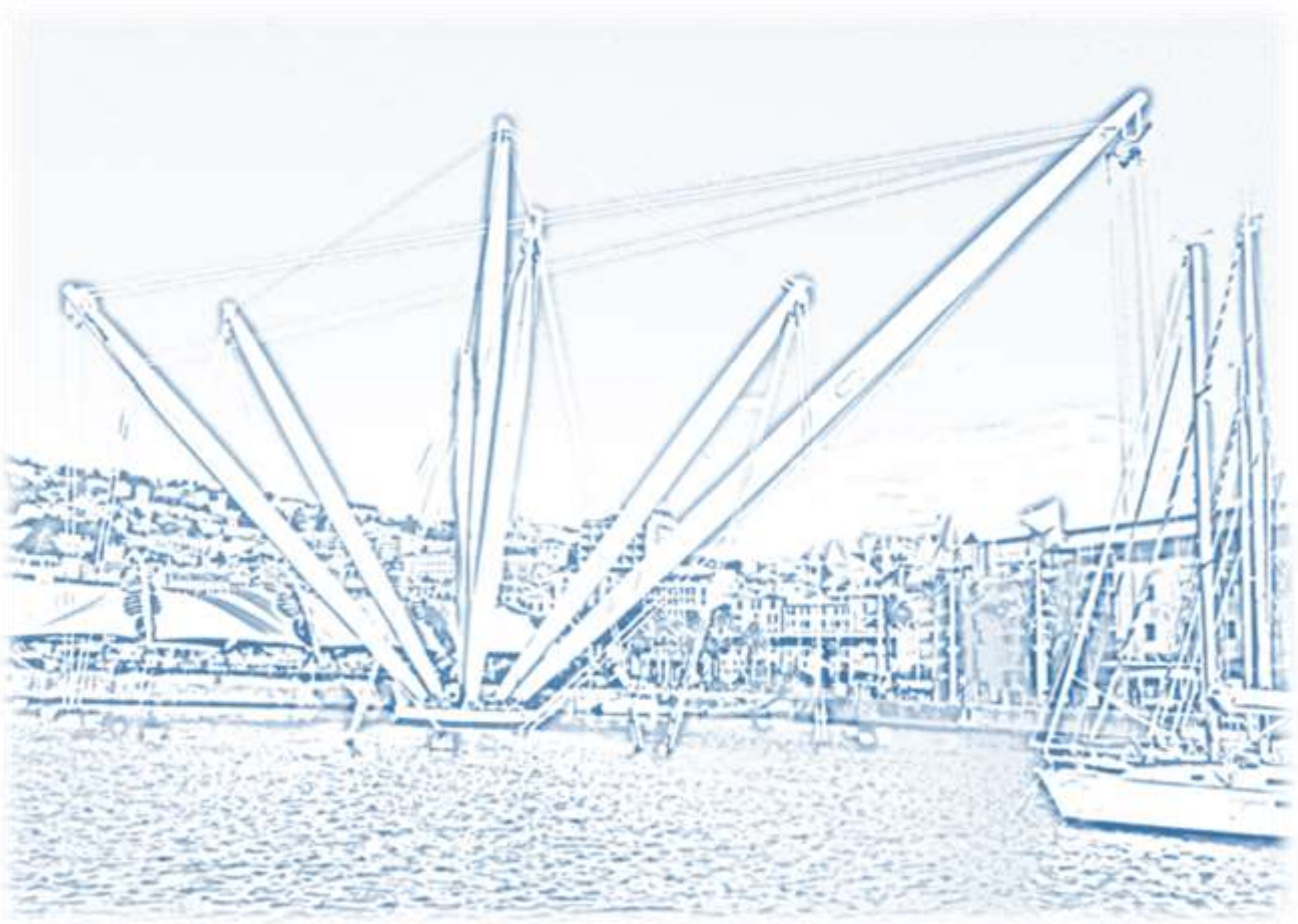

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GIC 2023

Catalysis as a golden lighthouse for green chemistry and energy related technologies

BOOK OF ABSTRACTS

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Fine Chemicals through Heterogeneous (and Supported) Catalysis: beyond recoverability.

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Key words: heterogeneous catalysis; fine chemicals; stereoselectivity; tandem processes

When heterogeneous catalysis is compared with the homogeneous one,[1] mainly when it is intended to be applied to fine chemicals synthesis, the typical desired advantage is related to the simplicity of separation from the reaction medium and the possibility of reuse, with or without reactivation of the heterogeneous catalyst. However, lower activity and selectivity are usually considered as the main disadvantages of heterogeneous catalysts, making their use difficult from a practical point of view. The supported catalysts, prepared by immobilization of homogeneous ones, are supposed to overcome part of those disadvantages, but it is considered that the catalytic site must be placed in a solution-like environment to get this result.

In this lecture, several examples will be presented showing how those ideas about heterogeneous and supported catalysis may be not so general. Examples of tandem processes will be shown, either using a combination of several heterogeneous catalysts, even mutually incompatible ones (such as an acid and a base), or by multifunctional catalysts in which the same catalytic sites play different roles in the successive reactions. In some cases unknown reactions in homogeneous phase were possible by using heterogeneous catalysts, for example by preventing isomerization equilibrium in solution.

Several examples dealing with the effect of support on stereo- and enantioselectivity with supported chiral catalysts will be shown. Although poorly understood, the presence of the support may produce significant changes in selectivity. Sometimes the presence of the support improves the result obtained with the homogeneous counterpart. In other cases, the support produces a reversal in the sense of selectivity and hence the heterogeneous catalyst promotes the formation of a different stereoisomer. The use of supported catalyst may even produce a significant selectivity in reactions where the homogeneous counterparts were totally unsuccesful. All those examples demonstrate that the situation of the catalytic site far from the support is good if the same selectivity as in homogeneous phase must be obtained, but the close proximity of the support may lead to interesting differences, making the supported catalysts complementary from their homogeneous counterparts.

Acknowledgements.
The financial support of Agencia Estatal de Investigación (project reference: PID2021-125762NB-I00) and Gobierno de Aragón (E37_20R group, co-financed with Feder 2014-2020 “Construyendo Europa desde Aragón”) is greatly acknowledged.

MgAPO-18 as key catalyst in the tandem conversion of CO_2toward valuable hydrocarbons.

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Key words: CO_2 valorization, Si/Mg-APO-18 zeotypes, MTO, Vibrational spectroscopies

The two-step conversion of CO_2 into hydrocarbons by methanol intermediate has been recently improved through the introduction of high pressure syngas (CO and H_2) co-feeding to move toward a unique tandem process for directly converting $CO/CO_2/H_2$ into light olefins over bifunctional catalysts.[1] In this study, SAPO-18 and MgAPO-18 zeotypes are tested as promising catalysts for the tandem process; therefore they are compared under the standard methanol to olefin conditions (MTO) and at high pressure reaction showing significantly different performances, as reported in Figure 1 a, b. For this reason, an extensive spectroscopic research was conducted in order to understand the origin of the different catalytic behavior depending both on the catalysts nature and the reactant gas composition. *In situ* IR spectroscopy coupled with probe molecules enabled to describe the different active sites populations, while the study of the reactions during *operando* experiments revealed different paths when the CO was co-fed with methanol. This is reflected in a different coke formation as emerged by analyzing the spent catalysts by ultraviolet Raman spectroscopy (Figure 1 c, d) that gives new insights for rebuilding the catalytic transformations occurring in MTO.

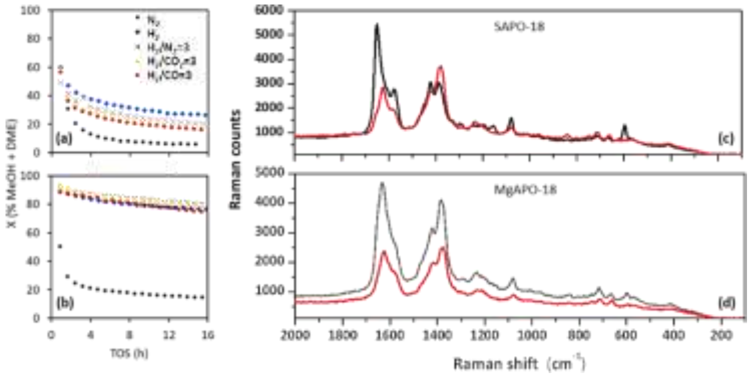

Figure 1. Left: Methanol conversion curves for growing time of stream of (a) SAPO-18 and (b) MgAPO-18 in presence of different co-feeding gasses as indicated in the legend of panel a (350 ºC, 20 bar, 1 bar methanol, WHSV 2.5 h^{-1}).[2] Right: UV Raman (λ = 244 nm) spectra of spent SAPO-18 (c) and MgAPO-18 (d) catalysts after methanol conversion in pure N_2 atmosphere (black spectra) or in high pressure H_2/CO environment (red spectra).

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Acknowledgements. Project funded by European Union's Horizon 2020 research and innovation programunder grant agreement no. 837733 (COZMOS)

Study of ceria-composite materials for high-temperature CO_2 capture and their ruthenium functionalisation for the application in methane production

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Key words: DFMs, CO2 valorization, CCUS, methane

The huge need to reduce the amount of atmospheric CO_2 connected with the energy sources demand due to the energetic crisis, drives the research to develop strategies to knock down this greenhouse gas converting it into a value-added product.[1] In this project, Dual Function Materials (DFMs) were developed to seize and *in-situ* convert a CO_2 feed gas to methane stream gas (synthetic natural gas) thanks to their chemical characteristics: high surface support (i.e., ZSM-5 zeolite and γ-Al_2O_3) to disperse a CO_2 adsorbent phase with high selectivity to methane (i.e., cerium oxide)[2] and the noble metal (i.e., ruthenium) characterized by a great capacity to activate H_2, and an optimum selectivity toward methane formation.[3] The ruthenium-ceria composite materials were prepared through consecutive impregnation depositions. Initially, three different percentages of cerium (10%, 20%, and 30%wt) were dispersed onto the two supports, and the adsorption capacities of the ceria-based materials were explored in a laboratory gas-adsorption implant at different temperatures (150, 200, and 250°C) at atmospheric pressure in order to optimize the amount of sorbet component. Thanks to these adsorption experiments, 30%CeO_2/Al2O3 and 30%CeO_2/ZSM-5 reached the best results and were selected as composite materials for the subsequent impregnation step to obtain the ruthenium-loaded catalyst (2 wt% Ru) employed in the catalytic tests. The catalysts were characterized by XRD, N_2 physisorption at -196 °C, TPDRO, ICP-MS, XPS, FESEM, HRTEM, and FT-IR. Methanation tests were conducted as follows: pretreatment in N_2 and then in H_2/ N_2 atmospheres, CO_2 adsorption phase, and a second hydrogenation step to convert the activated CO_2. Cyclic experiments were performed, simulating a real use of the catalysts. The Al_2O_3-supported ruthenium-ceria catalyst adsorbed approximately the same amount of CO_2 in each experiment and presented the best catalytic performances yielding a maximum of 94.9% of CO_2 converted and producing 123 µmol g^{-1} of CH_4. The zeolite-supported ones captured more than 300 µmol g^{-1} of CO_2 in each experiment and generated a maximum of 108 µmol g^{-1} of methane with an average yield of 29% during the testing campaign. The zeolite support increased the adsorption capacity of the material, but the CO_2 adsorbed does not participated completely in the catalytic process. Future tasks should focus on improving the adsorption capacities of the two catalysts working on the characteristics of adsorbent components. We will focus on the valorisation of the CO_2 captured by the zeolite-supported catalyst, incrementing the basicity of zeolite through, for example, an ion exchange procedure.

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CO_2 valorization through photothermo-catalytic strategies

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Key words: CO_2 use, photothermo-catalysis, zeolite, methane dry reforming, CuO_x,

Two different multi catalytic approaches were here investigated to valorize the CO_2. The first was the thermo-assisted solar photocatalysis applied for the CO_2 conversion into CO and CH_4, the second was the solar photo-assisted thermocatalysis for the CH_4 and CO_2 conversion into syngas (dry reforming). For the first reaction a low content of TiO_2 (10 wt%) was deposited on several zeolites to expose all the TiO_2 surface-active sites to the solar irradiation. The best sample (0.5wt% Cu_2O/TiO_2-mordenite) gave the 65% of CO_2 conversion at 120°C with the formation of 12 $\mu mol_{CO}/g_{cat}\cdot h$ and 4 $\mu mol_{CH4}/g_{cat}\cdot h$ (Fig. 1A). The Cu_2O co-catalyst, favoured the charge carriers separation generated on TiO_2 to efficiently convert the CO_2 adsorbed on the mordenite basic sites. Conversely, for the dry reforming an opposite strategy was adopted (the photo-assisted thermocatalysis) using Pd (0.3 wt%)-Ni (2% wt)/TiO_2. The exploitation of the visible part of the solar irradiation promoted by the Ni-Pd sites led to the decrease of the activation energy (E_a) of the syngas formation (the E_{aCO} and the E_{aH2} decreased from 29 and 27 kJ/mol of the thermocatalysis to 23 kJ/mol for both the products of the hybrid catalysis) and to increase the CO_2/CH_4 conversion at low temperature, 500°C (Fig. 1B), instead of the 600°C usually required. These new strategies with not-critical catalysts are promising to improve the solar fuels formation from the CO_2[1].

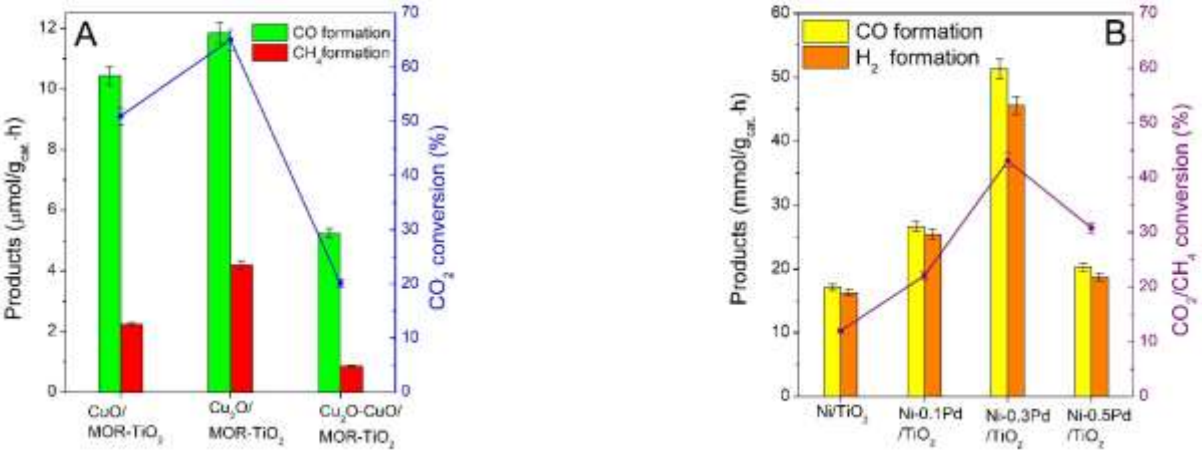

Figure 1: (A) Thermo-assisted photocatalytic CO_2 reduction at T =120°C, (B) Solar photo-assisted thermocatalytic dry reforming at T =500°C. The time of irradiation was 5 h in both the tests.

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One-pot lower olefins synthesis from CO_2 hydrogenation

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Key words: CCU, CO_2 hydrogenation, olefins, methanol, One-pot synthesis

Among the proposed CCU technologies, CO_2 hydrogenation to a high added value chemicals like lower olefins is particularly appealing. Olefins can be obtained from CO_2 with a 2 steps process involving the hydrogenation of CO_2 into methanol (CO_2-to-Methanol, CTM), followed by methanol conversion to olefins through the Methanol-to-Olefins (MTO) process [1]. Aiming at the development of a one-pot process for the synthesis of lower-olefins from CO_2 and H_2, in this study we have addressed the reactivity of bifunctional catalytic systems implementing In-based CTM catalysts and SAPO-34 MTO zeolites. These materials have been characterized and tested individually or combined in a fixed bed reactor, under relevant process conditions (T = 250 – 420°C, P = 0 - 40 barg, $H_2/CO_2/Ar = 73.5/24.5/2$ molar basis) to explore their potentiality in the one-pot synthesis of lower olefins.

The effects of the operating conditions were analyzed over the individual catalysts at first. The In-Zr coprecipitated CTM catalyst exhibited good selectivity to methanol and high activity, reaching thermodynamic equilibrium at 380°C at the investigated space velocities. The SAPO-34 sample showed high activity as well, but the presence of high H_2 partial pressures increased the paraffin selectivity at the expense of the olefins, especially for high contact times. Besides, the zeolite catalyst tends to deactivate at high methanol concentrations and low temperatures. It is therefore clear that a trade-off should be identified to guarantee satisfactory methanol formation and olefins production in the one-pot process.

The one-pot synthesis has been carried out using In_2O_3-ZrO_2 and SAPO-34 as sequential catalyst beds or by physically mixing the two catalysts. CO_2 conversion is the same regardless of the catalyst configuration; however, the mechanical mixture outperformed the sequential beds in terms of olefin selectivity thanks to the quick methanol removal from the reaction environment operated by the SAPO-34. This is able to push the selectivity of the reaction by reducing CO formation, but at the same time the H_2O produced by MTO cancels out the beneficial effect of methanol removal from CO_2 conversion. The best results obtained with the mechanical mixture were compared with those obtained according to a Fischer-Tropsch approach on a Fe-based catalyst [2]: interestingly, the two routes yield very similar CO_2 conversion levels but very different by-product selectivity (Figure1).

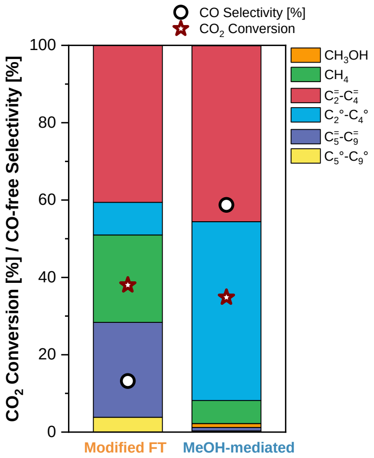

Figure 1. Comparison between CO_2 hydrogenation to lower olefins on a Fe-based catalyst (modified FT) or on a In_2O_3-ZrO_2 and SAPO-34 mechanical mixture (MeOH mediated).

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Nickel- and iron-based catalysts for CO_2/light alkanes pool tandem reactions

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Key words: CO_2 hydrogenation, alkane dehydrogenation, heterogeneous catalyst

According to International Energy Agency report [1], CO_2 emissions increased to 33 Gt in 2019, to then decrease by 5.8% in 2020 due to the pandemic and rise back in 2021 (36.3 Gt) and in 2022 (36.8 Gt), linked to the global economic output. For this reason, in recent years, the sustainable development of chemical processes and the reduction of CO_2 emissions is attracting more and more attention, accounting also for the EU target of net zero emission by 2050 [1]. In order to reach this target, the reduction of CO_2 emissions [2] is certainly one of the recognized key-challenges even if the Carbon Capture and Storage or Utilization technologies (CCS and CCU) are already under investigation.

Therefore, the aim of this work is to develop highly efficient heterogeneous catalysts to be used in the field of CO_2 utilization technologies and the evaluation of their possible exploitation in several reactions, i.e. methanation, reverse Water Gas Shift (rWGS) and more challenging tandem reaction (light alkanes oxidative dehydrogenation). In particular, tandem reaction allows to carry out a process without introducing hydrogen into the system thanks to the coupling of light alkanes dehydrogenation and rWGS reactions, increasing process efficiency and reducing the cost. According to the preparation reported in [3,4], Ni-, Fe- and (Ni, Fe)- supported catalysts on CeO_2 have been prepared through Incipient Wetness Impregnation (IWI) technique using an aqueous solution of metal precursor salts and then calcined at 723, 873 and 1023 K.

The prepared catalysts have been characterized by XRD, FE-SEM, FT-IR and UV-vis techniques before and after the catalytic tests. They have been tested in laboratory scale plant in a fixed bed quartz reactor both for methanation and tandem reactions in the temperature range 523-773 K and 773-973 K, respectively. The products stream was analyzed by GC and online FT-IR analysis in order to calculate reactant and product concentrations over time for each temperature steps. Moreover, thermodynamic equilibria have been evaluated successfully for all the tested reactions. (Ni, Fe)- and Fe-based catalysts are more active at $T > 623$ K in the rWGS reaction and bimetallic catalyst reaches a CO yield at 723 K close to the equilibrium one. Considering the tandem reaction system, bimetallic catalyst ensures the higher CO and olefins yields until 873 K, identifying Ni as suitable promoter for Fe. However, a significantly higher deactivation rate to rWGS and dehydrogenation reactions is observed at 973 K rather than that obtained with Ni-based catalyst. An analysis of process conditions allowed to set out the best parameters to evaluate performances of this catalytic system.

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Involvement of different catalytic sites in CO oxidation over Cu-doped ceria: a comprehensive spectroscopic study

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Key words: Redox catalysis, Cu-doped ceria, CO oxidation, active sites, lattice defects

Copper-ceria mixed oxides are widely considered promising catalysts for oxidation reactions, representing a viable and cost-effective alternative to supported noble metals. In particular, ceria can be especially useful when temporary O_2 shortage may occur, since lattice O^{2-} ions can act as the primary oxygen source[1]. However, the mechanistic understanding of copper-ceria catalytic systems is still incomplete, due to their considerable complexity. In fact, the addition of copper to ceria results in the formation of a significant number of different interacting sites in continuous evolution during the catalytic processes.

In the present study, pure and Cu-doped ceria samples were deeply investigated through complementary spectroscopic techniques, i.e. XPS, EPR, and in situ FTIR and Raman spectroscopy[2]. Through this systematic approach, the copper sites and lattice defects responsible for the enhanced CO oxidation activity of doped ceria were elucidated. In particular, four different copper species are present in Cu-doped ceria, as schematized in Figure 1. Cu^+ ions at the catalyst surface (i), detected via XPS and in situ FTIR spectroscopy, promote CO adsorption and its following oxidation. A similar function can be also carried out by some very small clusters of metallic Cu at the catalyst surface (ii), detected via in situ FTIR, which are however oxidized to Cu^+ under reaction conditions at high temperature. Isolated Cu^{2+} monomers well-dispersed in the ceria matrix (iii), revealed via EPR, can foster oxygen transfer thanks to the coupling of the Cu^{2+}/Cu^+ and Ce^{4+}/Ce^{3+} redox cycles; the latter species may occupy some oxidized substitutional sites detected via Raman spectroscopy. EPR also evidenced the presence of Cu^{2+} dimers (iv) in the bulk or sub-surface, which are able to strongly weaken the bonds of neighboring O^{2-} ions, improving the catalyst reducibility; in the proximity of such sites, oxygen vacancy clusters may form in sufficiently reducing conditions, as revealed by the Raman spectrum evolution during in situ measurements. Additionally, lattice oxygen mobility is also affected by the presence of Frenkel pairs, as interstitial sites may provide a path for oxygen transfer. All these findings shed new light on the complex mechanisms behind the activity of copper-ceria mixed oxides and provide valuable insights for the development of high-performance catalysts for oxidation reactions.

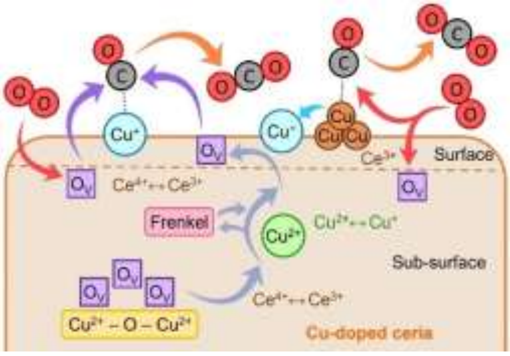

Figure 1. Scheme describing the different catalytic sites and reaction mechanisms involved in CO oxidation over copper-doped ceria

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PtNi-based catalyst for H_2 production from cellulose aqueous phase reforming

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Key words: Hydrogen, Layered double hydroxides, APR, Cellulose, PtNi

The development of green processes for green hydrogen production is needed in the framework of the H_2 transition. Among biomasses, cellulose can be directly transformed into hydrogen by aqueous phase reforming (APR). APR [1,2]. In particular, performing a one-pot process starting from cellulose, rather than cellulose hydrolysis followed by glucose APR, allows not only to intensify the process but also to hinder the polymerization of glucose derivatives by their fast consumption in intermolecular reactions that lead to small molecules and hydrogen production. However, glucose can easily decompose at those temperatures forming solid humins by polymerization, which block the catalytic sites and hinder hindering hydrogen generation. However, this approach requires the employment of tailored catalysts with both redox and acid base active sites are needed to perform the reforming and hydrolysis + C-C cleavage reactions respectively. To do so, NiMgAl LDH based catalysts were prepared by coprecipitation [2], then calcined to obtain the corresponding mixed oxides, that were then impregnated with Pt. The final catalyst, composed by Ni0 or PtNi over a MgAl mixed oxide was obtained by reduction under H2 atmosphere and the APR tests were conducted in an autoclave in batch configuration at 250°C.

The catalyst without Pt showed interesting hydrogen yields (up to 30%) in inert atmosphere while the addition of Pt to the catalyst allowed to decrease the reduction temperature (as shown by TPR), thus further pushing the reforming reactions, as well as C-C cleavage, increasing the hydrogen yield to 40%. The highest yield (>50%) was obtained under hydrogen atmosphere which allowed to increase the hydrolysis rate coupled with fast reforming given by the NiPt active phase The effect of reaction time was studied to identify and propose a reaction mechanism while reducing the catalysts at different temperatures allowed to identity the optimal reducing procedure. Finally, Pt was also impregnated over commercial support highlighting the better performances of the catalyst developed in this work.

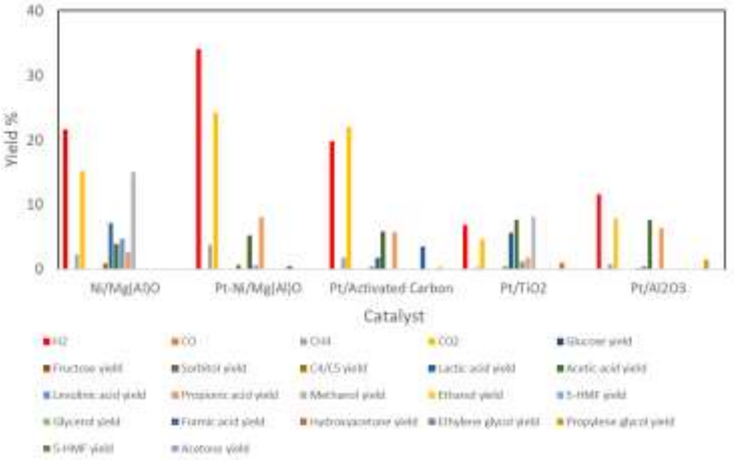

Figure 1. Gas and liquid phase products obtained over different Pt-based catalyst at 250°C for 3 h.

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Surface defects engineered Nano-Cu/TiO$_2$ photocatalysts for hydrogen production.

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Key words: photocatalysts, surface defects, H_2 production

H_2 production from alcohol photocatalytic reforming reaction is one of the most promising processes in the field of heterogenous photocatalysis[1]. Titania can be considered an ideal photocatalyst[2] but its wide bandgap (3.0-3.2 eV), the fast charge recombination and the presence of backward reactions are only few factors that negatively affect the development of H_2 production at a large scale. Tuning TiO_2 optical and electronic properties, by means of metal co-catalyst loading and by working on chemical surface composition can be a promising strategy to overcome these limits. The use of Cu co-catalyst can hinder the fast charge-carriers recombination and surface defects engineering can improve the overall photocatalytic efficiency, enhancing the separation of the photocarriers, promoting the sacrificial agent adsorption, and extending the light absorption range[3]. In this work, surface defects engineered nano-Cu/TiO$_2$ ($Cu_{2.0}$/gOx/P25X) photocatalysts have been synthesized through an easy and cost-effective microwave-assisted hydrothermal synthesis, followed by Cu co-catalyst loading through in-situ photodeposition procedure during reaction. Correlations between the photocatalytic activity and both physicochemical and optical properties of the materials were further made, by means of several techniques and $Cu_{2.0}$/gOx/P25X photocatalysts have been successfully used for hydrogen production through methanol reforming, showing an increased reactivity compared to bare $Cu_{2.0}$/P25 system (Fig.1).

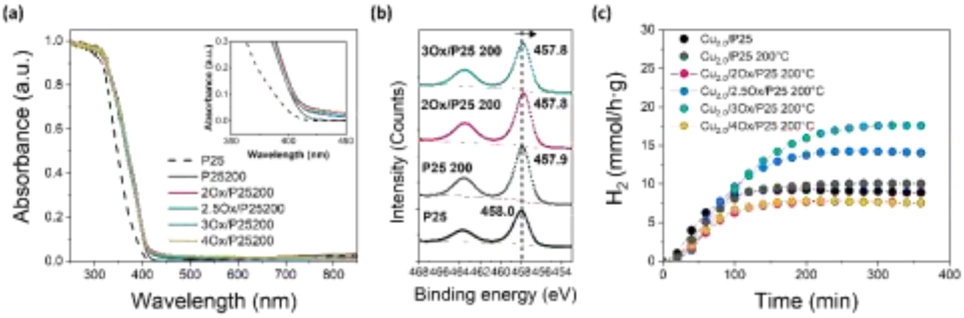

Figure 1. ***(a)*** *DRUV-Vis absorbance spectra of gOx/P25200 series samples.* ***(b)*** *Ti2p X-ray photoemission spectra for P25, P25200, 2Ox/P25200 and 3Ox/P25200 samples.* ***(c)*** *Photocatalytic H_2 production rates under UV light irradiation.*

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Vanadium Catalyzed Aerobic Oxidations

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Key words: aerobic oxidation, vanadium, lignin valorization, 1,2-diols,

Triphenolamines (TPA) are highly symmetric, modular molecules that form stable metal complexes with a wide variety of transition and main group elements.[1] TPAs metal complexes are highly active catalysts in important reactions like polymerizations, olefin metathesis, CO_2/epoxide cycloadditions, and oxygen transfer processes.[1]
Here our latest results related to the application of vanadium (V)-TPA complexes, as redox-catalysts for the aerobic oxidative cleavage of oxygen containing compounds (1,2-diols,[2] lignin models and lignin itself) will be reported. The catalytic system for the 1,2-diol and lignin models aerobic oxidative cleavage has been found effective not only under thermo-catalytic conditions in organic solvents and aqueous micellar conditions, but also activated by led visible light (Figure 1).[3] Optimization of the reaction protocols and applications of the catalytic system to a series of substrates of increasing complexity together with reaction mechanism studies will be presented.

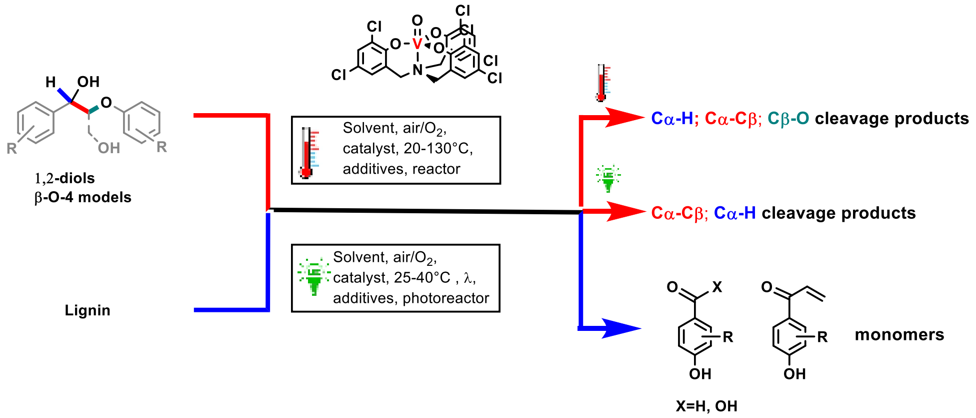

Figure 1. (V)-TPAs aerobic oxidation of lignin models and lignin under thermo and photocatalytic conditions

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Not Another Methanation Catalyst: Depleted Uranium Meets Nickel for a High-Performing Process Under Autothermal Regime.

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Key words: CO_2 methanation · depleted uranium · energy conversion · hot-spots control

Ni-based catalysts prepared through impregnation of depleted uranium oxides (DU) have successfully been employed as highly efficient, selective, and durable systems for CO_2 hydrogenation to substituted natural gas (SNG; CH_4) under an autothermal regime. The thermo-physical properties of DU and the unique electronic structure of f-block metal-oxides combined with a nickel active phase, generated an ideal catalytic assembly for *turning waste energy back into useful energy for catalysis*. In particular, Ni/UO_x stood out for its effective harvesting of the extra-heat originated by the methanation exothermicity turning it back into useful energy for the process itself. The appearance of net and positive hysteresis loops in the catalyst specific rate (λ) upon decreasing the reactor temperature setting (T_F) implies that the reaction exothermicity (constantly fed by reagents flow) is the main and almost self-sustaining heating source engaged for the CO_2-to-CH_4 conversion. Besides the outstanding methanation performance of Ni/UO_x setup recorded under ultra-mild conditions or even autho-thermal regime, our findings highlight the importance of heat diffusion control and material heat capacity for an effective "hot-spots" control in a process at the heart of decarbonization strategy (from CO_2 to substitute natural gas – SNG, CH_4).

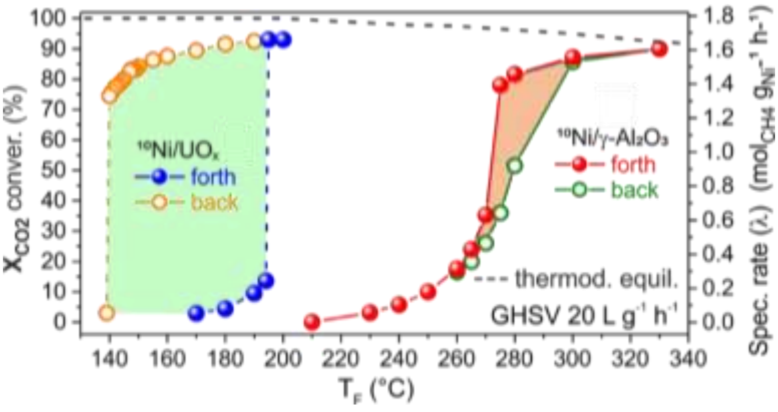

Figure 1. (A) CO_2 methanation with $^{10}Ni/R$ [R = UO_x or γ-Al_2O_3] as a function of the reaction temperature (T_F; Temp furnace). Reaction conditions: catalyst weight = 500 mg, GHSV (STP) = 20000 mL $g^{-1}h^{-1}$, [CO_2] = 20 vol%, [H_2] = 80 vol%, H_2/CO_2 = 4, total flow rate = 166.7 mL min^{-1}, atmospheric pressure. Full and empty spheres refer to the forth and back temperature scan, respectively. CH_4 selectivity (S_{CH4}, not shown in figures) was constantly 100% in the whole temperature range. Forth and back methanation profiles were recorded within 10–12 h and each temperature value was left to stabilize not less than 30 min before recording the data.

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$Ni@Ce_{0.5}Zr_{0.5}O_2$ bulk catalysts prepared through a novel surfactant-template method for systems subjected to coke deposition and sintering deactivation in CH_4 reforming processes

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Key words: coke deactivation, $Ni@Ce_{0.5}Zr_{0.5}O_2$, surfactant-template, methane reforming.

Ni-based catalysts have wide industrial applications in reforming processes due to their low cost, thermal stability, and ability to convert CH_4 and CO_2 in syngas. However, they show the important drawback of fast deactivation for carbon deposits formation or sintering [1]. Therefore, supports and promoters play the crucial role to overcome this obstacle. To date, two main strategies to overcome this issue are: increasing the metal-to-support interaction (MSI) and the support's oxygen storage capacity (OSC) [2]. This work aims to describe a new, fast, and organic solvent-free approach to prepare a catalytic system with such properties. High surface area $Ni@Ce_{0.5}Zr_{0.5}O_2$ catalysts were prepared by a surfactant-template method (Fig.1) in which both the active phase's and the CeZr oxide precursors were dissolved in water and added dropwise to a dodecyl sodium sulfate aqueous solution to obtain a homogeneous microemulsion.

Fig.1 Scheme of the preparation of $Ni@Ce_{0.5}Zr_{0.5}O_2$ bulk catalysts.

We can claim that this novel approach to synthetize $Ni@Ce_{0.5}Zr_{0.5}O_2$ catalysts could represent a better option, if compared to other classical synthetic procedures [3], in terms of sustainability (since no toxic, hazardous or CRM-based materials are used, and it is carried out in water) and cost-effectiveness (being faster and easily scalable). Reducible oxides, as CeO_2, are able to store and release oxygen due to the reversible oxidation state of the metal in a different extent according to its crystal phase [3]. This characteristic is the cause of the so called "self-regeneration" phenomenon through which the Ni sites, blocked with coke, are freed by the oxide's released oxygens which react with C by giving CO_x. Furthermore, with the addition of Zr and the obtainment of a $Ce_{0.5}Zr_{0.5}O_2$ stoichiometry, we further improved the thermal stability and the OSC of the oxide. Finally, our catalysts' MSI have been enhanced by our synthetic approach. Indeed, Ni is at first present in the CeZr oxide's same lattice, as confirmed by XRD analysis, and only after the exposition to a reducing atmosphere, it migrates from the catalyst's bulk to the surface. With TPR analysis we confirmed the migration of Ni, while Raman spectroscopy showed the obtainment of the mixed oxide's most favorable phase for the improvement of the OSC of the support.

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Metal-support interaction in methane dry reforming catalysts prepared via dry mechanochemical synthesis.

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Key words: ball milling, CeO_2, dry reforming of methane, metal-support interaction

Ni/CeO_2 catalysts represent one of the most studied catalysts for the simultaneous transformation of biogas (CO_2 and CH_4) to syngas (H_2 and CO) through the dry reforming of methane reaction[1,2]. In this study Ni/CeO_2 catalysts were prepared by mixing Ni nitrate and chloride precursors with high surface area CeO_2 via ball milling, a synthetic approach that have shown the ability to promote specific metal-support interactions[3]. Moreover, this technique matches with the principles of green chemistry being solvent-free and of easy scalability.

The effect of milling time on the surface area, structure and redox properties of the catalysts was studied by means of the physical nitrogen absorption technique (BET analysis), X-ray diffractometry (XRD) and temperature-programmed reduction (TPR) analysis in H_2. The catalysts were tested in the methane dry reforming reaction (DMR) and compared to those prepared by incipient wet impregnation (IW).

It was found that the mechanical action improved the catalytic activity regardless of the type of precursor, which affects the overall activity, with the nitrate precursor giving more active catalysts respect to the chloride. On the other hand, the effect of time of milling depended on the precursor used.

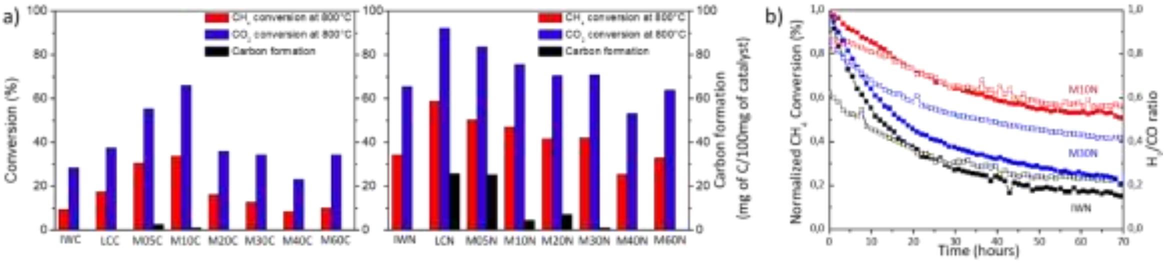

Figure 1.a) catalytic activity for the catalysts derived from the chloride precursor (left panel) and nitrate precursor (right panel); b) stability test of some representative N derived catalysts.

High-resolution transmission electron microscopy (HRTEM) and X-ray photoelectron spectroscopy (XPS) analyses reveal that the mechanical action causes a specific Ni-O-Ce arrangement responsible for their better catalytic performance, which resulted to be very surface-localized in the materials milled for shorter milling times.

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Vanadium role in the promotion of Ni/Al_2O_3 catalyst for Methane Dry Reforming

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Key words: Methane Dry Reforming, Vanadium doped catalyst, Nickel catalyst, Coke

Methane dry reforming (MDR) is a promising process to produce syngas from two of the main geenhouse gases (GHGs): CO_2 and CH_4 [1]. This could be a possible solution for reducing atmospheric carbon dioxide levels. The catalyst plays an essential role in this reaction, as it should encourage syngas formation while limiting coke deactivation.

This work focused on the effects of vanadium promoter in nickel-based catalysts [2]. In particular, the prepared Ni-V/Al_2O_3, was compared to the bare Ni/Al_2O_3. The fresh and spent catalysts were characterized via N_2-physisorption, TPR, XRD, TPO, TEM and SEM-EDX techniques to understand the morpho-physical features of the materials and to identify the causes of catalysts deactivation. The catalysts were tested for MDR at the temperature of 650 °C for 100h under non stress (CH_4:CO_2:He ratio 1:1:18) but also for 50h in stress conditions (CH_4:CO_2:He ratio 1:1:8).

Ni-V/Al_2O_3 showed a stable hydrogen yield of 45%, 81% conversion of CH_4 and 88% conversion of CO_2 in non-stress conditions and an improved activity both for methane and carbon dioxide conversion under stress conditions. The catalytic activity can be well explained by the characterization performed on the catalysts: vanadium ensures high metal dispersion and stronger interaction with the support compared to bare Ni/Al_2O_3, which is necessary for the stability of the catalyst against coking and deactivation. From the spent catalyst it is possible to observe that vanadium introduction favors the formation of only superficial carbon nanotubes which do not cover Ni active sites. This allows the catalyst to retain its activity for long time.

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SiC-based structured catalysts for a high-efficiency electrified dry reforming of methane

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Key words: Electrification, microwave, Joule heating, process intensification, SiC-based structured catalysts, methane dry reforming.

The process of dry reforming of methane (DRM) can allow the conversion of CH_4 and CO_2, the two main greenhouse gases, into syngas. However, the heat required for the reaction is obtained by combustion of fossil fuels, so CO_2 footprint of the process is significant. One more issue of the process concerns the heat transfer to the catalytic volume: for allowing the catalytic bed to reach and maintain the reaction temperature, the heating medium outside the tubes containing the catalyst must have a temperature higher than 1000°C. This work proposed the intensification of DRM process by combining (i) the use of electrification for the energy supply (microwave heating, MW, and ohmic electrification, OE) and (ii) the adoption of Ni-based structured catalysts with high thermal conductivity, prepared starting by a Silicon carbide (SiC) honeycomb monolith and a Si-SiC open-cell foam. The results of the experimental tests (Figure 1), performed at different space velocityvalues, have shown that the SiC monolith is more suitable than the Si-SiC foam for a MW- assisted catalytic test, with a higher energy consumption of the latter (8.29 kWh/Nm^3 H_2 and 4.2 kWh/Nm^3 H_2, for the foam and the monolith respectively). Moreover, the monolith-based catalyst approached the thermodynamic equilibrium values in terms of CH_4 conversion (X_{CH4}) in all the investigated temperature range, while in the same tests the foam-based catalyst reached these values only at the higher temperatures. Conversely, the foam-based catalyst has shown the best performance in the OE tests: the CH_4 conversion approached the equilibrium values in the investigated temperature range and, more important, the energy consumption value was of 2.6 kWh/Nm^3 H_2.

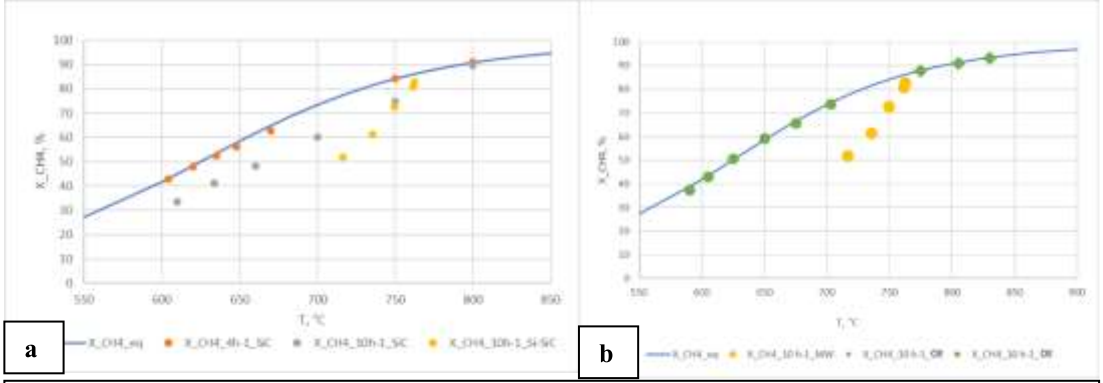

Figure 1. a) X_{CH4} vs T in MW-assisted experimental tests, b) Comparison in terms of X_{CH4} vs T for MW and OE experimental tests performed by using the Si-SiC based catalyst

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Study on new Ni based catalysts and catalytic membrane reactors in the Methane Dry Reforming and Reverse Water Gas Shift reactions

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Key words: Nickel, dry reforming, reverse water gas shift, catalytic membrane reactor

The mitigation of CO_2 emissions is a key issue in the European policies and researchers and companies are involved in research and project aimed at the CO_2 utilization. When a mixture of biogenic CO_2 and CH_4 is available then their conversion to syngas by the Methane Dry Reforming (DRM) reaction is attractive. When hydrogen is produced from renewable energy sources (e.g. solar, wind, etc.) another interesting reaction is the CO_2 hydrogenation to syngas through the Reverse Water Gas Shift (RWGS) reaction. Nickel based catalyst showed their activity in both the reactions and the nature of the catalyst along with the process parameter can show a prevalent selectivity in one or other of them.

In this study, a commercial Ni/Al_2O_3 catalyst, a Ni/Al_2O_3 catalyst prepared by the homogeneous precipitation method or by impregnation, and a new Ni-La-W catalyst synthesized by the citrate method were investigated in both the DRM and RWGS reactions either using a laboratory fixed bed or a catalytic membrane reactor.

The catalysts were characterized by FE-SEM/EDX, FTIR, XRD, physisorption and gas permeation tests. The reaction tests MDR and RWGS were performed at different temperatures in the range 450°C-650°C and the product were analyzed by gas chromatography. The catalytic membrane reactor was mainly studied in the forced flow configuration which constated in forcing the reactant feed to permeate through the membrane porosity. Post-reaction carbon formation on the catalysts was evaluated by electron microscopy (Figure 1).

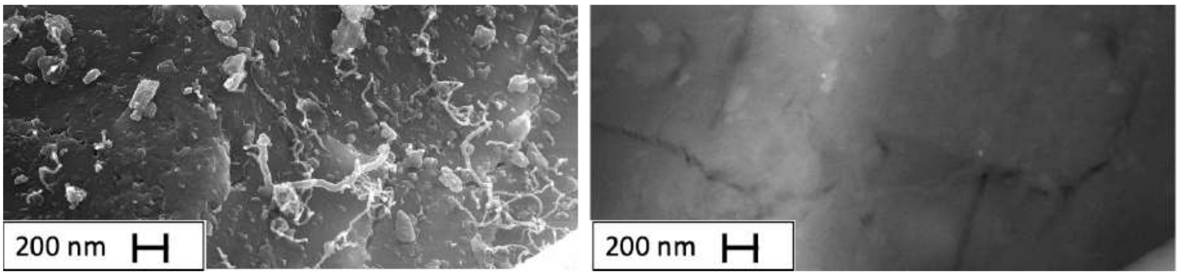

Figure 1. FE-SEM micrographs of the formation of carbon filaments on the surface of a Ni/Al_2O_3 catalyst prepared by the incipient wetness impregnation method. In-Lens detector (left) and back-scattering detector (right).

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The Laboratory of Electron Microscopy and the microscopist Laura Negretti are acknowledged.

Highlighting the key elementary step in olefin polymerization catalysis by time-resolved IR spectroscopy of insertion probes

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Key words: olefin polymerization, metallocene, Ziegler-Natta, IR spectroscopy, olefin insertion

Polyolefins (POs) are by far the most successful plastics today due to their attractive cost/performance ratio. Their outstanding economic success relies in the high versatility in terms of properties and applications, and in the high energy-, resource- and atom-efficiency of the catalytic processes used for their production. Catalysts evolution mainly occurred across a steady and patient day-by-day improvement, which is the kind of progress nowadays labelled as “incremental”, and taken as an indication of maturity. This perception has pervaded also the academic research. However, there is still plenty of room for improvement in this field. Understanding the key factors behind catalysts selectivity and developing more durable and functional POs are two among the most exciting challenges, which might benefit from the understanding of the structure of the active sites at a molecular level. Unfortunately, progresses in this field have been limited so far by the complexity of the catalyst formulation and in situ/operando spectroscopic studies on olefin polymerization catalysts are rare. The difficulties in understanding PO catalysts at molecular level arise mainly from their complexity, the small number of metal sites and even smaller number of active sites, as well as from their enormous air and moisture sensitivity. To overcome these difficulties, it is necessary to work in inert atmosphere and to use very sensitive techniques. This is where spectroscopies can contribute, due to their high sensitivity and robustness.

In this contribution we will present an innovative experimental methodology based on time-resolved IR spectroscopy with insertion probes, which allows to obtain simultaneously information on the catalyst properties at a molecular level and on their polymerization ability.[1] This is achieved by the synergetic use of insertion probe molecules (d-acetonitrile, carbon monoxide) and monomers (1-hexene and ethylene). Using insertion probe molecules instead of monomers has several advantages: 1) only one insertion event can happen vs. the thousands of insertion events occurring during the polymerization, meaning that there is no formation of a polymer layer at the catalyst surface, which greatly simplifies the application of optical spectroscopies; 2) insertion probes into the M-C bond follows much slower kinetics (from minutes to hours) than insertion of the monomer (milliseconds), which allows to collect spectra at a standard time resolution, without resorting to ultra-fast acquisition modes; 3) the occurrence of a single insertion event and the much slower kinetics contribute to avoid the problem of the exothermicity of the reaction. We will demonstrate that by performing systematic experiments on different industrial catalysts (metallocene-based and Ziegler-Natta) in the same experimental conditions, this approach allows to determine the relative fraction of accessible sites, as well as their inherent ability to insert the probe into the M-C bond.

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Beyond γ-valerolactone: from levulinic esters to C5 and C7 esters through innovative continuous-flow processes in the gas phase

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Key words: H-transfer; levulinic esters, ethanol; continuous-flow; heterogeneous catalysis.

Levulinic acid (LA) and its esters (LE) are important, polyfunctional molecules that can be obtained from lignocellulosic biomass through cellulose hydrolysis or alcoholysis, respectively.[1] Nowadays, the most common strategy for LA/LE valorization is the chemical reduction (i.e. hydrogenation with high pressure H_2) in order to obtain valuable compounds such as γ-valerolactone (GVL): a promising green solvent and bio-based fuel additive.[2] In this context, we recently reported on the possibility to enhance the catalytic transfer hydrogenation (CTH) of alkyl levulinates with ethanol (our reducing agent) in a continuous-flow, fixed bed, gas-phase reactor using a tetragonal ZrO_2 (120 m^2/g) as catalyst. In this way, by working at 250°C and atmospheric pressure with a contact time over the catalyst of just one second, methyl levulinate (ML) was completely converted promoting the formation of GVL with yield up to 70%,[3,4] finally avoiding any needs of working in liquid phase and batch system at high pressures.[5] Unfortunately, ZrO_2 undergoes to a progressive deactivation during the time-on-stream, due to the deposition of heavy carbonaceous compounds over the Lewis acid sites leading to parasite alcoholysis and transesterification reactions. Successively, we discovered that the deactivation rate is strongly affected by the zirconia crystalline phase, being the monoclinic one promptly promoting parasite oligomerization reactions of the intermediate angelica lactones. Nonetheless, an effective regeneration of the catalyst can be promoted *in-situ*, in the same reactor, by feeding air at 400°C, this way restoring the pristine catalytic activity. Finally, new efforts have been done toward the synthesis of improved catalytic systems based on zirconia mixed metal oxides (e.g. Ti, Si and W-doped zirconia) and by supporting low amount of noble metal over the same Zr-based supports with the aim of promoting both the catalytic activity and the stability of the material. Interestingly, in this way, we were able to obtain a much more efficient and sustainable continuous flow production not only of GVL but also, depending on both the reaction conditions and the catalytic system taken into account, of C5 (i.e. ethyl pentenoates and pentanoates) and linear and branched C7 esters by working at atmospheric pressure with a continuous-flow, gas-phase reactor using only ethanol as H-donor.

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Selective oxidation of substrate with heterogeneous catalysis:an alternative route to key fragrances ingredients

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Key words: dehydrogenation, heterogeneous catalysis, alcohols, aldehydes, fragrances.

In the world of fragrances, oxidation reactions play a key role in a wide variety of ingredient production.1 The selective oxidation with molecular oxygen of unsaturated substrates, namely long-chain complex alkenols, represents a testbed for promoting the sustainable production of aldehydes and ketones, crucial for perfume formulation. A heterogeneous catalysts' careful design and optimization may help to overcome the challenge of promoting selective, sustainable, and scalable oxidations.2

In this context, the continuous-flow, gas-phase oxidative dehydrogenation (ODH) of an actual mixture of decen-1-ol isomers, (“Isorosalva” alcohol) towards the corresponding mixture of aldehydes (decenal, “opalene”), has been investigated avoiding the use of Au and V based catalysts usually employed for similar reactions.3,4 In particular, using a copper ferrite (Cu0.6Fe2.4O4.2) as the catalyst the formation of the target product (opalene) was observed together with by-products derived from parasites reactions like aldol condensation, over-oxidation, and ketonisation reactions (Figure 1). Under reaction conditions (mol% isorosalva: O2:N2=2:1:97, 300°C), the catalyst undergoes progressive reduction promoting the formation of a new, highly dispersed Cu phase supported over a Fe-enriched copper ferrite. This phase proved to be very selective in the opalene formation (Y:30%, S:75%) for at least 9 hours of time on stream.

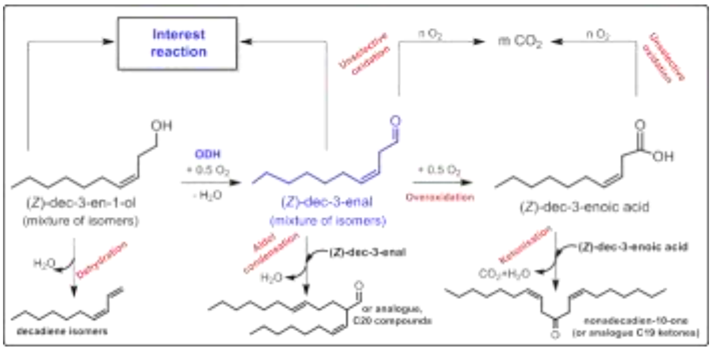

Figure 1. Isorosalva reaction scheme toward opalene andmain by-products.

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Ion exchange resins as selective catalysts for aromatic acylation.

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Key words: acid catalyst, MDB, acylation, ion exchange resins.

Introduction. Acylation reactions play an important role in fine chemical industries[1] and are tradionally carried out using inorganic compounds such as $AlCl_3$, $ZnCl_2$ and BF_3, posing serious environmental and economic issues[2]. Thus, the development of heterogeneous catalysts able to replace these compounds is of paramount importance. Starting from these premises, in the present work, the potential utilization of different Ion exchange resins as catalysts for the acylation of 1,3-benzodioxole (MDB) to 3,4-Methylenedioxypropiophenone (MDP1P, used in drugs and insecticides) were investigated.

Results and discussion. The acylation of MDB, using propionic anhydride (AP) as acylating agent, over acid macroreticular-type resins such as Purolite and Amberlite, showed that the best results in terms of MDP1P yield and selectivity were achieved at 120°C, hitting yields of ≈ 45% but with a high by-products formation. Conversly, Aquivion PW-87 (a perfluorosulfonic acid/gel-type resin) can efficiently catalyze the reaction at 80°C, showing a higher MDB conversion (53%) and a MDP1P selectivity of 79% (Figure 1a). The overall efficiency can be futher boosted by encapsulating the resin into a SiO2 matrix via a one-pot, sol gel synthesis. Moreover, It was found that, although the PW87/SiO2 ratio drives the MDB and AP conversion, the yields in by-products can be nearly halved using the new composite.

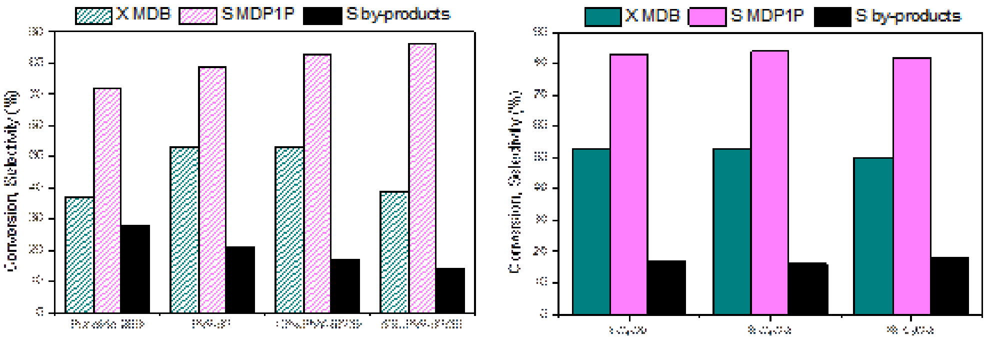

Figure 1: a) catalyst activity in terms of MDB conversion (X), MDP1P and By-products selectivity (S) and b) catalytic activity of 13%.PW-87/Si after each regeneration step with 20% HNO3 (aq). Reaction conditions: 80°C, 500 rpm, MDB:AP = 1 mol/mol, 1h, mol H+/ mol MDB = 0.007.

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Catalytic screening and kinetic investigation for DPA synthesis

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Key words: Levulinic acid, diphenolic acid, catalysis, kinetics

Diphenolic acid (DPA) is gaining much interest as bio-based alternative to the toxic and endocrine-disruptor bisphenol A in the synthesis of epoxy resins, polycarbonates and isocyanate-free polyurethanes [1]. Furthermore, DPA finds application as additive in fire retardant materials, in painting formulations as well as in antibacterial cotton fabric [2]. DPA is usually synthesized by solvent-free condensation of two molecules of phenol and levulinic acid in the presence of a Brønsted acid catalyst. Mineral acids such as hydrochloric and sulfuric acid are traditionally employed as homogeneous catalysts; however, they are highly corrosive and require wastewater treatment. On the contrary, heterogeneous catalysts provide a greener alternative thanks to their higher safety and easy separation from the reaction mixture.

Ethyl levulinate can be used as substrate in the reaction with phenol to increase DPA selectivity minimizing the occurrence of side reactions, but it has never been investigated until now.

In the present work levulinic acid and ethyl levulinate were compared as substrates in the synthesis of DPA. Sulfuric acid, zeolites i.e., H,Y-Zeolite and β-Zeolite as well as sulfonic acid resins i.e., Amberlite IR-120, Dowex 50WX8 and Amberlyst-15 were tested as catalysts. A proper kinetic study of the reaction between ethyl levulinate and phenol was conducted with the optimal catalyst i.e., Amberlyst-15 in a batch reactor. Reaction temperature, reactants molar ratio as well as catalyst loading were varied. Finally, the experimental data were elaborated to derive rate expressions based on plausible catalytic reaction mechanisms and a mathematical model was developed to determine kinetic parameters.

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Protecting a Pd/CB catalyst by a mesoporous silica layer for improving activity and selectivity in aldehydes hydrogenation.

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Key words: aldehydes hydrogenation, solvent effect, NMR relaxometry, Pd/C, mesoporous SiO_2.

In this work Pd nanoparticles supported on carbon black were encapsulated in a thin mesoporous silica layer and tested towards the hydrogenation of benzaldehyde and octanal, as reference aromatic and aliphatic aldehydes (Fig. 1a).

The hydrogenation and hydrodeoxygenation of aldehydes are important industrial processes for the production of a wide range of chemicals that find use as solvents, fuels and fine chemicals[1]. Aldehydes, in fact, can be found in several biomass-derived feedstock and their conversion is nowadays playing a crucial role, as the valuing of biomass-derived compounds is a critical step toward the replacement of fossil fuel as source of chemicals[2]. A vast body of work on the hydrogenation and hydrodeoxygenation of aldehydes using Pd-based catalysts is reported in the literature, due to the capacity of Pd to dissociate and easily activate molecular hydrogen[3].

Here, the activity, selectivity and stability of the naked Pd/C and of the Pd-protected catalyst have been compared.

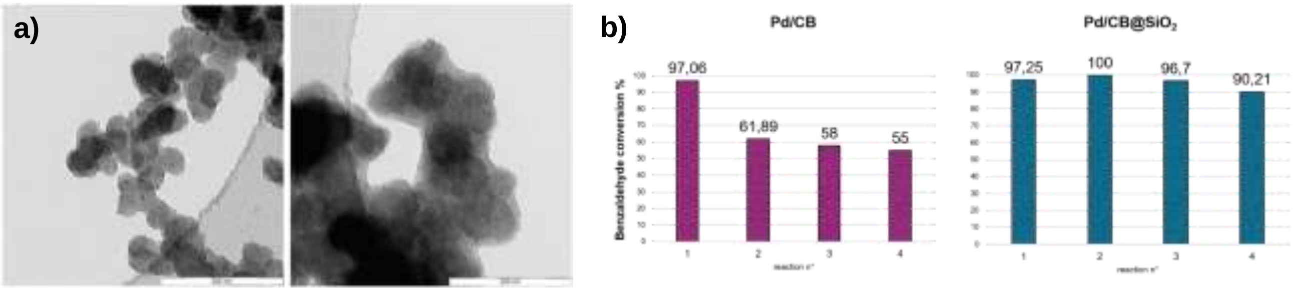

Fig. 1 TEM micrographs of Pd/CB and Pd/CB@SiO_2 (a)[4] and recycle tests in benzaldehyde conversion (b)

As main result we found that, overall, the SiO_2 does not negatively affect the catalytic activity and leads higher stability of the catalyst, as showed by recycling tests (Fig. 1b).

In addition, important aspects regarding the selectivity, the role of substrate and solvent and the influence of the silica layer on the adsorption of reactants were investigated, in particular using ^{13}C NMR relaxometry[5].

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Methanol, a potential energy carrier for the energy transition.

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AIDIC Working group on Energy Transition

Key words: Energy transition, methanol, critical minerals

The pressure exerted by the fear of climate change is accelerating actions for the reduction of CO_2 emissions and the replacement of fossil fuels with renewable ones.

The choice of energy carriers more compatible with the adoption of renewable energy sources also falls within this sphere.

Electric transport and Hydrogen seem to be the vectors of choice due to their "end of pipe" behavior. Even if electricity and hydrogen undoubtedly have an evocative charm, they are not the only ones that can cancel greenhouse gas emissions and therefore the most appropriate choice must be made on the basis of the behavior along the entire life cycle of the potential candidates.

In this presentation, the selection of alternative energy carriers will be discussed, which can involve products derived from biomass or from direct transformations of solar energy, where catalytic processes can play a role of primary importance.

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1.G. Bellussi LA CHIMICA E L'INDUSTRIA online | ANNO VI | N° 5 | SETTEMBRE/OTTOBRE 2022, DOI: http://dx.medra.org/10.17374/CI.2022.104.5.28

Lewis Acid-Catalyzed Regioselective Synthesis of Disubstituted1,2,3-Triazoles at Biological Activity

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Key words: 1,2,3-Triazoles, AAC, EAOC, F_1F_O-ATPase.

1,2,3-triazoles are five-member *N*-heterocyclic compounds bearing three nitrogen atoms in the ring that exhibit important biological properties, such as antibacterial, antifungal, anticancer, antiviral, anti-inflammatory, and anti-arrhythmic activities. Conventionally, 1,2,3-triazoles are synthesized through a 1,3-dipolar cycloaddition reaction between an azide and a terminal alkyne, the so-called AAC (azide-alkyne cycloaddition) reaction, but, generally, it is scarcely usable because provides a mixture of 1,4- and 1,5-regioisomers. The most important developments were achieved in this area by the copper catalyzed azide–alkyne cycloaddition (Cu-AAC) to obtain the 1,4-disubstituted isomer and the Lewis Acid azide–alkyne cycloaddition (LA-AAC) to achieve the 1,5-disubstituted isomer.

In this work, we report the regioselective synthesis of a variety of biologically active 1,5-disubstituted 1,2,3-triazoles by LA-catalyzed 1,3-dipolar cycloaddition, starting from azides as dipole and substituted triple or double bonds as dipolarophile [1]. For the latter, we also investigated the reactivity of propargyl nucleobases [2]. In addition, we performed the LA-catalyzed azide-alkyne cycloaddition to give regioselective synthesis of 1,4- or 1,5-disubstituted 1,2,3-triazoles to construct hybrid molecules with potential biological activity (Figure 1).

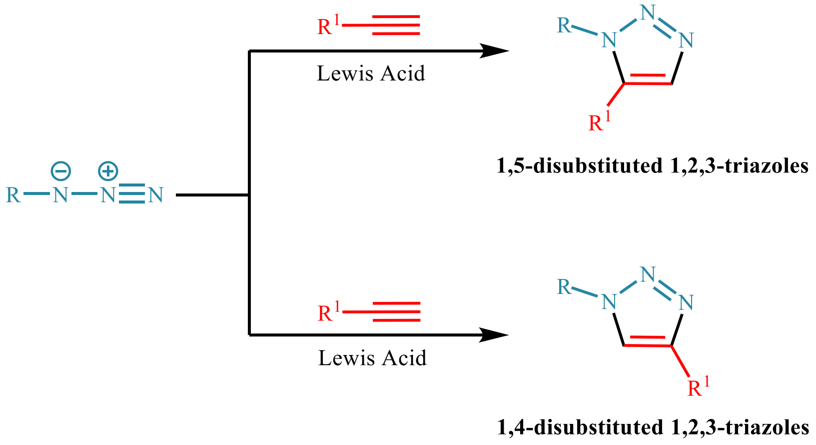

Figure 1. Regioselective synthesis of 1,4- and 1,5-disubstituted 1,2,3-triazoles.

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Hydrogenation of N-heterocycles at very mild conditions: the catalyst design makes the difference.

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Key words: Hydrogenation, non-noble metal catalysts, mild conditions.

Pincer ligands and their complexes are of high interest to organometallic and organic chemists due to their wide and successful application in catalysis [1]. As part of our on-going interest in the development of cheaper, more efficient non-noble metal-based catalysts for sustainable redox transformations, we have synthesized a series of phosphinoaminoimidazolyl pincer ligands and explored their coordination to earth-abundant metals (Figure 1). The ligands can be easily prepared in a one-pot two step synthesis from commercially available building blocks [2]; the pincer coordination confers improved stability to the resulting metal complexes. Additionally, due to the presence of an aliphatic NH group coordinated to the metal, the ligands can encourage cooperative catalysis with the metal.

These new catalysts have been characterized and studied by a combination of experimental and theoretical investigations, and their catalytic activities have been tested in several hydrogenation reactions with good to excellent performance. Importantly, the reduction of N-heterocycles can be performed under very mild conditions [3].

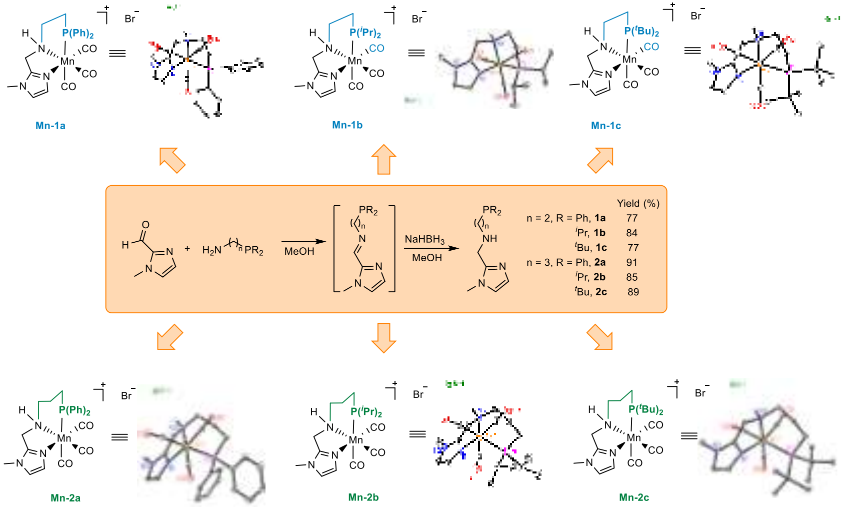

Figure 1. Preparation of N^{Im}N^{H}P-Mn(I) pincer complexes [3].

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Ammonium zincates as catalysts for the selective coupling of aziridines to yield piperazines.

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Key words: piperazines, aziridines, ammonium zincates, homogeneous catalysis, metallates

The piperazine ring is found in many drugs with central pharmacological activity.[1] Aziridines, on the other hand, are common synthetic intermediates, as their pronounced geometrical strain allows them to readily perform ring opening reactions under the stimulus of an appropriate nucleophile. With reference to ring opening reactions promoted by external nucleophiles, aziridines have been classified as activated if bearing a EWG group as substituent on the nitrogen atom, non-activated when having an EDG group. It is known that non-activated aziridines in the presence of Lewis acids undergo either dimerization to symmetric piperazines or polymerization.[2] In our recent investigation on the catalytic activity of ammonium ferrates and zincates in the CO_2 cycloaddition to epoxides[2] and aziridines[3] to yield, respectively, cyclic carbonates and carbamates, we disclosed that with the latter, symmetrical piperazines were formed as the only by-products when decreasing the CO_2 pressure. We decided to investigate this reaction with the aim to improve the yields of piperazine while reducing the amount of the polymeric by-products and we report here that in the absence of CO_2, ammonium zincates are suitable catalysts to promote the dimerization of aziridines to yield 2,5 disubstituted piperazines in good to excellent yields (**figure 1**). This method yields a 1 : 1 mixtures of two easily separable diastereoisomers, namely the (+/-)-form and the *meso* form, as the *meso* form readily crystalizes in excellent purity at the end of the reaction. The catalysts, ammonium zincates ($R_4N[ZnX_4]$, X = Cl, Br, I), can be easily and cheaply synthetized from readily available and inexpensive materials. Their scope extends over a number of substrates, ranging from *N*-alkyl to *N*-tosyl aziridines. Excellent yields and purity have been obtained by microwave heating (dielectric heating). We believe that this work represents a useful addition to the already large set of metallates catalyzed reactions.

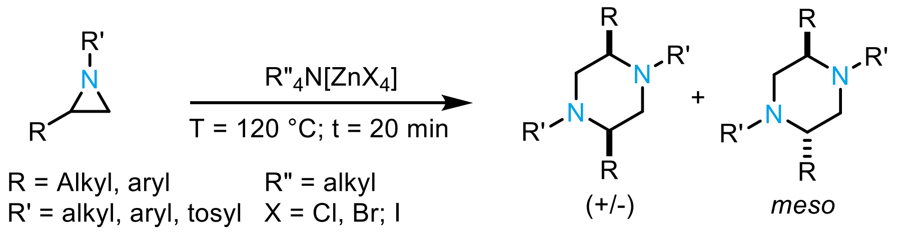

Figure 1. Synthesis of symmetric piperazines from aziridines catalyzed by ammonium zincates

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Circular economy practices in environmental catalysis: the case of Sn-hydroxyapatite and its multiple uses

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Key words: sustainability; water remediation; deNOx; air protection; reductive adsorption

Although adsorption is a simple and effective method to remove heavy metals from polluted water, disposing of the used adsorbents still poses significant challenges. Herein, we present "adsorbent to catalyst" strategy for the valorization of spent adsorbents. Specifically, calcium hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) is a waste-derivable eco-friendly material having well established adsorption ability towards several heavy metal ions. The functionalization of hydroxyapatite by tin(II) (Sn/HAP) produces a newly discovered class of ecofriendly reductive adsorbents effective in reducing Cr(VI) and adsorbing formed Cr(III). Cr(VI) removal up to 20 mg/g can be attained on Sn/HAP with 15 wt% Sn(II).[1] Such remarkable performances are maintained even in the co-presence of other ions (Fe(III), Al(III), Mn(II), etc.). Moreover, the Sn/HAP showed a good reuse capacity, although the removal efficiency gradually decreased over successive runs. To overcome the lack of regenerability, currently limiting the Sn/HAP materials, used adsorbents were tested as catalysts in selected environmental reactions for air-contaminant abatement (e.g. NH_3-SCR, NH_3-SCO, CH_4 oxidation). The upcycled adsorbents possessed a marked oxidizing capacity that could be exploited in selective total oxidation processes, such as VOC combustion. If properly optimized and improved, this strategy could assure simultaneous mitigation of both water and air pollution and have great potential for practical implementation, resulting in sustainable waste management and resource recovery (Fig. 1).

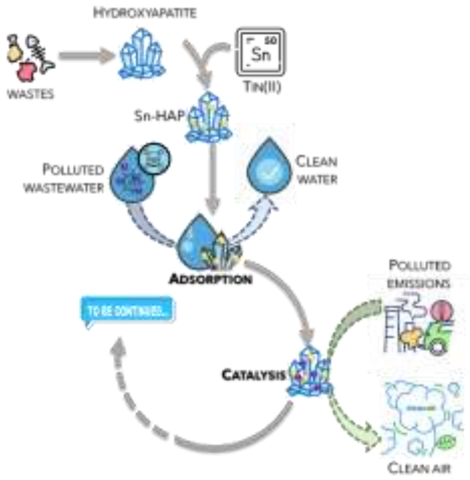

Figure 1. The hydroxyapatite-based circular approach in environmental catalysis

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Guaiacol acylation over a superacid catalyst in mild conditions.

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Key words: guaiacol, acetic acid, acylation, ion exchange resin, acid catalysis

The liquid phase acylation of guaiacol with acetic acid (both obtainable from renewable sources) to produce 2-methoxyphenyl acetate (O-acyl, perfumes, fragrances) and acetovanillone (C-acyl, anti-arthritis, anti-asthma, anti-inflammatory drugs) was study on a Perfluorosulfonic Acid Ion-Exchange resin. The experimental setup consisted of a two-neck round flask reactor equipped with a thermometer and a fixed-bed dehydrating section composed by Molecular Sieve 5A pellets placed below the reflux condenser. 5 mmol of Guaiacol, 50 mmol of Acetic acid and 200 mg of Aquivion PW87 were placed in the reactor and heated up in an oil bath under stirring at 120°C for different reaction time. The reaction products were analyzed through GC and GC-MS analyses.

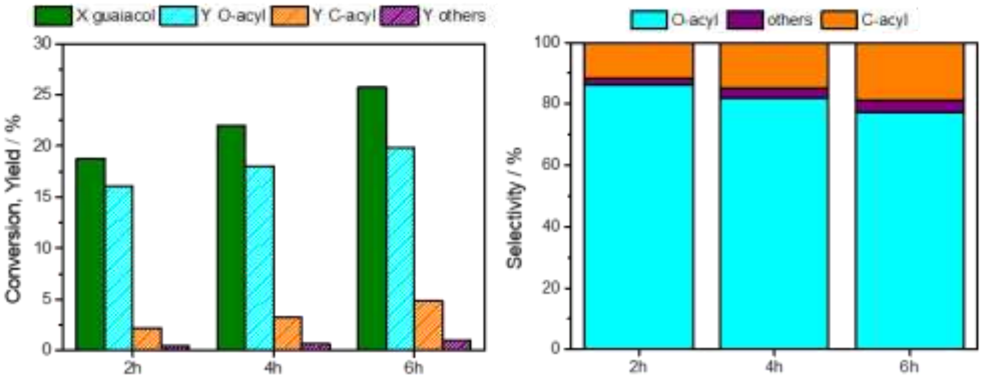

Figure 2. Catalyst performance in terms of Guaiacol conversion (X) and yields/selectivity of: acetovanillone (C-acyl), 2-methoxyphenyl acetate (O-acyl) and by-products (others).

The guaiacol conversion constantly increased with the reaction time (Figure 1), hitting a value of 27% at 6h. At the same time, the selectivity towards O-acyl decreased to a value of 77% in favor of the formation of acetovanillone that reached a selectivity of 20% and a yield of 6% after 6h of reaction. It is noteworthy that the formation of by-products was minimal and remained almost constant with the reaction time. The results obtained are in line with those observed in the literature for the gas phase reaction using zeolite catalysts[1,2] but in sensible harsher conditions of 250-270°C at which a higher formation of by-products (such as catechol and its derivatives) was observed. From the study of the reaction mechanism, it was possible to assert that, in these conditions, the acetovanillone is mainly formed through an intermolecular rearrangement of the O-acyl substrate with guaiacol, which will hardly undergo direct C-acylation by acetic acid. In conclusion, the continuous removal of water from the reaction enhanced the formation of the O-acyl that was the real acylating agent for the formation of acetovanillone with high purity (>95% of the C-acyl) and good yields.

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Supported Pt and Pt/Ni nanoparticles from metal carbonyl clusters as effective catalysts for biobased molecules valorisation

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Key words: Metal carbonyl clusters, supported metal nanoparticles, biomass valorization

In the last years, supported metal nanoparticles (NPs) have been widely employed in heterogeneous catalysis to obtain high-performance catalysts. Below 5 nm, nanoparticles chemistry has lots of connections with that of metal clusters: for instance, high-nuclearity clusters can be considered monodisperse and atomically defined metal nanoparticles. For this reason, metal carbonyl clusters (MCC) can play a role in better understanding and developing of the chemistry of ultrasmall NPs[1]. In particular, thanks to their chemical and structural composition, MCC have been considered promising precursors for the preparation of metal nanoparticles-based catalysts [2].

The main purpose of this work was to investigate the preparation of several heterogeneous Pt and Pt/Ni-based catalysts with the aim to minimize the use of Pt content, obtained by the effective decomposition of carbonyl cluster over TiO_2. Catalytic performances of the prepared catalysts were evaluated in the 5-hydroxymethyl-furfural (HMF) oxidation using base-free conditions and furfural reductive amination.

A series of random alloy carbonyl clusters $[NBu_4]_2[Pt_{6-x}Ni_x(CO)_{12}]$ with different Pt:Ni molar ratios were synthesised and supported on TiO_2 by wet impregnation, under nitrogen atmosphere.[3] The final catalysts were obtained through a decomposition of the cluster under controlled atmosphere and each sample was tested in the base-free oxidation of HMF. Some selected catalysts were also evaluated for the reductive amination of furfural.

IR spectra obtained on cluster modification during each synthetic step highlighted that carbonyl clusters were completely decomposed after a thermal treatment at high temperature. Moreover, the Pt and Ni distribution, evaluated by TEM analysis, confirms the formation of small and well dispersed Pt NPs, with an average diameter under 2 nm and narrow distributions, while Ni species appear to be dispersed on support surface suggesting the formation of a NiO_x layer. All Pt/Ni cluster-derived catalysts tested in base-free HMF selective oxidation to furandicarboxylic acid (FDCA) exhibited good performances: the presence of a Pt/Ni molar ratio of 5:1 improved HMF conversion up to 90% without the use of a base. This enhancement can be attributed to the formation NiO_x during cluster decomposition. Indeed, its basic properties can improve the catalytic activity. The presence of Ni species also contributes to the catalyst stability, in fact monometallic Pt catalyst presents an activity-loss after two reaction cycles, while bimetallic Ni/Pt materials remain stable for more cycles. The catalytic performances of the samples prepared using carbonyl clusters are significantly improved for HMF oxidation respect to similar systems prepared via incipient wetness impregnation of metallic salts. Moreover, these samples also present promising results for the reductive amination of furfural. This work highlighted that cluster decomposition on a support can be a suitable approach to design bifunctional active and stable catalysts promoting the formation of metallic nanoparticles over metallic oxide film.

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Catalytic performance of modified ZSM-5 zeolite for bioethanol conversion

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Keywords: Bioethanol, heterogeneous catalysis, H-ZSM-5

Over the last century, the use of fossil fuels has led to several environmental problems,such as increased greenhouse gas emissions, global warming and pollution. However, since our lifestyles are heavily dependent on hydrocarbon and chemical-based fuels, their production and consumption will not decrease in the future.

Bioethanol has been chosen for this work as a possible alternative to oil in the productionof hydrocarbons. According to literature [1], H-ZSM-5 catalyst allows to obtain C_3, C_4 and aromatic hydrocarbons, even though selectivity and optimization of process parametersare still important issues.

The aim of this work was to find out an alternative to fossil fuels in the achievement of environmentally friendly sources for hydrocarbon production and to explore if metal modified ZSM-5 can improve selectivity to different types of hydrocarbons. Whenbioethanol is used as a feedstock. Iron, zinc and tin have been chosen as exchanging metals. They were introduced into the ZSM-5 zeolite (CBV 5524 G, Zeolyst) by incipientwetness impregnation. Prior impregnation, parent protonic zeolite has been obtained bycalcination in dry air at 773 K for 4 h. In total, eight monometallic catalysts (with two different metal loadings) were prepared, as well as a bimetallic one. Catalysts were characterized by IR, UV-vis, SEM, XRD, TPSR and tested in similar conditions to thosereported in [2]. Reaction test were carried out by flowing 80 mL/ min and 8(v/v)% ethanolin nitrogen through a heated catalyst bed volume of 0.384 mL (60–70 mesh sieved). Reaction tests were performed by increasing the temperature by steps of 50 K in the range 423 - 773 K. Product composition was measured (GC-MS) when until steady statewas reached in each step.

It was seen that the different modifications of the parent zeolite did not enhance selectivity to heavy hydrocarbons, but instead product distribution improved, since several heavier hydrocarbons were produced upon catalyst modifications, observing remarkable selectivities for the product of interest.

Tin exchanged zeolites showed an improvement in the product distribution, since heavier hydrocarbons were produced. Moreover, they significantly improved selectivity to ethylene, while diethyl ether one was decreased. C_{3+} products were produced with a yield higher than 78% at 623 K over low loading tin modified zeolites.

Bimetallic Zn-Sn catalyst improved selectivity to diethyl ether, but it showed a lower products distribution, as well as a lower catalytic activity. Modification and effect on performances will be object of deep discussion.

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The Alternatives of Using Bioethanol as Hydrogen Source

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Ethanol, dehydrogenation, hydrogen, steam reforming

Bioethanol is a renewable, biodegradable, non-toxic raw material produced in an ever-larger amount as both a building block for chemicals and a base for a possible green transition to energy production. To the last purpose, ethanol can be a useful source of hydrogen. There are two different possibilities to produce hydrogen from bioethanol that are respectively: steam reforming and dehydrogenation. Steam reforming is based on the reaction:

$$C_2H_5OH + 3\ H_2O \rightarrow 2\ CO_2 + 6\ H_2$$

As it can be seen together hydrogen also CO_2 is obtained containing also small amounts of CO. Dehydrogenation reactions can be:

$$C_2H_5OH \rightleftarrows CH_3CHO + H_2$$

$$2\ C_2H_5OH \rightleftarrows CH_3COOC_2H_5 + 2\ H_2$$

In these cases, only pure hydrogen is obtained exempt of CO and CO_2 and both the reactions are reversible. According to Khamhaeng et al. [1] hydrogen produced by steam reforming is less expensive (1.58 USD/Kg H_2) than the production via acetaldehyde (1.97 USD/Kg H_2) or ethyl acetate (3.24 USD/Kg H_2). However, dehydrogenations have other advantages in particular the reaction to ethyl acetate. In fact, the reversibility of the involved reactions allows the possibility of using the couple ethanol-ethyl acetate as LOHC hydrogen carrier. The following successive reactions occur in the dehydrogenation [2]:

$$C_2H_5OH \rightleftarrows CH_3CHO + H_2$$

$$CH_3CHO + C_2H_5OH \rightleftarrows CH_3COOC_2H_5 + H_2$$

Then, ethyl acetate can be submitted to hydrogenation to repristinate ethanol with the following reaction: $CH_3COOC_2H_5 + 2\ H_2 \rightleftarrows 2\ C_2H_5OH$

Therefore, ethyl acetate can be hydrogenated to ethanol where there is an excess of energy production that cannot be used in place and converted into hydrogen by water hydrolysis. Hydrogen is so stored into the ethanol molecule for transportation toward place where hydrogen can be employed restoring by dehydrogenation ethyl acetate. In conclusion the ethanol-ethyl acetate system can be proposed as LOHC system. In this speech all the catalytic and kinetic aspects of the hydrogenation-dehydrogenation mentioned reactions will be discussed also considering the perspectives of catalyst performance improvements. The ethanol-ethyl-acetate LOHC system will be compared with others most studied LOHC system describing advantages and disadvantages of the mentioned systems.

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The PROMETH2eus project: from seawater to e-methanol

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Key words: Hydrogen, Electrolysis, SOECs, e-fuel, CO_2 capture

In July 2020, a primary role of hydrogen was established by the European Union, forecasting its growth in the energy mix from a value lower than 2% to 13-14% by 2050, with an underlying electrolysis capacity of 500 GW [1]. In synergy with the European Strategy, the Italian guidelines for the development of hydrogen were in turn outlined, citing among the levers that can be activated to achieve climate neutrality by 2050, that of a "radical change in the energy mix in favor of renewables (RES), combined with a profound electrification of end uses and the production of hydrogen, to be used as such or transformed into other fuels, also for the decarbonisation of non-electrical uses" [2]. Among all the methods for producing hydrogen, electrolysis of water is probably the cleanest when combined with a renewable energy source to produce electricity and solid oxide cell electrolysis (SOEC) has further advantages, due to the high operating temperatures: extremely fast process kinetics and potential integration synergies with downstream chemical syntheses, such as the production of e-fuels [3].

There is another aspect that deserves consideration. If we move away from the laboratory scale and envision extensive use of water as a source of hydrogen, it is conceivable that in coastal areas and hot arid regions where potable water is a scarce commodity, direct use of seawater constitutes a more reasonable choice; in any case, a direct use of seawater would make electrolysis extremely flexible [4].

According to these considerations, the social-economic motivation that leads to consider SOEC technology extremely promising in a new energy strategy is thus demonstrable, provided that the main challenges, such as performance, degradation and scale-up feasibility, are successfully addressed in a sufficiently rapid time [5].

The PROMETH2eus project pursues these aims and has as its main objective the manufacture of a solid oxide electrolyser with an innovative structure, fed with sea water, and its direct integration with a methanolation reactor fed with CO_2 from various sources. The took up challenges and the final objectives that the project intends to achieve will be presented.

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Green H_2 beyond electrolysis

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Key words: green H_2, H_2 vectors, carbon-negative H_2, PEC devices

Green" hydrogen will play a crucial role in the future of a carbon-neutral society, with multiple applications from carbon-intensive industries to transport, power and buildings sectors [1]. Thus, it is surprising that the discussion is focused almost only on electrolysis, an energy-intensive process. This lecture will discuss examples of alternative H_2 production and novel possibilities for hydrogen vectors to explore new opportunities in hydrogen production and distribution [2].

The lecture will discuss some examples of alternatives to electrolysis in producing green and even carbon-negative hydrogen. After introducing why it is necessary to go beyond electrolysis-only technologies, and briefly discussing the production of H_2 from waste [3], the concepts of i) H_2 from electrified SMR (steam methane reforming) and ii) green H_2 produced in a plasma-assisted process from bioCH_4 are presented. Both are just-started projects (EreTech and MECCA, respectively).

For hydrogen distribution (H_2 vectors), the catalytic hydrogenation of LOHC (Liquid organic hydrogen carriers) coupled with lignin derivatives oxidation to reduce LOHC production costs and links biowaste valorisation (biorefinery) to H_2 economy is introduced. This is also a just-started EU project (EPOCH). The final example regards the novel design of a PEC (photoelectrocatalytic) device integrating the chemical storage to allow a continuous (24h) production of green H_2. It is the first example of developing artificial trees for continuous or on-demand production of green H_2 in a distributed mode.

These examples highlight thus the many possibilities beyond the too-limited panorama of studies in the green H_2 arena. There is a need to accelerate innovative directions in green area production and distribution to address the challenge of a carbon-neutral society more effectively [1,2]. Catalysis and chemical engineering are crucial in realising this challenge [5,6].

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Novel possibilities to produce high-value chemicals from CO_2 by electrocatalysis

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Key words: CO_2, electrocatalysis, oxalic acid reduction, glycolic acid

The production of high-value chemicals by electrocatalytic reduction of CO_2 is one of the current challenges to fostering a fossil-free chemical industry based on renewable energy sources. While C1 products obtained by CO_2 reduction have a relatively low commercial value, C2+ chemicals are preferable from an industrial perspective [1]. The EU project OCEAN (Oxalic acid from CO_2 using Eletrochemistry At demonstratioN scale, ID 767798) developed, up to pilot scale, a new integrated process for producing high-value C2 chemicals from carbon dioxide using electrochemistry. The presentation will first introduce this project and also the pilot unit that has been realised to focus later the presentation on the specific aspect of developing advanced electrocatalysts for the selective electrocatalytic hydrogenation of oxalic to glycolic acid.

Electrodes prepared by anodic oxidation of Ti foils are robust and not toxic materials for the electrocatalytic reduction of oxalic acid to glycolic acid, allowing the development of a renewable energy-driven process for producing an alcoholic compound from an organic acid at low potential and room temperature. Coupled with the electrochemical synthesis of oxalic acid from CO_2, this process represents a new green and low-carbon path to produce added-value chemicals from CO_2 [1-3]. Various electrodes prepared by anodic oxidation of Ti foils were investigated. They were characterised by the presence of a TiO_2 nanotube array and small patches, debris, or TiO_2 nanoparticles [4]. The concentration of oxygen vacancies, the amount of Ti^{3+} measured by X-ray photoelectron spectroscopy (XPS) and the intensity of the anodic peak measured by cyclic voltammetry were positively correlated with the achieved oxalic acid conversion and glycolic acid yield. The analysis of the results indicates the presence of small amorphous TiO_2 nanoparticles (or surface patches or debris) interacting with TiO_2 nanotubes, the sites responsible for the conversion of oxalic acid and glycolic acid yield. By varying this structural characteristic of the electrodes, it is possible to tune the glycolic acid to glyoxylic acid relative ratio. A best cumulative Faradaic efficiency (FE) of about 84% with FE to glycolic acid around 60% and oxalic conversion ~30% was observed. The FE is highly dependent on the nanostructure of the electrode.

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Investigation of the behavior of different Cu-based gas diffusion electrodes for the CO_2 electroreduction in flow cells

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Keywords: CO_2 reduction, flow cell, gas diffusion electrode, ethylene

The electrochemical CO_2 reduction reaction is a promising technology to convert CO_2 into fuels and building blocks for chemicals using renewable energy. Cu is the only known metal catalyst converting CO_2 into a wide range of hydrocarbons and alcohols (mainly methane, ethylene, and ethanol).

To achieve higher production rates, flow cells employing gas diffusion electrodes (GDEs) instead of simple H-cells are needed. In a GDE, CO_2 diffuses through a porous gas diffusion layer and reaches the active sites located in the catalyst layer. The gas diffusion layer is thus an important element that only recently has attracted attention for the CO_2RR [1,2], while the role of its structure has been deeply studied for fuel cells.

With this regard, our work aims to establish how the structure of the gas diffusion electrodes affects the Faradaic Efficiencies (FEs) in a flow-cell CO_2 electrolyzer. We employed commercial Cu nanoparticles as electrocatalyst and selected a range of market-available carbon fiber papers to be used as gas diffusion layers.

We show that the structure, composition, and type of cracks of GDE greatly influence the FE of CO, H_2, and ethylene. For instance, larger and more abundant cracks are detrimental to ethylene production. Filling the cracks with higher carbon black to PTFE ratio changes the selectivity by increasing the CO to ethylene ratio. Using a crack-free GDE is advantageous for getting high ethylene FEs. The influence of these parameters on long-term stability will also be discussed.

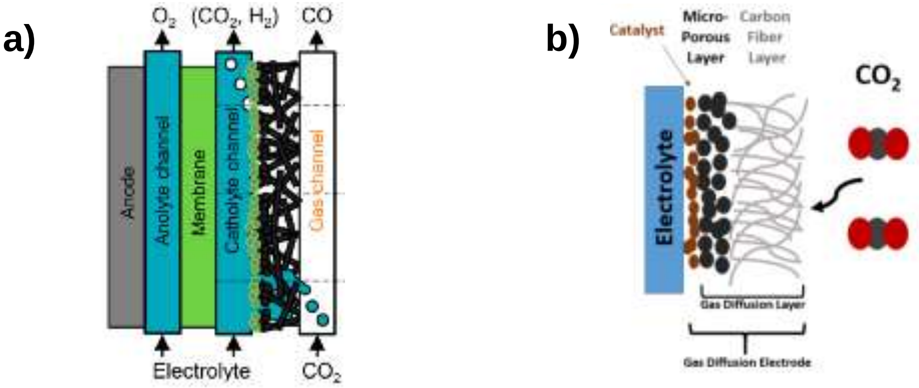

Figure 1. a) Flow cell CO_2 electrolyzer (ref. 3); b) scheme of gas-diffusion electrode.

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Metal-free Electrocatalysts for the Selective 2e$^-$ Oxygen Reduction Reaction: A Never-Ending Story?

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Key words: 2e$^-$ ORR · O-functionalized MWCNTs · electrochemistry · exohedral functionalization

In the recent years, the electrocatalytic oxygen reduction reaction (ORR) for the selective 2e$^-$ reduction path to give H_2O_2, has powerfully emerged as a cost-saving (ambient conditions) and environmentally benign technology (green and without organic wastes) alternative to the classical anthraquinone process.[1] The combination of this electrochemical technology with the use of renewable electricity sources (*i.e.* sun and wind) makes it an even more desirable alternative to existing production methods based on the use of fossil fuels. Metal-free carbon-based materials, in the form of light-weight hetero-doped networks (*i.e.* N, O) eventually featured by hierarchical porous architectures, are emerged as an effective, cheap and abundant alternative to the use of noble metal-based electrocatalysts for both a selective 4e$^-$ and 2e$^-$ O_2-reduction path.[2-3] Several "bottom-up" synthetic strategies have been applied to the production of O-enriched C-materials applied to for a selective 2e-ORR. However, the co-existence of different O-functionalities has made highly speculative any conclusion on their role on the ultimate process selectivity.

Herein, we report the "top-down" exohedral decoration of multi-walled carbon nanotubes (MWCNTs) with selected O-containing functionalities (*i.e.* carboxyl, carbonyl, ether and phenol/hydroxyl groups) for the fine tuning of the chemical and electronic surface properties of these complex carbon networks. Their use as metal-free electrocatalysts for ORR under alkaline environment (Figure 1) has spotted-light on the superior performance (onset potential and H_2O_2 selectivity) of samples containing dangling phenol groups as the most active functionalities engaged for a selective 2e$^-$ ORR. Details on the ORR mechanism at work and on the control on the process selectivity will be discussed.

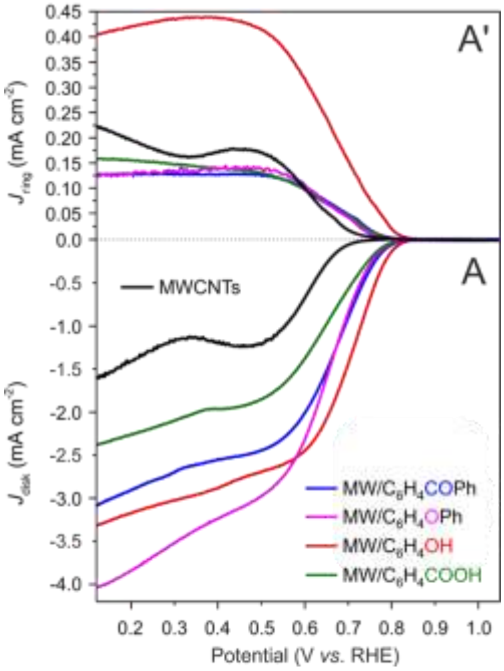

Figure 3 A) Disk and A') Pt-ring RRDE Linear Sweep Voltammograms of variably functionalized MWCNT samples and plain MWCNTs registered in an O_2-saturated 0.1 M KOH aqueous solution at 1600 rpm.

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Hydroformylation of olefines with CO_2 as CO precursor, an electrochemical-catalytic tandem approach.

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Key words: CO_2 reduction, electrochemistry, hydroformylation, olefines, aldehydes

Hydroformylation is with no doubt one of the key processes of the chemical industry since the production of oxo-products (aldehydes and alcohols) from olefines reaches more than 10 million metric tons per year[1]. Aldehydes are an extremely valuable product, and they also act as intermediate for the synthesis of many bulk chemicals; however, syngas utilization presents not negligible problems such as the under-pressure use of the toxic and flammable CO and H_2 stream, so the syngas replacement with a milder surrogate would be beneficial. Moreover, the process requires elevated temperatures, rendering the overall process conditions harsh and energy consuming. Among the possible surrogates CO_2 is extensively studied because of its inert nature and because of its primary role in the climate change processes as greenhouse gas.

Inspired by few numbers of recently published works concerning the coupling of eCO_2RR with hydroformylation/carbonylation reactions [2–4], a tandem double chamber set-up is under development. The idea is to produce syngas from the electrochemical CO_2 reduction that will be further used for the hydroformylation of waste olefines as 1-octene and D-limonene with a view to circular economy. The electrochemical set-up consists in a three electrodes system immersed in an organic electrolyte containing Ionic Liquids (1- Butyl-3-methylimidazolium triflate, BMIM.TfO) to both enhance the conductivity of the solution and the CO_2 capture; the gaseous products of the eCO_2RR are collected and quantified by µ-gascromatography. The reaction conditions in the two compartments are under development separately. The hydroformylation reaction is currently under study using $Rh(acac)(CO)_2$ as catalyst and diluting the syngas atmosphere with CO_2 to simulate the composition of the outstream gas from the electrochemical cell. A conditions screening hasbeen done to find the best parameters to couple the two reactions; different solvents, ligands, temperatures, pressures, catalyst/ligand and catalyst/substrate ratios have been studied to improve both the conversion of the substrate, the rate of the reaction and the selectivity towards the target products. The reaction products of the hydroformylation reaction are quantified by GC-MS spectrometry and ^1H NMR spectroscopy.

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Ruthenium Complexes as Efficient Catalysts for Transfer Hydrogenation Reactions

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Key words: ruthenium – transfer hydrogenation – carbonyl compounds

The employment of selective and productive ruthenium catalysts for transfer hydrogenation (TH) and hydrogenation of carbonyl compounds is a cost-effective and environmentally benign way for the production of alcohols. Since TH is a reversible reaction, these catalysts can be used for the Oppenauer-type oxidation of alcohols and related C-H activation reactions, namely alcohol racemization and borrowing hydrogen reactions.

In order to improve the catalytic activity and retard decomposition, the design of suitable metal systems based on chelating and non-innocent ligands appears crucial.

The preparation of ruthenium complexes and their use as efficient catalysts for TH of ketones and aldehydes, including biomass-derived molecules (5-HMF, ethyl levulinate),[1] Oppenauer-type alcohol oxidation,[2] amine alkylation with alcohols[3] and photochemical TH of carbonyl compounds are presented (Figure 1).[4]

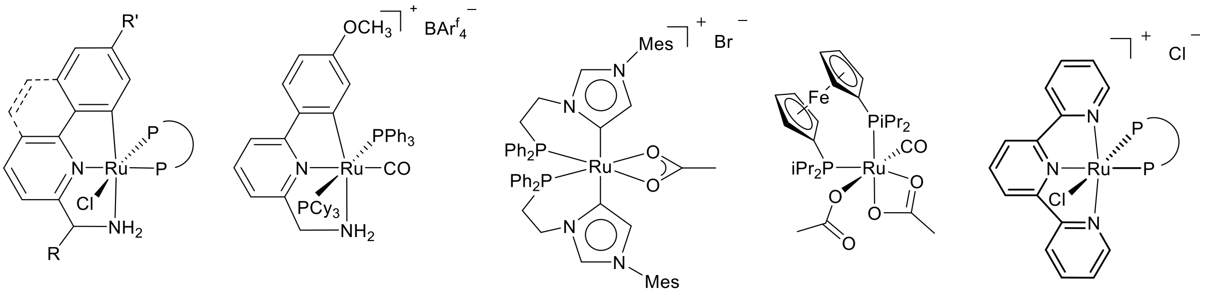

Figure 1

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Nickel nanoparticles as high selective and recyclable catalyst

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Key words: nanoparticles, nickel, green chemistry, green catalysis

Industrial valuable products such as aniline, nitroso benzene, azobenzene and azoxybenzene are often desirable and precious products for catalytic reactions. Aniline and secondary amines are important intermediates to produce fine chemicals, pharmaceuticals, polymers, herbicides, and more. Among intermediates, azoxybenzene is one of the most important and essential building blocks of naturally occurring compounds and functional materials due to its conjugated system and polar functionality. At the same time, biomasses are a useful source to produce energy and chemicals. The production of biofuel deriving from animal fats, vegetable oils and so on had an increasing scientific interest in the last few years. With the aim to set up new environmentally friendly synthetic methods to be performed under mild and sustainable conditions with high efficiency, herein we report the synthesis and characterization of a polymer supported Ni(II) complex (Ni(II)-pol). Ni(II)-pol was subsequently calcinated at 300°C to give polymer supported NiO (NiO-NPs) and/or Ni nanoparticles (Ni-NPs), depending on the calcination procedure employed. When the catalyst supported Ni-NPs, it was active, selective and recyclable for the for the synthesis of primary and secondary anilines[1,2], while when it supported NiO-NPs, it resulted active, selective and recyclable for the synthesis of azoxyderivates. Ni-NPs was also found to be active and highly selective catalyst for upgrading biodiesel deriving from waste cooking oil[3]. In all cases the catalysts were recycled for five catalytic runs without detecting a loss of activity and selectivity. They were fully characterized by STEM, IR and elemental analysis before, during and after several catalytic runs.

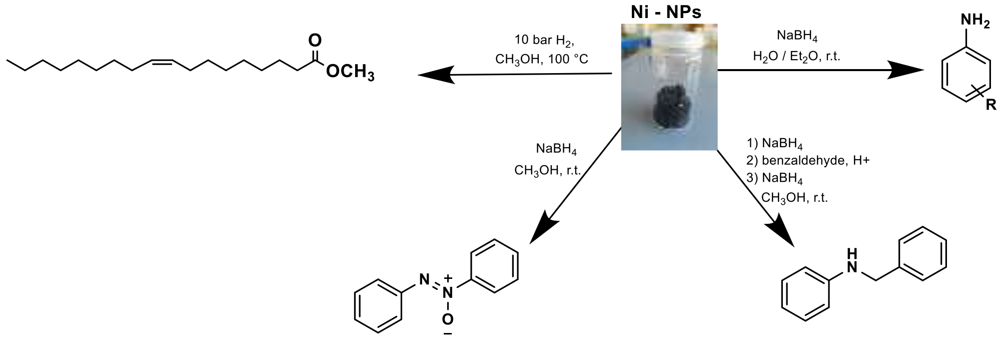

Figure 1. Catalytic applications of nickel nanoparticles

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Looking for stability: from aerosol Cu/SiO$_2$ catalysts to bimetallic NiCu/SiO$_2$ for the bioethanol dehydrogenation

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Key words: aerosol-assisted sol-gel process, bimetallic catalysts, bioethanol, dehydrogenation

Among the employed metals for dehydrogenation reactions, Cu has been largely studied in several industrial processes[1]. Particularly for the ethanol to acetaldehyde reaction, with the rise of biomass technology and bioethanol availability[2], many efforts have been carried out by researchers to develop new active copper-based catalysts[3]. Nevertheless, their rapid deactivation is still an unresolved challenge. For Cu supported catalysts, mainly metal sintering and coking are found to be detrimental for the catalyst lifetime[4]. Cu sintering causes a drop in active surface area and the exposure of the catalytically non-innocent support, with a consequent drop in acetaldehyde selectivity as well as the formation of side products that trigger fouling. Among the supports, silica is promising. In fact, Cu/SiO$_2$ catalysts are reported as highly selective to acetaldehyde because of the relative inertness of silica. Despite of this, SiO$_2$ is known to establish only weak interactions with supported metal nanoparticles, and the latter are therefore particularly prone to sintering. The design of deactivation-resistant catalysts that will demonstrate both high activity levels and long-term stability is still demanded in this domain. Thus, leveraging on an effective one-pot synthesis technique (Aerosol Assisted Sol Gel method (AASG)[5]), we firstly developed highly active and selective aerosol Cu/SiO$_2$ catalysts with a stronger intimacy between the active phase and the support[6]. With the teachings gained from a deep characterisation of fresh and exhausted catalysts, we identified the key parameters that govern both the high activity and the causes of deactivation. Then, we decided to further tailor the catalysts activity and stability by synthesizing bimetallic catalysts. Since Ni is reported[7] as a suitable candidate to improve thermal stability and catalytic activity of Cu, the effect of its addition has been investigated. A series of bimetallic Ni-Cu/SiO$_2$ catalyst was prepared. The synthesized materials have been tested in the ethanol dehydrogenation reaction and extensively studied looking also at the deactivation effects, by a complete characterization survey based on N$_2$ physisorption, XRD, FT-IR, DR-UV-VIS, XPS, TEM, TGA-MS. Remarkably, the bimetallic catalysts showed surface areas higher than 400 m^2/g and an homogeneous dispersion of the two elements, both in the bulk and at the surface. Furthermore, the best formulation, maintained stable and higher than 65% ethanol conversion at 523 K for 8 hours.

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Oxidation of cyclohexane to KA oil using noble metal-free Ce andZr-based mixed oxides

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Key words: KA oil, cyclohexane oxidation, mixed oxides, inverse microemulsion, heterogeneouscatalysis.

Cyclohexane oxidation is a crucial process in industrial chemistry. Despite its significance, the reaction is challenging due to kinetic and thermodynamic obstacles and operates via a complicated free radical mechanism. The existing industrial method employs a homogeneous Co-based catalyst and limits the conversion of cyclohexane at 4-5% conversion[1] for maintaining approximately 80% selectivity to KA oil. In recent years, numerous heterogeneous catalysts have been examined[2,3,6]. In this study, a series of non-noble metal (Cu, Fe) Ce and Zr-based mixed oxides has been found to be effective and promising as catalysts in cyclohexane oxidation.

The mixed oxides were prepared via inverse microemulsion[4], in order to obtain Ce or Zr mixed oxides that contain a lower amount of either Cu or Fe (1:9 molar to the amount of Ce or Zr). Additionally, a bare Ce-Zr mixed oxide with a 1:1 molar ratio was prepared. These mixed oxides were then subjected to reduction in the presence of $NaBH_4$ at 300°C to introduce defects in the structure of the oxides. The catalytic oxidation of cyclohexane was carried out at 120°C and 4 bars of O_2 using benzaldehyde (10 uL) as a radical initiator, similar to our previous work[5]. Different solid-state analytical techniques, such as STEM/EDX, XRD, BET, and XPS, were employed to characterize the catalysts.

The activity of the catalysts has been evaluated under mild conditions and the innovative use of benzaldehyde as radical initiator. Surprisingly we observed a strong dependence on the catalyst amount which allowed us to study the presence of a different reaction mechanism. Moreover, Cu-containing oxides resulted in favouring the more industrially valuable cyclohexanone[7] giving a $K/A>1.5$, while the other oxides gave a $K/A\leq1$. The reduction of the oxides boosted up the activity, and even the behaviour of the Cu and Fe-containing oxides differs significantly. After a careful characterisation (STEM/EDX, XRD and XPS) we were able to correlate the different productivity to structural alterations. As a result, modified Ce and Zr mixed oxides containing Cu and Fe are an appealing discovery in terms of ease of preparation, effectiveness, and stability.

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Effect of milling parameters on the chemistry, morphology, and CO oxidation activity of CeO_2 powders

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Key words: cerium oxide, mechano-chemistry, defects, reducibility, CO oxidation

The mechano-chemical activation of powder materials represents an interesting opportunity for the sustainable functionalization of heterogeneous catalysts,[1,2] by inducing meta-stable phase transformations on metal oxides[3,4] or promoting unique metal-support interactions on supported metal catalysts.[1,5] Here, the simple mechanical action on pure CeO_2 supports was investigated in terms of textural, morphological and redox properties, as a function of starting material and milling intensity, allowing for the prediction and design of CeO_2 powders properties for catalytic applications by dry milling.

Under mild energy milling, variations of the initial properties of the CeO_2 powders are observed only at long (> 2h) milling times, while the most significant changes in CeO_2 morphological properties are achieved by high energy milling. Most noticeably, the surface area of ceria powders tends to an equilibrium value (Fig.1a), due to crystallite breakage being induced on larger particles and agglomeration promoted on smaller particles.[1] Simultaneously, the mechanical action generates defects on the ceria surface,[4,5] highlighted by the appearance of a Raman band at 600 cm^{-1} (Fig.1b). Despite reduction in surface area (Fig.1a) and porosity (not shown), the increased amount of surface disorder leads to enhanced reducibility at low temperatures (>500°C, Fig.1c), which leads to improved catalytic performance in reaction where oxygen exchange is required and could potentially act as anchoring points for metals when used as a support oxide.

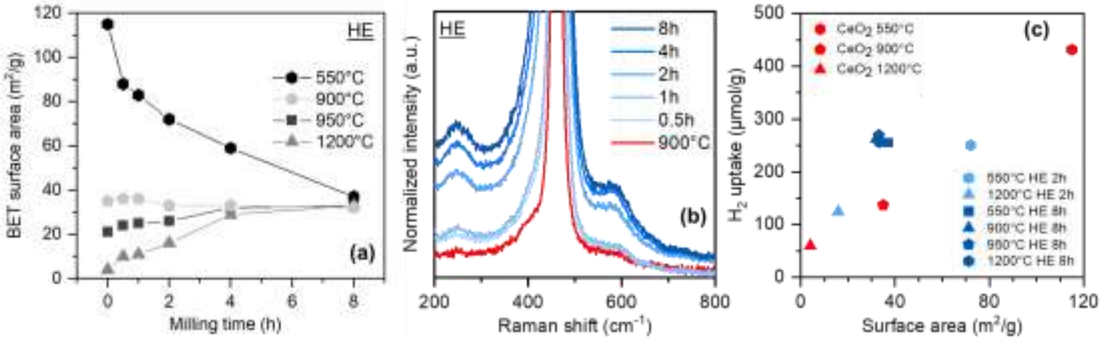

Figure 1. BET surface area (a), Raman spectra (b) and H_2 consumption below 500°C (c) as a function of milling time at high energy for selected samples.

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Heterogeneously catalyzed esterification of oleic acid with trimethylolpropane: a kinetic investigation

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Key words: bio-based lubricants; polyol esters; esterification reaction; heterogeneous catalysis; kinetics

There is a new interest in the use of lubricants obtained from vegetable oils due to growing concern over the environmental impact of fossil fuels. From a chemical point of view, bio-lubricants are composed of fatty acid alkyl esters. These products are currently derived from vegetable feedstocks (i.e., edible, non-edible, and waste vegetable oils) and they are characterized by low toxicity and high biodegradability [1]. Oleic acid is most frequently used to produce bio-based lubricants due to its huge abundance in the vegetable oils. On the other side, branched polyols, such as trimethylolpropane (TMP), have been widely used to produce polyol esters with enhanced thermal and oxidation stability thanks to the absence of β-hydrogen atoms in their structure and generally good flow properties comparable with those of mineral lubricating oils. For these reasons, they find different applications as engine lubricants, gear oils, hydraulic and pump oils [2].

The use of an acid heterogeneous catalyst is a key factor for the production of sustainable lubricants on an industrial scale. Acidic organic resins and zeolytes have been demonstrated to be inadequate for the esterification reactions involving large-sized molecules whereas supported heteropoly acids, sulphonated metal oxides and binary metal oxides showed better catalytic performances [3]. In particular, tungstic acid supported on silica (H2WO4/SiO2) has shown promising activities in the synthesis of bio-based lubricants [4]. At the actual state of art, literature is still scarce of articles dealing with the kinetics of heterogeneously catalyzed synthesis of polyol esters of oleic acid.

The aim of this work is to study in depth the kinetics of the esterification of oleic acid with trimethylolpropane catalyzed by H2WO4/SiO2. Several experiments have been performed in a batch reactor under different experimental conditions to investigate the effect of temperature, catalysts’ loading, agitation speed and reactant molar ratio.

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The impact of exsolution on chemical looping applications of $Sr_2FeMo_{0.6}Ni_{0.4}O_{6-\delta}$

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Key words: double perovskite, chemical looping, molybdates, exsolution

Chemical looping (CL) schemes for cyclically splitting CO_2/H_2O into CO/H_2 making use of solid oxygen carriers (OCs)[1] can be a valuable strategy in the context of the ecological transition to intensify processes such as reverse water-gas shift and steam/dry methane reforming. Notable examples of OCs at present are nonstoichiometric ceria and perovskites[2] that show very fast kinetics and long-term thermal stability compared with stoichiometric oxides. In this study, we explored for the first time the potential use of $Sr_2FeMo_{0.6}Ni_{0.4}O_{6-\delta}$ in chemical looping applications. The focus was on the effects of Ni exsolution on the performance of Reverse Water-Gas Shift Chemical Looping reaction (RWGS-CL). Following subsequent redox cycles, a core-shell perovskite @ Ni-Fe structure is formed and characterized by XRD and HRTEM analysis. It exhibited competitive performances[3] and excellent stability in RWGS-CL process. The best reduction and oxidation temperatures for maximizing the CO yield resulting from thermogravimetric tests are around 850 °C and 750 °C, respectively (Figure 1). The final composition was able to work steadily in isothermal conditions at 850 °C keeping a quite high CO production with time (around 1500 $\mu mol_{CO}/g$ after 350 h), comparable with or superior to most of the available yields reported in literature. Other CL schemes are currently under investigations for further applications.

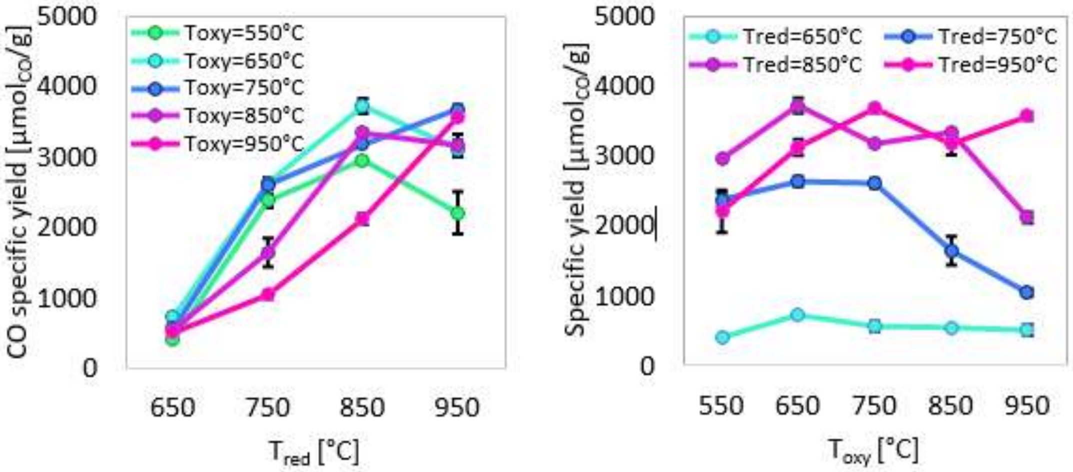

Figure 1 – CO specific yields calculated from thermogravimetry analysis (3-cycles-averaged values) as function of reduction and oxidation temperatures (average value ± 1 standard deviation).

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Cu-doped perovskites for the photo-reduction of CO_2

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6. **Key words:** photocatalysis; EXAFS; CO_2

Carbon capture and usage (CCU) technologies are amongst the alternative strategies aiming at buffering the environmental threaten posed by the increasing amounts of CO_2 in the atmosphere [1]. Due to the energetic inputs, CO_2 sequestration and conversion is still costly and therefore not yet industrially feasible [2]. Photocatalysis involves the use of light as energy source to enable a redox reaction via electronic excitation and consequent formation of electron-hole couples and, in this context, it could enable CO_2 conversion without additional energy and pollution [3]. Strategies such as doping, scaffolding or introduction of a co-catalyst often aim at reducing recombination and improve both selectivity and photo-responsiveness, which often limit the overall catalytic performance [4]. Although TiO_2 is on the most studied photo-active materials, low selectivity and yields still prevent its industrial application [5]. Alkaline-earth-metal-based perovskites have recently emerged as versatile photocatalysts, owed to the possibility to tune both their structure and stoichiometry [6]. Moreover, the intrinsic basicity of alkaline-earth-metal-based perovskites could favour CO_2 adsorption, thereby potentially improving the overall selectivity towards C-based products. CuO was extensively studied for the CO_2 reduction, and also proved to improve selectivity towards C-based products [7]. In this work, $BaTiO_3$ perovskite and CuO NPs were synthesized via hydrothermal method. Both $BaTiO_3$ and CuO-$BaTiO_3$ were tested for the photo-conversion of CO_2 into valuable products and their yields compared to a TiO_2 benchmark. Ambient pressure near edge X-ray absorption fine structure (AP-NEXAFS) investigation in *operando* conditions aimed at monitoring the electronic structure modifications occurring at the sample surface by addition of CuO nanoparticles (NPs). In fact, the formation of redox couples in +2/+1 in Cu co-catalyst is thought to participate to CO_2-direct reduction and therefore to increase the selectivity towards C-based products [7]. Moreover, the formation of heterojunctions in the CuO-TiO_2 and CuO-$BaTiO_3$ interfaces is proposed to play an important role in both a) the initial oxidation state of Cu and b) the photo-mediated inter-states charge exchange. As an in-depth understanding of the p-n junction behaviour in a CuO-$BaTiO_3$ system has not yet been achieved with regard to photocatalysis, the outcomes were related to the photocatalytic activity and to changes in the local chemical environment and oxidation state of the catalyst active sites, to obtain clues on the reaction mechanism.

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Reaction mechanisms of methanol *vs.* ethanol synthesis on Cu-based materials.

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Key words: Catalysis, DFT, CO_2 reduction, mechanisms of reaction.

The electrochemical carbon dioxide reduction reaction (CO_2RR) to chemicals and fuels has received great attention in the last few years. However, the key effects and catalytic mechanism for this reduction reaction on copper-based materials are still not entirely clear and deserve in-depth exploitation[1]. Among these materials, oxide derived Cu catalysts are unique because they reduce CO_2 to significant amounts of high-order hydrocarbons and alcohols[2]. In the present study, density functional theory (DFT) calculations have been performed to understand the role of metal in selective ethanol *vs.* methanol formation using doped and undoped models of some copper-based catalysts.

The DFT calculations obtained reveal what can reduce the C-C coupling reaction's barrier energies, determining for the synthesis of C_2 products. The findings herein reported may provide guidelines for the design of CO and CO_2 reduction active sites with enhancing *vs*. ethanol's selectivity than others chemicals.

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In-Cu binary oxides catalyst for CO_2 hydrogenation

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Key words: Cu-In, Methanol synthesis, CO_2 hydrogenation, Electrocatalysis, Thermo-catalysis

Hydrogenation reactions are an important catalytic process for valorising CO_2 waste. The CO_2 hydrogenation process has different possible product for instance methanol and formic acid. Methanol is a thermal-catalytic product and formate is an electrocatalytic product. To improve the methanol production in thermal-catalysis, in this work In-Cu binary oxides catalysts have been studied. According to the literature, In_2O_3-based catalyst has been investigated for its high selectivity into methanol [1, 2]. Otherwise, the industrial catalyst for methanol production is $Cu/ZnO/Al_2O_3$. This catalyst has the highest conversion of CO_2, but its selectivity to methanol is low. In this aim, a mixture of In-Cu oxide catalyst could improve the catalytic performance [3, 4]. At the same time, we tested this catalyst with electro-catalysis for producing formate. The In-Cu catalysts ($In_xCu_{100-x}O_y$) were synthetized via gel-oxalate coprecipitation by varying the atomic ratios between In and Cu. Afterwards, they were characterized with different techniques such as ICP-MS, N_2 physisorption, XRD, H_2-TPR, CO_2-TPD, SEM, TEM. What is more, with the purpose of determining the thermo-catalytic performance, the catalysts were tested in a fixed bed reactor (20 NL/g_{cat}/h, 2.1 MPa, $H_2/CO_2/N_2$ molar ratio equal to 15/5/1) at different temperature (200-300 °C). Furthermore, a 20-h stability test was done on each sample to study the deactivation phenomena. Subsequently, the spent catalysts were characterized to rationalise the catalytic results. Figure 1 summarizes the performance of In-Cu binary oxides catalyst during activity tests: $In_{90}Cu_{10}$ achieved a methanol yield of 3.25%, which is 51% of the equilibrium yield. In conclusion, we have observed that Cu could be a good promoter of the In_2O_3 for the methanol synthesis reaction.

At the same time, the catalysts have been tested in electro-catalysis for producing formate. As a result, we obtained that $In_{90}Cu_{10}$ has higher formate productivity (faradic efficiency 15%) compared to other In-Cu binary oxide catalyst. This efficiency is higher than CuO faradic efficiency, but comparable with In_2O_3 catalyst.

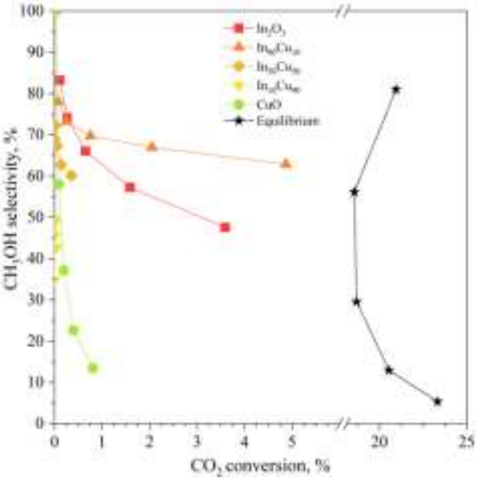

Figure 1. CO_2 conversion-selectivity map at 2.1 MPa, 20 NL/g_{cat}/h (inlet: $H_2/CO_2/N_2$ = 15/5/1) in temperature ranged from 200 °C to 300 °C.

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Unconventional photocatalysts for the H_2 production by solar photoreforming

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Key words: Carbon nitride, silicon carbide, Hydrogen, Photoreforming.

One of the green ways to obtain hydrogen is photocatalysis through solar photoreforming of water[1]. This process combines the water reduction with the organic oxidation on a semiconductor material. In this context, bisphenol A (BPA) and polyethylene terephthalate (PET), employed as sacrificial agents, can play an important role also considering the plastics water pollution. However, one of the necessary steps for the photoreforming reaction is the efficient solubilization of these organic substrates by various pre-treatments, that requires hard conditions which can deactivate the photocatalysts. The focus of this work is the study of uncommon photocatalysts as silicon carbide (SiC) coupled with graphitic carbon nitride (g-C_3N_4). To obtain the SiC-g-C_3N_4 composites, the commercial SiC was mixed with different amounts of urea and treated at 450°C for 5h with a 5°C/min ramp to favor the thermodegradation of urea and the formation of g-C_3N_4 with different wt%. The sacrificial agents were BPA (Sigma-Aldrich) and PET from commercial bottles.

From Fig. 1 it is possible to note as the SiC 0,5% g-C_3N_4 sample was the most active towards the BPA photoreforming providing at an alkaline pH (13), 12 μmol $H_2/g_{cat}\cdot h$. The same photocatalyst was the most active for the PET photoreforming, obtaining a minor amount of H_2 (2,7 μmol $H_2/g_{cat}\cdot h$). No H_2 was produced at acid pH for both BPA and PET. photoreforming

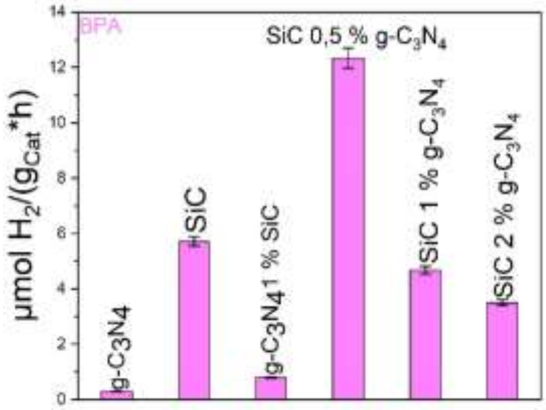

Figure 1 Photocatalytic H_2 production by BPA photoreforming (pH=13, 5 h of solar irradiation).

Interestingly, a higher amount of g-C_3N_4 was detrimental for the activity, due to the covering of the SiC surface sites by the excess of carbon nitride. The good interaction between unconventional photocatalysts as SiC and g-C_3N_4 allowed to explore new and green ways to produce H_2 from plastic wastes.

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Layered Double Hydroxides based photo-electrocatalysts for CO_2 conversion into solar fuels and chemicals

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Key words: CO_2 conversion, Photo-Electrocatalysis, Layered Double Hydroxides, solar fuels

Photoelectrochemical CO_2 valorization is a sustainable and promising way to reduce carbon dioxide concentration in atmosphere through its capture and conversion into fuels and chemicals. Tremendous efforts have been already made to identify the best materials and device configuration for efficient CO_2 reduction reaction (CO_2RR) in Photoelectrochemical Cell devices (PEC)[1]. Layered Double Hydroxides (LDHs) anionic clays represent an appealing option for such application thanks to their good affinity for CO_2 and tunable chemical composition[2]. This aspect allows to modify morphological, physical-chemical, and electrochemical properties of the material to provide good catalytic activity.

Ni, Cu and Fe containing LDHs films supported on a conductive glassy substrate (FTO) were produced through screen printing deposition of LDH powder-based ink. Bulk LDHs have been synthetized by coprecipitation method as described in a previous work of our group[3]. The photoelectrodes have been characterized with different techniques (XRD, SEM, UV-Vis, cyclic voltammetry (CV), Linear Sweep Voltammetry (LSV), Electrochemical Impedance Spectroscopy (EIS) and Mott-Schottky analysis. Photoelectrocatalytic CO2 reduction tests were performed in a three-electrodes PEC cell equipped with a quartz window.

The presence of LDH phase and the morphological homogeneity of the samples, both powder and films, were confirmed by XRD and SEM analysis. Band gap and electronic energy levels' position of the samples have been defined and confirmed compatible with standard potentials of CO_2RR thanks to UV-vis DRS and Mott-Schottky tests respectively. The characterization of the electron transfer ability, charge accumulation capability, and materials conductivity of the LDHs by CV, EIS and LSV showed that both NiFe 3:1 LDH and NiCuAl 3:1 LDHs provided an appreciable cathodic current density starting at -1.25 V vs Ag/AgCl, resulting promising materials for PEC electrodes.

These properties were linked to the photoelectrocatalytic activity of Ni, Cu, Fe containing LDHs toward CO_2 reduction. Higher selectivity for C-containing products i.e., formic and acetic acid, over hydrogen evolution was achieved at relatively low potential of – 0.8 V vs NHE (pH=7), while H_2 evolution was favored when higher potential was applied i.e., – 1.3 V vs NHE (pH=7).

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Thermocatalytic pyrolysis of methane over Fe/Al_2O_3 catalysts for hydrogen production

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Key words: methane pyrolysis, green hydrogen production

The indiscriminate use of fossil sources has led to the emission of large quantities of greenhouse gases, which are mainly responsible for climate change. The transition from fossil to renewable could represent a paradigm shift. Nevertheless wind, photovoltaic and hydroelectric plants, due to their nature, generate a difference between energy production and its consumption. In this way, in a temporary phase of the energy transition, it is necessary to replace the combustion of fossil fuels with other technologies that guarantee a reduction of carbon emissions and, at the same time, a programmable energy supply. Hydrogen represents one of the most promising energy carriers: its use guarantees a low environmental impact and flexibility of the energy system. Nowadays, the two main technologies adopted to produce hydrogen are the Steam Methane Reforming (SMR) and the electrolysis of water. SMR is the most widespread and economically advantageous technique. However, it is characterized by high greenhouse gas emissions. Electrolysis based on renewable sources has a low environmental impact but high production costs and a strong dependence on climatic fluctuations. Therefore, in the short term, it is necessary to develop low-cost techniques based on the exploitation of fossil fuels with a low carbon footprint. In this sense, a promising technological solution is represented by the Thermocatalytic Pyrolysis of Methane (TPM)(1). This process can be the main technology of energy transition towards a sustainable hydrogen economy. TPM involves the dissociation of the methane molecule into hydrogen and elemental carbon in the presence of a catalyst. The main advantage of this technique is the production of clean hydrogen with the formation of solid carbon as only by-product. Our work aims to analyze the production of hydrogen by TPM conducted on Fe/Al_2O_3 catalysts. In particular, the performance of two iron oxide-based catalysts (40% wt.) on alumina support (60% wt.), obtained through two different synthesis techniques such as Wet-Impregnation (WI)(2) and Solution Combustion Synthesis (SCS), were studied. Different characterization techniques were carried out in order to evaluate the composition and structural (XRD, BET, Raman), morphological (FESEM) and chemical (TPR) properties of the different analyzed samples. TPM tests were carried out under different operating conditions in order to evaluate the performance and catalytic properties of the two types of catalyst. Experimental results show how the catalyst obtained by impregnation is characterized by lower activity and at the same time greater stability than the catalyst obtained through SCS.

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Can biotechnology deliver cost effective liquid fuels from renewable feedstocks?

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Biofuels, CO_2 fixation, biotechnology, oil production, sustainability

The importance of liquid fuels in transportation is well established, yet, there are presently no viable options for their cost-effective production from renewable feedstocks. During the past 15 years we have been developing in my lab a system for the conversion of gas mixtures of hydrogen (or CO) and CO_2 to oils or alkanes. The system comprises anaerobic fixation of CO_2 and conversion of the CO_2 fixation product (for example, acetate) to lipids, from which biodiesel can be produced. In another application, the CO_2 fixation product is converted to alkanes. Our work includes both the engineering of the microbes *and* development of a process to achieve gas to liquid conversion in prototype systems. These systems are scalable, make no use of land (beyond what is needed for generating renewable electricity for hydrogen production), do not compete with food and are cost competitive based on high level cost analysis. I will present the essential features of this process in my talk; full details can be found in the 5 papers cited.

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Steam reforming reactions for the sustainable hydrogen production from biomass-derived raw materials

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Key words: Hydrogen; Steam Reforming; Heterogeneous catalysis

The world is—at last—heading toward the total decarbonization of the energy sector, and hydrogen has been identified as a key player in this scenario. This means that its production must keep pace with the forecasted surge in demand. While electrocatalytic production methods can direct harness sustainable energy inputs, like solar energy, thermocatalytic approaches will be as critical to this transition because of the much higher hydrogen production rates. But classical reforming catalysts have hard times when dealing with renewable resources, mainly because were conceived for converting methane. Often noble metals are used in the new catalytic formulations, so their content must be as low as possible without scarifying activity and stability. A strategy to achieve that is to limit the defectivity of the metal nanoparticles particles thus reducing the coke formation sites[1]. Alternatively, the (careful) addition of an acidic promoter can be used to improve the activation of organic reactants, like glycerol, to relief the noble metal of some work[2]. The exploitation of the right amount of acidity, which is somewhat counterintuitive for reforming reactions since coke formation is generally favored by these acid sites, can be also applied to non-noble metals, like Cu, whose unique properties allow for a fine tuning of its acidic characteristics. By modifying the reducibility of the support, for example, all the catalytic steps can be directed onto the Cu sites resulting in almost a four-fold higher hydrogen production rate[3]. When hydrogen purity is the goal, for instance for applications involving fuel cells, then all the reactions steps must be maximized in order to avoid the formation of byproducts such as carbon monoxide. To this end, adding In, which is an excellent methanol synthesis catalyst, to a Cu catalyst turned out to promote the hydrogen selectivity during the methanol steam reforming reaction. Through a series of investigations which included extended DFT calculations, it was possible to clarify that In in its oxide form facilitates the water activation—the Achille's heel of Cu catalysts—thus reaching an almost stochiometric hydrogen and carbon dioxide selectivity even at low temperatures[4].

Despite these and many other findings, much work is still needed before reaching acceptable catalytic performances in reforming reaction using renewable sources. Ditching noble metals for good while retaining the activity is certainly one target, but also improving the stability, especially as far as the coke resistance is involved.

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Gas-phase partial oxidation of fatty alcohols over CuO_x/γ-Fe_2O_3: a noble-metal free catalyst for the synthesis of perfume ingredients

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Key words: Rosalva, Costenal, Opalene, Oxidative Dehydrogenation, Cu-ferrite

The development of better gas-phase heterogeneously catalyzed processes plays a fundamental role in the struggle to achieve a more and more sustainable industrial production of fuels and chemical products. In fact, very often the successful industrialization of innovative gas-phase processes resulted in higher selectivities, safety improvement, less harsh reaction conditions, a significant reduction of waste and the use of less toxic or hazardous reactant. The production of acrylonitrile (the main monomer for the synthesis of acrylic fibers) to which Robert Karl Grasselli gave a fundamental contribution, represents a typical example. In this process, acrylonitrile is obtained in one-step in the gas-phase by reacting a mixture of propylene, NH_3 and oxygen (ammoxidation) over a $Bi_9PMo_{12}O_{52}/SiO_2$ heterogeneous catalyst. The development of this process allowed the large-scale production of cheap acrylonitrile and made obsolete the traditional IG Farben multistep synthetic process based on the addition of HCN (extremely toxic) to acetylene (explosive), with significant improvements form the points of view of safety and sustainability. During the course of several decades of career, Robert Karl Grasselli postulated seven principles (pillars) governing selective oxidation catalysis[1] (e.g., lattice oxygen, metal-oxygen bond, host structure, redox properties, multifunctionality of active sites, site isolation and cooperation of phases), which are herein applied in the description of the catalytic partial oxidation in the gas-phase of a mixture of fatty alcohols for the preparation of a valuable perfume ingredient. In particular, the continuous-flow, gas-phase oxidative dehydrogenation of a mixture of decen-1-ol isomers ("isorosalva" alcohol) to the corresponding aldehydes (decenal, "opalene") has been investigated over a series of innovative and cheap heterogeneous copper-based catalysts, thus avoiding the use of Au and V based catalysts usually employed in similar reactions[2,3]. It was found that when a Cu/Fe/O mixed oxide is used, the selectivity towards the desired product is poor. Nonetheless, the catalyst undergoes to a progressive segregation of metallic Cu during the reaction which lead, after a regeneration in air, to well-dispersed CuO particles, resulting in improved selectivity towards the desired product during a second run. Analogous results have been achieved by synthesizing *ad hoc* a CuO/γ-Fe_2O_3 catalyst by means of impregnation. The comparison between the performance of this material with those of CuO/SiO_2 and the bare γ-Fe_2O_3 support showed that the co-presence of Cu and Fe lead to a significant activity/selectivity improvement.

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New Catalysts to eliminate the use of HCN

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Key words: production acrylonitrile methacryilic acid, benzonitrile

I shall report all my publications realized in the field of oxidation catalysis in order to eliminate the use of HCN toxic substance. The ammoxidation of propylene to acrylonitrile (reaction with NH_3 and O_2) in alternative to the synthesis of acethylene and HCN has been was my first paper realized in Italy, after my coming back from Prague. After some month of the publication Robert K.Grasselli, the scientist from Sohio(USA) the industry that developed the first industrial process of ammoxidation of propylene come to visit me in Milan at the Politecnico.The visit of Grasselli was very important for me to remI ain to work in oxidation catalysis. In the field of ammoxidation of propylene I worked on the following catalysts: Bi molybdates (th first, Sn -Sb mixed oxides Bi tungstates , Bi_2O_3 on $Fe_2(Mo_4)_3$, Fe-Sb-Ti mixed oxides**.**

I worked in the ammoxidation of toluene to benzonitrile in alternative to the use of benzene iodide or benzene bromide with reaction with CuCN. I investigated as catalysts of ammoxidation< of toluene with NH_3 and O_2 the following catalysts : V_2O_5/TiO_2 ,; HZSM-11 and HZSM-5 zeolites impregnated with NH_4VO_3 and $VSbO_4$

I worked in the synthesis of methacrylic acid by oxidation of isobutane or isobutene in alternative to the reactions of acetone with HCN, and formation of acetone cyanidrin (toxic intermediate) and after other two reactions. I worked together with the French industry Elf Atochem (after Atofina and after Arkema) with the following catalysts:
potassium/ammonium salts of 12-molybdophosphoric acid (Keggin-type heteropoly compounds), V-Sb-Al-(W) mixed oxides Iron-doped, ammonium/potassium salts of 12-molybdophosphoric acid (Keggin-type polyoxometalates V/Te /Mo mixed oxides, Cr/V/Sb/Nb f

I worked with French industry Rhodia to realize a process of synthesis of adiponitrile alternative to the reaction of butadiene and HCN by dimerization of acrylonitrile. In order to reduce the prize of acrylonitrile I was working in the ammoxidation of propane to acrylonitrile with the following catalysts :$(VO)_2P_2O_7$, V-Sb and Fe- Sb mixed oxides , V-Sb-Al(W,Mo)-O mixed oxides V–Sb/Ti mixed oxides: $NiSb_2O_6$ Sn/V/Sb/O, Ti/V/Sb//Ce/ V mixed oxides and Cr/V/Sb/Nb mixed oxides

Effect of NO reduction on o-DCB oxidation.

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Key words: MnO_X-CeO_2, o-DCB, NO, NH_3

Chlorinated organic compounds (CVOCs) are hazardous compounds produced in industrial processes that involve combustion stages. Catalytic oxidation allows total destruction of this type of pollutants at a lower temperature than other techniques such as thermal combustion. In order to work with more environmentally friendly catalysts, MnO_X-CeO_2 catalytic formulation is being largely considered for CVOCs oxidation due to its excellent oxidation ability. This catalytic formulation is also under study for the selective catalytic reduction (SCR) of NO_X with NH_3 at low temperature, which brings the possibility of abating two different pollutants simultaneously. This work aims to assess the effect that SCR feeding has on CVOCs oxidation, using 1,2-dichlorobenzene (o-DCB) as a model compound. For that purpose, several catalytic tests and in-situ FTIR experiments were carried out with different feeding streams.

According to Figure 1, MnO_X-CeO_2 catalyst becomes active to carry out oxidation reaction around 250 ºC. Above that temperature, the presence of SCR feeding has a positive effect in o-DCB conversion, which allows to reach full conversion at a lower temperature. In order to elucidate the origin of the positive effect that SCR feeding has on o-DCB oxidation, this reaction was further performed separately in the presence of NO and NH_3, changing progressively the inlet concentration of these two compounds. The results of these experiments evidenced: (1) NO leads to increasing o-DCB conversion, although this effect disappears when NO is in excess; and (2) the increase in NH_3 concentration slightly increases o-DCB conversion and strongly decreases the production of chlorinated by-products. Therefore, the positive effect of SCR feeding is related to the presence of both NO and NH_3.

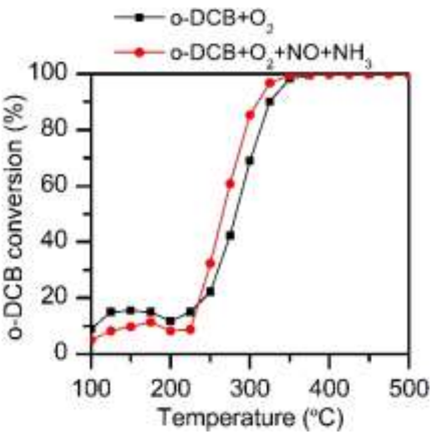

Figure 4. o-DCB conversion in the presence and absence of SCR feeding over a MnO_X-CeO_2 catalyst.

In-situ FTIR experiments were performed to understand catalytic activity results by studying the role of adsorbed NO and NH_3 species on o-DCB oxidation. NO adsorption led to nitrate species, which disappeared after o-DCB adsorption. This result suggests the involvement of adsorbed NO on the o-DCB oxidation pathway, probably in the step where the active sites are re-oxidized. On the other hand, NH_3 kept adsorbed after o-DCB adsorption, which evidences it does not participate in the oxidation pathway, although its presence slightly increased o-DCB conversion. The positive effect of NH_3 is proposed to be associated to the involvement of adsorbed NH_3 on the removal of adsorbed chlorine, which agrees with the strong decrease in the production of chlorinated by-products observed.

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Catalytic oxidative degradation of highly hazardous chemical and biological contaminants over sulfonic acid ion-exchange resins

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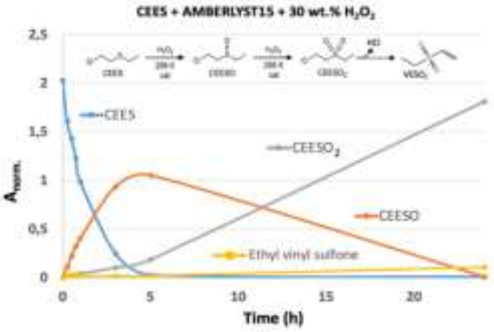
Keywords: decontamination, heterogeneous, sulfonic resins, virus/bacteria, chemical weapons

Heterogeneous catalysis opens promising paths towards an innovative approach to the mitigation of risks through the decontamination of highly hazardous chemical and biological contaminants. For this purpose, cation-exchange resins with acid sulfonic groups are a cheap, versatile, and effective tool for the *in situ* degradation of chemical warfare agents (CWAs)[1] and the inactivation of pathogenic viruses[2] and/or bacteria, in terms of safety, environmental sustainability and costs. The resins are first activated by contact with 30 wt.% aqueous H_2O_2 for 10 min, then filtered and dried, to give rise to the self-decontaminating materials featuring both oxidant and acid active sites. In particular, a styrene-divinylbenzene copolymer, Amberlyst 15 Dry (4.7 meq/g sites by dry weight) showed remarkable capabilities in the catalytic oxidative abatement of 2-(chloroethyl)ethyl sulfide (CEES), a CWA simulant of blistering sulfur mustard, and, in the inactivation of two bacteria, *E. coli* (Gram-) and *S. aureus* (Gram+), and *Monkeypox virus* (MPXV) a DNA virus. The activated Amberlyst 15/H_2O_2 system featured excellent conversions of CEES (up to *ca*. 89% after 3 h, Fig.1), with the gradual formation of the corresponding sulfoxide CEESO and further reaction to sulfone $CEESO_2$. Likewise, the same activated resin led to a decrease of >4 $\log_{10}$ of the viral titre and a decrease of 9 and 5 orders of magnitude of *E. coli* and *S. aureus* viability, respectively (Fig. 2). It is worth noting that these encouraging results were achieved over a unique catalytically-active system, exploiting a synergistic effect between H_2O_2 and H^+ sites, by following the same straightforward experimental activation protocol for the degradation of contaminants of chemical, bacterial and/or viral nature.



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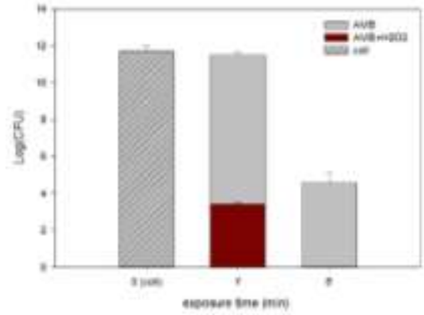

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Figure 1. *Oxidative abatement of CEES with H_2O_2 over Amberlyst 15. 14 mM CEES; 70 mM 30% aq. H_2O_2; ethyl acetate; 150 mg catalyst; 298 K.* ***Figure 2****. Viability of E. coli in presence of Amberlyst 15 (AMB) with (brown) or without (grey) H_2O_2 activation, at different contact times.*

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Non Thermal Plasma Catalysis for Water Treatment

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Key words: Catalytic Non-Thermal Plasma
Dielectric barrier discharge
Water treatment

Non thermal plasma (NTP) is one of the most promising technologies used for the degradation of hazardous pollutants in water. Recent studies have shown that various operating parameters influence the yield of the NTP-based process, but above all it has been highlighted that the presence of a catalyst, suitably placed in the NTP reactor, can guarantee a significant increase in process performance. For this purpose, several researchers have studied the ability of NTP coupled to catalysts for the removal of various categories of pollutants in aqueous solution, and the results obtained from these recent researches are absolutely interesting. In particular, by using a structured catalyst inserted in the discharge zone it is possible to increase the energy yield obtaining better results in terms of mineralization of the contaminant. Specifically, different active species (Fe_2O_3, CeO_2 with different amounts) supported on different materials (quartz spheres or Al_2O_3) were studied to obtain the best results in the degradation of the studied contaminants (dyes or herbicides).

The tests conducted made it possible to optimize the operating conditions of the system in terms of gas flow rate, voltage applied to the electrodes. Finally, the recyclability tests confirmed the reusability properties of the catalyst.

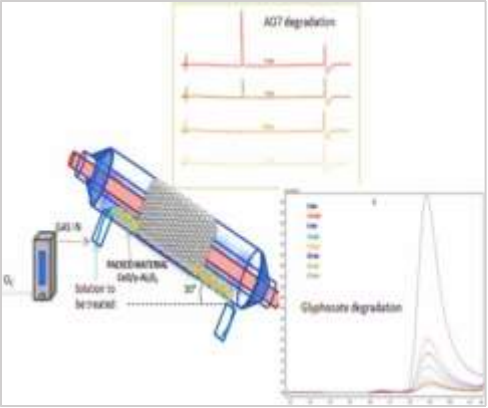

Figure. Experimental set up: DBD in plasma catalysis reactor, and the results in terms of Acid Orange 7 (AO7) and Glyphosate degradation.

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DMC synthesis from CO_2 over MOF and MOF-derived Ce and Ce/Zr oxides

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Key words: CO_2 valorization, Ce-MOFs, DMC synthesis, spectroscopic characterization.

The direct reaction between CO_2 and methanol (CH_3OH) to produce dimethyl carbonate (DMC) is a relevant process for short-term conversion of Mt/year of CO_2. Among the employed catalysts, CeO_2, ZrO_2 and their solid solutions presented the highest conversion/stability properties. The most recent publications reported as the presence of Ce^{3+} in $CeZrO_x$ solid solutions favoured CO_2 activation through bidentate carbonates formation. However, all redox roles of Ce^{3+} are not fully clear for this particular non-redox reaction. With all this in mind, we have synthesized and fully characterized defective Ce and Ce/Zr mixed MOFs and defective Ce and Ce/Zr oxides obtained via non-conventional oxidative calcination of MOFs (denoted as Ce/Zr-UiO-66). The data have been compared with pure CeO_2 [1] (Figure 1) and ZrO_2 oxides. The reaction has been followed by in situ IR spectroscopy in gas and liquid phases.

Different species, including formates (HCOO), methoxides (O-CH_3) and carbonates (CO_3) can be deduced from the reaction. MCR-ALS protocol was then applied to extract the spectral components. The species concentration profile has a complex evolution. However, it was observed that as soon as formate production begins, the rapid monomethyl carbonate (MMC) and DMC formation decreases, indicating as the former reaction hinders the latter. Moreover, the role of Ce^{3+} was monitored through NAP-NEXAFS in TEY mode. The Ce oxidation state in the pure CeO_2 did not change after reaction. Moreover, the FT-IR and NAP-NEXAFS results confirmed as CO_2 is reduced to CO oxidising Ce^{3+} whilst CH_3OH/CH_3O^- are oxidised to $HCOO^-$ hence reducing Ce^{4+}. Ce^{4+} reduction increases at higher ZrO_2 content.

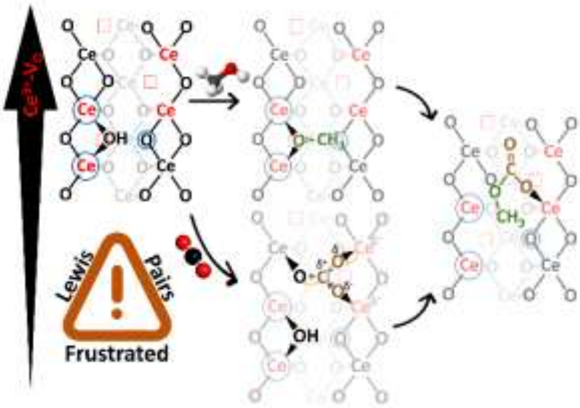

Figure 1: Pictorial representation of the formation of Mono Methyl Carbonate on the defective CeO_2 surface.

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Modelling of cyclic CO_2 adsorption and in situ methanation overdual function materials: a parametric study

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Key words: CO_2 Capture, CO_2 Methanation, DFM, Reactor Modelling.

The Power-to-Gas (PtG) technology seems to be a promising technology to obtain syntheticmethane by exploiting renewable hydrogen and CO_2 captured from flue gas. However, catalytic conversion of CO_2 is generally linked to heat management problems due to the exothermicity of the reactions. In this perspective, a possible solution may be represented by dual function materials (DFM), that can provide active sites for both CO_2 capture and hydrogenation towards hydrocarbons. Farrauto et al.[1,2,3] have proposed DFM catalysts made of alkaline or alkaline-earth metal sites on which the CO_2 capture is possible (Fig.1). The captured CO_2 is then hydrogenated on the reaction active sites (Fig.2), made of Ruthenium. The overall process can be carried out at atmospheric pressure by feeding a CO_2-lean gas stream (e.g., flue gas) during the adsorption phase to produce a CH_4-rich stream during the methanation phase. The aim of this work is to create a mathematical model that describes the atmospheric methanation of CO_2 from a flue gas stream. A parametric study on the kinetic parameters allows us to select the optimal characteristics of the materials to be used for cyclic CO_2 adsorption and methanation. A fixed-bed reactor hasbeen modelled where adsorption and reaction occur in sequence. The adsorption kinetic has been assumed as Langmuir type while reaction kinetics evaluates both methanation and Reverse Water Gas Shift (RWGS) reactions. A parametric study of the model evaluates how the system responds varying main parameters of the kinetics. Optimal results show high CO_2 recovery and conversion without reaching temperature over 400 °C which is a fundamental aspect to avoid catalytic deactivation. It is desirable to find combinations of adsorption and methanation active phases that allow a cyclic process to be developed for the capture and conversion of CO_2 to CH_4. This would lead to high purity methane obtainedfrom waste streams (e.g., a flue gas) without spending huge quantities of heat for the CO_2 separation and with an easier heat management of the process (i.e., avoiding hot spot).

Figure 1. Adsorption phase: (a) adsorption of CO_2 on M_xO and (b) formation of M_xCO_3.

Figure 2. Methanation phase: (a) adsorption of H_2 on Ru and (b) reaction of M_xCO_3 with H_2 to produce CH_4, H_2O and M_xO.

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LPMO immobilization on Carbon nanotubes: a first investigation toward higher stability and catalytic activity

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Key words: Lytic polysaccharide monooxygenases (LPMOs), Carbon nanotubes, Biocatalyst

Thanks to their excellent functional properties, enzymes are able to catalyze several complex chemical processes under mild conditions and are potentially excellent catalysts for a more sustainable chemical industry. However, limitations, such as low stability and a tendency to be inhibited by substrates, products or solvents, limit their application for nonbiological purposes. One way of tailoring enzymes for industrial applications is immobilization onto a suitable carrier, following simple and cost-effective protocols, in order to increase enzyme stability. Lytic polysaccharide monooxygenases (LPMOs) are mononuclear copper-containing enzymes found in the majority of cellulolytic fungi and actinomycete bacteria that are able to oxidize C–H bonds of the glycoside linkages in polysaccharides[1–3]. However, LPMOs are prone to oxidative damage, particularly in the absence of an adequate substrate[2]. The aim of this contribution is to develop a possible bio-catalyst for C-H activation reactions, based on bioconjugation of LPMOs to Carbon Nanotubes (CNTs), which is done to stabilize the biological partner without jeopardizing its catalytic ability. CNTs have been selected since they are conductive, thus allowing the electron transfer processes that are needed to optimize the LPMO activity. After the optimization of the immobilization protocol with different model proteins, two different LPMOs were selected, *Sc*AA10C, from *Streptomyces coelicolor* A3 and LsAA9A from *Lentinus similis*. Oxidized CNTs were firstly activated by using N-(3-dimethylaminopropyl)-N′-ethylcarbodiimide hydrochloride (EDC) and N-Hydroxysuccinimide (NHS) and then mixed under stirring with the enzyme solution. After the reaction, the suspension was dialysed and the bioconjugates were analyzed by means of UV-Vis spectroscopy, fluorescence spectroscopy and circular dichroism. Lastly, the catalytic activity of the LPMO bioconjugates was assessed by determining their oxidase[4] and peroxidase[5] activities, which are known side activities of LPMOs involving small molecule substrates.

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Cu-MOFs as potential oxygenation catalysts: redox performances from a XAS study

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Key words: Oxygenation catalysis; metal organic frameworks; copper; redox performances

The activation of C-H bonds is a key challenge in modern chemistry, e.g., the conversion of light hydrocarbons to corresponding alcohols could revolutionize the bulk chemicals market. Cu catalysts, either from biological or synthetic origin, proved their effectiveness in such processes. Nonetheless, they are far from real applications, due to stability and/or productivity issues. Cu-based metal organic frameworks (MOFs), featuring the stability of inorganic systems and a local Cu environment mimicking that of efficient enzymatic systems (e.g., LMPO [1]) could overcome such limitations. Their potential application as oxygenation catalyst is expected to strongly depend on their redox properties, in particular the cyclability between Cu(I)/Cu(II) states, in analogy with Cu-zeolites [2]. In this study, a set of Cu-MOFs based on the UiO-66/67 frameworks modified to host Cu-anchoring sites were characterized by means of XAS. The redox activity of the Cu sites, i.e., the capability of cycling between the Cu(I)/Cu(II) oxidation states under different gas feeds (inert, oxidizing, reducing), was assessed. Some of the considered materials (e.g., the Cu-UiO-67 modified by substituted bipyridine linkers, inspired by redox active homogenous complexes [3], shown in Figure 1) presented interesting features, as prominent reduction/reoxidation compared to literature examples at mild temperature (150 °C) [4]. An enhanced evaluation of the spectroscopic data was achieved by exploiting advanced data analysis techniques, namely Multivariate Curve Resolution (MCR) and wavelet transform EXAFS analysis.

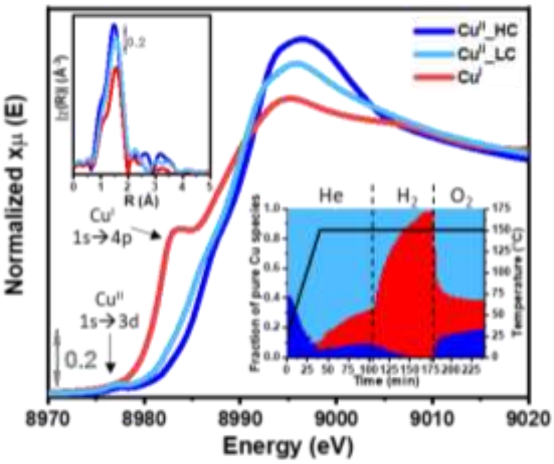

Figure 1: MCR reconstruction of XAS for bipyridine modified Cu-UiO-67 along reduction/oxidation stages, including XANES and EXAFS spectra and concentration profiles of pure Cu species.

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Role of Hydrogen and Oxygen Complexes in Water Splitting Reaction on Single-Atom Catalysts

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Key words: SAC, DFT, HER, OER

The electrochemical water splitting is a promising route for the energy transition. The reaction can be divided in two semi reactions. In the first, protons are reduced to molecular hydrogen, in the second water is oxidized releasing molecular oxygen. Recently, a lot of attention has been dedicated to the Hydrogen Evolution (HER) and Oxygen Evolution (OER) Reactions on Single Atom Catalysts (SAC).[1] The activity of SACs for water splitting is usually rationalized or predicted using the seminal model proposed by Nørskov and co-workers, where the free energy of key intermediates adsorbed on an extended metal surface is used to explain the catalytic activity.[2]

SACs differ substantially from metal surfaces and can be considered analogues of coordination compounds. In coordination chemistry, at variance with metal surfaces, stable complexes of hydrogen and oxygen can form.[3,4] We show that the same can occur on SACs and their formation may change the kinetics of the process.[5] This can be estimated by extending the original kinetic obtaining a multi- dimensional volcano plot for the HER and OER on SACs. DFT numerical simulations of dozens of models demonstrate that the formation of the suggested complexes may lead to different conclusions about the activity of SACs in the water splitting reaction. The results are validated against selected experimental cases. The work provides an example of the important analogies between the chemistry of SACs and that of coordination compounds.

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Types and amount of functional groups in activated carbonsused in catalysis

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Key words: Activated Carbon, Functional Groups, DRIFT, TPD

Activated carbons (ACs) find large application as catalytic supports and as catalysts on theirown. They consist of very heterogeneous ensembles of graphitic domains, exhibiting a large degree of irregularity both in terms of physical defects (i.e. curvature, vacancies…) and of chemical composition (i.e. functional groups). The choice of the precursors, of the activationprocedure and of the post-activation treatment can largely influence the final properties of the ACs, with severe repercussions on their behaviour under reaction conditions.[1-2] Thus, the systematic physico-chemical characterization of various AC samples is imperative for a better understanding of their role in the functioning of a catalyst. In this contribution we identified and quantified the O-containing functional groups in ACs by systematically applying a large number of complementary techniques on a consistent set of samples. TheACs were provided by the company Chimet S.p.A. and differ for the carbonaceous precursor(wood or peat), the activation procedure (physical or chemical), and the possible post- activation oxidation treatment with HNO_3. The employed techniques include infrared spectroscopy in DRIFT mode (Figure 1A), TPD (Figure 1B), TGA, elemental analysis, Boehm titration and DFT simulations. Our results demonstrate that no single technique is able to provide a complete characterization of the surface chemistry of ACs, while the complementary use of multiple techniques is essential. The collected data are significant forthe choice of the most suited AC supports for different applications in catalysis.

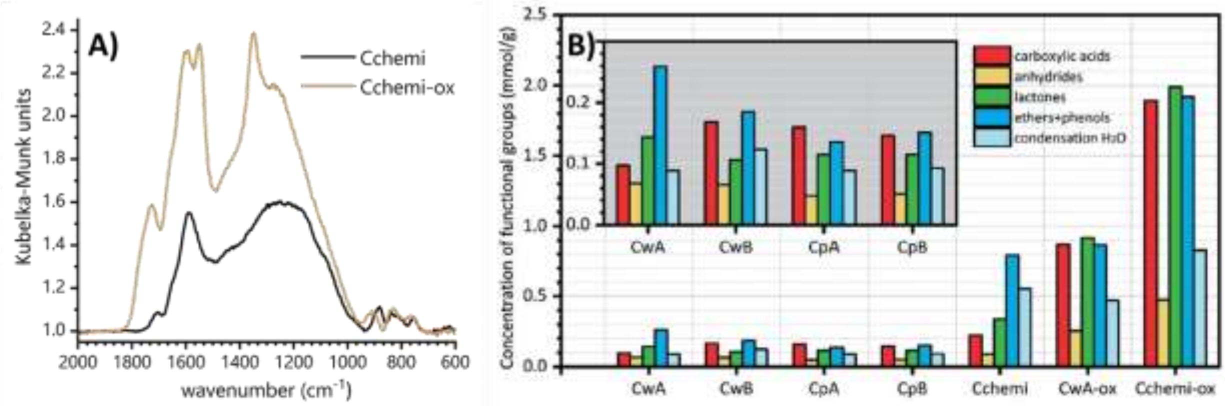

Figure 1. A) Infrared spectra of the parent AC (Cchemi) and of the corresponding AC oxidized in HNO_3(Cchemi-ox). B) Result of the quantification of the functional groups thermally decomposing at a temperature lower than 700°C for various AC samples.

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Modulated Excitation Spectroscopy: A Powerful Tool to Study Catalytic Mechanism of Reaction.

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Key words: Modulated Excitation, operando X-ray absorption spectroscopy, DRIFTS, catalytic CO oxidation, photocatalytic hydrogen production

Modulated Excitation Spectroscopy (MES),[1,2] achieved through periodic switching of a parameter effecting a catalyzed reaction (e.g., gas composition, light intensity, temperature, etc.), has been successfully combined with time resolved in situ spectroscopic techniques (DRIFTS; XAS and XRD) in order to study the mechanism of reaction occurring on the surface of solid catalysts.

In particular, MES has proven to be a powerful tool to bring surface sensitivity to hard X-ray based techniques.[3] Indeed, MES exploits the Phase Sensitive Detection (PSD) algorithm to filter the signals of spectator species (including the background) and the noise, significantly enhance the active species response and enabling extraction of kinetic information. This is particularly important to reveal structural information of working nanoparticles which is often contained in weak signals. An example is reported in Figure 1 obtained during the investigation of the catalytic CO oxidation over Pd/Al_2O_3, where the difference time-resolved XAS spectra at the Pd K-edge are compared with the corresponding phase-resolved spectra. The noise removal after demodulation revealed enhanced information, especially in the EXAFS region, due to subtle variation at the Pd surface, i.e. surface passivation and CO adsorption.

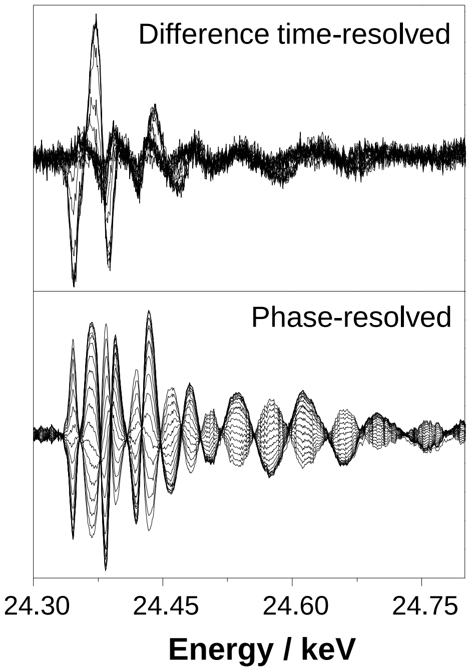

Figure 1. Comparison between difference time-resolved and phase-resolved XAS spectra at the Pd K-edge

In this talk, we discuss the origin and theory of MES will be presented together with some application to thermal- (CO oxidation on Pd/$Ce_{1-x}Zr_x$)[4] and photo-catalytic (methanol steam reforming for hydrogen production)[5] reactions.

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Pyrolysis and hydrotreatment of Kraft Lignin: catalytic hydrodeoxygenation of pyrolytic oil

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Key words: Kraft Lignin, Pyrolysis, Hydrotreatment

The importance in the recovery and valorization of lignin is due to the high content of aromatic compounds which can be used for the production of biofuels or chemical intermediates [1,2,3]. Kraft lignin is one of the most produced types of commercial lignin –it is obtained as a by-product in paper and pulping industry and burnt for heat recovery. In the first part of this work, fast-pyrolysis experiments have been carried out to produce bio-oil from Kraft lignin. The produced oil presents different oxygenated compounds such as methoxyphenols which can be further upgraded via hydrotreatment [4,5]. For this reason, a catalysts screening approach will be performed to evaluate the best catalysts for hydrodeoxygenation (HDO) reactions. Then hydrotreatment of pyrolysis bio-oil will be performed with the more efficient HDO catalyst with the aim to produce bio-based phenols.

Kraft lignin valorization is done by pyrolysis at 550 ˚C with a continuous N_2 flow of 2 L/min. The heating system allows to reach 550 ˚C in 3 min, with a maximum peak of temperature around 600 ˚C. For each test, 30 g of biomass is positioned in the heating zone of the reactor after a drying step in the oven at 110 ˚C to limit the production of water during the pyrolysis. Condensable gases pass through a series of cooling steps allowing the condensation of bio-oil, which is further collected in acetone as washing solvent.

After the evaporation of the solvent the oil was analyzed using GPC, GC-MS, 2D-GC, and NMR analysis. Also, the water content of the oil was evaluated by Karl-Fisher titration. The yield of the pyrolytic oil obtained is around 30%, the char around 35%, and the gas yield 35% (calculated by difference).

The hydrodeoxygenation (HDO) reaction will be performed considering different catalysts such as NiMoP, NiMoS, and Ru/C known for their HDO activity and sulfur resistance. The sulfur poisoning of the catalysts will be an issue during HDO of the pyrolytic oil, and for this reason catalytic deactivation will be monitored during the reaction. Hydrotreatment will be performed on the oil obtained from fast pyrolysis using batch autoclave (Parr) reactor and catalytic performances in terms of conversion and selectivity towards phenols will then be evaluated.

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Sustainable synthesis of biomass-derived catalysts: hydrochars and pyrochars in the perspective of acid applications

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Key words: hydrochar, pyrochar, sulfonation, acid properties, 5-(hydroxymethyl)furfural

Lignocellulosic biomass is one of the more important renewable sources and it will play a strategic role in many future markets [1]. Deconstruction of lignocellulosic biomass can be carried out through hydrothermal processes and, among them, the highly versatile hydrothermal carbonization promotes the progressively deoxygenation of the biomass, under relatively mild reaction condition [2]. This is an environmentally and low-cost treatment, thus resulting suitable for any type of biomass, including wet and waste ones. The obtained solid-rich product, called hydrochar, can be used in a wide range of applications, such as adsorption, energy storage, CO_2 sequestration, catalysis etc. In this last field, within the project PRIN 2020 LEVANTE "LEvulinic acid Valorization through Advanced Novel Technologies" (2020CZCJN7), different hydrochars have been synthesized starting from cellulose and the effects of the main reaction parameters, such as reaction time, temperature and substrate loading, have been investigated employing statistical modelling. The adopted central composite design has allowed us to identify the best reaction conditions (220°C for 5h, with 20 wt% of cellulose loading), in order to maximize both the hydrochar yields and its reactive functionalities. For this purpose, the synthesized hydrochars have been characterized by elemental analysis, SEM, EDS, FT-IR, TGA, whereas the recovered liquid phase has been analyzed by HPLC. Under the selected set of processing parameters, the hydrochar yields were in the range 38-48 wt%, with a carbon content of 60-70 wt% and corresponding higher heating values amounting to 17-27 MJ/kg, confirming the successful conversion of cellulose into a carbonaceous material. Moreover, Boehm titration has been applied to quantify acidic functional groups, whose amount increases under more severe reaction conditions. The best reaction parameters have also been adopted for the synthesis of hydrochars starting from glucose and xylose as reference model compounds and from hazelnut shells as real biomass. Finally, also pyrochars derived from the pyrolysis treatment of the synthesized hydrochars have been prepared and characterized, working at 600°C with a heating rate of 10°C/min, in order to increase the aromatization degree and the surface areas. All the obtained hydrochars and pyrochars were then sulfonated and successfully tested as heterogeneous acid catalysts in the conversion of fructose to 5-(hydroxymethyl)furfural, thus confirming their promising potential as acid catalysts for biomass circular exploitation.

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Development of biochars as supports of new catalysts for the future biorefinery

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Key words: biochar, biorefinery, Pd catalyst, Ru catalyst, Ni catalyst

Biochars are a promising option as catalytic supports since they are carbon rich materials with suitable and tunable properties and a chemical composition of various doped and functionalized elements. In this work, activated carbons derived from biomasses were selected as novel supports for different metal catalysts for biomass valorization reactions that would be useful in the future biorefinery.

Biochars were obtained by pyrolysis of different biomasses from vegetal (hazelnut shells, vine wood waste, barley waste, rice husks, and *Sargassum*, macroalgae of Venetian lagoon) and animal (leather tannery waste) origins. The activation was performed either by CO_2- or steam-physical treatment at high temperature.

The following samples were investigated:

i) Ru based catalysts for the selective hydrogenation of 5-hydroxymethylfurfural to 1-hydroxy-2,5-hexanedione[1];
ii) Ni based catalysts for conversion of levulinic acid to γ-Valerolactone;
iii) Pd based catalysts for benzaldehyde hydrogenation to toluene[2].

The metal active phases were added by wet methods, namely wet impregnation or deposition-precipitation. In some cases, alumina as Lewis acid site for dehydration step was incorporated to the supports too.

Biochar-based supports and metal catalysts were characterized by AAS, elemental analysis, FTIR, N_2 physisorption, selective gas chemisorption, SEM EDS, TEM, TPD, TPR techniques. The catalytic efficiencies of the biochar-based systems and of commercial references were evaluated and compared in the different processes.

The chemical and textural properties of the biochars were strongly affected by the origin of the starting biomass, pyrolysis condition and activation process. In fact, all such points highly influenced the chemical, textural and morphological properties of activated biochars and therefore of final catalysts.

In all examples biochars proved to be an interesting option as supports for the different reactions of the future biorefinery.

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Design and assessment of Ni- and Ru- supported catalysts for CO_2 methanation

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Keywords: molten salt, graphene nanoplatelets, CO_2 methanation, carbon-supported catalysts

The combustion of fossil fuels is widely recognized as one of the main contributors to global warming, due to the release of CO_2 into the atmosphere. CO_2 hydrogenation to methane by using renewable hydrogen is considered a promising solution for the recovery and reduction of CO_2 emissions. This reaction is conventionally performed in the presence of Ru or Ni-based catalysts supported on oxides such as SiO_2, and more often Al_2O_3[1]. In the optic of sustainable and green chemistry, carbon-supported catalysts, particularly, graphene, are currently attracting researchers' interest[2]. In this context, graphene has been used as support for both monometallic and bimetallic nanoparticles, displaying exceptional catalytic activity in several reactions[3]. Nevertheless, studies concerning the utilization of graphene as catalyst support for the preparation of heterogeneous catalysis are limited[3] and moreover, the conventional graphene production methods require harsh chemicals[4]. Recently, simple, eco-friendly, and cost-effective graphene syntheses were developed by using molten salts, in which the latter act both as reaction medium and templating agents[5]. In this study, molten salt method was used for the synthesis of high-quality Graphene nanoplatelets (Gnp) as catalyst support for the preparation of Ni and Ru-based catalysts for CO_2 hydrogenation reaction. Moreover, their catalytic performances will be compared with conventional catalysts. Briefly, graphite powder was mixed with a eutectic salts mixture (NaCl/KCl) and heated in an Ar atmosphere up to 1023 K [6]. Then, Gnp was recovered by washing off molten salts. Gnp was successfully achieved with a yield of 30-40 wt.%. Active metals (Ni or Ru) were then added to the support (Gnp or γ-Al_2O_3) via wetness impregnation technique using ethanol as solvent. Carbon-based and supported catalytic materials have been characterized by SEM, XRD, and FT-IR techniques. They have been tested in a laboratory-scale plant and CO_2 hydrogenation products have been evaluated by online FT-IR and GC analysis at each investigated temperature step. Prepared Ni/Al_2O_3 catalysts showed comparable catalytic activity to those reported in the literature[1]. Ongoing research includes the optimization of metal loading, exploration of single-atom catalyst design, and evaluation of their catalytic activity.

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MOF-based Materials for Electrocatalytic Water Splitting Reaction

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Keywords: MOF, Electrocatalysis, WSR.

The modern challenge of fully green and renewable energy sources is pushing the limit of fundamental and applied research up and up. The current global economy is terribly hungry for energy therefore is important to develop efficient technologies and materials to convert electric energy into chemical energy. One of the most promising platform molecules for this goal is hydrogen, however its production nowadays relies principally on cracking of fossil fuels. One of the most accessible hydrogen sources in the world is water, but its exploitation for this purpose is far from simple due to the enormous stability of the water molecule, consequently its split requires a large amount of energy. In recent years, progress has been made in the electrochemical sector and it has been shown that the water split reaction (WSR) occurs on metal dimers/clusters on the amorphized surface of the electrodic materials[1]. On this way, we would like to take advantage of a peculiar class of materials: Metal Organic Frameworks (MOFs), highly ordered porous materials constituted by metallic clusters and organic linkers connecting them together[2]. Their one-pot self-assembly synthesis, together with extremely tailorable choice of either linkers or metals for the nodes, make them ideal candidates for such reaction. By tuning the metal species in the clusters and their coordination number, with either defect engineering or framework variations by changing the nature of the linkers, it is ideally possible to recreate the best local environment for any reaction[3]. Here we introduce some basic ideas standing behind this project to be implemented in the near future.

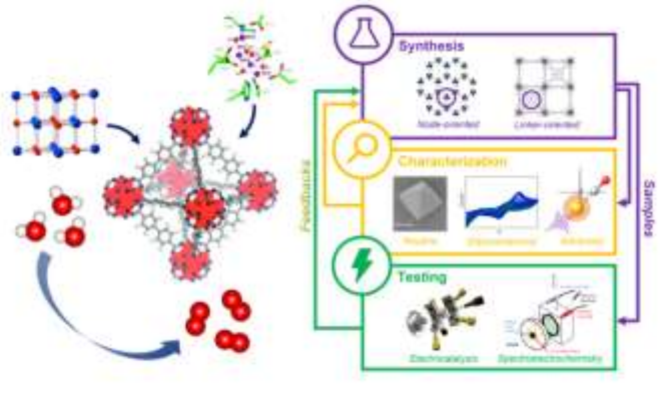

Figure 1. Overall schematization of the ideal project from materials rational design, their preparation and characterization, concluding with catalytic tests.

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Perovskite as novel photocatalytic material for CO_2 utilization

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Key words: CO_2 photoreduction, perovskite, barium titanium oxide, calcium titanium oxide, carbon and nitrogen doping

Solar energy comes up as an abundant, clean, and secure source to pursue a sustainable development. The efficient transformation of solar energy to chemical energy is considered as one of the most attractive topic in energy storage. Hence, utilization of CO_2, H_2O, and sunlight in a photocatalytic transformation to produce chemical fuels has been a "hotspot" research field [1]. In this regard, the aim of present work is to formulate efficient photocatalysts for conversion of the CO_2 emitted from industry to H_2, CO, CH_4 as fuel source for the same industrial sector. In particular, we focused on the photocatalysts development meaning formulation of the photocatalytic materials through different techniques and their basic characterizations such as DRS, FT-IR, TPD, and N_2-Physisorption, SEM/EDX and TEM. Therefore, different alkaline based oxide semiconductors (perovskite) namely $BaTiO_3$ and $CaTiO_3$, and their N- and C-doped structures were formulated and characterized for proposed photocatalysis application. The N_2 adsorption–desorption isotherms and pore-size distribution of all samples exhibited type-IV isotherm (IUPAC classification) suggesting the presence of mesopores and also some macropores. the BET surface area of C-doped and N-doped samples showed an increase and decrease, respectively compared to pure perovskites. These can suggest different interactions of C and N with pure structure which was also confirmed by morphological characterization (SEM,TEM). Optical properties of all photocatalysts obtained by UV−vis diffuse reflectance spectroscopy showed an absorption edge bellow 400 nm, which corresponds to the absorption in UV region. The band gap energies were determined using the Tauc plots for indirect band gap of all samples. The calculated band gaps were 3.1 eV and 3.4 eV for $BaTiO_3$ and $CaTiO_3$, respectively [2,3]. In addition, the results confirmed the indirect band gap narrowing of both $BaTiO_3$ and $CaTiO_3$ through C and N doping procedure. Gas phase photocatalytic tests in a batch reactor have been carried out at 40°C for 6 h with a CO_2/H_2O ratio of 13.3. The materials were active for CO_2 photoreduction in these conditions, and the products detected by gas chromatography were CH_4 and H_2. From the photocatalysts characterization results, it is expected that doping of both pure perovskites with C and N can efficiently affect their photoactivity in the mentioned reaction conditions which will be deeply discussed in the conference. Finally, the result obtained from synthesized photocatalysts were compared with that of the commercial one (P25).

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Fe-Ceria catalyst for Volatile Organic Compounds oxidation.

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Keywords: VOC combustion, FT-IR spectroscopy, Ceria-based catalyst, Iron oxide.

A series of ceria-based catalysts have been prepared at Politecnico di Milano in the form of powders and also deposited onto open cell ceramic foam. Nickel, cobalt, iron and copper were selected as representative active phases, to be supported over commercial high surface area (HS) and low surface area (LS) cerium oxides[1]. Among the different formulations studied, 7% wt Fe-Ceria HS powdered catalyst, prepared by incipient wetness impregnation, has been fully characterized and tested in the oxidation of ethanol and methanol by using in situ IR spectroscopy and Temperature Programmed Surface Reactivity (TPSR). Indeed, in recent years, alcohols have been considered a promising alternative fuel, thus the application of catalytic combustion in controlling emission from their oxidation deserves further study[2]. Characterization data by FT IR spectroscopy, UV Vis.-NIR DR spectroscopy, XRD, and SEM techniques indicate the formation of mainly Fe_2O_3 particles interacting with cerium oxide component, and lowering the basicity of the surface, while new OH groups are formed, other than those of pure ceria. Moreover, the impregnation procedure from nitrate salt appears to slightly change support particle morphology that becomes more irregular than pure ceria.

In situ IR spectroscopy shows reactive adsorption of both ethanol and methanol at the surface of Ceria and Fe-Ceria HS. As first step, alkoxide species are formed, strongly adsorbed at both surfaces already at room temperature, with an indication of alkoxide species interacting selectively with iron oxide particles and traces of carbonyl compounds. The evolution of adsorbed species at increasing temperatures, and without molecular oxygen, shows the formation of carboxylate and carbonate species, likely precursors of combustion products, together with partial oxidation products. Thus, the activity of lattice oxygen has been proven in these experiments. Preliminary IR studies on in situ oxidation of 2-chloropropane compound over Fe-Ceria HS catalyst indicate that a nucleophilic substitution readily occurs at the catalyst surface already at room temperature, and leads, once again, to the formation of strongly adsorbed alkoxy species, prone to further oxidation steps to CO_2. In our conditions, TPSR experiments show that alcohols total oxidation is not greatly increased by Fe doping, at least at the metal loading of the tested catalyst. However, the addition of iron oxide seems to lower the selectivity to partial oxidation products, for instance CO, which formation is, indeed, a drawback in the combustion processes.

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In-situ and ex-situ thermocatalytic pyrolysis of plastics: a comparison of two different approaches

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Key words: Catalysis, Pyrolysis, Polymers, Fuels, Green Chemistry

Plastics are considered one of the greatest technological innovations of the past century and their production overcomes most man-made materials. Geyer et al. estimated that 407 million metric tons (Mt) of virgin plastics were produced worldwide in 2015, and in the same year, 302 Mt left the "use phase" and became waste [1]. Currently, only about 20% of plastic wastes are recycled, while 25% and 55% are respectively incinerated and discarded [1]. In the last few decades pyrolysis of plastic became an interesting alternative to valorise plastic wastes by producing a wide range of products, from fuels to platform molecules, like olefins and BTX [2,3]. The implementation of a catalytic stage allows a reduction in working temperatures and thus energy consumption compared to a purely thermal solution. Furthermore, the use of a catalyst could also improve the selectivity towards the product fractions of greatest interest compared to the thermal solution. An advantage can therefore be expected in terms of both energy efficiency and production effectiveness. Acid catalysts (i.e. zeolites) can effectively reduce polymers' decomposition temperature and guide the reaction toward the desired products [4]. Two different operating modes were reported in the literature to promote a catalytic pyrolysis: an "*in situ*" mode, in which the catalyst is loaded inside the pyrolysis reactor and an "*ex situ*" mode with a dedicated, heated reactor placed afterward [4]. Despite being the simplest, the *in situ* approach has some drawbacks: i) the non-ideal contact between the fused polymer and the solid catalyst leads to mass and energy transfers limitations and ii) the recovery of the catalyst from the pyrolysis residue is challenging and, in some cases, not possible. To avoid these drawbacks, an *ex situ* mode could be implemented, e.g. by pre-treating the polymer to obtain partially cleaved molecules, in order to use the catalyst placed in a fixed-bed reactor, improving mass transfer. Furthermore, in the case of physical separation of these two phases, the conditions of each phase can be optimised. Coke formation is a known cause of catalyst deactivation, but since it is already physically separated from the melted polymer, the catalyst could be readily regenerated. Some preliminary tests have been carried out in a "kettle type" reactor using zeolites and an *in situ* approach. They showed very promising results on the degradation of LDPE and HIPS in different experimental conditions. All considered, the project aims to investigate multiple catalytic systems in a pyrolytic process to obtain the desired output. The final goal is to chemically recycle the "Plasmix" (plastic mix derived from waste sorting) to obtain useful products that can be reintroduced as feedstock in the chemical industry.

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An innovative catalytic pathway for the synthesis of acyl furans: the cross-ketonization of methyl 2-furoate with carboxylic acids

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Key words: 2-acetyl furan, methyl 2-furoate, cross-ketonization, continuous-flow, gas-phase.

The cross-ketonization between methyl 2-furoate (MF) and acetic acid (AA) was investigated with the aim of selectively synthesizing 2-acetyl furan (AF), a well-known flavor/fragrance and pharmaceutical intermediate.[1] This approach towards AF (figure 1), in respect to the traditional Friedel-Crafts acylations with homogeneous Lewis acid catalysts, would benefit from continuous operation, a much easier work-up, and the use of bio-based feedstocks (e.g. AA and furfural-derived MF). All catalytic tests were carried out in the gas-phase using a continuous-flow fixed-bed reactor. Unreacted reactants and products were quantified by means of GC-TCD (online) and GC-FID (offline). Unknown products were identified by means of GC-MS. Monoclinic ZrO_2 was prepared adapting a precipitation technique from the literature.[2] The synthesis of AF was preliminarily carried out over ZrO_2 by feeding an AA/MF/N_2 = 1/1/98 mixture at 350 °C, contact time = 1 second. In these conditions MF conversion was ≈ 70 % and AF yield was ≈ 43 %; at the same time, AA conversion was complete, meaning that the homo-ketonization of AA towards acetone competed with the desired reaction, subtracting AA and limiting the achievable yield of AF. Therefore, the excess of AA in respect to MF was increased by increasing the molar fraction of AA in the feed up to 4 %: in these optimized conditions the conversion of MF was complete and a 70 % yield of AF in respect to MF was achieved. The versatility of this synthetic route towards acyl furans was further investigated by carrying out the cross-ketonization between MF and carboxyilic acid with different chain-lengths (i.e. propionic and butyric acid), thus extending the substrate scope of the method to the propionyl- and butyryl-derivatives of furan, which were obtained with 70 and 80 % yield respectively.

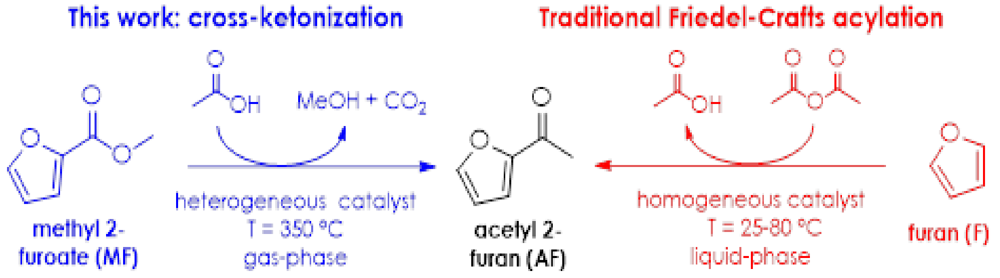

Figure 1. AF synthesis by means of cross-ketonization between MF and AA compared to the traditional synthesis by means of Friedel-Crafts acylation of furan with acetic anhydride.

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Sustainable synthesis of dymethyl adipate fromcyclopentanone and dimethyl carbonate

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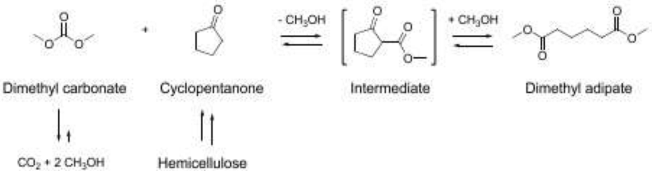
Key words: heterogeneus catalysis, organic carbonates, cyclopentanone, diesters.

Dimethyl adipate (DMA) and adipic acid find wide industrial application in the production of nylon 6,6 (>10 Mton/y), a polyamide extensively used by the textile industry. Nowadays, adipic acid is mainly produced via nitric acid oxidation of KA oil, which is a mixture of cyclohexanone and cyclohexanol obtained from the oxidation of fossil-based benzene. The environmental impact of this process is extremely high, due to the emissions of NO_x and N_2O.[1] In this context, we decided to investigate and develop an alternative synthetic pathway for DMA production starting from cyclopentanone (CPO) and dimethyl carbonate (DMC) by working in liquid phase using a multifunctional heterogeneous catalyst to promote the reaction. This process meets the principles of Green Chemistry, in fact it can be conducted without the need of an external solvent (i.e. an excess of DMC behaves both as reagent and solvent) and it has a 100% atomic efficiency. Furthermore, both reagents can be obtained through a sustainable way, in fact CPO can be obtained from the processing of hemicellulose,[2] while DMC from the condensation of methanol and CO_2.[3] This alternative synthetic strategy is scarcely investigated in literature.[4] Therefore, we decided to investigate the catalytic activity of different metal oxides and mixed metal oxides in the target process. Interestingly, by working at 260°C in autoclave in the presence of a Mg/Zn mixed oxide a DMA yield of 40% was obtained after 5h of reaction. Deepening the mechanism investigation, we found that the limiting step is the low availability of the co-formed methanolfor the nucleophilic attack over the beta-ketoester intermediate (carboxymethylcyclopentan-2-one). Indeed, this consecutive reaction step (Scheme 1), was investigated separately anda 92% yield of DMA was obtained in the optimized conditions (MeOH:Int =150 :1, cat: Zn/Mg/O 20%wt, T=160°C, t=3h, P=20 bar). Subsequently, the assisted tandem catalysis strategy has been investigated. Using the same catalyst, the reaction has been performed in two steps, adding methanol between the two and obtaining a further improve in DMA yield.



Scheme 1. Reaction scheme for the production of DMA from CPO and DMC.

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Catalytic combustion of waste biomass from wood-processing industry in a conical spouted bed combustor

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Key words: catalytic combustion, conical spouted bed combustor, energy valorization, waste biomass

Aiming for the EU to be climate-neutral by 2050 (European Green Deal), in line with the Paris Agreement, the renewable energy target must reach at least 45 % by 2030 (COM/2022/230 final). With a share of nearly 60%, biomass for energy, mostly forestry waste (logging waste, wood-processing waste, fuelwood, etc.), is the largest renewable energy source in the EU. Wood processing industry, such as sawmills, generates a large amount of biomass wastes, mainly sawdust, chips, and slabs, which can be a renewable resource for energy production (heat and electricity)[1].

Spouted Beds technology may be a sustainable and alternative for exploitation of biomass waste as a renewable energy source. Thermal exploitation of biomass wastes was previously performed in conical spouted beds for the drying of industrial sludge[2-3], and agroforestry waste[4] and the combustion of paper industry sludge[5], fruit tree pruning waste[6], vineyard pruning waste[7], and avocado waste[8].

In this study, a conical spouted bed combustor was used for combustion of sawdust waste from the wood processing industry in the spouted bed regime at 550 ºC by using $Pt/A_{l2}O_3$. Combustion efficiency was determined from the flue gas concentration data[3,6-9] monitored by Testo 350 gas analyzer during combustion process.

Higher combustion yield values and lower minimum combustion temperatures in conical spouted beds were got with $Pt/A_{l2}O_3$ catalyst than without it.

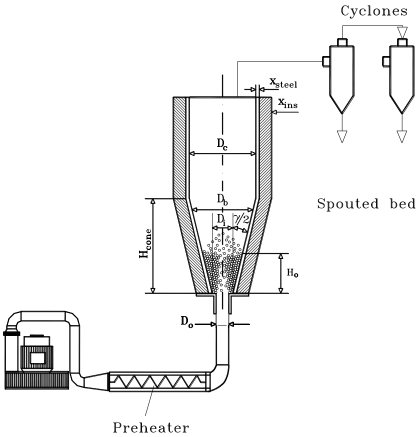

Figure 1. Schematic diagram of the experimental plant

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CO_2 methanation: role of V, Co and Fe over Ni/Al_2O_3 catalysts

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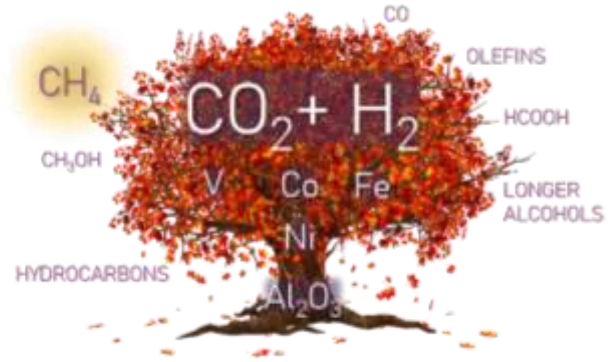
Key words: CO_2 hydrogenation, carbon coke, nickel, vanadium

Nowadays, the world is facing up with an urgent issue: global warming. One of the most abundant greenhouse gases responsible is CO_2. Researchers are developing technologies to capture and trap the CO_2 from atmosphere but then it must be used or converted. One way to convert it is through hydrogenation. From this reaction it is possible to obtain very useful products such as methane, methanol, hydrocarbons, olefins and so on[1]. This is a huge advantage, as these products are all mainly obtained from fossil resources. Methane is obtained from natural gas, that is one of the most pollutant industries. To produce it from CO_2 is fundamental to tune the catalyst's properties, to maximize its selectivity but also inhibit coke deposition and catalyst sinterization. The most used non-noble metal is nickel, which is highly apt to both these problems[2]. From previous works, is reported that vanadium can inhibit carbon formation[3]. In addition, metals like cobalt and iron should help doing this too[4], but they can also affect catalyst's selectivity[5]. Three different catalysts were prepared by incipient wetness impregnation: $Ni\text{-}V/Al_2O_3$, $Ni\text{-}V\text{-}Fe/Al_2O_3$, $Ni\text{-}V\text{-}Co/Al_2O_3$, and compared with Ni/Al_2O_3. The samples obtained were tested for CO_2 methanation at 350°C, GHSV= 6000 h^{-1}, CO_2:H_2:He = 4:1:5. Fresh and spent catalysts were characterized by TPR, N_2 physisorption, SEM-EDX, XRD and TPO. The activity results reported an optimal stability for all the catalysts over 50 h, and highlighted how the introduction of different promoters influences activity and selectivity. With the addition of cobalt and iron a major activity was reached but with different selectivity: cobalt enhances methane while iron increases also carbon monoxide yield.



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Toward boronated biomass-derived carbons as hydrogen storage systems

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Key words: hydrogen storage, green economy, activated carbons, boron doping

The search for sustainable and efficient energy storage solutions has led to the development of hydrogen fuel cells, which require a reliable and efficient method for hydrogen storage. Carbon-based materials, such as activated carbons, have shown promise as potential hydrogen storage materials. However, their low storage capacity has limited their practical application. Activated carbons doped with boron have emerged as a potential solution to increase their hydrogen storage capacity. Indeed, the latter have been shown a discrete variation in terms of hydrogen storage performance, in comparison to undoped ones, thus suggesting promising improvements (Figure 1).[1] In our work, the main aim was to design and synthesize hydrogen storage systems, under environmentally friendly conditions. In this perspective, the activated carbons subjected to boronation are carbons derived from waste biomass and the synthetic methodology was carried out under the mildest possible conditions compatible with the reaction requirements. The samples have then been characterized and tested. Preliminary hydrogen absorption tests have shown promising results.

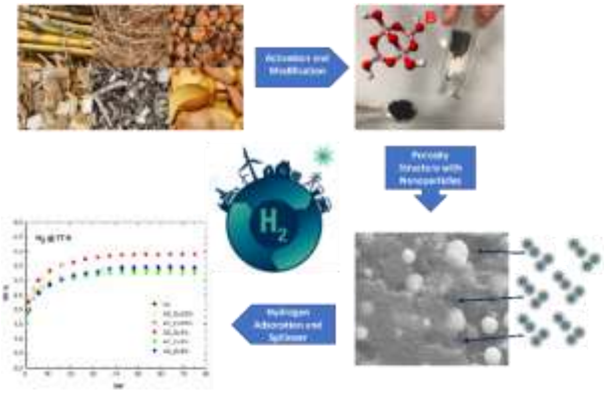

Figure 1. Schematic representation of boronation of biomass-derived activated carbon

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Carbon nitrides for α-oxidation of *N,N*-functionalized anilines

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Key words: carbon nitride, *N*-phenylformamides, photo-oxidation, oxygen

Oxidation of substituted amines by means of photo-activated pathways is a versatile process, widely mentioned in literature[1,2].

However, only few protocols concerning the formylation of *N,N*-disubstituted anilines have been reported, mostly involving metal-based catalysts[3] or the use of harsh conditions (such as ultraviolet light)[4]. Milder and greener strategies must be endeavored to upgrade the environmental impact around the production of such important industrial precursors, which are key compounds for pharmaceutical and chemical industries.

Carbon nitride (CN)-based materials represent a viable opportunity to overcome these limitations[5]. On this regard, we performed the oxygen-mediated one-step synthesis of a series of *N*-phenylformamides, up to obtain yields superior to 80% on a considerable range of organic substrates.

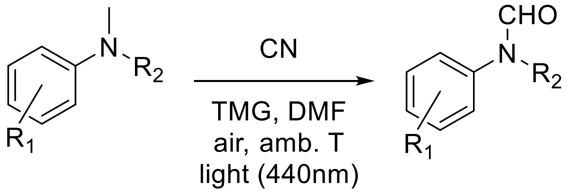

Figure 1. Scheme of the target reaction

Particular attention has been devoted to the screening of several different structural modifications on CN (namely, amorphization, reduction and mild oxidation) to explore the features that critically affect the reaction, in order to define an accurate structure/activity nexus that will allow rational design of CN-based materials with enhanced performance.

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Microwave-assisted selective alkyne semi-hydrogenation over commercial gold catalysts

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Key words: Alkyne semi-hydrogenation, Gold catalysts, Microwave, Sustainable process

Alkynes are a versatile class of compounds broadly used by the fine chemical and pharmaceutical industries. Although the semi-hydrogenation of alkynes is knowns since decades,[1] this selective reduction remains still a challenge. In a typical industrial semi-hydrogenation, alkynes are hydrogenated in the presence of a Lindlar catalyst,[2] which contains Pb, and sometimes modifiers such as amines.

Therefore, the search for more sustainable catalysts that allow highly selective alkyne semi-hydrogenation is of high interest. Nowadays, environmentally benign non-conventional enabling technologies are widely studied to foster process intensification and combine safer protocols, cost reduction and energy savings[3]. The use of modern microwave (MW) equipment working at 2.54 GHz affords an easy, safe, rapid, and efficient heating of reaction medium due to dielectric loss.[4] MW has also been used in chemical synthesis for their ability to induce synergy with heterogeneous metal-based catalysts via the creation of localized hotspots[5]. Moreover, the use of Au-supported catalysts for alkyne semi-hydrogenation has been reported[6]. In this work, many different commercial Au supported catalysts (with 1 wt% Au loading) have been tested in the MW-assisted alkyne semi-hydrogenation.

Au catalysts supported on Fe_2O_3, CeO_2 and Co_3O_4 were found to be the most active. The catalytic activity followed the trend: $Au/Co_3O_4 > Au/CeO_2 > Au/Fe_2O_3$, while the observed trend for selectivity was $Au/Fe_2O_3 > Au/Co_3O_4 > Au/CeO_2$. In particular, Au/Fe_2O_3 afforded a >95% conversion and a >90% alkene selectivity, affording slightly better results with respect to those observed with a commercial Lindlar catalyst (in the same relatively short reaction time (2 hours). An extensive characterization (TEM, FESEM, XRD, DR UV-Vis spectroscopy) was carried out to establish structure-activity relationships.

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Catalysts for the total conversion of VOCs: Mn-Cu oxides prepared by Solution Combustion Method

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Key words: Oxidation catalysis; VOC oxidation; Copper oxide; Manganese oxide

Volatile organic compounds (VOCs) are molecules that are emitted as pollutants from various sources, such as transportation and industrial processes. They have negative impacts on the environment and exposure to VOCs is hazardous to human health[1]. As a result, different strategies have been designed to regulate and reduce their emissions. Catalysts based on noble metals have the highest activity toward VOC oxidation, but they are very expensive and are subject to deactivation by poisoning or sintering[2]. Therefore, transition metal oxides are considered alternatives to noble metals for this application[3]. In particular, manganese oxides exhibit high oxidation efficiency at low temperatures. Moreover, their efficiency can be further enhanced by the copresence of different oxide phases that interact[4].

In this work, Mn-Cu oxides with a Cu/Mn atomic ratio ranging from 0 to 100 were synthesized through the solution combustion synthesis method. The physico-chemical properties of the prepared catalysts were characterized using different techniques, such as N_2 physisorption at -196 °C, XRD, HR-TEM, Raman spectroscopy, temperature programmed analyses (H_2-TPR, O_2-TPD, and NH_3-TPD), and XPS. Results are not reported for the sake of brevity.

The synthesized samples were then tested for the oxidation of ethylene, propylene, and toluene. The catalytic test outcomes showed that the probe molecules were completely oxidized below 310 °C in presence of Mn-Cu oxides. The results suggest that the VOCs tested follow different oxidation mechanisms. Specifically, ethylene oxidation sems mainly favored by oxygen mobility (oxygen vacancies and chemisorbed oxygen species) and redox ability (Mn^{4+}/Mn^{3+} ratio and Cu^{+} species), while propylene and toluene oxidations seem mainly favored by the presence of acidic sites. Further analyses demonstrated that the most effective catalysts exhibited good catalytic stability over a time-on-stream of 7 hours and generally low water vapor inhibition (5 vol.% in the gas stream).

These findings suggest that Mn-Cu oxides possessing the appropriate composition have promising potential as catalysts for the oxidation of VOC. Furthermore, their catalytic properties can be further investigated for the treatment of waste gas emanated from stationary industrial plants.

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Synthesis and characterization of multifunctional Fe-based catalysts for efficient hydrogenation of CO_2 to hydrocarbons

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Key words: CO_2 conversion, Fe-based catalyst, core-shell

Currently, the emission of CO_2 is having detrimental social and environmental effects onclimate change. To mitigate this issue, there is potential to capture and transform CO_2 into value-added chemicals, and the modified Fischer-Tropsch synthesis (FTS) is a promising process for this purpose[1]. One effective approach involves using Fe_3O_4-based materials toconvert CO_2 directly into fuels, typically promoted by alkali metals[2]. This study investigated the concentration and distribution of sodium in Fe_3O_4, as well as the effects of coupling different zeolites to the iron-oxide on stability and hydrocarbon distribution. Two samples of impregnated pure Fe_3O_4 ($1NaFe_3O_4$_IW and $5NaFe_3O_4$_IW)[3,4] were compared with a sample of coprecipitated Fe_3O_4 with NaOH ($5NaFe_3O_4$_CP)[2]. In addition two physically mixed samples ($5NaFe_3O_4$_CP+HZSM5 and $5NaFe_3O_4$_CP+HZ) with a 1:1 mass ratio of oxide to zeolite were prepared in order to be compared with three core-shell configurations(ZF1, ZF2, and HZF1) synthesized using a physical adhesive technique[5]. Comparing the three different Na-promoted oxides, it is worth noting that $5NaFe_3O_4$_CP shows the best performances. This aspect has been ascribed to the best distribution of Na on the surface of the catalyst (see Figure 1a). Furthermore, the addition of zeolite, respectively commercial HZSM-5 and homemade HZ, allows to modulate the distribution of the products to gasoline-like-products. As expected, the physical mixture with the hierarchical zeolite (HZ) shows superior performances, due to the presence of mesopores that favor the diffusion of the products. In contrast he three core-shell configurations (ZF1, ZF2 and HZF1) show a decrease of the CO_2 conversion and an increase in CH_4 selectivity. This behavior can be ascribed to water diffusion problems, favoring Na migration phenomena. This assumption was evaluated and confirmed through characterizations like H_2-TPR and NH_3-TPD on fresh and aged samples. The good coverage of the core-shell structures was instead evaluated using FESEM-EDS images (see Figure 1b), cutting a slice from the core-shell structures. Further investigation should be carried out to avoid diffusion problems.

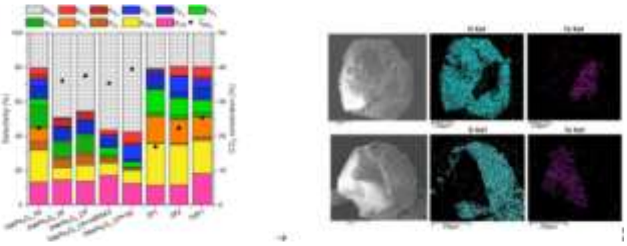

Figure 1. a) CO_2 conversion and product selectivity over different $NaFe_3O_4$/zeolite catalysts (Reaction conditions: $H_2/CO_2=3$, 330 °C, 2.3 MPa and 21.96 NL h^{-1} $g^{-1}NaFe_3O_4$); b) FESEM-EDS images of ZF1 and ZF2

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Heterogeneous catalysts for the ketalization of ethyl levulinate with glycerol

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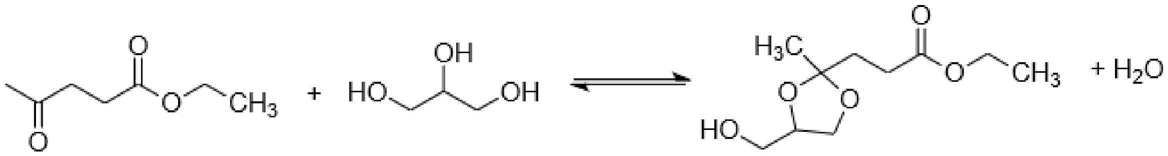
Key words: Ketalization, Ethyl Levulinate, acid solid catalysts

Alkyl Levulinates (Als) are important platform molecules, easily derivable from biomass, which can be converted into valuable chemicals [1]. The reaction of Als with alcohol leads to the formation of the ketals, which have found widespread application as flavorings, plasticizing agents, and fuel additives. Mineral acids are usually applied as catalysts for the reaction. The use of heterogeneous catalysts could overcome environmental and technological issues, reducing downstream costs [2]. A suitable catalyst should be not only active but also selective, promoting exclusively the ester condensation reaction and not the parallel transesterification reaction.

A suitable catalyst should be not only active but also selective, promoting exclusively the ester condensation reaction and not the parallel transesterification reaction.

This work is aimed at the synthesis of ethyl levulinate ketals, through an acid heterogeneous catalysis. For this purpose, different acid solids have been investigated as active and selective catalysts, such as zeolites, acid ionic exchange and sulfonated materials. Beyond the higher acidity, a strong influence of the presence of water, formed in the reaction, on the activity was found. The gel-type resin such as Dowex was shown to be more active, as the water causes the swelling of the resin, enhancing the exposure of the active sites. While among the studied zeolites, the most hydrophilic one, zeolite Y, showed higher activity. Sulphated zirconia also showed a good activity in the investigated reaction.

Fig



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Synthesis of methyl-levulinate catalyzed by an ion-exchangeresin: a kinetic investigation.

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Key words: levulinic acid; biomass; esterification; kinetics; heterogeneous catalysis.

The depletion of fossil fuels has pushed towards the use of renewable raw materials. Among these, biomass is widely used. Lignocellulosic biomass is a starting material for obtaining important platform chemicals such as levulinic acid (LA) which has been classified by the United States Department of Energy as one of the best chemical compounds for the synthesis of many value-added products for its versatile chemistry [1]. The esterification of LA with primary alcohols (i.e. methanol, ethanol, etc.) is of great interest since, the derived esters, such as methyl levulinate, find many applications as green solvents, fuel-additives, fragrances component, medical drugs synthesis, plasticizers, etc.[2]. Homogeneous acidic catalysts (e.g. liquid mineral acids like HCl, HNO_3, H_2SO_4) have been widely used in the esterification reactions because they ensure high yield of esters, but such catalysts suffer from disadvantages such as difficult recovery and product extraction, equipment corrosion and environmental pollution. Therefore, over the past decade, solid acids (e.g. zeolytes, metal oxides, HPAs and ion-exchange resins) have gained broad prospects as efficient heterogeneous catalysts for the esterification of LA given the advantages of environmental friendliness, mild reaction conditions, high yield, selectivity, easy recovery, and reusability. In this regard, resins, due to their high acidity and long-lasting activity, are attractive heterogeneous catalysts to be employed in the synthesis of levulinates.

The present work reports the kinetics of the esterification of levulinic acid with methanol catalyzed by DOWEX® 50-WX8, an ion exchange resin produced in the form of thin spherical beads whose gel-type lattice consists of a styrene- divinylbenzene copolymer. Several experiments have been carried out in a batch reactor at different experimental conditions to study the effect of the temperature, the agitation speed, the catalyst bulk density and the LA-to-methanol ratio on the reaction kinetics.

A mathematical model has been developed to simulate the behavior of the system, considering also the intraparticle diffusion limitations and the experimental data have been submitted to nonlinear regression analysis to obtain kinetics and thermodynamic parameters.

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Ni-containing intermetallic catalyst precursors for CO_2 hydrogenation

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Key words: intermetallics, CO_2 hydrogenation, Ni catalysts, chemical bonding, power-to-methane

Ni and Ru are commonly recognized as active phases of supported catalysts for CO_2 hydrogenation process; however, Ni-based catalysts could generally suffer of deactivation for metal sintering, coke deposition and, in many cases, of a lowered selectivity to methane due to the CO production as a by-product. Since best catalysts formulation is still matter of debate together with mechanistic implication, intermetallics might be of interest as catalysts for CO_2 hydrogenation, especially considering the encouraging results recently obtained in other reactions[1,2].

In this work, Ni-based (Ni-Al, Ni-La and Ni-Ce) intermetallic compounds have been prepared by arc melting under argon atmosphere, characterized by means of XRPD and FESEM techniques and then tested in the 523-773 K temperature range at atmospheric pressure in diluted conditions, keeping a GHSV of 55000 h^{-1}.

Tested intermetallics were found to be active in the CO_2 hydrogenation, foreseeing the production of CH_4 through the Sabatier reaction and/or CO, arising from the reverse water gas shift reaction. In the tested conditions, Ni-Ce intermetallic results the most performant catalysts, achieving a methane yield of 50% at 723 K.

XRPD and FESEM analyses carried out on catalysts after their use, revealed that both $LaNi_5$ and $CeNi_5$ completely decompose into metallic Ni and La_2O_3 or CeO_2, even during pre-reduction treatment under H_2 flow.

To shed light on this, the chemical bonding of both compounds was investigated by means of cutting-edge position-space techniques, and the results so obtained will be discussed. The bonding outcomes enabled a surface simulation, revealing that while H_2 molecules dissociate as hydrides, penetrating the bulk, Ni atoms diffuse toward the surface, well in line with experimental results.

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On the role of hydroxyapatite as a key component in cathode materials to drive the electroreduction of CO_2 to CH_4

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Key words: electrometanogenesis; power-to-gas; electrocatalysts; interfaces; biomaterials

In the ongoing efforts to recycle carbon dioxide (CO_2) emissions on a large-scale, the production of methane from CO_2 using electrochemical reduction systems and renewable energy represents a promising technology in a power-to-gas (P2G) concept. To fully exploit the potential of P2G, advances in process engineering and development of effective materials for electrodes are still required.[1]

Here, we present our recent results in the combination of chemical and microbial CO_2 reduction processes, experimenting an innovative and cost-effective composite material, consisting of porous carbon (biochar) doped with copper (Cu) and hydroxyapatite ($Ca_5(PO_4)_3OH$, HAP) nanoparticles. The composition of cathodes has been optimized by application of the D-optimal factorial Design of Experiments (DoE) with the final aim to maximize methane production. Electromethanogenesis tests in mesophilic (45°C) conditions were performed in double-chamber experimental set-up. Strains of hydrogenotrophic microorganisms of *Metanobacteriaceae* enriched from the inoculum collected from a biogas plant. High methane production was achieved on cathodes made of biochar doped with Cu 20 wt.% and HAP 10 wt.%, with a max. of 866±199 mmol m^{-2} d^{-1} (projected cathode area, coulombic efficiency of 64%). These tests revealed the synergistic action of composites and microorganisms, favoring the selective reduction of CO_2 to CH_4.

The characterization of electrodes, before and after use, revealed that HAP plays a pivotal role in stabilizing the pH of the interface, in favoring the adhesion of microorganisms and in the adsorption and stabilization of reaction key-intermediates (e.g. carbonate and formate).

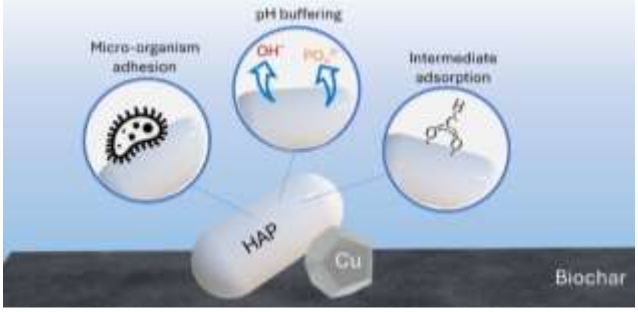

Figure 1. Schematic diagram of the role of hydroxyapatite on CO_2 electroreduction

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A study on the catalytic decomposition of Hydrogen Peroxide onNiFe/CeO_2 catalysts

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Keywords: Non-PGM catalysts, Nickel, Oxygen Evolution Reaction Catalysts, Hydrogen Peroxide Decomposition, Reaction Kinetics

Ni has been investigated as a stable and inexpensive electrocatalyst for oxygen evolution reaction (OER) in electrolysers. Several recent studies have shown that Fe addition to the Ni catalyst results in a higher OER catalytic activity[1]. A successful OER catalyst must be active and stable in alkaline and oxidant environments. Catalytic decomposition of hydrogen peroxide has been extensively studied andits kinetics depends on the operating conditions (concentrations, temperature and pH), on the catalystsand, for heterogeneous catalysts, on their surface properties. Moreover, this reaction has been used asa model reaction for evaluating the catalytic activity in correlation with catalyst surface features.

In this work, NiFe/CeO_2 catalysts with different Ni and Fe ratios were prepared through a chemical reduction method using sodium borohydride. The morphology and structure of these catalysts were characterised by Scanning electron microscopy, x-ray diffraction, Fourier transform infrared spectroscopy, N_2 adsorption/desorption physisorption. Their catalytic performance was preliminarily investigated by evaluating the catalytic decomposition of hydrogen peroxide. The catalysts were also compared in terms of activity (Figure 1) at different pH values. At higher pH, the catalyst stability was investigated. Our results show that NiFe/CeO_2 catalysts can be promising and stable catalysts.

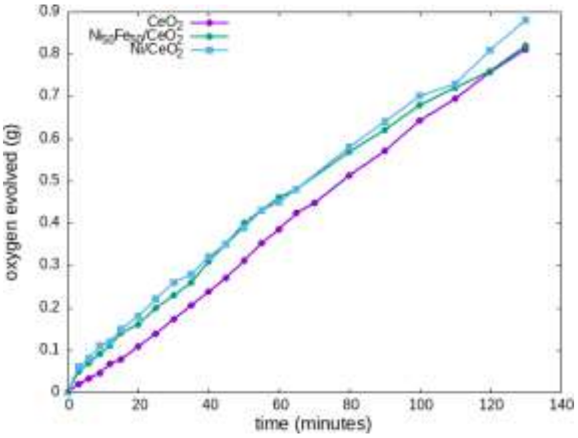

Figure 1. The weight of oxygen evolved as a function of time for Ni/CeO_2, $Ni_{50}Fe_{50}/CeO_2$, and CeO_2

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Catalytic valorization of cheese whey through renewable hydrogen production

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Key words: aqueous phase reforming, cheese whey, hydrogen, lactose, waste valorization

The cheese-making industry is one of the most important sectors within food processing. Cheese whey is a major byproduct of this production route, being generated in large quantities globally: it is estimated that for every kilogram of cheese produced, nine kilograms of whey are generated (1). Its composition is a complex mixture of proteins, lactose, minerals, and vitamins, and if not managed properly, it can pose significant environmental challenges because of its high organic load, high biological oxygen demand (BOD), and chemical oxygen demand (COD). For example, if discharged untreated into water bodies, whey can deplete oxygen levels, leading to the death of aquatic life and causing eutrophication. Therefore, it is essential to find sustainable and cost-effective solutions for the management, and possibly valorization, of cheese whey.

In this work, we investigated the aqueous phase reforming (APR) of a lactose solution to produce hydrogen. Lactose is the most present molecule in cheese whey, and it was used as representative compound in this preliminary assessment. APR is catalytic reaction which exploits the thermodynamic tendency of oxygenated hydrocarbons to produce hydrogen at much lower temperature, and in the liquid phase, than steam reforming (2). The tests were conducted in a batch set-up, examining several reaction conditions. Both the liquid and gaseous phase were characterized to get information on main indicators such as lactose conversion, hydrogen selectivity and hydrogen yield. Moreover, the spent catalyst (Pt/C) was characterized to determine possible modification in its properties. The APR of the lactose solution showed the preferential production of a solid phase, namely humins, attributed to the dehydration of 5-HMF. This pathway was found linearly correlated with the initial lactose concentration, i.e., with a first-order reaction. In order to increase the selectivity towards hydrogen production, two routes were investigated which could avoid the formation of 5-HMF as intermediate, and hence humins production. In the first route, lactose was firstly subjected to hydrogenation to lactitol, and hence subjected to APR; in the second route, lactose was firstly hydrolised to glucose and galactose; this sugar-laden solution was further hydrogenated to sorbitol and galactitol, respectively, and further subjected to APR. Scope of this investigation is hence determining the possibility to have a positive net hydrogen production. The results showed that carrying out the two pretreatments it was possible increasing the hydrogen selectivity from 10% (standard case) to 70%, and reducing the solid yield from 40% to less than 5%; however, the net hydrogen production remained negative, pushing for further optimization in the hydrogenation/APR reaction conditions.

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Hydrotalcite-derived Ni/Mg(Al)O mixed oxides for CO_2 methanation: performances, surface studies and kinetic development

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Key words: CO_2 hydrogenation, Ni-based catalyst, Kinetic study

CO_2 emissions into the atmosphere represent one of the main environmental problems of the modern day. In this contest, CO_2 emissions achieved a high value of 36.3 Gt in 2021, causing an increase in greenhouse gases concentration and correlated global warming[1]. The CO_2 conversion to produce methane by using renewable hydrogen through the so-called Sabatier reaction represent a possible strategy to mitigate this environmental problem. This reaction is conventional performed on Ru or Ni supported catalyst, but both present several concerned that need to be solved, i.e high Ru prize, Ni deactivation by coke formation or particle sintering [2-4]. For these reasons new catalyst formulations need to be investigated to overcome these limits. In this work, $NiO-MgO-Al_2O_3$ mixed oxides have been prepared by the decomposition of corresponding layered double hydroxides of the hydrotalcite family. Ni content was kept constant at 24 mol.%, while the molar ratio of the Mg and Al precursors was varied (Mg 51-56 mol.% and Al 25-20 mol.%). The prepared catalysts have been characterized in terms of XRD, FT-IR, UV-vis-NIR, BET, TPR and TPD techniques. After catalyst pre-reduction in situ, at two different temperatures (773 and 923 K), the catalytic test has been carried out in a tubular fixed-bed silica glass reactor with 80 NmL/min of gaseous reactant mixture, with H_2/CO_2 ratio of 5, and GHSV of 55000 h^{-1} in the temperature range 523-773 K. The reaction has been also performed in static condition in IR cell using a press disk of pure catalyst. Moreover, kinetic studies have been carried out under differential reaction conditions to evaluate apparent activation energies and CO_2 and H_2 reaction orders. Characterization results confirmed that hydrotalcite-type Ni,Mg-Al layered double hydroxides allow the production of homogeneous mixed oxides constituted by a rock-salt type $Mg_{1-x}Ni_xO$ solid solution with Al^{3+} in tetrahedral interstices of the cube close packing of oxide anions. IR spectroscopy data showed that on the reduced catalysts, CO_2 adsorbs in the form of hydroxycarbonates, which convert in carbonates and strongly adsorbed linear and bridging carbonyl species on metallic nickel at high temperature. Catalytic data showed that these materials are more active than $Ni/\gamma\text{-}Al_2O_3$ catalysts at low temperatures, approaching the thermodynamic equilibrium at 623 K.

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Creating and Scaling Nano-Enabled Bio-Based Materials for a Circular Economy; The BIOMAC Project experience.

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Key words: BIOMAC, Bio-based materials, Nano-enabled, Sustainable, Circular economy

The European Union is aware that changing how products and services are produced and consumed significantly is necessary to move towards a sustainable and low carbon economy[1]. To achieve this transformation, it is crucial to develop novel technologies that are both environmentally sustainable and can effectively reduce these adverse effects. Simultaneously, these technologies should also contribute to the growth of the economy and facilitate the creation of employment opportunities[2]. This transformation necessitates the production of cutting-edge, environmentally friendly technologies, including the development and use of nanomaterials, that lessen industry's negative effects on the environment while fostering economic growth and employment creation[3]. Sustainable manufacturing and the reduction of industrial impacts are strongly supported by Catalytic processes, on the other hand, nano-enabled bio-based materials, applied in green technologies and energy transition, can further support the circular economy, leading to a more sustainable and environmentally friendly future[4].

The European Sustainable BIO-based nanoMAterials Community (BIOMAC) is a Horizon2020 project that aims to establish an Open Innovation Test Bed (OITB) for the development, testing, and upscaling of materials and products in the field of nano-enabled bio-based products and materials. The project brings together 26 partners from 13 European countries, including research institutions, universities, and industry partners. The ultimate goal of BIOMAC is to promote the use of nano-enabled bio-based materials in various industries, reducing the environmental footprint of industries and contributing to sustainability.

The BIOMAC Ecosystem provides open access to its facilities, including 17 highly innovative Pilot Lines and complementary services required for the development and upscaling of materials and products. The Pilots Lines cover the whole value chain, from biomass fractionation and intermediate chemicals to final nano-enabled bio-based materials (NBMs). By validating the BIOMAC ecosystem through internal test cases in the fields of automotive, agricultural, food packaging, construction, and printed electronics industries, the project aims to boost and sustain innovation in the European bio-economy industries by reducing the time-to-market of novel nanotechnologies.

Through its Open Innovation Test Bed, BIOMAC provides open access to its facilities and complementary services to promote the use of nano-enabled bio-based materials in several industrial domain, thus creating an ideal platform for innovating biocatalytic processes and products.

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Hydrocyclization of levulinic esters to γ–valerolactone using ZrO_2-based catalysts *via* catalytic transfer hydrogenation

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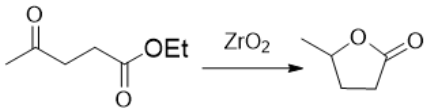
Key words: Levulinic acid/esters; γ-valerolactone; zirconia catalysts; valeric esters.

Lignocellulose is an attractive source of biomass, because of its abundance and it does not compete with food production. Levulinic acid (LA) and its esters (LEs), which can be obtained by lignocellulosic waste, can be hydrogenated to γ–valerolactone (GVL)[1], a platform molecule with many applications (green solvent, biofuel precursor, fuel additive, building block for chemicals). The traditional hydrogenation using molecular hydrogen requires high H_2 pressure and expensive supported metal catalysts. On the contrary, the catalytic transfer hydrogenation (CTH) represents a valid alternative[2], which employes a liquid organic molecule (i.e. bio-alcohols) as hydrogen donor allows one to work in safer and cheaper conditions. Here, the conversion of ethyl levulinate (EL) to GVL *via* CTH was carried out in a batch reactor (autoclave), under 4 bar of N_2, between 150 and 250 °C by using either 2-butanol or ethanol as hydrogen donor, in the presence of Zr-based heterogeneous catalysts[3]. In particular, best results have been obtained by using ZrO_2-WO_3 and ZrSi30 catalysts. The acid-base characterization is currently under investigation to understand the reasons of their superior activity.



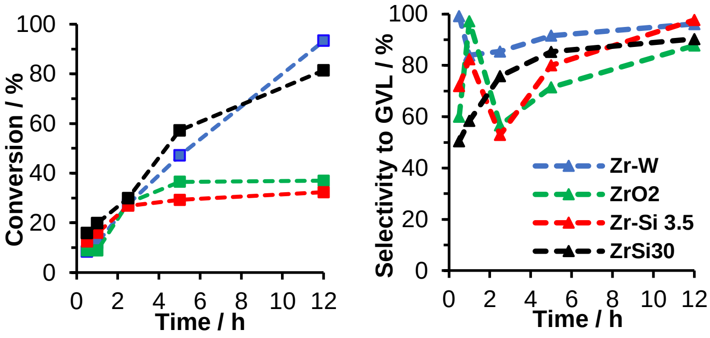


Figure 1. Reaction profiles for the hydrocyclization of EL to GVL on different ZrO_2 based catalysts with 2-BuOH (175 °C).

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Artificial Impregnation of a Freeze Tape Cast YSZ Scaffold for Solid Oxide Cells (SOCs): Electrode Design Optimization

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Key words: freeze tape casting, impregnation, finite element method, nano-holotomography

This work focuses on the manufacturing process and morphological characterization of hierarchical porous fuel electrodes for Solid Oxide Cells applications. The proposed innovative electrodes architecture is produced by combining the freeze tape casting technique (Scotti & Dunand, 2018) to shape the ion-conducting scaffold and the artificial impregnation method for the decoration of the backbone walls with the electrocatalyst. The graded porous scaffolds are made out of 8 mol% Yttria Stabilized Zirconia (8YSZ) and 10 mol% Gadolinium Doped Ceria (GDC10). The microstructure of an 8YSZ freeze tape cast backbone was reconstructed by synchrotron X-Ray nano-holotomography and X-Ray micro-tomography for two regions of the hierarchical scaffold. In-house codes implemented in MATLAB R2022b were employed to extract microstructural properties such as volume fraction, interfacial specific surface area, particle size distribution and tortuosity factor. The raw reconstruction of the backbone was also employed to build a synthetic microstructure featuring the experimental scaffold architecture decorated with electrocatalyst nanoparticles, as shown in Fig.1a and Fig. 1b. The generation of a synthetic solid phase simulating the distribution of Ni nanoparticles aims at the identification of key parameters to engineer an electrode with optimized electrochemical properties, thus providing insightful indications to the impregnation manufacturing process (primarily, required volumetric percentage of the electrocatalyst for sufficient electronic percolation, density of active sites).

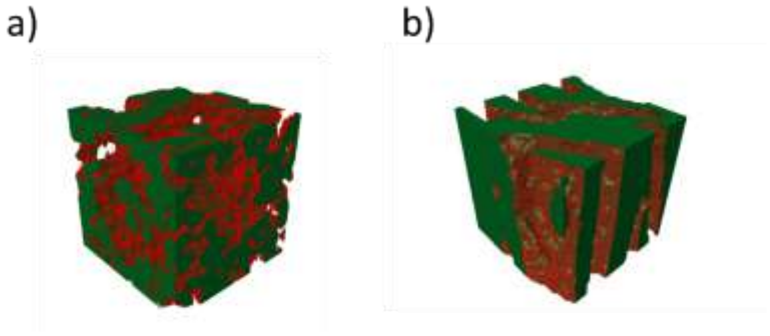

Figure 5: a) 3D reconstruction of the Representative Volume of Interest of a) the synthetically infiltrated YSZ functional layer and b) synthetically infiltrated YSZ supporting layer (red: Ni nanoparticles, green: YSZ scaffold);

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The authors acknowledge the PROMETH2eus project, funded by the European Union – Next GenerationEU, for the work on freeze tape cast electrodes and Dr. Peter Cloetens at the ESRF (Grenoble) for providing assistance in using beamline ID16A.

Ag_3PO_4/Fe_3O_4 for photocatalytic removal of water pollutants

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Key words: solar photocatalyst, silver phosphate, water remediation, heterostructures

Silver phosphate is a high efficiency visible light photocatalyst, and exhibits excellent capabilities in oxidative degradation of organic pollutants.[1] However, the practical application of Ag_3PO_4-based catalyst is limited by the high cost, the slight solubility in water and the self-photocorrosion phenomenon.[2] In this study, core shell Ag_3PO_4/Fe_3O_4 structured heterojunction was prepared for water purification.[3]

The combination of Ag_3PO_4 with magnetic Fe_3O_4 has many advantages: easy separation after the use, improving the visible light response of material, achieving a cheaper material as well. The photocatalytic activities of Ag_3PO_4, Fe_3O_4 and Ag_3PO_4/Fe_3O_4 were comparatively evaluated for the photocatalytic removal of different types of pollutants: green acid 25, diclofenac and hexavalent chromium species. Ag_3PO_4/Fe_3O_4 showed better activity towards both green acid blue 25 and diclofenac oxidation, and high reduction ability in term of Cr(VI) photoreduction. The deactivation tests showed that Ag_3PO_4/Fe_3O_4 is more stable than bare Ag_3PO_4. Based on the scavenging experiments, it was suggested that a Z-scheme heterojunction could be formed at the interface of the Ag_3PO_4/Fe_3O_4 composite, with metallic Ag^0 acting as an electron mediator for enhancing the separation of charges. Results shows the advantages of combined Ag_3PO_4/Fe_3O_4 compared to bare materials in terms of photocatalytic activity, suspension use and stability.

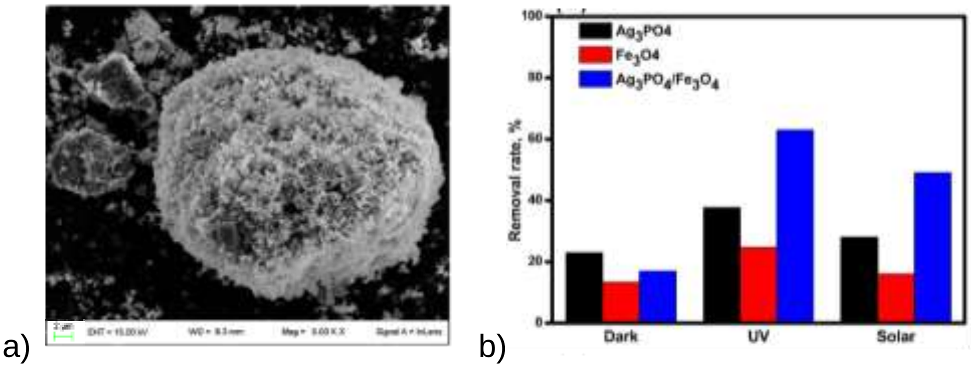

Figure 1. a) SEM image of Ag3PO4/Fe3O4; b) Dark adsorption and photocatalytic oxidation of green acid 25 under UV-A and solar light irradiation.

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Synthesis of biosurfactants from ketals of ethyl levulinate

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Key words: biosurfactants, levulinic acid, ketals, heterogeneous catalysts

Levulinic acid (LA), is a building block that can be produced by acid catalysis from sugars and waste materials[1]. A wide variety of products can be obtained from LA using different types of chemical reactions, and chemicals that can be made include levulinate esters, bio-based chemicals that have strong potential to be used in various applications[1]. In addition, the discovery of highly selective ketalization of alkyl levulinates is enabling the development of new monomers and bio-derivatives with applications ranging from solvents, lubricants and plasticizers to polyols, thermosets and thermoplastics. Levulin ketals are thermally and chemically stable chemical compounds, which can be easily functionalized and used as building blocks for sustainable materials as biosurfactants.

Recently, work has been published showing that levulinic acid ketals with 1,2-dodecandiol are excellent candidates as biosurfactants[2]. However, the information available in the literature on these compounds is limited. The aim of this thesis work is the synthesis and subsequent characterization of the reaction product between ethyl levulinate and 1,2-dodecanediol. For the synthesis, homogeneous catalysts, such as sulfuric acid, and heterogeneous catalysts, such as acid resins (Amberlyst-15) and zeolites (Zeolite Y) were used. The product obtained was characterized by foaming test in order to test the foaming properties of the biosurfactant obtained.

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On the stability of structured foam catalysts for bioethanol reforming.

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Key words: hydrogen, bioethanol reforming, foams, bimetallic catalysts

In this work, the long-term stability of a bimetallic foam catalyst was investigated between 500 and 600°C during the oxidative reforming of fuel grade bioethanol. The detailed preparation procedure of the catalyst was reported elsewhere [1]. Ni-Fe foams were coated with an Al2O3-based washcoat and successively impregnated with ceria, Ni and Pt solutions. The sample contained 35 wt% CeO2 as well as 10 wt% Ni and 3 wt% Pt. The catalyst durability was studied under a reacting stream of 10 % fuel grade ethanol, 40 % water and 5 vol% O_2 in Ar under a WHSV of 12 h_{-1}. Stability tests were followed by a regeneration cycle under a 5%O_2 in Ar stream from 25°C to 600°C. Such test also allowed evaluating the CFR [2].

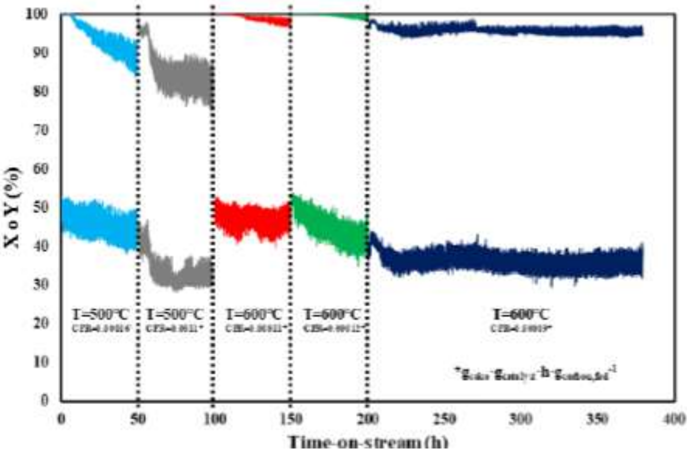

Figure 1. Ethanol conversion (X) and hydorgen yield (Y) measured during bioethanol reforming over a foam bimetallic catalyst (refers to CFR measured in* $g_{coke}\cdot g_{catalyst}\cdot h^{-1}\cdot g_{carbon,fed}^{-1}$).

Foam stability was preliminary investigated at 500°C for 50 h (Figure 1). Total ethanol conversion (X) and a stable H_2 yield (Y) was recorded for 10 h; thereafter, a slight and gradual activity loss was observed and X as well as Y were reduced to 88% and 45%, respectively, after 50 h. At this point, the sample was cooled down and regenerated as described above, measuring a CFR of 0.00016 $gcoke\cdot gcatalyst\cdot h^{-1}\cdot gcarbon,fed^{-1.}$ The regenerated sample was subjected to a further 50 h-cycle of stability test at 500°C; which caused a CFR growth of 1 order of magnitude. The following 3 steps involved catalyst testing under an higher reaction temperature (600°C), which assured a clear performance improvement: ethanol conversion was above 99% in the last part of the experiment; moreover, Y was attested to 45%. CFR was strongly reduced and a similar performance was also measured during the fourth cycle. Finally, after the regular oxidation and reduction, a final 170 hours-test at 600°C was performed. In the latter test, almost constant X and Y values, attested to 95% and 35%, respectively. Moreover, the carbon formation rate was practically unaffected by the time-on-stream during the last 270 h, highlighting the promising durability of the developed structured catalyst.

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An effective synthesis route for efficient UV/VIS photocatalysts: Fe-CeO₂ NPs for Ibuprofen degradation

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Key words: mesoporous nanoparticles, Fe-doped Ceria, reverse micelles, ibuprofen, solar light

Over the past 30 years, there has been an intensive research effort in the field of photocatalysis, and titanium oxide has been ubiquitously studied. However, the rapid recombination rate of e^-/h^+ pairs, low efficiency and low reactivity in the solar spectrum range may obscure its promising characteristics and limit its full-scale deployment as a photocatalyst for environmental remediation applications.

In this scenario, CeO_2 arises as excellent candidate for photocatalysis. One of the most intriguing features is the possibility of self-doping with the generation of oxygen vacancies due to the reversible conversion between Ce^{4+} Ce^{3+} valence state [1]. Furthermore, doping with other metals can increase the ceria photoactivity creating defect states in the band gap or introducing energy levels in it, moving the E_g to solar range value. As part of the modification strategies, iron has been selected as metal dopant because its trivalent cation is able to replace a small fraction of Ce^{4+}, decreasing the activation energy of oxygen release and becoming a powerful tool for rational defect engineering. In the perspective of enhancing the performance of Fe doped ceria nanoparticles, we propose a reverse micelles (RMs) approach [2]. The use of the RMs approach provides an aqueous core that acts as a nanoreactor for the controlled nanoprecipitation of CeO_2 and simultaneously allows the dispersion of Fe species increasing the extent of doping. A one-pot synthetic route was designed to prepare samples of both pure ceria and iron-doped ceria with metal contents of 0.5, 2.5, 5 and 10 (nominal molar percentage) by using a non-ionic surfactant. An in-depth characterization was conducted to identify the structural, textural and morphological properties, as well as the optical properties.

The samples were successfully exploited for ibuprofen photodegradation, and the results compared to the benchmark TiO_2 counterparts. The massive use of ibuprofen as daily use drug is reflecting to its accumulation in surface water and wastewater. The presence of this compound, together with personal care products (PPCPs), nowadays presents a serious risk to human health and the environment with still unknow effects. The Fe-CeO_2 synthetized has shown an ibuprofen concentration reduction of 70% under solar light, paving the way for a novel efficient photocatalyst.

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Visible Light Driven Degradation of Ceftriaxone by Light Modulation Techniques

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Key words: Photocatalysis, Duty-Cycle Dimming, Visible Light Modulation, Co-doped Titania.

The aim of this work was to analyze the effect of visible LED Fixed Duty dimming duty-cycle modulation technique in a photocatalytic system for ceftriaxone (CEF) degradation, using a visible light structured photocatalyst. For this purpose, a flat-plate photocatalytic reactor, irradiated by white-light LEDs matrix controlled by a system for light dimming, was used. The structured photocatalyst consisted of an iron-nitrogen-doped titania photocatalystdeposited on a polystyrene plate (Fe-N-TiO_2/PS). Photocatalytic tests evidenced the stability of the photocatalyst, in fact, after various cycles of tests using Fixed Duty-cycle light modulation, the photocatalytic activity has not been altered, showing the CEF degradation efficiency of about 64.76% under 180 min of visible light irradiation. Furthermore, photocatalytic tests have demonstrated the improvement of the process efficiency using thelight modulation technique and a further improvement using the optimal parameters of the modulation of the light. Precisely, the optimal light modulation was the one achieved throughthe Sinusoidal Variable Duty-cycle light modulation; in fact, it presented a CEF degradationequal to 75.3% after 180 min of visible irradiation with a value of the apparent degradation kinetic constant equal to 0.0082 min^{-1}. Finally, the experimental results obtained confirmedthe advantage brought by the modulation of light in terms of photocatalytic activity and energy costs of the system by comparing the energy costs required for the photodegradationof 90% of the CEF in 1 m^3 of the photocatalytic system used in this work compared to the others found in the literature[1-4].

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Catalysts for the conversion of CO_2 to methanol

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Key words: Methanol, cardon dioxide, hydrogen

Fossil fuels, nowadays, are still the major sources for energy production. Because of their nature, they are the main responsible for greenhouse gasses (GHG) emission, such as CO_2, CH_4 and NO_x, which contribute to global warming. Because of this problem, the world is moving towards more sustainable solution such as hydrogen or methanol. Between the two of them, due to the high costs of hydrogen purification and difficulties in storage and transport, the best competitor to fossil fuel results to be methanol that can be used as energy carrier for hydrogen storage and transportation. It is also an important compound which can be transformed into more complex chemicals as acetic acid, dimethyl ether (DME), methylamine or into intermediate and synthetic hydrocarbons including polymers and single-cell protein. Moreover, because of its high octane number, can be mixed with gasoline without any modification in the vehicle engine. So, Methanol can be considered the most promising building blocks in the chemical industries in order to obtain different products.

Methanol synthesis have been studied for years starting from different carbon-containing feedstock such as natural gases, coal, biomass or synthesis gas. An interesting solution can be atmospheric CO_2 and electrolytic H_2 feedstock conversion that can solve both the need for methanol production and the reduction of CO_2 in the atmosphere.

Because of byproduct formation such as higher alcohol or hydrocarbons, a selective catalyst is needed for methanol synthesis.

In this work, Cu/ZnO-based catalysts have been studied for methanol production starting from gasesous stream containing CO_2 and H_2. The performances are evaluated and compared with commercial Cu/ZnO catalyst in methanol selectivity, methanol yield, activity, stability and also operating condition.

Microwave-assisted catalytic dehydrogenation of propane to propylene

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Key words: structured catalysts; process intensification; microwaves; propane dehydrogenation.

The catalytic dehydrogenation of propane (PDH) to propylene is an endothermic process that requires high operating temperatures[1]. Due to the considerable heat flux to be supplied to the system, the heat transfer to the catalytic volume is a critical aspect that could be overcome by replacing the conventional heating method with the microwave (MW) heating. Since the MW heating capacity depends only on the dielectric properties of the materials[2], this technique allows to obtain a selective and fast heating of the catalytic volume. Furthermore, the application of MW irradiation as alternative heating method can be a promising path for the electrification of industry, aiming at sustainable processes and lower carbon footprint[3]. In this work, a novel approach for PDH process through MW catalysis was developed. To this end, MgO-modified Pt-Sn-based structured catalyst was prepared (Figure 1), characterized, and tested. Since silicon carbide (SiC) absorbs excellently MW irradiation, a SiC honeycomb monolith was used both as structured supportfor the catalyst and as heating medium.

Dip-coating procedure was used to deposit on the SiC monolith an Al_2O_3-based washcoat, while the active species were loaded through wet impregnation. The catalyst was characterized by means of several chemical-physical and analytical techniques: Scanning Electron Microscopy (SEM), N_2 adsorption at -196 °C for the specific surface area (SSA) determination, Hg intrusion porosimetry, ultrasound adherence test, Raman spectroscopy. The MW-assisted experimental tests were performed in a peculiar reactor configuration characterized by a restriction in correspondence of the catalytic section as shown in Figure 5. The cone-shaped geometry at the inlet and the outlet allows to intensify the electric field of microwaves in the catalytic zone, minimizing reflected radiation phenomena. The performance of the system was evaluated in temperature range of 450-600 °C, at different weight hourly space velocity (WHSV) values, by feeding a gaseous stream containing propane and helium (20 vol%). In order to appreciate the features of the innovative system, the prepared catalyst was tested by using both the MW-heating method and the conventional one. The reactor outgases stream was analyzed by means of a mass spectrometer, and the performance of the catalytic system were evaluated in terms of C_3H_8 conversion and selectivity to C_3H_6.

Figure 1 Structured catalyst: $Sn/Pt/MgO/Al_2O_3/SiC$

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Study on the catalytic hydrogasification reaction of carbonaceous materials into methane-rich stream in a fixed bed reactor

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Key words: catalytic hydrogasification, methane, substitute natural gas

Carbonaceous materials, such as biomass and non-recyclable plastics, are currently an attractive resource to produce energy or green compounds, alternative to fossil fuels, such as syngas, biodiesel, bio-methane and others. Among the different treatments throughout these materials are converted, the catalytic hydrogasification, which involves biomass pyrolysis and char and volatiles hydrogasification, allows to store renewable energy, and obtain an energetic recovery without combustion. In this process hydrogen is used as gasifying agent, which can be produced with an electrified steam reforming or water electrolysis steps, limiting so the environmental impact. The gaseous stream produced is a methane-rich with a high energetic value product (synthetic natural gas), which can be used as a green alternative to natural gas.

High reactivity and conversion efficiency of char can be achieved under high hydrogen pressure and high reaction temperature conditions (850°C and 30 bar). However, owing to the exothermicity of the reaction forming methane the char-hydrogenation equilibrium is limited with reaction temperature rises. The catalytic approach could effectively promote the char reactivity and conversion efficiency under milder conditions as lower temperature and pressure, thus decreasing the hydrogasification costs.

In this work, the use of a suitable catalyst is analyzed in order to increase the methane yield of biomass hydrogasification at mild conditions in a fixed bed reactor where the catalytic zone was thermally insulated from the biomass zone to prevent the biomass pyrolysis before the activation of catalyst. A comparison between a commercial pellets catalyst (Ni/alumina) used for the methanation of complex systems and a 40%Ni/CeO_2 powder catalyst, prepared in laboratory, was carried out to identify the best catalytic system in terms of CH_4 and TAR yields. The results showed that the commercial catalyst can achieve a maximum of 50 vol% of methane yield at 500°C using a catalyst:biomass ratio of2/3 and 160 Ncm^3/min (95 vol%H2 – 5 vol%Ar). In particular, the optimization of heating system has allowed simultaneously to reduce the content of organic compound in the liquidresidue and to minimize the carbonaceous solid residue. Preliminary tests on the catalyst coke resistance have showed very promising results, in particular for the 40%Ni/CeO_2 sample, even if further studies focused on the catalyst formulation optimization in terms of activity and stability will be done evaluating the addition of promoter compounds such as calcium-based ones.

UV-Assisted Photocatalysis for Simultaneous Valorization and Treatment of Olive Mill Wastewater

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Key words: Olive mill wastewater valorization, Photocatalysis, supported catalyst, H_2 production

The heterogeneous photocatalysis is a process widely studied to treat different types of waste in water. An interesting approach involves not only the degradation of pollutants that are difficult to biodegrade, but also their valorisation through transformation into molecules of interest. This is why this study illustrates how to valorize olive mill wastewater (OMW) with a photocatalytic process able to produce hydrogen and simultaneously break down the polluting load of this waste. To achieve this objective, a comparison between the performances of commercial TiO_2 and home-made sol gel TiO_2 on olive mill wastewater was first carried out. The hydrogen production and the ability of the catalyst to remove the organic matter present in wastewater were considered, with particular attention to the best combination (in terms of processing time and experimental phase sequence) between the anoxic phase (for the hydrogen production) and the oxidative phase (for the degradation of the organic residue). Once the best combination was identified, the photocatalyst in powder form was transferred on the surface of polystyrene pellets in order to make the catalyst easily separable and recyclable. The photocatalytic activity tests demonstrated that the proposed photocatalyst showed very good stability after ten reuse cycles, even in the presence of real OMW, assuring a hydrogen production of about 16954 μmol/L after four hours of UV irradiation. During the tests the liquid sample were analyzed also with UHPLC technique that evidenced the phenol degradation and the presence of only hydroquinone as by-product.

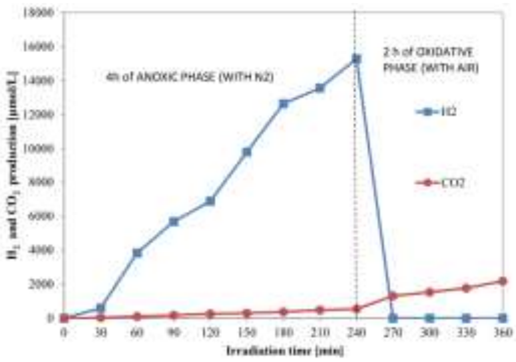

Figure. Behaviour of H_2 and CO_2 production during the “doble stage test” (anoxic phase (4 hours) and oxidative phase (2 hours), on PS/TiO_2 III impregnation catalyst. Phenol aqueous solution:100 mg/L.

Ru- and Rh- based catalysts for CO_2 methanation assisted by non-thermal plasma

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Key words: non-thermal plasma; methanation; sustainability; electrification

The need to reduce the concentration of CO_2 in the atmosphere is becoming increasingly necessary since it is considered the main factor responsible for climate change. Carbon Capture and Utilization (CCU) technology offers the opportunity to obtain a wide range of chemicals using this molecule as a raw material. In this work, the catalytic Non-Thermal Plasma (NTP)-assisted hydrogenation of CO_2 to CH_4 (methanation reaction) in a Dielectric Barrier Discharge (DBD) reactor was investigated. Four different Ru- and Rh-based catalysts were prepared starting from γ-Al_2O_3 spheres, characterized and tested in both thermal and NTP-assisted methanation under different operating conditions. The experimental tests evidenced the very positive effect of the NTP application on the catalytic performance, highlighting that for all the catalysts the same CO_2 conversion was reached at a temperature 150 °C lower with respect to the conventional thermal reaction. Among the prepared catalysts, the bimetallic ones showed the best performance, reaching a CO_2 conversion of 97% at about 180 °C with a lower energy consumption with respect to similar catalysts present in the literature.

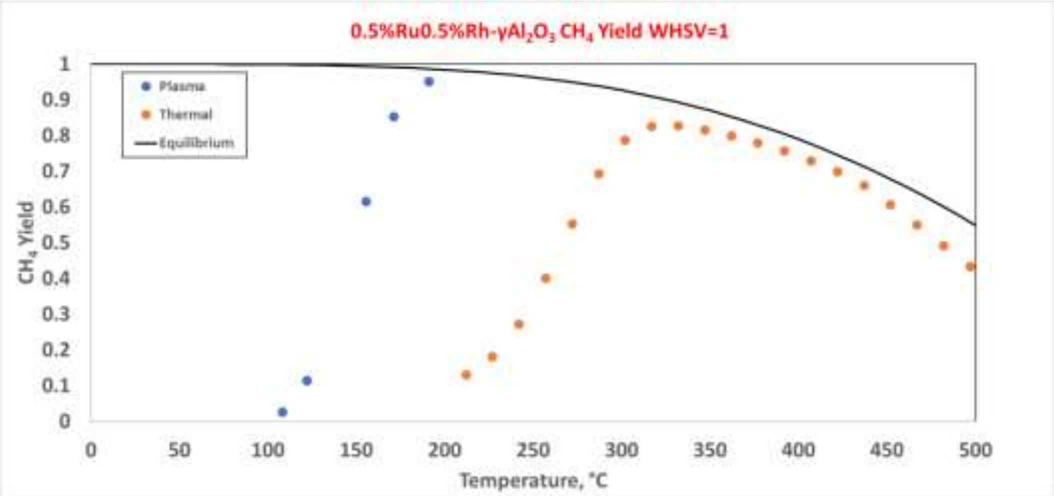

Figure 1. RuRh-γAl_2O_3 CH_4 yield comparison for both thermal and non-thermal-plasma-assistedtests at WHSV = 1 NL/g_{cat}h.

The ability to activate the CO_2 molecules at lower temperatures results in the possibility of reaching yields that would be impossible to reach due to thermodynamic limitations. Furthermore, it is also fundamental to note that it is possible to obtain CH_4 yields similar to the thermal ones at temperatures about 100 °C lower, which would result in a considerably lower energy expense.

INDEX OF CONTRIBUTORS
Surname page (o oral, p poster, KN keynote, PL plenary)