, microwave, GC-MS, biomass*

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References

- [1] Undri, A.; Rosi, L.; Frediani, M.; Frediani, P. *Fuel* **115** (2014) 600
- [2] Bartoli, M.; Rosi, L.; Frediani, M.; Frediani, P. *European Journal of Mass Spectrometry* **22** (2016) 199
- [3] Undri, A.; Abou-Zaid, M.; Briens, C.; Berruti, F.; Rosi, L.; Bartoli, M.; Frediani, M.; Frediani, P. *Fuel* **153** (2015) 464
- [4] Frediani M., Bartoli M., Rosi L., Frediani P., Giovannelli A., *Waste Management & Research* (2019) accepted

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Michela	Signoretto	Università di Venezia
Giorgio	Strukul	Università di Venezia
Tommaso	Tabanelli	Università di Bologna
Francesco	Taddeo	Università di Napoli Federico II
Riccardo	Tessser	Università di Napoli Federico II
Sebastiano	Tieuli	Università di Venezia
Giorgio	Tofani	Università di Anversa
Marilena	Tolazzi	Università di Udine
Ferruccio	Trifirò	Università di Bologna
Rosa	Turco	Università di Napoli Federico II

Vincenzo	Venditto	Università di Salerno
Vincenzo	Villani	Università della Basilicata
Rosa	Vitiello	Università di Napoli Federico II
Maria	Vocchia	Università di Salerno
Marco	Zanetti	Università di Torino

“MEDAGLIA CHIUSOLI”

Chiara Bisio (Università del Piemonte Orientale)

When physical chemistry meets catalysis: stories around the active site

MASTER THESIS AWARDS

MSc-01: Francesco Taddeo (Università di Napoli)

Chemicals production from biosuccinic acid

MSc-02: Silvia Giorgi (Università di Firenze)

Crosslinkers for polyvinyl alcohol based formulations

PhD THESIS AWARD

PhD-01: Gioele Pagot (Università di Padova)

Electrode and electrolyte materials for the development of advanced lithium and magnesium secondary batteries

ORAL COMMUNICATIONS

O-01: Ferruccio Trifirò (Università di Bologna)

Types of microreactors to study in laboratory oxidation catalysts

O-02: Giorgio Ferrari (MAPEI)

A new calcium aluminate phase in hydrated portland cement paste

O-03: Biagio Naviglio (OCF)

The circular economy in the tanning industry

O-04: Anna Maria Raspolli Galletti (Università di Pisa)

Valorization of papermill wastes for the production of levulinic acid and butyl levulinate

O-05: Pierpaolo Prosini (ENEA)

Development of high capacity lithium sulphur batteries

O-06: Tommaso Tabanelli (Università di Bologna)

Glycerol carbonate as an innovative alkylating agent for phenolics

O-07: Enrico Catizzone (ENEA)

DME production by one-pot CO₂ hydrogenation: key factors affecting the behaviour of CuZnZr/zeolite

O-08: Melissa Galloni (Università di Milano)

Iron functionalized hydroxyapatite: effect of iron speciation on the catalytic performances in the NH₃-SCR reaction

O-09: Stefano Cattaneo (Università di Milano)

Carbonaceous materials for the selective hydrogenation of HMF

O-10: Alessandro Rossini (Università di Genova)

Biogas purification process by adsorption on activated carbon

O-11: Claudio Imparato (Università di Napoli)

Synthesis of defective TiO₂ materials for hydrogen production

O-12: Vincenzo Villani (Università della Basilicata)

Rheology of PDMS liquid or rubber blends

O-13: Matteo Gastaldi (Università di Torino)

Azo-based functional polymers for 3D printing

O-14: Wanda Navarra (Università di Salerno)

Photocatalyst/polymer aerogels for the removal of water organic pollutants.

O-15: Rinaldo Psaro (CNR ISTM)

The periodic table of elements turns 150 years old: how metals have marked and still mark today the civilization of man

POSTERS

P-01: Giulia Balestra (Università di Bologna)

Study of the catalytic hydrogenation of 5-(hydroxymethyl)furfural

P-02: Federico Bella (Politecnico di Torino)

Biosourced Polymers and Lignocellulosic Materials for Eco-Friendly Electrochemical Energy Conversion and Storage Devices

P-03: Danilo Bonincontro (Università di Bologna)

Au/Pd-Decorated Electrospun Membranes as Catalytic Systems for Selective HMF Oxidation

P-04: Fabrizio Caldera (Università di Torino)

Dextrin-based nanosponges for environmental applications

P-05: Sofia Capelli (Università di Milano)

Bio adipic acid production from sodium muconate and muconic acid

P-06: Alice Cappitti (Università di Firenze)

Synthesis and characterization of innovative materials from renewable resources

P-07: Simona Cuglietta (Università della Calabria)

New Synthesis of Benzothiophene Derivatives by Pd-Catalyzed Oxidative Carbonylation of (2-Alkynyl)(methylthio)benzenes

P-08: Jacopo De Maron (Università di Bologna)

Innovative bifunctional catalytic system for methyl methacrylate synthesis: the peculiar role of gallium

P-09: Serena Esposito (Politecnico di Torino)

Ceria-Zirconia as an effective support to stabilize catalytically active and stable molybdenum species in the epoxidation reaction

P-10: Viviana Ferretti (Università di Napoli)

Realization of a pilot plant for the on-line monitoring of a water network that focuses to the disinfection product (DBP) for human consumption

P-11: Marco Frediani (Università di Firenze)

Synthesis platinum containing PLLA macrocomplex and catalytic performances in hydrogenation of α,β -unsaturated carbonyl compounds

P-12: Giorgio Grillo (Università di Torino)

Microwave-assisted catalytic conversion of cellulose: synergistic effect of sulfated zirconia and zeolites

P-13: Nicole Mariotti (Università di Torino)

Eco-design for photovoltaic materials

P-14: Daniele Martella (European Laboratory for Non-linear Spectroscopy)

3D printing of Photoresponsive Polymers for Microrobotics

P-15: Marcella Mazzocca (ARPA Campania)

Chemical and Morphological Identification of Microplastics in the Marine Environment

P-16: Federica Menegazzo (Università di Venezia)

Effects of supports for Nickel based catalysts in Methane Dry Reforming

P-17: Rossana Miliè (Università della Calabria)

Carbonylative Regio- and Stereoselective Synthesis of (Z)-2-(2-Oxopyrrolidin-3-ylidene)acetates

P-18: Maria Grazia Musolino (Università di Reggio Calabria)

Effect of the dopants on the α -Fe₂O₃/rGO nanocomposites as anode materials for sodium-ion batteries

P-19: Emilia Paone (Università di Reggio Calabria)

Transfer hydrogenolysis of aromatic ethers and lignin promoted by the bimetallic Pd/Co catalyst

P-20: Gianguido Ramis (Politecnico di Torino)

Surfactant assisted sol-gel synthesis of silica supported cobalt catalysts for ethanol steam reforming

P-21: Carmelina Rossano (Università di Napoli)

Kinetics of the levulinic acid esterification with ethanol in the presence of Amberlyst-15

P-22: Vincenzo Russo (Università di Napoli)

Catalytic hydrogenations to high value-added products

P-23: Clorinda Salvi (Università di Napoli)

Fluoride adsorption for wastewater treatment

P-24: Annalisa Sacchetti (Università di Bologna)

Effect of mesoporous zeolites for the selective conversion of carbohydrates

P-25: Antonella Salvini (Università di Firenze)

*Biorefinery from *Nannochloropsis oceanica**

P-26: Michela Signoretto (Università di Venezia)

Materials for CO₂-to-valuable-products photoconversion: efficiency optimization in mild reaction conditions

P-27: Sebastiano Tieuli (Università di Venezia)

Hydrodeoxygenation of isoeugenol over Ni-SBA-15: Kinetics and modelling

P-28: Giorgio Tofani (Università di Anversa)

Alternative approach in the filler recovery from recycled paper waste stream

P-29: Maria Voccia (Università di Salerno)

Mechanistic insights into the Pd-catalyzed intermolecular alkyne hydroarylation reaction: the role of the ligand on activity and selectivity unveiled

P-30: Silvia Giorgi (Università di Firenze)

Study of polymeric formulations for gels and adhesives

P-31: Francesco Taddeo (Università di Napoli)

Kinetic study of solketal formation from glycerol and acetone - Chemicals production from biosuccinic acid

P-32: Marco Frediani (Università di Firenze)

Low temperature microwave assisted pyrolysis of olive pruning residue