CARBOCATVIII

8TH INTERNATIONAL SYMPOSIUM **ON CARBON FOR CATALYSIS**

PORTO, PORTUGAL

JUNE 26 – 29, 2018

Book **of** Abstracts

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26-29 JUNE 2018

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Porto - Portugal

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PREFACE

Dear Participant,

On behalf of the Carbon Group of the Portuguese Chemical Society (C@SPQ) we are pleased to welcome you in the city of Porto to attend the 8th International Symposium on Carbon for Catalysis, CarboCat-VIII.

Following the previous CarboCat meetings held in Lausanne (2004), Saint-Petersburg (2006), Berlin (2008), Dalian (2010), Brixen (2012), Trondheim (2014) and Strasbourg (2016), CarboCat-VIII will be devoted to new developments and fundamental advances on carbon materials (conventional and nanostructured carbons) for catalytic applications.

The Scientific Program includes 3 Plenary Lectures, 4 Keynote Lectures, 33 Oral Communications and 85 Posters. In addition to the two general poster sessions, several post-graduate students will be able to present their posters also as Short Oral Communications. Several awards are available to distinguish the best poster presentations.

You are also invited to visit Porto, with its historical center (UNESCO World Heritage Site), the river Douro and the famous Port Wine cellars.

Finally, we would like to thank all the sponsors and participants, whose contributions made this event possible.

On behalf of the Organizing Committee,

José Luís Figueiredo

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SCIENTIFIC PROGRAM

Tuesday, 26th of June, 2018

13:00-15:00	**Registration**
15:00-15:20	**Opening session**
15:20-16:00	**KN1** “Oxidative dehydrogenation over nanocarbons: Recent mechanistic study” Siglinda Perathoner and Gabriele Centi (*Università degli Studi di Messina, Italy*) Dangsheng Su (*Dalian Institute of Chemical Physics, China*)
16:00-16:40	**KN2** “Going green with black: Oxygen reduction carbon electrocatalysts” Magdalena Titirici (*Queen Mary University of London, United Kingdom*)
16:40-17:00	**OC1** “Involvement of Pd single atoms in Pd/C catalyzed terpene hydrogenation in continuous reactor” Philippe Serp (*LCC-CNRS, France*)
17:00-17:20	**OC2** “Carbon-supported Au nanoparticles: Catalytic activity ruled out by carbon support” Laura Prati (*Università degli Studi di Milano, Italy*)
17:20-17:40	**OC3** “Acid porous carbons involved in the green synthesis of benzodiazepines” Inês Matos (*LAQV/REQUIMTE, Portugal*)
17:40-18:00	**OC4** “Sustainable carbocatalyst with atomically dispersed Fe-N-P-C complex active sites for superior oxygen reduction” De Chen (*Norwegian University of Science and Technology, Norway*)
18:00-20:00	**Welcome reception**

Wednesday, 27th of June, 2018

09:00-10:00	**PL1** "Catalysis using carbon-based nanomaterials" Graham Hutchings (*Cardiff Catalysis Institute, United Kingdom*)
10:00-10:20	**OC5** "Carbon supported metal-carbides and metal-phosphides for biomass-based conversions" Johannes Hendrik Bitter (*Wageningen University, The Netherlands*)
10:20-10:40	**OC6** "Effect of the nature of carbon support in Pd/C catalysts on the reaction routes of aqueous-phase hydrogenation of furfural" Roman Mironenko (*Institute of Hydrocarbons Processing, Russia*)
10:40-11:10	**Coffee break**
11:10-11:30	**OC7** "Aziridine functionalized carbon nanotubes as highly efficient electrocatalysts for the selective CO_2 reduction to CO" Giuliano Giambastiani (*ICCOM-CNR, Italy*)
11:30-11:50	**OC8** "Palladium-nickel on tin oxide-carbon composite supports for electrocatalytic hydrogen evolution" César Sequeira (*CeFEMA/IST, Portugal*)
11:50-12:10	**OC9** "Nitrogen-doped carbon materials derived from cellulose for the oxygen reduction reaction" Martin Muhler (*Laboratory of Industrial Chemistry, Germany*)
12:10-12:30	**OC10** "Cu and Pd nanoparticles supported on a graphitic carbon material as bifunctional HER/ORR electrocatalysts" Diana Fernandes (*REQUIMTE/LAQV, Portugal*)
12:30-12:50	**OC11** "Bifunctional oxygen reduction/evolution activity of Fe/Co/Ni mixed oxide nanoparticles supported on oxidized carbon nanotubes" Mariya Kazakova (*Novosibirsk State University, Russia*)
12:50-14:00	**Lunch break**
14:00-14:20	**OC12** "Graphene aerogels as catalyst support for nanodiamonds and metal nanoparticles" Enrique García-Bordejé (*ICB-CSIC, Spain*)
14:20-14:40	**OC13** "Tomography analysis of Ru supported on micro and mesoporous carbon: A correlation between morphology and catalytic activity" Marta Stucchi (*Università degli Studi di Milano, Italy*)
14:40-15:00	**OC14** "Cobalt catalysts on graphene nanoflakes and carbon nanotubes in Fischer-Tropsch synthesis: effect of the support oxidation and N-doping" Sergei Chernyak (*Lomonosov Moscow State University, Russia*)
15:00-16:00	Short oral communications **SOC1** "Confinement of iron and promoters in carbon nanotubes for direct selective synthesis of lower olefins from syngas over Bi and Pb promoted iron catalysts" Bang Gu (*University of Lille, France*)

SOC2 “Manganese promoter effects in carbon-supported copper-based ester hydrogenation catalysts”
Rolf Beerthuis (*Debye Institute for Nanomaterials Science, The Netherlands*)

SOC3 “Highly selective conversion of methanol to propylene: design of a MFI zeolite with selective-blockage of (010) surfaces”
Dali Cai (*Tsinghua University, China*)

SOC4 “Hydrodeoxygenation of vanillin over carbon supported noble metal catalysts”
Jose Santos (*Instituto de Ciencia de Materiales de Sevilla, Spain*)

SOC5 “Tracking the paths for the sucrose transformations over bifunctional Ru-POM/AC catalysts”
Nadia Bosch (*UNED, Spain*)

SOC6 “Tailoring the catalytic properties of Mo_2C/CNF catalysts for the HDO of guaiacol: Influence of carburization time”
Elba Ochoa (*ICB-CSIC, Spain*)

SOC7 “Au nanoparticle size control over few layer graphenes”
Valérie Caps (*ICPEES, France*)

SOC8 “Development of mesoporous, graphitic carbons as flexible catalyst platform for metal-free oxidative dehydrogenation reactions”
Felix Herold (*Technische Universität Darmstadt, Germany*)

SOC9 “Bayer-Villiger oxidation and esterification reaction catalyzed by sawdust biochar”
Tiago Duarte (*CQE/IST, Portugal*)

SOC10 “Nickel nanoparticles decorated nitrogen doped carbon nanotubes as an efficient catalyst for CO_2 methanation”
Wei Wang (*ICPEES, France*)

SOC11 “Photocatalytic behaviour of ZnO nanoparticles and their composites with graphene”
Sandra Román (*ICB-CSIC, Spain*)

SOC12 “Carbon-supported Cu and Cu_2O nanoparticles for CO_2 electroreduction”
Marisol Rosales (*Debye Institute for Nanomaterials Science, The Netherlands*)

16:00-17:00 Posters & Coffee break

17:00-17:20 **OC15** “Comparative study of CoMo/MWCNT and CoMo/Al_2O_3 hydrotreating catalysts prepared with citric acid”
Maxim O. Kazakov (*Boreskov Institute of Catalysis, Russia*)

17:20-17:40 **OC16** “N-decorated carbon nanotubes as a metal-free heterogeneous catalyst for mild CO_2 chemical reduction to methanol”
Tuci Giulia (*ICCOM-CNR, Italy*)

17:40-18:00 **OC17** “Fine-tuning of metal-carbon complex catalysts: Learning from natural catalysts”
Xuezhi Duan (*State Key Laboratory of Chemical Engineering, China*)

Thursday, 28th of June, 2018

09:00-10:00	**PL2** “Carbon-supported catalysts – Assembly, characterization and performance” Krijn P. de Jong (*Utrecht University, The Netherlands*)
10:00-10:20	**OC18** “Direct formation of nanometals and nanooxides within pristine bulk graphitic matrices” Valérie Caps (*ICPEES, France*)
10:20-10:40	**OC19** “The tunable effects of dopants on the nanostructured carbon on the catalytic property of the supported single metal atom catalysts revealed from first principle calculations” Bo Li (*Institute of Metal Research, China*)
10:40-11:10	**Coffee break**
11:10-11:30	**OC20** “Pd nanoparticles supported on functionalized carbon nanotubes for the liquid-phase aerobic oxidation of ethanol” Baoxiang Peng (*Laboratory of Industrial Chemistry, Germany*)
11:30-11:50	**OC21** “Surface functionalized carbon nanotubes as molecular oxygen carrier for liquid-phase aerobic oxidation reaction” Yuefeng Liu (*Dalian National Laboratory for Clean Energy, China*)
11:50-12:10	**OC22** “Macroscopic oxidized graphite felts containing palladium nanoparticles as an efficient liquid-phase hydrogenation catalyst with easy recovery” Zhenxin Xu (*ICPEES, France*)
12:10-12:30	**OC23** “Strong effect of the surface properties of carbon supports in Au-catalyzed reactions” Baira Donoeva (*Debye Institute for Nanomaterials Science, The Netherlands*)
12:30-12:50	**OC24** “Nanocarbons as supports for the gold catalyzed glycerol oxidation” Ana Paula Ribeiro (*CQE/IST, Portugal*)
12:50-14:00	**Lunch break**
14:00-15:00	**PL3** “Carbon materials in chemical energy conversion” Robert Schlögl (*Fritz Haber Institute of the Max Planck Society, Germany*)
15:00-15:20	**OC25** “Metal free oxidation of glycerol over nitrogen containing carbon nanotubes” Alberto Villa (*Università degli Studi di Milano, Italy*)
15:20-15:40	**OC26** “Tuning properties of ultrafine Pd nanoparticles supported on multiwalled carbon nanotube” Zinfer Ismagilov (*Institute of Coal Chemistry and Materials Science, Russia*)
15:40-16:00	**OC27** “Au/C catalysts for 2,5-furandicarboxylic acid production” Svetlana Ivanova (*Instituto de Ciencia de Materiales de Sevilla, Spain*)
16:00-17:00	**Posters & Coffee break**
17:40-20:30	**Social event**
20:30-23:30	**Conference dinner**

Friday, 29th of June, 2018

09:00-09:40	**KN3** “Nitrogen-doped carbon nanofibres: What are the requirements for application in PEM fuel cells?” Magnus Rønning (*Norwegian University of Science and Technology, Norway*)
09:40-10:00	**OC28** “Sulfonated hydrothermal carbons as catalysts for organic reactions” José Fraile (*ISQCH, Spain*)
10:00-10:20	**OC29** “Carbon materials in cyclohexane catalytic oxidation” Marta Andrade (*CQE/IST, Portugal*)
10:20-10:40	**OC30** “Effect of carbon support on selective hydrogenation by concave platinum nanocubes” Katerina Soulantica (*LPCNO, France*)
10:40-11:10	**Coffee break**
11:10-11:30	**OC31** “Surface-modified nanocarbons as metal-free catalysts for catalytic oxidation” Shaobin Wang (*Curtin University, Australia*)
11:30-11:50	**OC32** “Modified carbide-derived carbons used in the catalytic wet peroxide oxidation of oily wastewaters” Jose Díaz de Tuesta (*Instituto Politécnico de Bragança, Portugal*)
11:50-12:10	**OC33** “Highly nitrogen-selective Pt-In/C catalysts in the reduction of nitrites in water” Enrique V. Ramos Fernandez (*Universidad de Alicante, Spain*)
12:10-12:50	**KN4** “Catalytic layers of Proton Exchange Membrane fuel cells based on carbon xerogel supports” Nathalie Job (*University of Liège, Belgium*)
12:50-13:10	**Closing session**
13:10-14:00	**Executive lunch**

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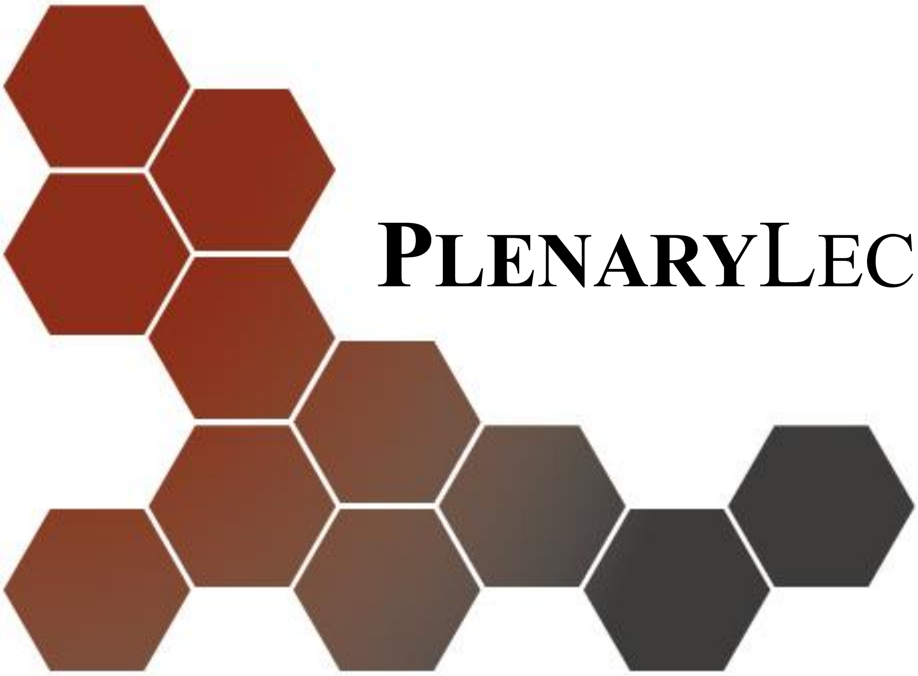

PLENARYLECTURES

(PL)

CARBOCATVIII

CATALYSIS USING CARBON-BASED NANOMATERIALS

Graham J. Hutchings

Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Cardiff, UK CF10 3AT
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Catalysis is of crucial importance for the manufacture of the goods and infrastructure necessary for the effective wellbeing of society. Catalysis plays a key role in the manufacture of chemical intermediates but in a wider context contributes in some way to the production of over 80% of all manufactured goods and contributes to over 25% of global GDP. In this respect, the design of catalysts with improved performance is of key importance and this is the topic of this lecture. The use of carbon as a catalyst and as a support for catalysts will be explored in this presentation. In particular, the use of graphitic oxide as a catalyst for alkene epoxidation will be described. Selective oxidation is challenging research, as the key aim is to restrict overoxidation to carbon oxides and water. The use of carbon-supported gold catalysts for acetylene hydrochlorination will be described. This catalyst has recently been commercialised in China and the timeline between catalyst discovery and commercialisation will be described. For all examples, the importance of the catalyst preparation methodology will be emphasised.

CARBON-SUPPORTED CATALYSTS – ASSEMBLY, CHARACTERIZATION AND PERFORMANCE

Krijn P. de Jong

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Carbon-supported catalysts are widely used in industry and investigated in academia. Academic research benefits from the use of carbon since often it is chemically inert and the properties can be varied over a wide range. Here we discuss the use of carbon nanotubes (CNT) and surface oxidized carbon nanotubes (CNT-ox) to synthesize supported cobalt and iron catalysts used for the Fischer Tropsch synthesis.

Cobalt catalysts supported on CNT and CNT-ox were prepared via impregnation and drying and proper selection of cobalt precursor, solvent and support. Identical sizes of cobalt nanocrystals were obtained with different crystal structures leading to large differences in surface-specific activities [1].

Colloidal iron oxide nanocrystals (Fe-NC) were deposited on skeins of CNT. The macropores in the skeins facilitated diffusion of Fe-NC to obtain uniform distributions of iron particles over the support. The ligand concentration in the solution played a key role too [2].

For assembly of cobalt nanocrystals on CNT it appeared necessary to apply mild oxidation to deposit CoO-NC rather than Co-NC to mitigate magnetic interactions [3].

Finally, we will show very first results of assembly of carbon-supported iron catalysts in real time using liquid-phase in situ TEM [4].

[1] T.O. Esschemann et al., J. Catal. 328 (2015) 130−138.
[2] M. Casavola et al., Adv. Funct. Mater. 25 (2015) 5309−5319; M. Casavola et al., ACS Catal. 7 (2017) 5121−5128.
[3] T.W. van Deelen et al., Chem. Commun. 54 (2018) 2530−2533.
[4] N.A. Krans et al., in preparation.

CARBON MATERIALS IN CHEMICAL ENERGY CONVERSION

Robert Schlögl

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4 – 6, D-14195 Berlin, Germany)
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The versatility of carbon in its allotropes and nanostructured variants gave already rise to multiple applications in the wider field of energy-related processes including as reagent in steel and aluminum industry, as indispensable part of water purification and in moving electrodes. New are extensions of the field of electrode applications in water splitting. The possibility to generate carbon from biomass into an electrode may open the pathway to sacrificial water splitting in the OER reaction. Pyrolysis of biomass and fossil hydrocarbons may lead to hydrogen and solid carbon that can be used for a variety of bulk applications such as road surfaces or deposited as “carbon capture and solid storage”. This application of carbon may become a very large driver for carbon chemistry when waste organic materials or biomass can be converted using its intrinsic energy content to a form of environmentally stable carbon “biochar”. Such a process could open a safe path for sub-zero CO2 emission control. Carbon polymers from the CxNy family are recently intensely researched as photo-catalysts and as electrode materials. A very large number of realizations of carbon-metal mixed compounds are advocated as electro- or photo-catalysts. Batteries and fuel cells cannot work with a wide variety of functional carbon materials.

All these applications have in common that a precise control of structure in the bulk and at the surface is required if a rational development should replace the still frequent phenomenological approach. Progress in analysis and functional testing that is exemplified in the talk nourishes the expectation that the pertinent challenge of developing structure-function correlations in large-volume carbon materials may be met in the foreseeable future although we recognize that the number of efforts in phenomenological material science vastly exceeds those in advancing our functional understanding.

KEYNOTE

COMMUNICATIONS

(KN)

OXIDATIVE DEHYDROGENATION OVER NANOCARBONS: RECENT MECHANISTIC STUDY

Siglinda Perathoner[1], Gabriele Centi[1], Dang Sheng Su[2,3,*]

[1]University of Messina, ERIC aisbl and CASPE/INSTM, Messina, Italy
[2]Dalian National Laboratory for Clean Energy (DNL), Dalian Institute of Chemical Physics, CAS, Dalian 116023, China;
[3]Shenyang National Laboratory for Materials Science (SYNL), Institute of Metal Research, CAS, Shenyang 110016, China
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Sustainable and environmentally benign catalytic processes are vital for the future to supply the world population with clean energy and industrial products. The replacement of conventional metal or metal oxide catalysts with earth abundant and renewable nonmetallic materials has attracted considerable research interests in the field of catalysis and material science. The stable and efficient catalytic performance of nanocarbon materials was discovered at the end of last century, and these materials are considered as potential alternatives for conventional metal-based catalysts. With its rapid development in the past 20 years, the research field of carbon catalysis has been experiencing a smooth transition from the discovery of novel nanocarbon materials or related new reaction systems to the atomistic-level mechanistic understanding on the catalytic process and the subsequent rational design of the practical catalytic reaction systems.

In this presentation, we will summarize the recent progress in the kinetic and mechanistic studies on nanocarbon catalyzed alkane oxidative dehydrogenation (ODH) reactions [1,2]. We will attempt to extract general concepts and basic regularities for carbon catalytic process directing us on the way for rational design of novel efficient metal-free catalysts. The nature of the active sites for ODH reactions has been revealed through microcalorimetric analysis, ambient pressure X-ray photoelectron spectroscopy (XPS) measurement, and in situ chemical titration strategies. The detailed kinetic analysis and in situ catalyst structure characterization suggests that carbon catalyzed ODH reactions involve the redox cycles of the ketonic carbonyl−hydroxyl pairs, and the key physicochemical parameters (activation energy, reaction order, and rate/equilibrium constants, etc.) of the carbon catalytic systems are proposed and compared with conventional transition metal oxide catalysts (Figure 1). The proposal of the intrinsic catalytic activity (TOF) provides the possibility for the fair comparisons of different nanocarbon catalysts and the consequent structure-function relation regularity. Surface modification and heteroatom doping are proved as the most effective strategies to adjust the catalytic property (activity and product selectivity etc.) of the nanocarbon catalysts. Nanocarbon is actually a proper candidate platform helping us to understand the classical catalytic reaction mechanism better, since there is no lattice oxygen and all the catalytic process happens on nanocarbon surface. We will also exhibit the importance of the in situ structural characterizations for heterogeneous nanocarbon catalysis. The research strategy and methods proposed for carbon catalysts may also shed light on other complicated catalytic systems or fields concerning the applications of nonmetallic materials, such as energy storage and environment protection etc.

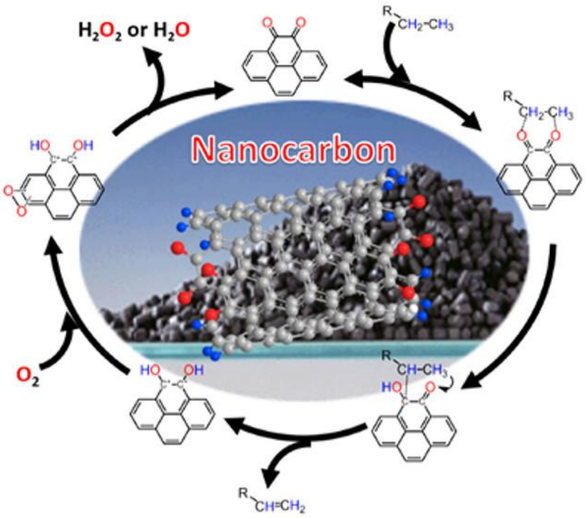

Figure 1. Schematic drawings of alkane ODH reaction mechanism for nanocarbon.

[1] W. Qi, W. Liu, X. Guo, R. Schlögl, D. S. Su, *Angew. Chem. Int. Ed.*, 54 (2015), 13682-13685.

[2] W. Qi, P. Yan, D. S. Su, *Acc. Chem. Res.*, 2018, 10.1021/acs.accounts.7b00475

GOING GREEN WITH BLACK: OXYGEN REDUCTION CABON ELETROCATALYSIS

Magdalena Titirici*, Kathrin Preuss, Mo Qiao, Jingyu Feng

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As the limitation of climate change poses a pivotal challenge nowadays, avoidance of carbon dioxide emission is desirable. One solution would be the shift from a carbon-based energy economy to hydrogen based, where hydrogen could be won from renewable energy resources and used in fuel cells, to produce electricity and heat. Polymer Electrolyte Membrane (PEM) Fuel Cells have an electrical efficiency of up to 60% and are thus a promising opportunity for future applications.

Currently, electro-catalysts for the oxygen reduction reaction (ORR) at cathodes of PEM fuel cells involve Pt/Pt-alloys, which show a number of shortcomings, such as slow ORR kinetics, low availability and high cost, which is why alternative catalytic materials are highly desirable.

Heteroatom doped carbon materials have recently emerged as a promising class of electrocatalysts allowing to completely avoid the use of platinum.

Here we present different design strategies towards the synthesis of effective heteroatom doped carbon materials from renewable precursors engineered with the right porosity, functionality and conductivity to allow a comparable or even superior performance to Pt-based catalysts for the ORR reaction in fuel cells. We also present the correlations between the structure and the electro catalytic properties of these sustainable nanocarbons.

We also present a new concept where we can manipulate the interface at the triple point between the catalyst, electrolyte and the oxygen gas.

NITROGEN-DOPED CARBON NANOFIBRES: WHAT ARE THE REQUIREMENTS FOR APPLICATION IN PEM FUEL CELLS?

Magnus Rønning*

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Proton-exchange membrane fuel cells (PEMFCs) have been the focus of research and development for decades, but only recently started to penetrate real markets in application areas such as automotive transport, distributed power generation and auxiliary power units [1].

Many of the critical technological challenges for the implementation of fuel cells in automotive applications are on their way of being resolved, with the notable exception of cost. A significant contributor to the high cost is the use of platinum, and other platinum group metals (PGMs) as catalysts. Between 20 and 40% of the total PEMFC cost is the cost of Pt/C catalyst for the oxygen reduction reaction (ORR) at the cathode [2,3]. So far, only platinum and platinum group metal (PGM) catalysts were successfully utilized in commercial PEMFC cathodes, as no other material could demonstrate comparable combination of ORR activity and durability in the acidic conditions of PEMFCs.

Platinum group metals are listed by the European Commission as critical raw materials, and resources are limited and expected to be depleted by the end of the 21st century regardless of the introduction of fuel cell vehicles. Therefore, it is important to find catalysts based on more sustainable catalyst materials.

Nitrogen-doped carbon nanomaterials containing a non-PGM metal such as iron or cobalt (Me-N-C) have received substantial attention as potential alternatives as ORR catalyst [4,5]. These materials are highly conductive, corrosion resistant and can be produced in large quantities at only a fraction of the cost of PGM. Such Me-N-C catalysts have been shown to have superior ORR performance to commercial Pt catalysts in alkaline electrolytes. However, they are less active in acidic electrolytes such as H_2/O_2 PEM fuel cells, which is currently limiting their large-scale practical applications.

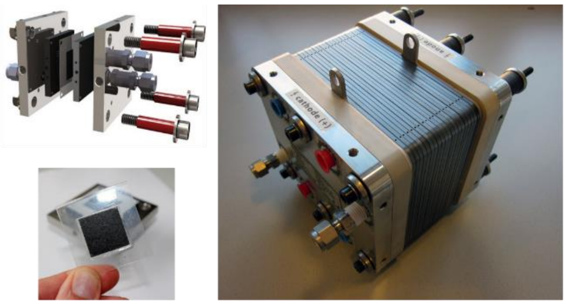

Figure 1. Illustration of a test cell and membrane-electrode assembly (MEA) used in single cell experiments, and a 10-cell PEM FC stack using a Fe-N-C ORR catalyst [9].

There are several reports on promising single PEM cell performance for such catalysts, both in terms of activity and durability [6,7,8]. We have recently reported the performance and durability of Fe-N-C (carbon nanofibres, CNF) catalyst for ORR in PEMFCs in both single cell and a 10-cell FC stack [9]. A 10-cell stack with a cell active area of 75 cm^2 was produced and tested for 400 hours. The Fe-N-C catalyst is applied to the cathodes of the MEAs by a conventional method and at relatively high loadings (1-10 mg cm^{-2}). By using the test results, a simple market application model was established based on calculation of the total cost of ownership of a 1 kW PEM FC backup power unit with Fe-N-CNF cathodes. In conclusion, even a near-complete elimination of the cathode catalyst cost by substitution of platinum with a carbon-based catalyst cannot produce a cost competitive product unless both the performance and the durability of the fuel cell with the new catalyst are close to that of the state-of the art system [9].

The requirements for commercialisation of Fe-N-C PEMFC catalysts are discussed. A review of recent literature on the topic highlights the challenge that not only intrinsic activity is crucial for obtaining the required performance: Among other factors, MEA assembly, mass transfer limitations and durability are also often limiting factors.

Acknowledgements

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CATALYTIC LAYERS OF PROTON EXCHANGE MEMBRANE FUEL CELLS BASED ON CARBON XEROGEL SUPPORTS

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Carbon materials are commonly used as electrode components in electrochemical systems. Carbon black remains the most widespread support to prepare catalytic layers of Proton Exchange Membrane Fuel Cells (PEMFCs). The composition and the pore texture of these carbons are key variables to the device performance, through (i) the ability of the support to disperse metal atoms, (ii) the electrolyte/carbon contact and (iii) the reactant/product mass transport within the porosity [1]. However, in the case of carbon black, the mastering of these properties is not easy. In particular, the pore texture of the final electrode is not controllable since it largely depends on the electrode processing (*i.e.* electrode pressing), and not on the material itself.

Replacing these conventional carbons by nanostructured materials, such as carbon xerogels (CXs), allows for improving their performance and understanding the impact of the pore texture on the catalytic layer performance [2]. CXs are obtained by drying and pyrolysis of aqueous organic gels, and their pore texture can easily be tailored within a very wide range by adjusting the synthesis variables at an adequate value [3]. The final carbon is made of interconnected spherical-like microporous nodules, the size of which is controlled by the gel synthesis variables. As a result, one can obtain very pure carbons with meso-macropore sizes ranging from a few nm to a few µm, with pore volumes as high as 3 cm^3/g and large specific surface area (~600 m^2/g). In addition, the micropore texture and surface chemistry can be modified via post-treatments in order to tune these properties independently [4, 5]. CXs are thus very interesting candidates to replace carbon blacks with a catalyst support with tunable (surface) chemical composition and adequate pore texture, which both impact the performance of PEMFC catalytic layers.

The synthesis of CX-supported Pt catalysts has been studied and optimized [6]. Pt catalysts with excellent dispersion (particle size ~3-4 nm, Fig. 1a) and high mass fractions (min. 40% wt.) supported on texture-tailored carbon materials (pore size from 20 to 500 nm) were prepared using simple impregnation-reduction processes in liquid phase. Final catalysts are obtained from the powdery support and the metal precursor within about 1 h. They display excellent intrinsic catalytic activities and can be used to prepare Membrane-Electrode Assemblies (MEAs) with interesting mass transport properties compared to those elaborated from supported catalysts on carbon black.

The same type of nanostructured carbon can be used to synthesize supported hollow PtCo nanoparticles (Fig. 1b) [7]. The addition of Co leads to the Pt lattice contraction, and thus to much higher catalytic activity while the hollow structure allows for good metal utilization ratio despite the large particle size. These catalysts were thoroughly characterized using physico-chemical and electrochemical techniques, including Accelerated Stress Tests (ASTs) on rotating disk electrodes. The hollow PtCo/CX catalysts display much better stability than Pt/CX and Pt/carbon black samples, probably due to the particle size. PtCo/CX catalysts were also tested in Membrane-Electrodes Assembly configuration for at least 200 h, which allowed comparing the overall stability of the samples. ASTs were performed and results show that the stability of the hollow PtCo/CX catalysts are far more stable than Pt nanoparticles, whatever the support used: indeed, while the performances of Pt nanoparticles continually decrease with ageing time, the current-voltage curves obtained with PtCo/CX hollow particles stabilize after a while.

Current research goes towards the modification of the carbon surface properties, for instance by nitrogen doping *via* plasma treatments. The goal is to improve the nanoparticle stability and increase further the catalysts lifetime.

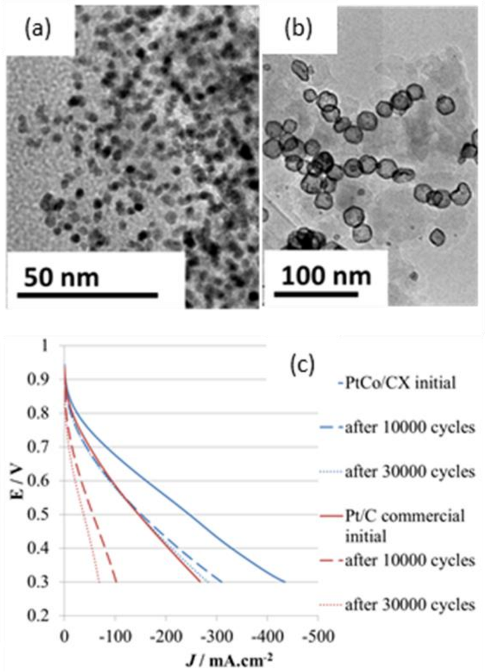

Figure 1. (a) TEM picture of a Pt/CX catalyst (40% wt.) prepared by impregnation-reduction process. (b) TEM picture of hollow PtCo/C nanoparticles. (c) Comparison between commercial Pt/carbon black and hollow PtCo/CX catalysts in MEA (H_2/O_2); the Pt content is constant (0.033 $mg_{Pt}/cm^2_{electrode}$), and cells were cycled up to 30,000 times between 0.6 and 1.0 V to accelerate ageing.

Acknowledgements. NJ thanks the Walloon Region for funding (project HYLIFE, grant n° 1410135).

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ORAL COMMUNICATIONS (OC)

INVOLVEMENT OF Pd SINGLE ATOMS IN Pd/C CATALYZED TERPENE HYDROGENATION IN CONTINUOUS REACTOR

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The major uses for terpenes are in the flavour and fragrance industries, as a solvent, and in the manufacture of polymers and adhesives. Most of the terpenes are obtained as co-products of the paper or food processing industries. Recently, metabolic engineering has been successfully used to produce these valuable compounds in microbial hosts which enables their production on a larger scale [1] and for some of them opens the way for a potential use as a biofuel. Some applications of terpenes (e.g. cosmetics and fuel) require fully hydrogenated products obtained with a complex network of exothermic catalytic reactions [2]. In the first part of this study, the development of new Pd catalysts supported on innovative carbon supports is presented. Several carbon supports were investigated including a screening of their pre-treatments in order to identify the best catalytic material in comparison to a reference Pd/Al_2O_3 commercial catalyst. Myrcene ($C_{10}H_{16}$) was used as a model substrate because of the presence of conjugated double bonds that could lead to thermally activated by-products. Squalene ($C_{30}H_{50}$) and β-farnesene ($C_{15}H_{24}$) have also been studied as a strategic substrate. Squalane and farnesane, obtained by full hydrogenation of squalene and β-farnesene, are key ingredients in the cosmetic, nutraceutical, pharmaceutical and biofuel industries [3]. For these substrates, hydrogenation can be the subject of external/internal mass and heat transfer issues, leading potentially to a decrease in selectivity, productivity and safety. Thus, another part of this work is focused on the development of an intensified continuous reactor involving highly porous foams that are suitable to promote the highest apparent activity of the best identified catalysts in neat or concentrated media without alteration of the selectivity and/or safety.

Five kinds of carbon materials were studied: carbon nanotubes (CNTs), nitrogen-doped carbon nanotubes (N-CNTs), filamentous carbon (FC), carbon nanofibers (CNFs), and few layer graphene (FLG). 4 pretreatments are also compared: no pretreatment (-), oxidation with nitric acid (-COOH); high temperature annealing (-HT) and a combination of nitric acid oxidation followed by high temperature annealing (-COOH-HT). All the catalysts were characterized by different techniques (TEM, STEM-HAADF, TPD, XRD, BET, ICP, TGA, etc.) and present a Pd loading between 1-2 wt.% with mainly 2 nm well dispersed nanoparticles. The screening was conducted in a mechanically stirred tank reactor of 200 mL at 120°C with pure H_2 atmosphere at a constant pressure of 20 bar with a 1M substrate solution in heptane. Continuous experiments were conducted in a stainless steel tubular reactor made of several 10 cm long segments in order to investigate some mass and heat transport effects with various superficial velocities at constant contact time.

Different double bond reactivity have been observed (conjugation, steric hindrance, etc.) including some complex interplay with external gas-liquid and possible internal mass transfer limitations for the more reactive ones. All the catalysts were compared regarding two profiles: reaction progress and apparent turn over frequency (based on H_2 consumption rate per mol of Pd). The highest activities are encountered with CNF, FC, FLG and CNTs supports (Figure 1a). This can be explained by a lower internal limitation (highly mesoporous supports) and by a possible better intrinsic activity due to particular metal-support interactions. The acidic pretreatment of the carbon supports was found to be efficient for many catalysts (Figure 1a). For support presenting a high edge/basal plane ratio such as CNF or FC, the high temperature annealing treatment was also very efficient. This results is not in favor of an involvement of –COOH groups in the catalysis. We have demonstrated by STEM-HAADF the presence of stable single electropositive Pd atoms on the most active catalysts. DFT calculations performed on a model system and a kinetic study have shown that this single atoms play a role in the parallel isomerization of some "hard to reduce" double bonds. These bi-functional catalysts are also extremely active for squalene and farnesene hydrogenation (Figure 1b).

Finally, a successful coating method of metallic foams with the best catalysts has been developed, allowing continuous experiments in a home-made well-instrumented stainless steel tubular reactor.

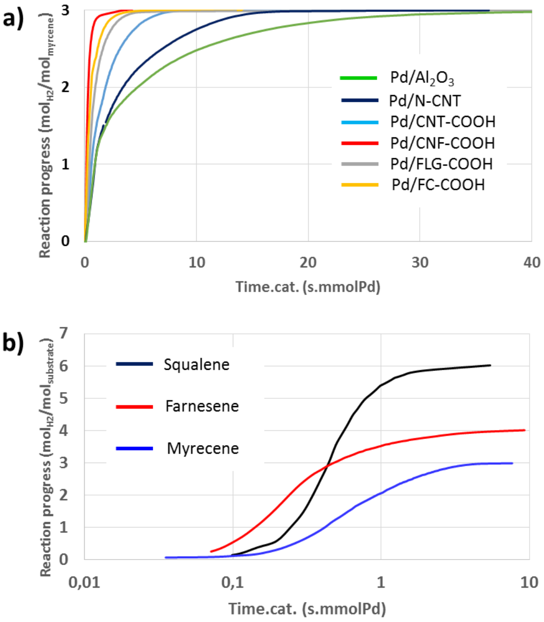

Figure 1. a) Comparison of catalysts in myrcene hydrogenation; b) comparison of substrates on Pd/FLG-COOH catalyst.

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CARBON-SUPPORTED Au NANOPARTICLES: CATALYTIC ACTIVITY RULED OUT BY CARBON SUPPORT

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Background. The catalytic oxidation of glycerol produces high added value chemical products [1; 2]. Gold NPs have been shown to be active, selective and stable against deactivation [3]. Particle size and shape affects the catalytic activity [4]. Complementarily, the role of the support showed to be decisive in modulating gold activity and stability [5]. Demirel-Gulen et al. investigated the liquid phase oxidation of glycerol over carbon supported gold catalysts; comparing carbon black and activate carbon, they found that the activity was higher for the first mentioned support [6]. Other studies on the specific interaction between Au and graphite reported about the change of the catalyst structure and stability of Au clusters [7]. Overall, the whole catalyst properties come from the specific properties of the support together with the synthesis approach for depositing NPs. Gold-supported carbon materials have been deeply explored, but the range of possibilities for modulating their properties still require efforts.

Here, we deposited Au NPs on three different commercial carbon supports (Vulcan-XC72R, X40S and Norit GSX) by SMAD technique for investigating the support effect on size, dispersion, catalytic activity/selectivity and catalyst stability in glycerol oxidation. In addition, in order to better clarify the influence of the preparation technique, we also prepared Au catalyst on the same supports by Sol Immobilization (SOL) technique in the presence of polyvinyl alcohol (PVA) as stabilizing agent. The morphological and structural features of each catalyst were deeply investigated disclosing the importance of the synthetic procedure on the whole material physico-chemical properties. These latter were related to the catalytic results in the selective glycerol oxidation highlighting that also the nature of the support play an important role.

Experimental. In SMAD, gold vapors generated by resistive heating of an alumina crucible filled with ca. 100 mg of gold (beads) were co-condensed with acetone. After, the Au-SMA solution was added to the relative suspensions containing each carbon support. Each catalyst contained 1.0 wt.% of Au. Sol method requires the preparation of an aqueous solutions of metal precursor (HAuCl4·3H2O) and PVA (1 % w/w). Then we dripped NaBH4 (0.1 M) and Au reduced immediately. Immobilization of Au NPs occurred by adding each carbon support under magnetic stirring.

A LIBRA 200FE ZEISS at 200 kV equipped with a high-angle annular dark field detector (HAADF) provided HRTEM and STEM measurements. Gold loadings were determined by ICP-OES (ICAP6300 Duo purchased from Thermo Fisher Scientific). XPS (KRATOS XSAM 800 XPS machine equipped with an atmospheric reaction chamber) scanned the surface composition and oxidation state of the metals.

Glycerol oxidation occurred in a glass reactor, at 50 °C and oxygen pressure of 3 atm. The catalyst was suspended in 10 ml of a glycerol solution 0.3 M and NaOH/glycerol molar ratio 4, having a glycerol/metal molar ratio of 2000. Sample was analyzed by HPLC (Alltech OA-10308, 300 mm × 7.8 mm).

Discussion. TEM and XPS analyses showed that the size and distribution of the AuNPs on the different supports varied according to the density of surface oxygen-containing groups. However particle size also depends on the immobilization time, being the longer producing larger particles. Sol-derived catalysts always showed higher activity in the glycerol reaction (Figure 1).

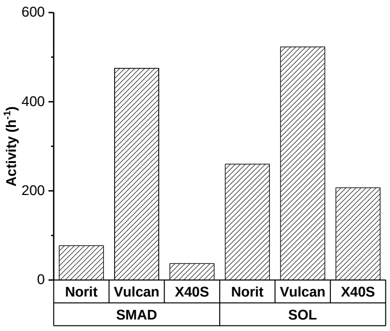

Fig. 1 Comparison of the initial activities for i) Norit, ii) Vulcan and iii) X40S carbon by SMAD and Sol method, respectively. Reaction conditions: 10 ml 0.3 M; NaOH/GLY 4:1; GLY/Metal molar ratio 1:2000, $P(O_2)$ 3 atm, T=50 °C,

[a]Activity calculated at 15 min as moles converted/moles of metal x h.

Conclusions. We observed that the higher O-containing functionalities of the support determines a higher exposure of Au nanoparticles at the surface but also an increase of particle size due to a lower rate of immobilization on the support.

We found that the highest activity was shown by AuNPs on Vulcan, samples that showed the lowest exposure of Au but the smallest particle size. Comparing SMAD and SOL prepared samples on Vulcan, beside a very similar particle size and distribution, a different activity and also selectivity was observed. Moreover, SOL sample on Vulcan showed a pretty good stability on recycling.

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ACID POROUS CARBONS INVOLVED IN THE GREEN SYNTHESIS OF BENZODIAZEPINES

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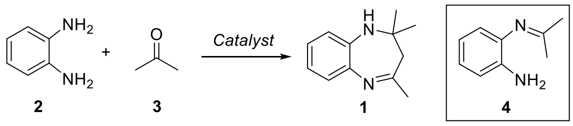
Carbon materials due to their properties such as high surface areas, chemical inertness and thermal stability, tunable textural properties and surface chemistry, are almost ideal supports for catalytic purposes, providing the appropriate chemical environment to produce fine chemicals [1].

In order to continue with our ongoing investigations, we seek to develop a new family of porous carbon materials as active catalytic systems for the green synthesis of relevant nitrogen heterocyclic systems [2, 3], particularly benzodiazepines. Benzodiazepines and derivatives are fine chemicals exhibiting interesting therapeutic properties. A huge number of synthetic methodologies for the preparation of benzodiazepines using porous catalysts have been reported. However, the carbon materials have been barely explored in the synthesis of this class of compounds. In this context, we selected three carbons exhibiting different structures and porosities. These carbons were treated with different acids such as HNO_3 or H_2SO_4, denoted as N or S, respectively.

The carbon materials selected were: i) commercial activated carbon, particularly Norit RX3 (N), ii) xerogel (X), and iii) meso-ordered carbon (CZ). In this communication, we report herein a new family of carbon materials found to be highly efficient, environmental-friendly and alternative catalysts for the synthesis of benzodiazepines **1**, from *o*-phenylendiamine **2** and acetone **3**, under mild reaction conditions (Scheme 1).



Scheme 1. Synthesis of benzodiazepine **1** catalyzed by acid carbon catalysts, at 50 °C, under solvent-free conditions.

We observed that although carbon supports are involved in the reaction, all of them resulted in low selectivity to **1**. Concerning this an analysis of the ^{1}H NMR spectra of the reaction crude, at different reaction times, showed the presence of a new product which was assigned to an intermediate compound **4**.

Figure **1** depicts the conversion values and selectivities obtained when using carbon materials modified with HNO_3. We observed that the presence of oxygenated groups on the carbon surface notably increase both the conversion and selectivity to benzodiazepine **1** at shortest reaction times. As a result, the N-N and N-S carbon catalysts, exhibiting mainly microporous character and therefore the highest surface area, showed slightly higher conversion values (80%) but also higher selectivity to **1**, 80 and 90%, respectively, in comparison with unmodified support.

The obtained results demonstrated the strong effect of the porosity on the catalytic performance. Thus, the selectivity to **1** increased when diminishing the porous size, the selectivity order being N-N > X-N > CZ-N, where N-N is a microporous carbon whereas X-N and CZ-N are mesoporous samples. Analogous catalytic behaviour was observed when using the modified samples with H_2SO_4. In these cases, while X-S was found to be the most active catalyst, N-S was the most selective one, exclusively to the corresponding benzodiazepine **1**. It is important to note that N-S was totally recyclable during two cycles maintaining its activity.

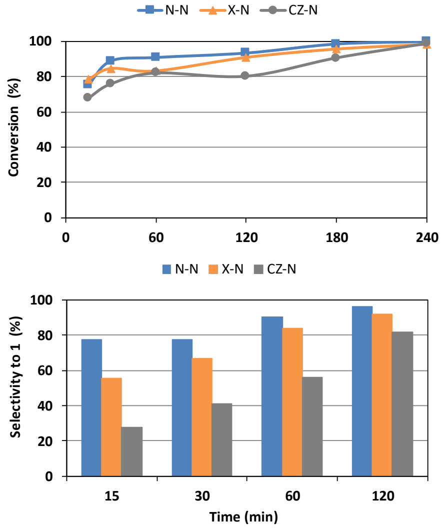


Figure 1. Synthesis of benzodiazepine **1** catalyzed by acid carbon catalystS, at 50 °C, under solvent-free conditions.

In summary, our results demonstrated that both acidic functions and the porosity of the catalysts are determinant factors influencing the catalytic performance. We also confirmed the involvement of the carbon support in the reaction but mainly to catalyse the first step of the reaction leading to the intermediate compound **4**. Nevertheless, the oxygenated functional groups at the catalyst surface seem to have an important role in the second imination and electrocyclization reaction, allowing the formation of benzodiazepine **1** with increased selectivities.

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SUSTAINABLE CARBOCATALYST WITH ATOMICALLY DISPERSED Fe-N-P-C COMPLEX ACTIVE SITES FOR SUPERIOR OXYGEN REDUCTION

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Development of efficient, low-cost and stable electrocatalysts to replace precious platinum catalysts for the oxygen reduction reaction is of great importance to boost the applications of green energy devices such as fuel cells and metal-air batteries 1-5. Here we report a sustainable and highly active oxygen reduction reaction (ORR) electrocatalyst with atomically dispersed Fe-N-P-C complex structure, prepared by a simple impregnation-pyrolysis in ammonia process directly from renewable woody biomass.

The linear scan voltammetry of as obtained Fe, N and P tri-doped biomass derived carbon catalyst (Fe-NPC) using a setup with rotating disk electrode is displayed in Figure 1. The onset and half-wave potential of Fe-NPC are both surpassing those of 30 % Pt/C, suggesting exhibited extraordinary ORR activity.

Characterizations were carried out to explore the origin of the excellent ORR activity. Aberration-corrected HAADF-STEM (Figure 2a) image indicates the existence of Fe single atoms (some of them are indicated by the red circles), while the Fe edge and P edge EXAFS (Figure 2b and 2c) reveal the existence of Fe-N, Fe-P and Fe-O-P bonds. Based on the results of these characterizations, a unique atomically dispersed Fe-N-P-C complex (Figure 3) is proposed using DFT calculations. The removal of adsorbed OH* is calculated to be the rate determining step for the ORR catalysed by Fe-N-P-C complex (Figure 4 inset). The optimized configurations of the intermediates for the ORR on Fe-N-P-C complex (Figure 4) and the corresponding reaction pathway were further analysed to reveal the origin of its high ORR activity. It is reveal that the associated Fe-O-P bond can significantly lower the stability of strongly adsorbed OH* on the catalytically active sites and thus give rise to enhanced ORR performance.

The atomically dispersion Fe-N-P-C complex structure is analogue to the nature catalysts where the reactivity of the metal active sites can be tuned by the coordination and ligands. The strategy demonstrated here illustrates a promising and efficient way to design the molecule-like heterogeneous ORR catalyst, which could be widely applied in preparing various atomically dispersed, highly efficient catalysts in electrochemical energy technologies.

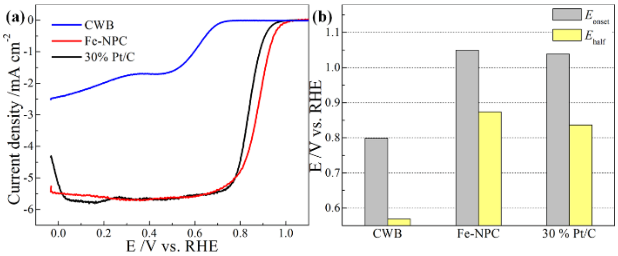

Figure 1. (a) LSV curves of Fe-NPC, CWB and 30 % Pt/C in O_2-saturated 0.1 M KOH at a scan rate of 10 mV/s with rotating rate of 1600 r.p.m. (b) bar chart of Eonset and Ehalf of Fe-NPC, CWB and 30 % Pt/C.

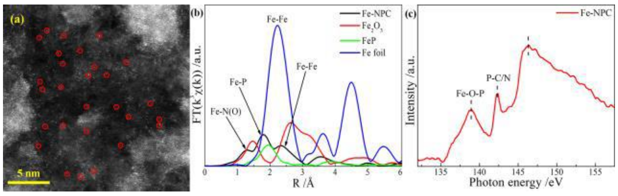

Figure 2. (a) Aberration-corrected HAADF-STEM images of Fe-NPC. (b) the k^3 weighted $\chi(k)$ function of the EXAFS spectra for Fe-NPC, Fe_2O_3, FeP and Fe foil. (c) TEY of P $L_{2,3}$-edge XANES spectrum of Fe-NPC.

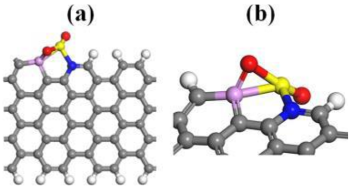

Figure 3. Front view (a) and side view (b) of the optimized structure of Fe-N-P-C complex.

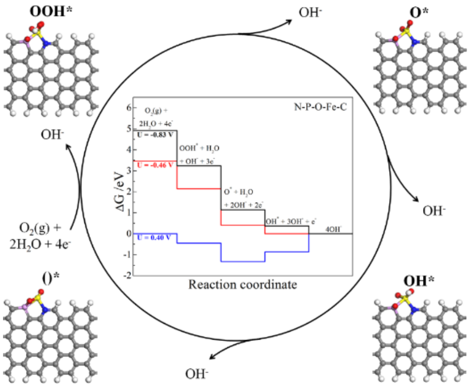

Figure 4. Schematic of the ORR on the N-P-O-Fe-C catalyst. The inset in cycle shows the free energy diagram for oxygen reduction reaction on this catalyst in alkali medium. For U < -0.46 V (vs. NHE), all steps are thermodynamically accessible. Inset: Free energy diagram for ORR on Fe-N-P-C complex at different potentials.

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CARBON SUPPORTED METAL-CARBIDES AND METAL-PHOSPHIDES FOR BIOMASS-BASED CONVERSIONS

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Catalysts are at the heart of industrial chemical transformations and approximately 90% of all chemical industry products require a catalytic step. In 2014, the global demand of catalysts was about US$ 33.5 billion and a steady increase in this demand is expected in the next years.

To secure catalyst supplies, diversification of catalysts is required. In that view the replacement of the already scarce noble-metal based catalysts by non-noble metal based catalysts is an essential step. Here we focus on the replacement of Pd, suitable for deoxygenation of vegetable oil/fat based feedstocks [1], by Ni-phosphides and W-carbides.

To advance this field of catalysis it is essential to understand the relationship between catalyst properties and performance. It is well known that transition metal carbides and phosphides are efficient catalysts for reactions involving hydrogen transfer, thus they are a potential substitute of noble metals. Therefore, we studied the relation between transition metal carbide and phosphide properties and their performance for deoxygenation reaction. We focus here on the nature of the active site in these catalysts and we investigated the effects of particle size and support over the performance on stearic acid deoxygenation.

The effect of Ni_2P/AC particle size (10, 20 and 30 wt% Ni_2P/AC – 8, 12, > 30 nm, respectively) on the activity and product distribution of deoxygenation of stearic acid was investigated. We concluded that although the particle size does not influence the catalyst intrinsic activity it influences the product distribution.

Both the decarbonylation/decarboxylation (DCO) and hydrodeoxygenation (HDO) routes occur over the nickel phosphide. However, oxygenates are the major products over 10 wt% Ni_2P/AC while C17 are the major products over 20 and 30 wt% Ni_2P/AC at low conversion (< 10%) (Figure 1). This result indicates that the HDO route is more significant over 10 wt% Ni_2P/AC catalyst which has smaller phosphide particles (8 nm) and that the DCO route is more significant over big particles (12 and >30 nm). We suggest that this difference in product distribution is related to differences in concentration of Ni(1) and Ni(2) sites in the catalysts.

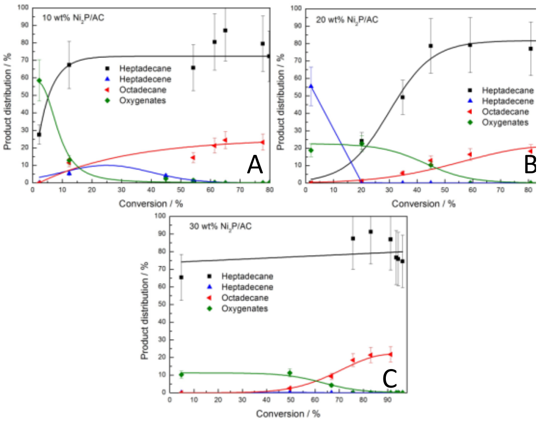

Figure 1. Product distribution as function of conversion of stearic acid HDO at 350 ºC and 30 bar H_2 in batch mode over 10 (A), 20 (B) and 30 (C) wt% Ni_2P/AC catalysts.

Also, for Mo-carbides the nature of the active site can be tuned by either the carbide loading (as was the case for phosphides) or the carburization conditions. For Mo-carbides two phases exist i.e. the cubic α-phase and the hexagonal β-phase. These two phases could be prepared by either carbothermal reduction (reaction between the W-precursor and the carbon of the support in an inert atmosphere) which results in the β-phase, or by carburization in methane, which results in the α-phase (Figure 2).

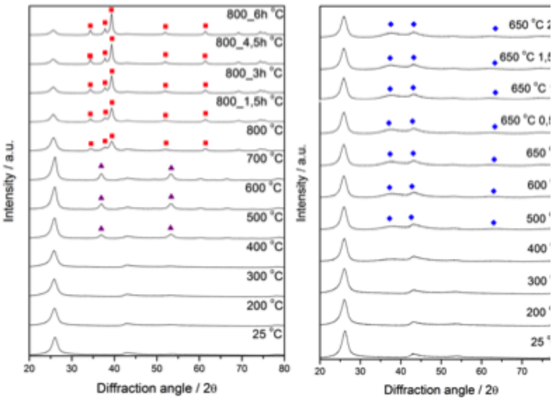

Figure 2. Left: In situ XRD for 7.5 wt% Mo_2C/CNF synthesized via carbothermal reduction with argon ■ hexagonal β-Mo_2C ▲ MoO_2. Right: In situ XRD for 7.5 wt% Mo_2C/CNF synthesized via carburization with 20% CH_4/H_2 gas mixture ♦ cubic α-MoC_{1-x}

Catalytic results of stearic acid hydrodeoxygenation showed that both phases (loading of 7.5 wt% Mo) displayed similar intrinsic activities (TOF: 3 s^{-1} for alpha phase and 4 s^{-1} for beta phase). However, α-MoC_{1-x}/CNF reached 80% of stearic acid conversion after 240 min of reaction while the 7.5 wt% β-Mo_2C/CNF catalyst only reached the same conversion after 360 min of reaction. CO TPD results indicated that while α-MoC_{1-x}/CNF has only Mo atoms terminating the surface of the catalyst, β-Mo_2C/CNF has both Mo and C atoms terminating the surface of the catalyst. However, since reaction results showed that α-MoC_{1-x}/CNF and β-Mo_2C/CNF displayed the same selectivity at the same conversion, it was concluded that only the Mo atoms terminating the surface play a role in the HDO reaction. DFT calculations using the probe molecule butyric acid indicated that the adsorption enthalpy over Mo sites of β-Mo_2C phase (-51 kcal mol^{-1}) is higher compared to that over Mo sites of α-MoC_{1-x} (-27 kcal mol-1). This might result in a stronger interaction between the active sites and reactant molecule over the β-Mo_2C/CNF catalyst which can explain the lower reactivity of the β-Mo_2C/CNF compared to α-MoC_{1-x}/CNF.

Clearly for both metal-phosphides and metal-carbides the details of the structure of the catalysts determine their performance in the deoxygenation of vegetable oil/fat based feedstocks.

EFFECT OF THE NATURE OF CARBON SUPPORT IN Pd/C CATALYSTS ON THE REACTION ROUTES OF AQUEOUS-PHASE HYDROGENATION OF FURFURAL

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Furfural is an important platform compound produced commercially from lignocellulosic biomass. The catalytic hydrogenation of furfural yields a wide range of value-added products. By now, numerous supported catalysts containing noble metals have been proposed to perform this reaction [1]. Various types of graphite-like carbon materials are often used as supports of these hydrogenation catalysts. This is due to advantages of carbon materials, such as high specific surface area, developed pore space providing the transfer of reactants and products of the catalytic reaction, controlled surface properties. The formation of metal clusters and nanoparticles (NPs), their state and catalytic performance can vary significantly depending on the nature of the chosen support. Therefore, variations in the composition, morphology, and physicochemical characteristics of the support can be regarded as an efficient tool for regulating the structure and catalytic properties of active sites in order to achieve high selectivity for the desired product of catalytic reaction.

Our work presents the results of studying the effect of the nature of carbon support on the activity and selectivity of Pd/C catalysts in the aqueous-phase hydrogenation of furfural. Palladium catalysts containing 0.5, 1 and 2 wt.% of Pd were prepared using carbon materials of various origin and morphology: carbon nanotubes (CNTs) and different kinds of carbon nanoglobules (CNGs) (Figure 1). The structure of the supports was studied by XRD, TEM and low-temperature nitrogen adsorption. The surface acid-base properties were estimated by FTIR spectroscopy. The formation of Pd NPs on the supports was monitored by H_2-TPR. Dispersion of Pd NPs was determined by CO chemisorption and TEM. XPS was used to estimate the oxidation state of palladium in the reduced catalysts.

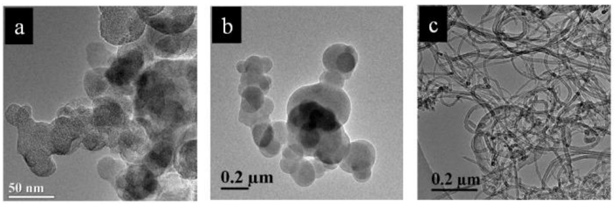


Figure 1. TEM images of the carbon supports: CNGs-1 (a), CNGs-2 (b), CNTs (c).

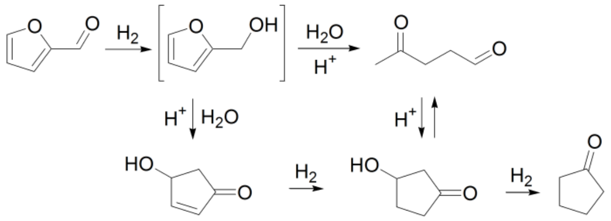
The hydrogenation of furfural over Pd/C catalysts was performed in the periodic reactor at a temperature of 423 K and pressure of 3 MPa. The reaction products were identified by ^{1}H and ^{13}C NMR. The quantitative composition of the reaction mixtures was determined by GC.

As can be seen from Table 1, all of the Pd/C catalysts are highly active in furfural hydrogenation. The samples based on CNTs and CNGs-2 allow achieving almost complete conversion of furfural. For the first time, we established that hydrogenation of furfural in aqueous solution over Pd/C catalysts under chosen conditions proceeds *simultaneously* through two competitive routes involving acid-catalyzed steps of opening the furan ring under the action of water (Scheme 1). One of the directions ends with the furan ring rupture giving mainly 4-oxopentanal (**1**), while the other is associated with the Piancatelli rearrangement and successive formation of 4-hydroxy-2-cyclopentenone (**2**), 3-hydroxycyclopentanone (**3**), 2-cyclopentenone (**4**) and cyclopentanone (**5**).

Table 1. Catalytic properties of Pd/C samples in the aqueous-phase hydrogenation of furfural at 423 K, 3 MPa for 1 h

Catalyst	TOF (mol H_2 mol Pd_s^{-1} min^{-1})	X (%)[a]	S (%)[b]	
			1	**5**
0.6%Pd/CNTs	undefined	93.0	11.7	57.0
1.0%Pd/CNTs	237.1	98.0	20.7	49.4
2.0%Pd/CNTs	undefined	97.9	17.5	48.0
0.5%Pd/CNGs-1	275.5	52.5	60.6	18.4
1.0%Pd/CNGs-1	191.5	71.7	57.6	21.1
2.1%Pd/CNGs-1	172.9	93.7	54.6	18.4
0.4%Pd/CNGs-2	385.8	72.5	62.6	25.2
1.0%Pd/CNGs-2	345.9	98.4	56.9	22.0
2.0%Pd/CNGs-2	271.1	98.9	60.9	17.3

[a] Conversion of furfural according to GC. [b] Selectivities for 4-oxopentanal (**1**) and cyclopentanone (**5**) according to GC.



Scheme 1. Reaction pathways of aqueous-phase hydrogenation of furfural over Pd/C catalysts.

It is important that the reaction route is determined by the nature of carbon support in the catalyst (Table 1). So, the catalysts based on CNGs were selective for **1** (up to 63 %), while the Pd/CNTs catalysts give mainly **5** (up to 57 %). The predominance of the latter route over Pd/CNTs catalysts is confirmed by the presence in the reaction mixtures such intermediates as **2**, **3** and **4**. In contrast, in the presence of Pd/CNGs catalysts, the formation of **5** proceeds mainly via intramolecular aldol condensation of **1** (Scheme 1).

The reasons for the observed differences in catalytic properties of Pd/C samples may be due to the effect of the nature of carbon support on the electronic state (XPS data) and the dispersion of supported Pd (TEM and CO chemisorption), as well as to the differences in the acid-base properties of carbon supports (FTIR spectroscopy data).

The obtained results can be useful for the development of efficient catalysts for hydrogenation of biomass-derived furfural to value-added chemicals.

Acknowledgements. The study was financially supported by FASO Russia (Project No. AAAA-A17-117021450099-9).

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AZIRIDINE FUNCTIONALIZED CARBON NANOTUBES AS HIGHLY EFFICIENT ELECTROCATALYSTS FOR THE SELECTIVE CO_2 REDUCTION TO CO

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The steady state increase of CO_2 levels in the atmosphere as a result of main anthropic activities is directly linked to climate change, leading to, for example, erratic weather patterns and rising ocean temperatures.[1] Multiple approaches need to be implemented to curb with these phenomena, including carbon sequestration, electrification of the transportation sector and switching from the use of fossil fuels to renewable energy.

One interesting method to mitigate CO_2 impact while providing a means of mass energy storage, is the electrochemical reduction of CO_2 into chemicals and fuels, which can be stored and used on demand.[2] However, electrocatalysts for the CO_2 conversion into products, such as CO, formic acid, methanol, and small hydrocarbons, still suffer of moderate productivity and/or poor selectivity. To date, Ag and Au-based electrocatalysts exhibit the best performance for the conversion of CO_2 to CO although, from a sustainable viewpoint, metal-free systems have recently emerged as highly attractive candidates to replace metal-based systems in the process. Relatively few examples of metal-free catalysts for CO_2 reduction exist, most of them raising from the class of light-heterodoped carbon nanomaterials (CNMs). In particular, a series N-doped systems (N-CNMs) have been investigated, although the role of nitrogen doping and its configuration as "catalytically active species" in the process still remain controversial.[3]

Recent findings from our group have demonstrated how a tight control of the surface properties of carbon-based nanomaterials can be conveniently achieved by chemical functionalization of their outer surface with tailored N-containing heterocycles.[4,5] The chemical approach allows for a fine control of N-dopants in terms of N-configuration and electronic charge distribution at the heterocycles, and it offers a unique tool for the in-depth comprehension of the role of specific N-functionalities in the activation of small molecules and their subsequent (electrochemical) conversion.

In this contribution we discuss the chemical decoration of MWCNTs with NH-aziridine functionalities (MW@N^{Az}) and their application as highly efficient and selective metal-free electrocatalysts for CO_2 reduction into CO.

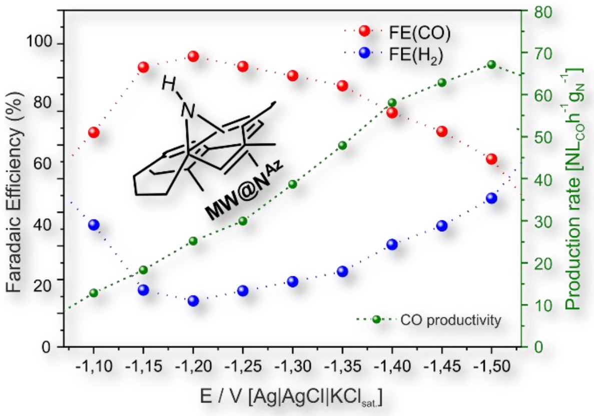

Figure 1. FE and CO productivity of MW@N^{Az} in 0.1M $KHCO_3$.

With a Faradaic efficiency (FE) close to 90% at -1.2 V (vs. Ag/AgCl/KCl sat.) and productivity as high as 25 $NL_{CO}h^{-1}g_N^{-1}$, MW@N^{Az} ranks among the metal-free systems with the highest performance reported so far. Catalyst synthesis, stability and performance in the process will be discussed.

Acknowledgements. Authors thank the TRAINER project (*Catalysts for Transition to Renewable Energy Future* - Ref. DGPIE/MOPGA/2017-589) and the Italian MIUR (PRIN 2015, Project SMARTNESS 2015K7FZLH) for financial support.

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PALLADIUM-NICKEL ON TIN OXIDE-CARBON COMPOSITE SUPPORTS FOR ELECTROCATALYTIC HYDROGEN EVOLUTION

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In recent years, numerous studies have been devoted to the renewable energy sources in order to replace the human kind dependence on fossil fuels, which face limited availability and lead to global warming. Hydrogen obtained by renewable energy sources is a green fuel, as its production and use does not release greenhouse gases or any other pollutants [1]. Among the hydrogen production methods, water electrolysis has a remarkable industrial importance. The main challenge in the development of alkaline water electrolysis systems is finding low cost electrode materials, which possess efficient and durable performance [2].

The electrode material is not only made of the electrocatalyst material, but also of the support on which it is anchored. Among the non-noble metals, palladium and its alloys, e.g. PdNi, is attractive for hydrogen evolution reaction (HER), due to rather good catalytic activity, low cost, and chemical and mechanical stability. In particular, Pd retains a great part of the intermediate hydrogen binding energy and high exchange current density of Pt. Moreover, electrocatalysts based on PdNi nanoparticles (NPs) show much higher catalytic activity than its bulk form [3].

In recent years, composites of metal oxides and smaller quantities of carbon blacks, are functioning as supports and co-catalysts in the electrolysis process due to electronic and bifunctional mechanisms. In this work, four different supports, SnO_2-KB600, SnO_2-KB300, SnO_2-graphene, and Vulcan XC72, were synthesised by precipitation using a hydrothermal method described in the literature [4,5]. These support materials were then decorated with PdNi (90:10). The composition of the carbon supported PdNi NPs was investigated by inductive coupled plasma optical emission spectrometry (ICP-OES), and it was found to be $Pd_{94}Ni_6$, $Pd_{92}Ni_8$, $Pd_{92}Ni_8$ and $Pd_{95}Ni_5$ for the PdNi/(SnO_2-KB600), PdNi/(SnO_2-KB300), PdNi/(SnO_2-graphene), and PdNi/Vulcan XC72 electrocatalysts, respectively. Electrocatalytic inks of these prepared materials were deposited on 0.07 cm^2 glassy carbon (GC) electrodes, whose electrochemical activity for HER in 8 M KOH, at temperatures from 25 ºC to 85 ºC, was investigated using linear scan voltammetry (LSV) and chronoamperometry (CA). XRD was also used to characterise the electrodes.

LSV of the four prepared electrodes lead to polarisation plots from which the charge transfer coefficients, the Tafel slopes, the exchange current densities, the current densities at overpotential of -0.1 V, and the overpotentials at -10 mA cm^{-2}, were calculated. At 25 ºC, the Tafel slope was always close to 120 mV dec^{-1}, indicating a rate determining Volmer step. The PdNi/(SnO_2-graphene) catalysts showed exchange current densities of 0.03 and 1.52 mA cm^{-2}, at 25 and 85 ºC, respectively. CA measurements confirmed the catalysts' kinetic behaviour. For the HER activation energies, unexpected higher values were shown by the graphene catalysts, but this issue was largely counterbalanced by the overall LSV/CA results, and the high currents obtained at higher temperatures.

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NITROGEN-DOPED CARBON MATERIALS DERIVED FROM CELLULOSE FOR THE OXYGEN REDUCTION REACTION

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Introduction. The oxygen reduction reaction (ORR) has attracted increasing attention due to its technological importance in industrial electrolysis processes as well as in electrochemical devices such as fuel cells. At the current stage, Pt-based materials are the most practical catalysts. As these Pt-based catalysts are too expensive for large-scale applications, extensive research over the past several decades has aimed at developing alternative catalysts, including non-noble metal catalysts or metal-free catalysts. Nitrogen-doped carbon materials are among the most promising candidates as alternatives to high-cost Pt catalysts for fuel cell applications.[1] The hydrothermal carbonization (HTC) of cellulose is a cheap and easily applicable method to synthesize carbon materials with defined composition. [2] The HTC-derived carbon materials already contain 30 wt.% of oxygen in various functional groups as shown by ATR-IR and NMR measurements.[3] Hence, gas-phase treatment in ammonia can be directly used to introduce nitrogen.

In our study, we present the nitrogen functionalization of HTC. The NH_3 treatment was performed at different temperatures in the range from 300 °C to 800 °C with different concentrations (10 % NH_3/He and 100 % NH_3). The synthesized samples were characterized with respect to composition and structure and tested as ORR catalysts.

Results and Discussion. The introduction of nitrogen into the carbon network at all treatment temperatures in both NH_3 atmospheres was confirmed by elemental analysis. The carbon content increases with increasing treatment temperature, whereas the oxygen content decreases. It is concluded that during the thermal treatment in NH_3 the sample is also pyrolyzed. The loss in oxygen-containing functional groups enables the doping of nitrogen into defect sites of the material. In general, the incorporation of nitrogen at a given temperature is more effective using 100% NH_3 compared with 10% NH_3/He. The combination of carbonization, pyrolysis, nitrogen functionalization and activation of the carbon network increases the surface area with increasing temperature. The release of volatile compounds and the etching of the carbon network by the NH_3 increase the porosity of the samples, enabling more active sites for the ORR.

Thermal gravimetric analysis (TGA) measurements in oxidative atmosphere showed that with increasing treatment temperature and increasing nitrogen content, a thermally more stable carbon material is formed during pyrolysis in NH_3 compared with nitrogen-free HTC pyrolyzed in inert gas. The deconvolution of the N 1s X-ray photoelectron spectroscopy (XPS) signal displayed that mostly pyridinic and pyrrolic N was incorporated at the edges. The ratio of pyrrolic N to pyridinic N ranged between 1.06 and 1.36.

Linear sweep voltammograms (LSV) recorded for the HTC samples treated in 100% NH_3 at temperatures ranging from 300 to 800 °C are presented in Figure 1. As expected, the HTC material does not show any significant ORR activity (red line in Figure 1), since it is known that carbon black reduces O_2 mainly to H_2O_2. [4] Thermal treatment of HTC in the presence of 100% NH_3 at temperatures up to 500 °C has no impact on the catalytic performance of the material, although 4 mol% N were present in the material. A further increase of the treatment temperature above 600 °C clearly improves the ORR performance. The potentials at which the investigated electrocatalysts generate a current density of -1 mA cm^{-2} are gradually increasing with 0.83 V vs. RHE being achieved by the HTC-derived carbon material treated in 100 % NH_3 at 800 °C (100N8/HTC). This potential is among the highest values reported in literature for metal-free carbon catalysts.[5]

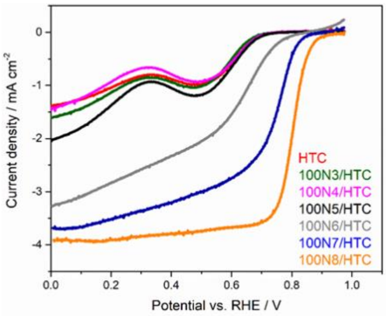

Figure 1. Linear sweep voltammograms recorded in O_2-saturated 0.1 M KOH solution with 5 mV/s scan rate at a rotation of 1600 rpm.

The higher electrocatalytic activity of 100N8/HTC correlates with the higher amount of pyridinic N in good agreement with Nakamura and co-workers[6] who found that pyridinic carbon decreases the adsorption energy of O_2 and is an important catalytic center for the reduction of H_2O_2 to H_2O. Both rotating disk electrode (RDE) and rotating ring disk electrode (RRDE) measurements indicate that the ORR on NH_3-treated catalysts at 800 °C takes place through an intermediate mechanism between 2 + 2 electrons, where H_2O_2 is produced, and 4 electrons, and that the overall reaction rate is limited by the coverage of O_2 and O_2^- species.

Conclusions. NH_3-treated carbon obtained by hydrothermal carbonization is a readily available, almost metal-free (below 10 ppm) and active catalyst as an alternative to traditional carbon-supported Pt catalysts for the ORR. Nitrogen functionalization not only improves the electrocatalytic activity, but also increases the stability against oxidation.

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Cu AND Pd NANOPARTICLES SUPPORTED ON A GRAPHITIC CARBON MATERIAL AS BIFUNCTIONAL HER/ORR ELECTROCATALYSTS

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In the face of challenges such as climate change, significant and continuous increase of environmental pollution and decrease of fossil fuels, the research for new cleaner energies is of vital importance for the forthcoming years. The development of novel renewable energy storage and conversion technologies (metal–air batteries, water splitting, fuel cells), has therefore been extensively studied both from the fundamental to the practical point of view [1-3]. Although mechanisms may differ, their core relies on a series of electrochemical reactions which include the hydrogen evolution reaction (HER) and oxygen reduction reaction (ORR), where electrocatalysts (ECs) play a key role. Hydrogen is a potentially clean and renewable alternative for fossil fuels in the future and electrocatalytic reduction of water to molecular hydrogen may provide a simple and efficient solution to forthcoming energy demands. On the other hand, fuel cells have been acknowledged as efficient and viable alternative energy sources and ORR plays a key role in these systems. For both reactions, Pt and its alloys are considered the most effective ECs [4]. However, there are still some relevant drawbacks like scarcity, high cost, poor stability/durability, and probable Pt deactivation by methanol poisoning (in the case of ORR) that have hampered its large-scale application. So, it is urgent to develop alternative HER/ORR electrocatalysts. Among the several candidates exploited so far, transition metals (e.g. Fe, Co, Cu) supported on carbon-based materials are promising ones for ORR [4]. Huge effort have also been devoted to develop efficient HER ECs, like POMs/metal oxides/sulfides/phosphides and metal-free ECs (pristine/doped carbons).[5]

This work explores the application of metal nanoparticles (NPs) – of Pd, Cu or Cu/Pd - supported on high surface area graphite (HSAG), as bifunctional HER/ORR electrocatalysts. The metal/HSAG composites were prepared by wetness impregnation technique, followed by generation of metal nanoparticles using NaBH4 as reducing agent. The HSAG, Cu/HSAG, Pd/HSAG and Cu-Pd/HSAG electrocatalytic properties towards HER were evaluated in acidic medium using cyclic voltammetry (CV) and linear sweep voltammetry (LSV) while for ORR these were performed in alkaline medium.

HER results (**Figure 1a**) shows that HSAG and Cu/HSAG are not active while the Pd/HSAG and Cu-Pd/HSAG nanocomposites present good HER electrocatalytic activity with low overpotentials, η_{10}, (η for a current density j = 10 mA cm^{-2}) of 0.063 and 0.146 V, respectively. Under the same experimental conditions, the reference Pt/C shows an overpotential of 0.024 V. These two nanocomposites also present low Tafel slopes suggesting a Volmer-Heyrovsky HER mechanism, implying that hydrogen desorption is the rate-limiting step. As for HER, Pd/HSAG and Cu-Pd/HSAG ECs (**Figure 1b**) exhibit the most promising ORR performances with E_{onset} = 0.91 and 0.84 V and a higher diffusion-limiting current densities of $j_{\mathrm{L,\,0.3\,V,\,1600\,rpm}}$ = -4.2 and -3.5 mA cm^{-2}, respectively.

This proof-of-concept resulted in a new set of bifunctional HER/ORR electrocatalysts.

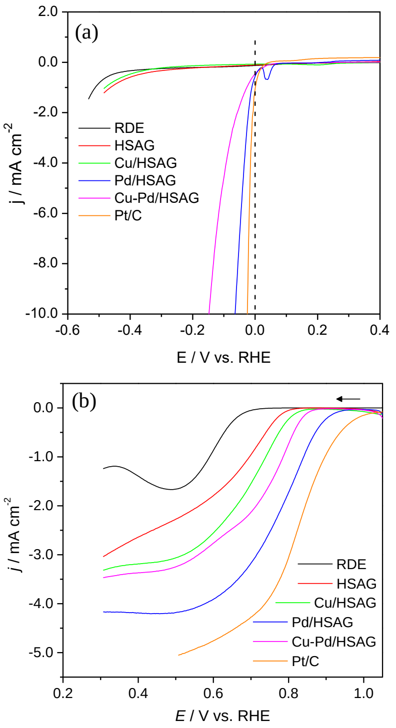

Figure 1. LSVs for bare RDE, Pt/C and different electrocatalysts (HSAG, Cu/HSAG, Pd/HSAG and Cu-Pd/HSAG) in 0.5 moldm^{-3} H_2SO_4, HER (a) and in 0.1 moldm^{-3} KOH, ORR (b) at a ν = 0.005 V^{-1}.

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BIFUNCTIONAL OXYGEN REDUCTION/EVOLUTION ACTIVITY OF Fe/Co/Ni MIXED OXIDE NANOPARTICLES SUPPORTED ON OXIDIZED CARBON NANOTUBES

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The fabrication of highly active and low cost bifunctional oxygen electrodes is a bottleneck for wide-spread utilization of renewable energy technologies such as unitized regenerative fuel cells (URFC) and metal-air batteries, such as Zn-air, Al-air and Li-air among others. The main challenge is to achieve high performance and reversibility of the oxygen evolution reaction (OER) and the oxygen reduction reaction (ORR), that are both kinetically sluggish and possess numerous intermediates. Moreover, the pH of the electrolyte drastically influences the performance of the catalyst due to change in the formation mechanism of the underlying intermediate reactions. Only a few noble metals like Pt are active for the ORR at low pH conditions as they can provide the high free energy for O_2 adsorption [1]. Other compounds such as transition metal oxides possess promising ORR activity in basic electrolytes due to the easier activation of oxygen molecules in alkaline media [2]. The combination of ORR and OER catalysts into a composite aims at producing materials that can retain their individual properties or even slightly alter their activity due to a synergetic effect [3]. However, to date most bifunctional catalytic systems suffer from lack of activity of one of the reactions leading to a wide gap between overpotentials for the OER and ORR, along with low stability or high cost.

Here, we present a facile strategy for synthesis of Fe, Co and Ni mixed metal oxide nanoparticles with variable metal ratios supported on, and embedded inside high purity oxidized multi-walled carbon nanotubes (MWCNTs) of narrow diameter distribution as effective bifunctional catalysts able to reversibly drive the oxygen evolution reaction (OER) and the oxygen reduction reaction (ORR) in alkaline solutions. Fe, Co and Ni mixed oxide samples were prepared by impregnation of MWCNTs with aqueous solutions of Co(II), Fe(III) and Ni(II) salts followed by calcination under an inert gas atmosphere. The samples with different metal ratios and combinations were investigated by TEM, XRD and XPS methods.

As an example, variation of the Fe:Co ratio resulted in a pronounced trend in the bifunctional ORR/OER activity as was previously shown in [4]. Among the prepared Fe_xCo_{1-x}/MWCNT systems, samples with Fe:Co ratio close to 1 demonstrated the lowest overpotentials between the ORR and the OER in alkaline electrolytes (Fig. 1), as well as a high selectivity for preferential reduction of oxygen to OH^- during the ORR. However, addition of the other transition metals, such as Ni, led to other pronounced trends in OER and ORR activity.

The improvement of the bifunctional activity for the mixed oxide nanoparticles can be ascribed to a synergetic effect, as well as film conductivity and active site density of the bi- and tri-metallic systems. Moreover, this work investigates the size and localization of the mono- and multi-metal nanoparticles (inside the tube core and on the surface of the MWCNTs) that can vary with the ratio, concentration and combination of metals, and, as a result, strongly influence the catalytic performance.

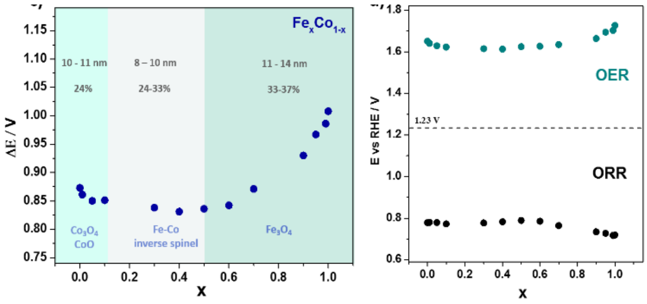

Figure 1. Dependence of the bifunctional parameter ΔE (V) and dependence of the ORR and OER activities (obtained at -1 and +10 mA cm^{-2}, respectively) on the metal content (x) in 13.5% Fe_XCo_{1-X}/ MWCNTs. Data obtained in O_2 - saturated 0.1 M KOH at a scan rate of 5 mV s^{-1} and at 1600 rpm electrode rotation speed.

Importantly, high bifunctional ORR/OER activity, and ORR selectivity towards the 4-electron reduction of O_2 to OH^- were achieved without functionalization of the catalyst with nitrogen, thus unveiling a design approach for efficient noble metal-free ORR/OER electrocatalysts. Additionally, the optimized mixed-oxide catalysts sustained at least 400 charge-discharge cycles at 15 mA cm^{-2} in 6 M KOH measured in a 3-electrode configuration set-up, using teflonized carbon cloth as a gas diffusion layer, without any visible loss in performance, which makes these systems very promising for reversible oxygen electrodes with potential application in metal-air batteries among others.

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GRAPHENE AEROGELS AS CATALYST SUPPORT FOR NANODIAMONDS AND METAL NANOPARTICLES

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Graphene aerogels have emerged as a promising flow-through reactor for adsorption and catalysis due to its high porosity, fluidynamic characteristics and amphiphilic character [1]. Despite these advantages, the application of graphene foams in catalysis is still very scarce [2-3]. One of the challenges when preparing metal catalyst on graphene is stabilising metal nanoparticles on the low defective graphene surface. To enhance the stable attachment of metal nanoparticles different approaches can be used such as, e.g. the introduction of defects or doping. The preparation of graphene from GO reduction has the advantage that GO has many surface functional groups for doping and the creation of defects.

Herein, we have prepared graphene aerogels by hydrothermal treatment of graphene oxide (GO) dispersions in an autoclave. In the autoclave a process of reduction-auto-assembly of GO nanosheets takes place leading to phase separation and precipitation of a hydrogel. The hydrogel transforms into an aerogel after freeze drying. The pore size and surface chemistry of the resulting aerogel can be controlled by manipulating the pH of the synthesis and the time of hydrothermal treatment [4]. The preparation at pH=11 leads to aerogels with higher pore volume (~200 cm^3g^{-1}) consisting mainly of macropores and more reduced than at pH=3. The graphene nanosheets have a flat morphology at pH=3 while they are bent and more reduced at pH=11, leading to more open porosity (Figure 1). In addition, aerogels with a 7% of nitrogen mainly of pyridinic-type have been prepared at pH=11 by adding NH_3.

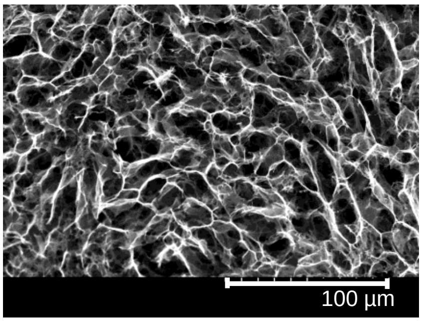

Figure 1. Representative SEM image of a cross-section of a graphene aerogel prepared at pH=11

Using one-pot preparation, nanodiamonds have been dispersed on the graphene nanosheets of the aerogel and they have been used as catalyst for the oxidative dehydrogenation of propane [5] (Figure 2). The nanodiamonds supported on graphene aerogels provided higher specific propene yield than CNT and graphene itself. Moreover, the graphene aerogels contribute to prevent the aggregation of the nanodiamonds during reaction.

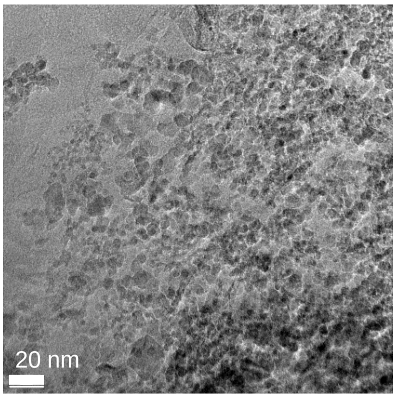

Figure 2. 5 wt% nanodiamons dispersed on graphene sheet

In another piece of research, a layer of N-doped carbon derived from polydopamine has been coated on the graphene nanosheets by one-pot polymerization. A 5 wt% of Ru nanoparticles have been dispersed on the N-doped carbon coating and used for the aerobic oxidation of benzyl alcohol. The catalyst prepared on the N-doped support exhibited higher efficiency to benzaldehyde than Ru supported on uncoated graphene aerogel and also higher than a commercial Ru on alumina catalyst with the same loading.

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TOMOGRAPHY ANALYSIS OF Ru SUPPORTED ON MICRO AND MESOPOROUS CARBON: A CORRELATION BETWEEN MORPHOLOGY AND CATALYTIC ACTIVITY

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Background. Ruthenium (Ru) based catalysts effectively hydrogenate aromatic compounds, olefins, aldehydes, ketones and other carbonyl compounds [1]. Ru/C reached conversion and selectivity over 90 % for the hydrogenation of levulinic acid (LA) to γ-valerolactone (GVL) [2]. However, solvents and supports greatly affect activity and selectivity [3]. Ru/graphite, Ru/zeolite, or a mixture of Ru/graphite and zeolite showed very different GVL yields [4]. Depositing Ru on four graphitized carbon materials differing in their surface area, different Ru dispersion has been produced which lead to different catalytic activities in CO methanation, as reported by Truszkiewicz et al. [5]. However, even if the control of selectivity has been roughly achieved, the stability of Ru-based catalysts is still insufficient. Villa et al. [6] studied the hydrogenation of levulinic acid at 70°C by Ru supported on functionalized mesoporous carbons, showing a good stability. On the contrary the same catalysts showed a decreased activity after three consecutive cycles when the reaction was performed at higher temperature (200°C) [6]. Deactivation mainly has been addressed to Ru leaching, Ru particle aggregation or carbon deposition on them [7]. Therefore, characterization analyses of the support morphology and surface, as well as of the metal particle size, shape and dispersion, are critical to understand how certain factors can modulate the catalytic properties.

Here, we synthesized Ru nanoparticles supported on two different types of carbon, i.e. ordered mesoporous carbon (OMC) and activated carbon (AC). STEM tomography analyzed Ru particles size and distribution, showing different NPs confinement inside the pores. HAADF STEM electron tomography sets the material 3D structure and improved the identification of the preferential NPs allocation which strongly affects catalytic activity.

Experimental. Activated carbon (AC) was from Norit (GSX). Ordered mesoporous carbon (OMC) was synthesized as reported in [6]. Ru was added by incipient wetness impregnation as having a final Ru loading of 1 %wt. The catalysts were tested in hydrogenation of levulinic acid and glucose. The samples have been examined by using a FEI Titan 80-300 electron microscope equipped with CEOS image spherical aberration corrector, Fischione model 3000 HAADF STEM detector and EDAX SUTW EDX detector. The microscope was operated at an accelerating voltage of 300 kV in TEM mode for HRTEM and in STEM mode for STEM and EDX spectrum imaging. Nitrogen adsorption isotherms were measured at −196 °C using TriStar 3000 volumetric adsorption analyzer manufactured by Micromeritics Instrument Corp (Norcross, GA).

Discussion. Median particle size was 1.2 nm for Ru/OMC and 1.5 nm for Ru/AC. However, size distribution was narrower for Ru/OMC because of NPs agglomeration on AC support. STEM clearly showed that Ru NPs were mostly inside the pores of OMC support, while agglomerations were on the outer surface of the AC support (Fig. 1). The different preferred anchoring site of particles affects the catalytic activity as expected (Tab. 1); particles inside pores are more difficult to be reached by the reactant and therefore result less active. The higher confinement of Ru nanoparticles observed on OMC produced a very stable catalyst as determined by recycling experiment. On the contrary, Ru/AC continuously lost activity during the consecutive runs.

Table 1. Catalytic hydrogenation of LA

	Conversion (%)	Selectivity	
		GVL	Pentanoic acid
1% Ru/OMC	83	96	3
1% Ru/AC	>99	97	2

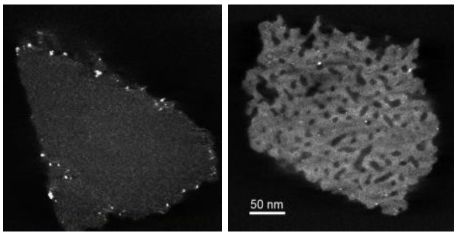

Figure 1. STEM images for 1%wt Ru on AC (a) and on OMC (b)

Conclusions. STEM-tomography clarified the allocation of similarly sized Ru particles on OMC and AC. The different exposition to the surface results in a different catalytic activity, being the confined ones less active. However, the same effect that limits the activity, greatly increased the stability of the catalyst in levulinic to GVL hydrogenation. The NPs confinement is a key factor to improve the catalyst reusability.

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COBALT CATALYSTS ON GRAPHENE NANOFLAKES AND CARBON NANOTUBES IN FISCHER-TROPSCH SYNTHESIS: EFFECT OF THE SUPPORT OXIDATION AND N-DOPING

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Fischer-Tropsch synthesis (FTS) is an industrial process of coal, natural gas and biomass conversion into hydrocarbons, alcohols, ethers, etc. via catalytic CO hydrogenation. Cobalt catalysts on oxide supports are widely used in FTS, but at the same time they possess several disadvantages, for example, difficult reducibility and low thermal conductivity. Structured carbon supports such as carbon nanotubes (CNTs), nanofibers and different types of graphene do not interact with metal due to their chemical inertness and prevent local overheating owing to the high thermal conductivity. N-doped carbon nanomaterial supports show even better characteristics in Co-based FTS catalysts compared to undoped ones, since nitrogen atoms affect electronic structure and defectiveness of carbon material [1]. At the same time, despite the promising properties of the catalysts supported on the above mentioned carbon materials, some challenges have not been overcome yet, such as structure instability towards high-temperature treatment by air (catalyst preparation stage) or hydrogen (catalyst reduction stage) [2].

In this work we investigate the cobalt catalysts supported on CNTs and graphene nanoflakes (GNFs). We focus mainly on the influence of oxygen and nitrogen functional groups localized in the support on the structure and catalytic performance of Co-based systems in FTS. Evolution of the support structure and surface composition is also studied by TEM, XPS, nitrogen adsorption and Raman spectroscopy. Raw, oxidized and/or N-doped CNTs and GNFs were synthesized by the pyrolysis of hexane or acetonitrile as well as by post-doping NH_3 treatment, while Co-based catalysts were obtained by the impregnation of the supports with Co nitrate ethanol solution. Catalytic experiments were carried out in a stainless steel vertical reactor at 1 and 20 bar and 180–220°C.

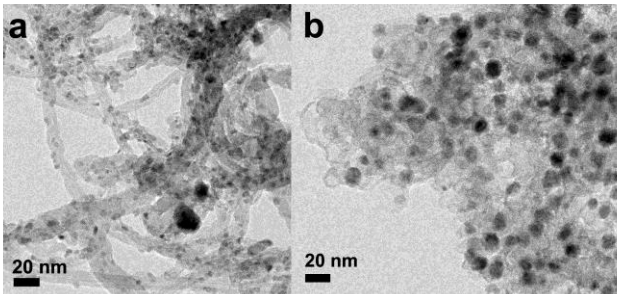

Figure 1. TEM images of Co/CNT (a) and Co/N-GNF (b) catalysts contained 15 and 10 mass. % of Co, respectively.

TEM images of reduced catalysts are shown in Fig.1. It was found that the functionalization of carbon surface by oxygen and nitrogen affects Co particle size apparently due to the different acidic properties of O- and N-groups. Strongly acidic carboxyls facilitate higher Co dispersion and the formation of small particles of 2–6 nm (Fig.1a). At the same time, amides, pyrrols, pyridines and N-oxide groups are less acidic and the catalysts supported on N-doped GNFs contain Co particles mostly of 10–15 nm (Fig.1b). It is known that Co particle size of 8–10 nm is the most suitable to achieve the highest activity and selectivity in FTS [3], thus the N-doping of carbon support provides the optimal size of Co particles uniformly distributed over a carbon support.

Annealing and reduction significantly change the structure of carbon support, especially on the surface [4]. The content of oxygen and nitrogen species (especially carboxyls, anhydrides, lactones, NO_x and amides) changes as a result of thermal treatment in the presence of Co particles, while air oxidation and methanation by hydrogen lead to the etching of carbon surface. For example, in the case of N-doped materials amide groups either partially decompose or transform into pyridines/graphitic nitrogen (Fig. 2). Such results are crucial for the understanding of the role of functionalities in the catalytic performance (activity and selectivity) of cobalt FTS catalyst. To reveal the influence of the functionalization of a real surface on the readsorption of intermediates and hence the selectivity of catalysts the adsorption properties of CNT and N-doped CNT supports after reduction of Co catalysts were also studied by the dynamic vapor sorption technique towards hexane as a model hydrocarbon. Initial oxidation does not significantly change the adsorption properties of support after reduction due to the defunctionalization proceeded under hydrogen treatment. Thus, the selectivity of Co/CNT catalysts depends mostly on Co particle size and structure, whereas the functionalities and surface defects ensure metal dispersion at the impregnation stage and further particle stabilization.

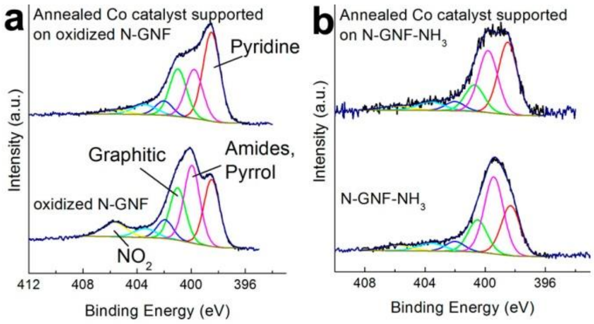

Figure 2. N1s XPS spectra of the oxidized N-GNF (a) and NH_3 post-doped N-GNFs supports and corresponding annealed catalysts contained 10 mass.% of Co.

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COMPARATIVE STUDY OF CoMo/MWCNT AND CoMo/Al_2O_3 HYDROTREATING CATALYSTS PREPARED WITH CITRIC ACID

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Hydrotreating processes are largely carried out over sulfided Co(Ni)Mo catalysts supported on alumina, which has good thermal, mechanical and textural properties and provides high dispersion of the active metal components. However, the main drawback of alumina is strong interaction with the active components, which hinders the complete sulfidation of supported metals and decreases the number of active sites. There are number of approaches for preparation of hydrotreating catalysts with enhanced activity. Among them, the addition of chelating agents, especially, citric acid as a relatively inexpensive chelating agent, has been widely used in the hydrotreating catalysts preparation. Unlike alumina, carbon materials hydrophobic surface limits the metal support interaction, which facilitates the sulfidation process. Multi-walled carbon-nanotubes (MWCNT) have drawn a lot of attention since their discovery due to their unique properties. In this work the effects of MWCNT and γ-Al_2O_3 supports on the properties and hydrodesulfurization (HDS) activity of corresponding CoMo catalysts prepared with citric acid is studied.

MWCNT were synthesized by CVD of ethylene decomposition over the bimetallic Fe-Co catalysts at 680°C. The functionalized MWCNT containing surface carboxylic groups (0.76 groups per 1 nm^2) were obtained via boiling in concentrated nitric acid. For CoMo/MWCNT catalyst preparation the functionalized MWCNT were used. The Al_2O_3 support was prepared by extrusion of boehmite paste using plunger extruder with subsequent drying of obtained trilobe extrudates at 120°C and calcination at 550°C. CoMo/MWCNT and CoMo/Al_2O_3 catalysts were prepared by impregnation with aqueous solution prepared from cobalt hydroxide, ammonium heptamolybdate and citric acid. Impregnated catalysts were dried at 120°C. The catalysts contained 12.0 ± 0.2 wt% of Mo and 3.2 ± 0.1 wt% of Co. The sulfidation of the catalysts was carried out in H_2S flow for 4 h at 200°C and 400°C at atmospheric pressure. The catalysts in sulfide form were studied by N_2 physisorption, XPS and HRTEM. The catalysts were tested in simultaneous dibenzothiophene (DBT) HDS and naphthalene hydrogenation in fixed-bed reactor under the following conditions: $t = 280°C$, $P = 3.5$ MPa, LHSV 20 h^{-1}, H_2/feed = 500 nm^3/m^3.

Figure 1 shows HRTEM data for sulfide CoMo/MWCNT and CoMo/Al_2O_3 samples. For both catalysts the unsulfided species of active component are not observed. Active phase is uniformly distributed on Al_2O_3 surface in CoMo/Al_2O_3 catalyst. For CoMo/MWCNT the presence of active phase both inside and outside the CNT channels is observed. The average stacking number and slab length were calculated for each catalyst using not less than 500 slabs. It is defined that the average stacking number for CoMo/MWCNT and CoMo/Al_2O_3 samples is close and equal to 1.035±0.015. The average slab length is 2.88 nm for CoMo/Al_2O_3 and 3.75 nm for CoMo/MWCNT.

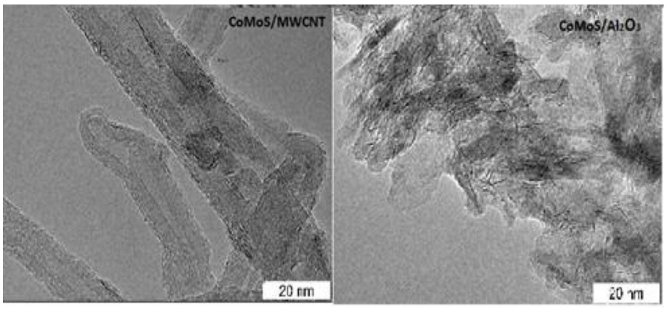

Figure 1. TEM micrographs of sulfide CoMo/MWCNT and CoMo/Al_2O_3 samples

The formation of active CoMoS phase on the surface of supports was confirmed by XPS. For both catalysts Mo3d spectra contain an intensive peak with binding energy of 229±0.1 eV and Co2p spectra contain an intensive peak with binding energy of 779.0±0.1 eV. According to Mo3d spectra decomposition the amount of Mo^{4+}, which is related to molybdenum in sulfur surrounding in sulfide catalysts, is higher for CoMo/MWCNT sample: 77% versus 63% for CoMo/Al_2O_3. The decomposition of Co2p spectra shows that the amount of CoMoS phase is 73% for CoMo/MWCNT and 63% for CoMo/Al_2O_3.

Table 1. DBT and naphthalene conversion over CoMo/MWCNT and CoMo/Al_2O_3 catalysts

Sample	Conversion, %	
	DBT	Naphthalene
CoMo/MWCNT	91.6	12.4
CoMo/Al_2O_3	80.8	8.8

The results of catalysts testing in hydrotreating of model feed (Table 1) show that CoMo/MWCNT has higher activity in HDS of DBT and hydrogenation of naphthalene.

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N-DECORATED CARBON NANOTUBES AS A METAL-FREE HETEROGENEOUS CATALYST FOR MILD CO_2 CHEMICAL REDUCTION TO METHANOL

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Exploiting carbon dioxide for the production of chemicals and fuels is one of the hottest topics of current sustainable catalysis with a relevant societal impact. Indeed, carbon dioxide is a cheap, non-toxic and renewable C_1 carbon source that can be transformed into products of added value with the assistance of a catalyst.[1] On this ground, the conversion of carbon dioxide to methanol is a very important chemical process that allows the production of an alternative energy vector (MeOH). However, the CO_2 molecule is extremely stable and its chemical conversion to target chemicals is difficult. Therefore, the preparation of new and efficient catalysts for promoting the process remains a challenging matter. Many reducing agents (hydrogen, hydrosilanes and hydroboranes) in combination with transition metal based heterogeneous catalysts have been employed successfully for the conversion of CO_2 into products of added value.[2] Anyway, such a heterogeneous technology faces with economic and environmental impacts linked to the use of metals. On a longer term vision, a sustainable technology for CO_2 reduction based on a cheap alternative is offered by metal-free catalysts. Recently, a variety of organocatalysts operating under *homogeneous* conditions has emerged for CO_2 reduction into valuable products.[3,4] Among these, N-heterocycles featured by N-[5] or C-[6] basic sites have been reported as good *homogeneous* candidates for CO_2 reduction to methanol in the presence of various hydroboranes at ambient conditions.

Following our experience on metal-free N-decorated carbon nanomaterials (N-CNMs) successfully employed in several key catalytic transformations,[7] carbon nanotubes grafted with pyridine groups have been scrutinized as the first *heterogeneous* metal-free systems in the challenging CO_2 hydroboration to methoxyborane. The prepared materials showed high catalytic activity with high TONs and complete recyclability thus candidating as a heterogeneous benchmark for the process (Figure 1).[8] In addition, on the joint basis of experimental data and *ab initio* simulations, a reaction mechanism has been proposed suggesting the key role of the carrier as an electronic reservoir for the dangling pyridine active arms.

Figure 1. CO_2 selective hydroboration to methanol catalyzed by pyridine-decorated carbon nanotubes.

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FINE-TUNING OF METAL-CARBON COMPLEX CATALYSTS: LEARNING FROM NATURAL CATALYSTS

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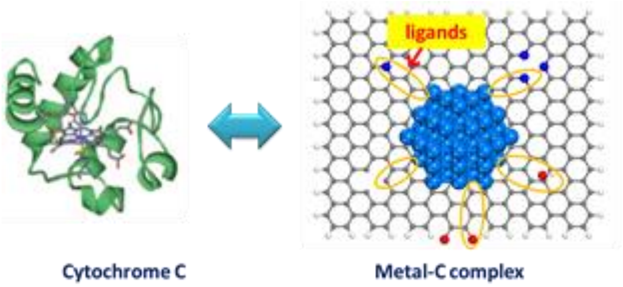
Conductive carbon supports in comparison to conventional metal oxides endow the catalysts with a unique, effective electron transfer system toward unexpected activity, selectivity and stability patterns[1]. However, the development of carbon supported catalysts is still far from rational design, because the complex surface properties (e.g., defects and heteroatom groups) of the carbon add a new dimension and thus lead to a particularly intricate interaction with metal NPs. This would delay fine-tuning of the catalysts and maximizing of metal utilization efficiency. Herein, the new concept of metal-carbon complex (MCC) catalysts which we propose is inspired by natural catalysts such as enzymes (Scheme 1.), whose function is determined by the overall system made up of both the metal center and the ligands. To mimic the enzyme catalysts, the surface properties of carbon could act as the ligands.



Scheme 1. New concept of MCC catalyst design inspired by enzyme catalysts.

On some typical reaction systems including hydrogen production, preferential oxidation of CO in H_2 and glycerol oxidation, the catalytic performance is fine-tuned by engineering both the metal properties and the ligand properties, aiming to obtain highly durable MCC catalysts with maximum mass-specific reactivity[2-9]. The plausible catalyst structure-performance relationship is established by combining kinetic and isotopic analyses, advanced characterizations and theoretical studies, where the catalytic reaction rate is expressed as the number of the active sites (i.e., N_T) times the quality of the ones (i.e., TOF). The insights revealed here could guide the rational design and optimization of the MCC catalysts.

Acknowledgements. This work was financially supported by the Natural Science Foundation of China (21776077), the Shanghai Natural Science Foundation (17ZR1407300 and 17ZR1407500), the Shanghai Rising-Star Program (17QA1401200), the Program for Professor of Special Appointment (Eastern Scholar) at Shanghai Institutions of Higher Learning, the Open Project of State Key Laboratory of Chemical Engineering (SKL-Che-15C03), and the 111 Project of the Ministry of Educationof China (B08021)

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DIRECT FORMATION OF NANOMETALS AND NANOOXIDES WITHIN PRISTINE BULK GRAPHITIC MATRICES

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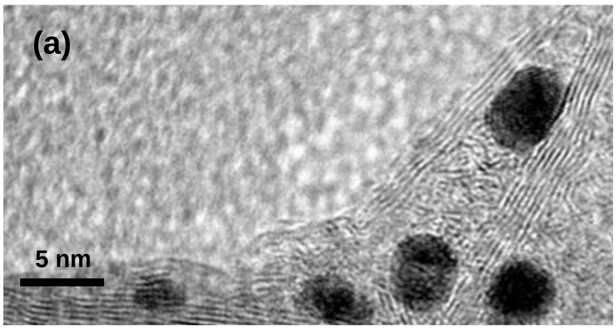
Pre-exfoliated graphene surfaces may be decorated with metal nanoparticles (M NPs) *via* a variety of covalently-bound [1, 2] and non-covalently-bound chemical linkers [3], such as pyrene-ended molecules [4]. The thermal transformation of strongly anchored molecular complexes may also lead to graphene-supported M NPs [5]. However, the decoration of bulk graphite systematically includes a pre-exfoliation step which maximizes the accessible graphitic surface by breaking down the highly stacked graphitic structure into smaller packs of layers. The most convenient way to achieve that is to oxidize the graphitic structure in the bulk by Hummers-type methods [6]. The resulting change in the chemical structure and composition of the planes indeed results in deep exfoliation of the carbonaceous structure [7]. Besides, the numerous, out-of-plane, covalently-bound and widely accessible oxygen functions of the resulting graphite oxide (GO) may straight-forwardly be used as anchoring points for metal salts [8, 9]. The reduction of such composite to obtain M NPs is however not always sufficient to restore the chemical structure of graphene, which exhibits a significant amount of in-plane defects [10]. Softer, less permanent exfoliation methods have been developed, based on the straight-forward sonication of graphite in a suitable organic solvent [11]. In these non-oxidative processes, the solvent molecule intercalates between the sonically-destabilized basal planes, generating 3D systems in solution, in which the interlayer space is largely occupied by the stabilizing organic molecules [12].

Here we show that bulk natural graphite (NG) may straight-forwardly be both exfoliated and decorated in its bulk with *in situ* formed M NPs by adding a metal precursor and $NaBH_4$ to sonochemically-destabilized NG suspensions. We will present an extensive parametric study involving a series of metal nitrates (Co, Ni, Fe, Mn, Cu) and noble metal salts ($NaAuCl_4$, K_2PtCl_6). Systematic chemical and structural characterization (ICP, FTIR, Raman, XRD, TGA) of the metal/oxide/borate, borax and graphitic phases of the resulting nanocomposites shows that the incorporation process relies on the formation of a Na^+-BH_4^- ion pair (solvent effect), which drives the insertion of Na^+-BR_4^--protected metal seeds inside the solvent-stabilized graphenic architecture *via* a Na^+-π hydrophobic interaction. This is the first example of $NaBH_4$-type molecules as chemical linkers between a M NP and a pristine graphenic surface. Advantages of such soft decoration over a π-π-driven exfoliation and NP formation based on metal phthalocyanines will be discussed in terms of particle size control, quality of the resulting graphitic matrix and catalytic properties (Figure 1).



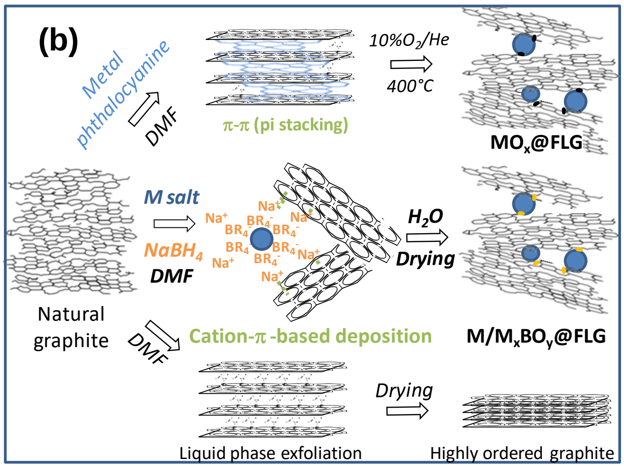


Figure 1. (a) HRTEM of Au@FLG. (b) Mechanistic pathways in the non-covalent-driven exfoliation and decoration of bulk NG with *in situ* formed nanometals and nanooxydes

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THE TUNABLE EFFECTS OF DOPANTS ON THE NANOSTRUCTURED CARBON ON THE CATALYTIC PROPERTY OF THE SUPPORTED SINGLE METAL ATOM CATALYSTS REVEALED FROM FIRST PRINCIPLE CALCULATIONS

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The nanostructured carbon material is one of the most important supports for the metal catalysts due to their unique properties such as chemical stability, easiness to recover metal etc[1]. The boron and nitrogen atoms have the similar radius with the carbon atom which can enter carbon matrix and they are the most often observed dopants on the nanostructured carbon materials. As boron or nitrogen has one less or more valence electron compared with carbon, it is expected that the different effects induced by the boron or nitrogen doping. In this work, the tunable effects from boron and nitrogen dopants on the carbon nanotube and graphene on the catalytic property of supported single Au and Pt atom catalysts in CO oxidation and propane direct dehydrogenation are revealed from the first principle calculations[2,3].

For CO oxidation on the single Au, the results reveal that boron and nitrogen doped SWCNTs can enhance the binding strength and catalytic activity of Au catalysts compared with the pristine SWCNTs. Moreover, the boron and nitrogen doping donate or withdraw charges to and from the Au atom. The excess positive or negative charges on Au can significantly modify its interactions with CO and O_2 molecules. We have found that O2 binds stronger than CO on Au/B-SWCNTs, but weaker than CO on Au/SWCNTs and Au/N-SWCNTs. The adsorption preference of CO and O2 molecules on the doped SWCNTs gives a distinct coadsorption pattern of the reactants which is closely related to the dopant configurations. Furthermore, the calculations reveal that the reactions proceed via either the bi-molecular Langmuir–Hinshelwood (BLH) mechanism or the bi-molecular Eley–Rideal (BER) mechanism with a relatively low energy barrier of 0.22 and 0.28 eV. The peroxide-like (OOCO) complex is a key intermediate in the reaction pathway in both BER and BLH mechanisms. Besides the traditional BLH and BER mechanisms, a tri-molecular Eley–Rideal (TER) mechanism is also observed, which is almost a barrierless process on Au/B-SWCNTs.

For propane direct dehydrogenation on single Pt, The nitrogen on the graphene support withdraws electrons from Pt, but boron donates electrons to Pt. Consequently, the d-band center of Pt atom is modified by either nitrogen or boron doping. The nitrogen doping shifts the d-band center of Pt atom closer to the Fermi level compared with the boron doping and the pristine ones. On the other hand, the d-band center has a significant influence on the C-H bond dissociation energy and reaction barrier. Therefore, better reactivity of Pt is found on the support with more nitrogen dopants as the d-band center is closer to the Fermi level. Also the calculated dissociation energy and the first C-H bond activation barrier obey the BEP rule. The different ratios between nitrogen and boron on the codoped graphene can continuously adjust the electronic structure of supported Pt and deliver the dissociation energy and reaction barrier in between the pure nitrogen- and boron-doped cases. Among various investigated supports, the graphene doped by pyridine nitrogen is predicted to be the most effective for enhancing Pt catalytic performance.

From these calculations, it is demonstrated a practical way to adjust properties of the supported single metal atom catalysts by rational doping.

Table 1. Binding energy, E_b and Bader charge, Q calculated for the most stable configurations of O_2 and CO adsorbed on a SWCNT supported Au atom. Q represents the charge on Au.

System(SWCNT)	Au		O_2-adsorption		CO-adsorption	
	E_b	Q (|e|)	E_b	Q (|e|)	E_b	Q (|e|)
Pyridine AuN	-0.89	+0.4	-1.10	+0.52	-2.55	+0.5
Pyridine AuB	-2.12	-0.55	-1.73	-0.27	-1.26	-0.3
Axial AuN	-1.79	+0.9	-0.29	+0.52	-1.06	+0.54
Axial AuB	-2.09	-0.44	-1.45	-0.25	-0.7	-0.004
Pristine SWCNT	-0.38	-0.08	-0.69	+0.19	-1.03	+0.22

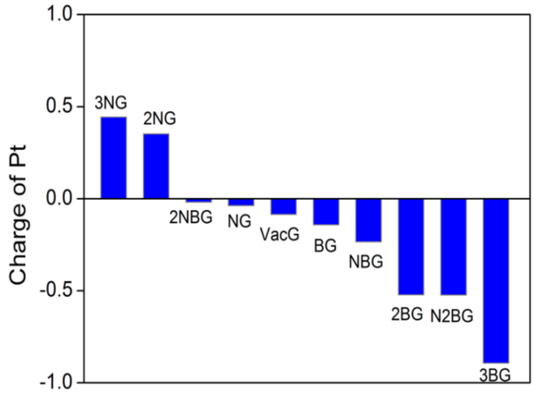

Figure 1: Bader charge analysis on the single Pt atom supported on the undoped and doped graphene.

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Pd NANOPARTICLES SUPPORTED ON FUNCTIONALIZED CARBON NANOTUBES FOR THE LIQUID-PHASE AEROBIC OXIDATION OF ETHANOL

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Introduction

Carbon nanotubes (CNTs) are promising materials in many fields due to their unique geometric, mechanical and electronic characteristics. By introducing heteroatoms or defects on the CNT surface, the interaction between the deposited metal species and the CNTs can be optimized, leading to favorable catalytic performance. The aerobic oxidation of alcohols to the corresponding carbonyl compounds is an important reaction in organic synthesis.

In the present study, surface functionalization of CNTs with a KOH and steam co-treatment to generate more basic functional groups with high thermal stability was systematically investigated. Nitrogen-doped CNTs (NCNTs) were also selected as support due to their ability to improve the dispersion and, more importantly, modify the electronic structure of the supported metal NPs. The prepared Pd NPs supported on KOH-steam co-treated CNTs and NCNTs were tested in the selective oxidation of ethanol in the liquid phase.

Experimental section

OCNTs were prepared by treating purified CNT in HNO_3 vapor, and the subsequent treatment of OCNT in NH_3 produced NCNTs. CK samples were obtained by a thermal treatment in the presence of pre-adsorbed KOH and steam at 350–550 °C. The Pd/CNT catalysts were synthesized by a colloidal deposition method described elsewhere.[1] The aerobic liquid-phase oxidation of ethanol was carried out in a multiple parallel operating autoclave system with 10 mL of 5 wt% aqueous ethanol solution at 160 °C and 30 bar synthetic air.

Results and discussion

Steam and KOH co-treatment of CNTs resulted in a synergistic effect on the functionalization of the carbon surface with –CO– groups having high thermal stability and basicity. Owing to the electron-donating properties of the introduced functional groups and the additional Brønsted basicity, Pd nanoparticles supported on the co-treated CNTs were found to be strongly anchored leading to a high degree of Pd dispersion and a high resistance to sintering.[2] The Pd nanoparticles on the co-treated CNT support produced at 450 °C and 550 °C showed the highest activity and yields of acetic acid in the aerobic oxidation of aqueous ethanol reaching almost full conversion after 5 h in the absence of additional base (Table 1). In addition, the KOH-steam co-treatment was found to enhance the recyclability of the Pd/CNT catalysts.

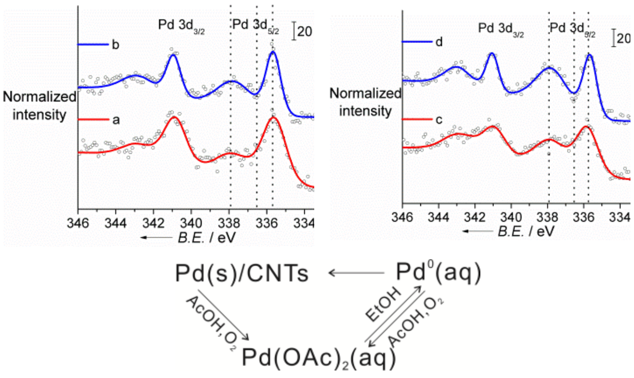
Table 1. Comparison of conversion and yield of acetic acid over Pd/CNT catalysts during aerobic ethanol oxidation.[a]

Catalyst	1st run				2nd run	
	After 1 h (%)		After 5 h (%)		After 5 h (%)	
	Conv.	Yield	Conv.	Yield	Conv.	Yield
Pd/OCNT	16	2	62	39	60	35
Pd/CK-im	58	26	88	55	69	33
Pd/CK05-350	47	20	78	42	68	46
Pd/CK05-450	50	20	96	71	88	55
Pd/CK05-550	64	29	95	67	88	63

[a] Reaction conditions: ethanol/metal=2000 (mol/mol), 10 mL of 5 wt% aqueous ethanol, 30 bar of synthetic air, 160 °C.

Compared to OCNTs, NCNTs were found to act as a better support for the Pd nanoparticles by efficiently stabilizing and recapturing the Pd species, which resulted in higher activity and selectivity to acetic acid for ethanol oxidation over the whole temperature range (80-180 °C).[3] X-ray photoelectron spectroscopy (XPS) measurements showed that Pd was largely in the metallic state for the freshly reduced Pd/CNT catalysts (Figure 1a and 1c), while an increase in the intensity of the peak at a binding energy of 338 eV attributed to $Pd(OAc)_2$ was observed especially for Pd/NCNT after reaction (Figs. 1b and 1d). $Pd(OAc)_2$ species were generated under the oxidizing conditions according to Eq. (1). The strong interaction between $Pd(OAc)_2$ and the surface N species played an important role in both the formation and stabilization of $Pd(OAc)_2$ under the reaction conditions. In summary, the dissolution and redeposition (or release and catch) of the Pd species shown in Figure 1e was identified to be responsible for the overall reactivity under reaction conditions, bridging the gap between heterogeneous and homogeneous catalysis.

$$Pd + 1/2\ O_2 + 2\ AcOH \longrightarrow Pd(OAc)_2 + H_2O \qquad (1)$$



(e)

Figure 1. XP Pd 3d spectra of the Pd/CNT catalysts before and after reaction: a) Pd/OCNT, b) Pd/OCNT-AR, c) Pd/NCNT-NH_3, d) Pd/NCNT-NH_3-AR; e) evolution of Pd species during aerobic ethanol oxidation in the liquid phase.

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SURFACE FUNCTIONALIZED CARBON NANOTUBES AS MOLECULAR OXYGEN CARRIER FOR LIQUID-PHASE AEROBIC OXIDATION REACTION

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Developing an environmental friendly process for fabrication of imines and their derivatives is a very important synthetic approach in chemistry as well as in biology as the products can be extensively utilized as intermediates in the synthesis of pharmaceuticals, fine chemicals and biologically chemicals. such catalytic protocol usually requires metal-based catalysts even in the presence of base to purchase higher selectivity and yield. However, such catalytic process alwasys suffer the high cost problems as well as the harmful impurities from resident metals in the final products, especially for the production of pharmaceuticals. It is known that carbon materials have been used as supports or even catalysts for many reactions such as selective oxidation and dehydrogenation reactions, where their surface chemical properties play key roles in activating reactant molecules and achieving efficient performances[1,2]. Current strategy to decorate oxygenated groups on carbon surface is through oxidation treatments[2], which are however at the expenses of harsh reaction conditions and large amount of acidic waste, hindering the process to be upscaled for industrial production. Ozone (O_3) as a strong oxidant is considered as a good oxidizing agent without environmental concern and corrosion problems, unless systematic investigations concerning the potential catalytic application of ozone functionalized CNT are still lacking.[3] Here in this work, we focus on the facile ozone treatment with vapor assistance under near ambient conditions on the functionalized groups and catalytic performances for aerobic oxidation of benzylamine to imine on both CNT and nitrogen(N)-doped CNT. Such moderate oxidation treatment process could efficiently transfer the molecular oxygen on the surface of nanocarbon materials that could efficient act as active site for oxidative coupling reaction.

As shown in Figure 1, the proper functionalization of NCNT causes the light breakage of the outside wall and formation of defects, where initial nanotube structure is also very well kept. The changes in the surface structure after the ozone treatment acts only a few layers (as shown in the inset of Figure 1b) of the graphitic walls of NCNT.

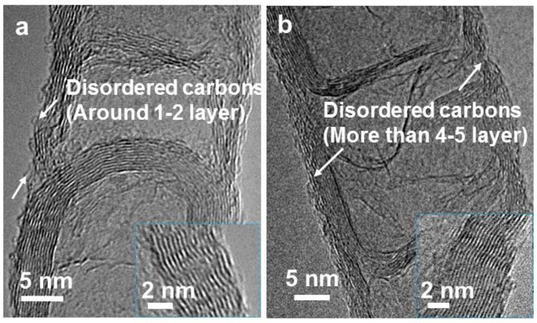

Figure 1. a, b) HR-TEM images of initial NCNT and functionalized oNCNT samples.

Typical CNT with and without nitrogen doping are functionalized by ozone in the presence of vapor and tested directly as catalysts for the aerobic oxidation of benzylamine in the absence of either base or solvent. It can be seen that CNT has selectivity for imide as high as 99% despite of the functionalization. Ozone functionalized oCNT gives much higher conversion of benzylamine, which is similar to that of NCNT. However, the secondary ozone functionalization based on nitrogen doped CNT (oNCNT) as catalyst leads to the boosting off of the conversion of benzylamine and the reaction rate, revealing the possibility that the aerobic oxidation of benzylamine ought to be a double-active sites controlled process. Temperature-programmed desorption is also carried out to understand the formation of surface functional groups as well as the relationship between functional groups and catalytic performances. No matter how, the ozone functionalization is economical and fairly effective for industrial use in carbon modification for catalysis purposes.

Table 1. Solvent-free aerobic oxidation of benzylamine to imine over nanocarbons.[a]

Catalyst	S_{BET} [m^2/g]	Conv. [%][b]	Sel. [%][b]	$\gamma_{catal.}$ [$mmolg_{catal.}^{-1}h^{-1}$][c]
-	-	n.a.[d]	n.a.	n.a.
CNT	223.4	3.9	> 99	0.7
oCNT	308.7	28.1	> 99	5.2
NCNT	101.7	26.7	> 99	5.6
oNCNT	97.9	66.0	> 99	12.9

[a] Reaction conditions: benzylamine (7.5 mmol), catalyst (20 mg), O_2 balloon, 10 h, 100 ºC. [b] Determined by gas chromatography methods using toluene an internal standard and confirmed by ^{1}H NMR. [c]$\gamma_{catal.}$ is expressed as the amount of imine formation per weight of catalyst per hour. [d] Not available.

In this work, we used a green and facile strategy of ozone treatment in the presence of vapor to functionalize CNT materials, which were then applied catalyst as oxygen carrier. The formation of defects, the breakage degree of outside wall, as well as the evolution of oxygenated and nitrogen functional groups can be controllably varied based on the ozone functionalization. Moreover, the method is green and economic, which is superior either in the environmental part or the lower raw cost, comparing with the conventional acid treatment or any other liquid-phase ozone treatment. The as-obtained oCNT and oNCNT performed great efficiency for aerobic oxidation of benzylamine to imine. Characterizations including temperature-programmed desorption, Raman spectra, kinetics experiments, as well as X-ray photoelectron spectroscopy were also carried out for further understanding the mechanism and relationship between the surface functional groups and catalytic performance.

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MACROSCOPIC OXIDIZED GRAPHITE FELTS CONTAINING PALLADIUM NANOPARTICLES AS AN EFFICIENT LIQUID-PHASE HYDROGENATION CATALYST WITH EASY RECOVERY

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Hierarchical catalysts with surface functionalization have received an ever increasing scientific and industrial interest since the last decades in several catalytic processes, especially for liquid-phase reactions. Such systems ensure several advantages such as: i) an easy transport and handling, ii) a high efficiency in the recovery of the catalyst along with iii) low diffusion of the reactant and product in and out of the catalyst bed thanks to the hierarchical structure which prevents secondary reaction. In this work a hierarchical catalyst based on entangled graphite felts (GFs) decorated with defects and containing palladium will be investigated as selective liquid-phase hydrogenation catalyst.

The GFs was pretreated with gaseous HNO_3 to generate OGFs with defects functionalized with oxygenated groups. The defects play the role of anchorage sites for the dispersion of Pd nanoparticles as evidenced by the TEM analysis of the Pd catalyst supported on untreated GFs (Pd/GFs) and acid-treated GFs (Pd/OGFs) presented in Fig. 1A and B. According to the TEM results the Pd particles with homogeneous diameter (ca. 4 nm) are well dispersed on the OGFs support (Fig. 1B and C).

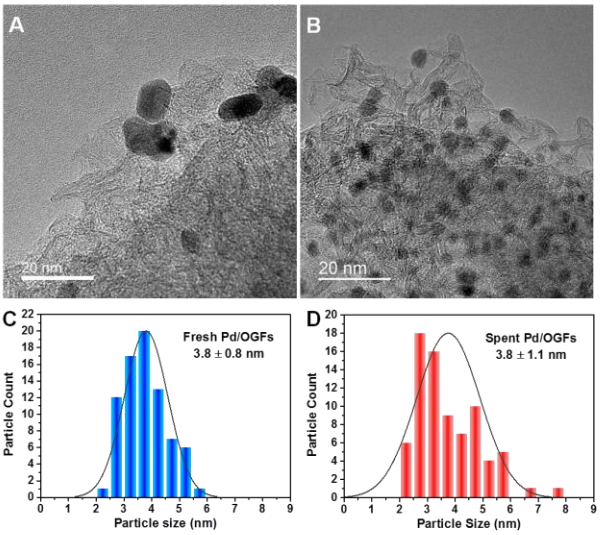

Figure 1. TEM micrographs of the fresh Pd/GFs (A) and Pd/OGFs (B), and Pd particle size distributions of fresh (C) and spent (D) Pd/OGFs.

The Pd/OGFs catalyst displays extremely high hydrogenation activity compared to that obtained on the untreated Pd/GFs catalyst under severe reaction conditions, i.e. low H_2 partial pressure where H_2 dissociation on metal sites is the limiting step (Fig. 2A). The Pd/OGFs catalyst also displays high stability as a function of recycling tests compared to the Pd/GFs and commercial Pd/activated charcoal catalysts (Fig. 2B). The Pd/OGFs catalyst displays a similar hydrogenation activity, expressed in terms of cinnamaldehyde conversion, during the fifteen cycling tests while the Pd/GFs and commercial catalysts display about 60% and 50% activity loss after four and two cycles (Fig. 2B). Such high stability was confirmed by statistical TEM analysis (Fig. 1C) which shows the complete absence of metal particle sintering on the Pd/OGFs catalyst.

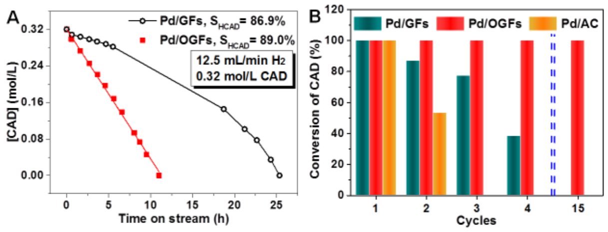

Figure 2. (A) Cinnamaldehyde (CAD) conversion under severe reaction conditions on Pd/OGFs and Pd/GFs catalysts. (B) Cinnamaldehyde conversion as a function of the cycling tests on Pd/OGFs, Pd/GFs and commercial Pd/AC catalysts. Conditions: 80 °C, 50 mL/min H_2, 1 atm, 375 rpm and 0.08 mol/L of CAD.

In conclusion, gaseous acid treated graphite felt leads to the formation of a macroscopic support with oxygenated function defects evenly distributed on the surface. Such defective support displays a high density of anchorage sites for hosting, and stabilizing, metal nanoparticles and contributes to the development of new hierarchical catalyst for liquid-phase reaction with high efficiency and easy recovery.

Acknowledgements. Zhenxin Xu and Bing Li would like to thank the Chinese Scientific Council for grants during their stay at the ICPEES.

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STRONG EFFECT OF THE SURFACE PROPERTIES OF CARBON SUPPORTS IN Au-CATALYZED REACTIONS

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Summary. Support materials are well-known to affect catalytic performance of metal nanoparticles in metal-catalyzed reactions. We have recently demonstrated that surface properties of the carbon supports play a vital role in determining activity, selectivity and stability of Au catalysts. [1] In this contribution, we will provide a detailed discussion on how and why the surface properties of carbon supports affect the performance of Au catalysts in the oxidation of 5-hydroxymethylfurfural (Figure 1), an important reaction for the production of bio-based polymers.

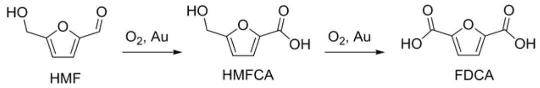

Figure 1. Oxidation of HMF to furandicarboxylic acid (FDCA).

Introduction. Carbon materials are highly promising catalyst supports for metal nanoparticles, particularly for fuel cell catalysts and catalysis in the aqueous phase. Surface properties of carbon materials can greatly differ depending on the preparation method and post-treatments. For example, carbon surface can be easily functionalized by incorporating other elements, such as oxygen and nitrogen,[2,3] which in turn would affect surface polarity and acid-base characteristics. These parameters are expected to strongly impact activity, selectivity and stability of supported metal catalysts.

In this work, we investigated a series of similar 2−4 nm gold nanoparticles supported on high-surface-area graphite (HSAG) materials with different surface chemistries, but the same morphology, in the oxidation of 5-hydroxymethylfurfural (HMF). We demonstrate that the surface properties of the carbon supports strongly influence the performance of gold catalysts.

Results and discussion. Table 1 gives an overview of the surface properties (chemical composition, point of zero charge, PZC) and textural properties (surface area and pore diameter) for the commercial and functionalized HSAG materials.

Table 1. Properties of the HSAG support series

Material	S_{BET}, m^2/g	d_{pore}, nm	O/C (XPS)	N/C (XPS)	PZC
HSAG	502	5.4	0.059	-	4.0
HSAG-ox	443	5.8	0.145	0.005	2.6
HSAG-H	507	5.4	0.034	-	7.7
HSAG-N	506	5.5	0.013	0.009	9.9

A series of Au/HSAG-x catalysts with similar particle sizes have been prepared by depositing 2-3 nm colloidal Au nanoparticles on these supports.

Study of the Au catalysts for HMF oxidation showed that the activity (TOF_{Au}) and the yield of FDCA strongly increased with the support PZC (Figure 2). On the other hand, Au catalysts supported on acidic HSAG (HSAG and HSAG-ox) were highly selective towards the intermediate HMFCA. Gold nanoparticles were substantially more stable on HSAG supports with lower concentration of surface oxygen groups, while Au nanoparticles on HSAG and HSAG-ox with oxygen-rich surfaces showed severe particle growth during reaction.

The observed differences in activity and selectivity between catalysts immobilized on modified HSAG supports primarily originate from the differences in the reactant and intermediate adsorption on the surface of the catalysts, as will be discussed in more detail in the conference contribution.

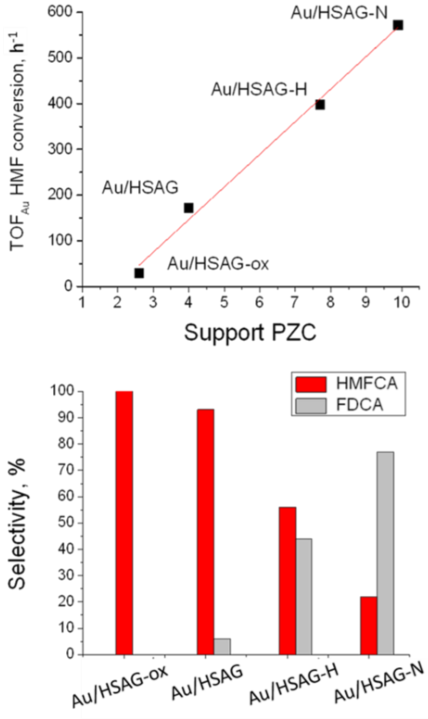

Figure 2. Activity and selectivity of Au/HSAG-x in HMF oxidation.

Conclusions. Surface properties of carbon materials have a strong impact on the performance of supported gold catalysts. A detailed discussion on the reasons behind such a strong impact, as well as the guidelines for the rational design/choice of optimal carbon supports for highly active, selective and stable Au catalysts will be given in the conference contribution.

Acknowledgements. European Commission for funding from the European Union’s Horizon 2020 research and innovation program under the Marie Skłodowska-Curie grant agreement No 703861; and NWO Vici (N. 16.130.344) are gratefully acknowledged.

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NANOCARBONS AS SUPPORTS FOR THE GOLD-CATALYSED GLYCEROL OXIDATION

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One of the main by-products obtained during the production of biodiesel is glycerol, a highly functionalized bio renewable molecule [1]. The effective utilization of glycerol and its efficient conversion into various value added products will have positive effects on the economics of biodiesel production, resulting in increased production and increased utilization of this alternative fuel resource.

The selective oxidation of glycerol follows a complex reaction pathway yielding different C_3 products (glyceric acid (GLYA) dihydroxyacetone (DHA), and tartronic acid (TA)), C_2 products (glycolic acid (GLYCA) and oxalic acid (OXA)), and even C_1 products (formic acid (FA)) (Figure 1). Most of these products are useful intermediates in organic synthesis, but they presently have a limited market [2].

In a previous work by Zope et al. [3], it was proposed that gold required the presence of NaOH to perform the H-abstraction, the first step of the dehydrogenation pathway. In subsequent studies [2]?, Davis and co-workers, using labelling experiments with $^{18}O_2$ and $H_2{}^{18}O$ for glycerol oxidation over supported Au catalysts, demonstrated that oxygen atoms originating from hydroxide ions are incorporated into the alcohol during the oxidation reaction, instead of those from molecular oxygen.

Furthermore, Carretin et al. [4] concluded that the gold particle size is crucially important in determining the activity and selectivity of the gold catalyst in glycerol oxidation. But, the effect of the support is still understudied and it can also modify the activity of Au nanoparticles. Therefore, it is an important parameter for improving the catalytic process.

In previous works, we had studied the effect of carbon materials as supports for gold nanoparticles in relevant reactions using cyclohexane [5-7]. Also the oxidation of glycerol had already been tested using Au on other carbon materials, such as carbon nanotubes [8-9] and xerogels [10]. The aim of the present work is to better understand the way in which the metal active sites interact with the substrates and products, that will lead to the development of better catalysts and better control of activity/selectivity parameters in the oxidation of glycerol.

In this work, different carbon materials were loaded with 1% Au using a sol immobilisation method, described in previous papers [5-7]: single walled carbon nanohorns (1%Au-NHS), graphene oxide (1%Au-GROX), reduced graphene oxide (1%Au-RGROX) and graphene nanoplatelets (1%Au-GRNPLS). Some experimental results are shown in Table 1.

Table 1. Oxidation of glycerol using Au/nanocarbon catalysts[a]

	Conversion %	Mono-acid selectivity %
1%Au-NHS	30	50
1%Au-GROX	70	100
1%Au-RGROX	45	30
1%Au-GRNPLS	65	80

[a] 60 ºC, 2 mL water in an autoclave, stirring speed 1200 rpm, 1.2-mmol substrate, 1.2-mmol NaOH, 20-mg catalyst, 3 bar pressure of oxygen.

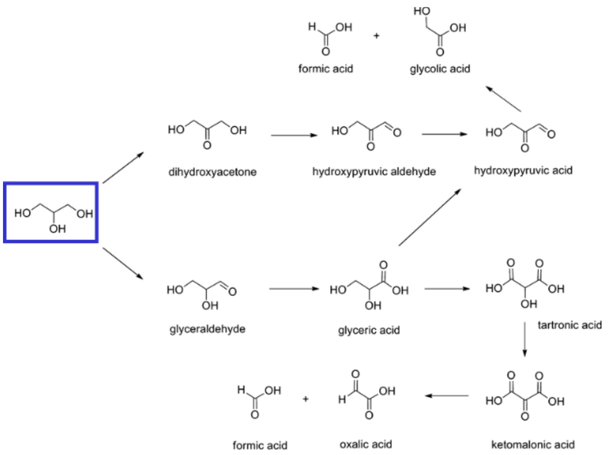

Figure 1. Reaction scheme for glycerol oxidation under basic conditions.

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METAL FREE OXIDATION OF GLYCEROL OVER NITROGEN CONTAINING CARBON NANOTUBES

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Sustainable development requires use of biorenewable feedstocks to produce clean fuels and commodity chemicals. In this respect glycerol is of significant interest, which is available widely as a primary by-product during biodiesel production.[1] Glycerol can be converted through oxidation process to a variety of valuable chemicals.[2] For example, the oxidation of a primary alcohol group in glycerol leads to glyceric acid (GLYA), a multifunctional building block compound.[2] The oxidation of a secondary hydroxyl group produces dihydroxyacetone (DHA), a specialty chemical used as a sunless tanning agent in the cosmetics industry.[3] Noble metal based catalysts (Au, Pd, Pt, etc.) are largely reported in literature for attaining good activity selectivity, but due to the high costs non-metal analogues should be explored. Recently, metal free nitrogen doped carbon materials have been shown to be good candidate to replace noble metal free catalysts for the oxidation of alcohols.[4] In particular, it was reported that the presence of graphitic nitrogen enhances the catalytic activity in alcohol oxidation modifying the electronic structure of the adjacent carbon atoms.[4] In this work, we report the utilization of NCNTs as metal free catalyst for the selective oxidation of glycerol to DHA.[5] Two CNTs with high N content were synthesized by catalytic chemical vapour deposition (CVD) method over Fe–Mo–Al catalyst synthesized through hydrothermal process and imidazole as carbon/nitrogen feedstocks at 700 and 800°C. The obtained N-doped CNTs were flagged as NCNT700 and NCNT800, respectively. HRTEM analysis show nanotubes with an inverted cup pile structure, with an average diameter of ~20 nm (Fig.1a). X-ray Photoelectron spectroscopy (XPS) was used to investigate the carbon surface. NCNTs700 showed a higher amount of nitrogen on the surface compared to NCNTs800 (atomic % of 13.7 and 2.3, respectively). For different nitrogen functional groups, pyridinic-N, pyrrolic-N/pyridone-N, quaternary-N/pyridinic-N–H and pyridinic-N$^+$–O$^-$, were identified. A high concentration of pyridinic groups were detected on NCNT700 (45.8%) (Fig.1b), whereas the major N specie present on NCNT800 was pyridinic-N$^+$–O$^-$ (36.5%).

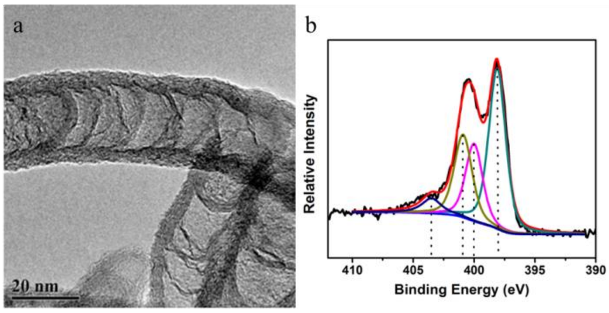

Figure 1. a) HRTEM image and b) XP-Spectra of NCNT700.

The catalysts were evaluated in the selective glycerol oxidation using tert-Butyl hydroperoxide (TBHP) as oxidant. Non functionalized CNTs were almost inactive whereas nitrogen functionalized CNTs reached a conversion of 8.3%, and 36.5% after 6h, for NCNTs800, and NCNTs700 respectively (Table 1). Correlating the activity with the surface properties showed that the most active catalyst is NCNTs700, which contains the highest amount of pyridinic groups (13.4%) compared to NCNTs 800 (1.9%) and CNTs (0%). All the catalysts showed dihydroxyacetone, as main product with a selectivity of 84.3% and 73.8% for NCNTs700 and NCNTs800, respectively (Table 1). Quantum-chemical calculations were performed to understand the mechanism of reaction and to calculate the reaction barriers. The catalytic activity of the NCNT was assigned to the pyridinic groups present on its surface that are most probably converted into N-O groups formed by edge oxidation of N-doped active carbon by TBHP.

Table 1. Glycerol oxidation using NCNT700 and NCNT800.

Catalyst[a]	Conversion[b]	Selectivity	
		GLYA	DHA
CNT	0.5	-	-
NCNT700	36.5	84.3	0.2
NCNT800	8.3	73.8	14.2

[a] Reaction conditions: Glycerol 3 mmol, TBHP 6 mmol (TBHP 70% in water), glycerol/catalyst 5/1 wt/wt, 60°C, 1250 rpm

[b] conversion after 6h

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TUNING PROPERTIES OF ULTRAFINE Pd NANOPARTICLES SUPPORTED ON MULTIWALLED CARBON NANOTUBE

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Carbon materials (CM) have been successfully used as supports for metallic and oxide particles [1]. Doping of the carbon supports opens up the possibility of regulating its chemical, electronic and mechanical properties. The introduction of heteroatom into the carbon structure leads to the formation of specific adsorption centers for metal species. In particular, it was found that the adsorption energy of Pt on carbon nanotube (CNT) increases in the next row of doping atoms (X): pristine < N < B < O [2]. Improvement of the functional properties of metal particles deposited on X-CNT is associated both with an increase in their dispersion and a change in their electronic state. In this work the influence of Pd-CM composition (CNT, N-CNT, Pd = 0.2-2.0 wt.%) and reduction conditions (H_2/Ar, 100-300^{o}C) on the material properties was studied. The characteristics of materials and their performance in nitrobenzene hydrogenation reaction are compared.

The synthesis of carbon materials (CNT, N-CNT) was carried out by the method described in [3]. Ammonia was used as a precursor to nitrogen in N-CNT. The nitrogen content was 4 wt.%. For the synthesis of Pd/CNT and Pd/N-CNT catalysts the support was impregnated with an acetone solution of palladium acetate of the given concentration. Then the samples were dried in air atmosphere and reduced in H_2/Ar mixture. The content of Pd was varied in the range from 0.2 to 2.0 wt. %. The nitrobenzene hydrogenation reaction was carried out at 40^{o}C and 1 atm.

According to the CO chemisorption the dispersion of Pd is regulated by support composition, Fig. 1.

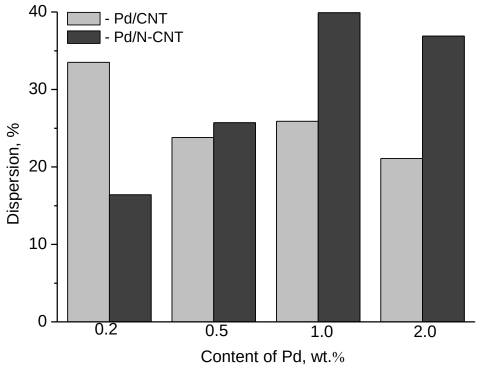

Figure 1. Effect of support composition on the Pd dispersion at different content of Pd. Reduction temperature is equal to 100^{o}C.

For a series of Pd/CNT samples by increasing the content of Pd ranging from 0.2 to 2 wt.% dispersion decreases from 34 to 21%. On the contrary, in the case of Pd/N-CNT samples, the increase in the content of Pd is accompanied by an increase in dispersion of the active component. This effect can be connected with stabilization of ionic/electron-deficient Pd subnanoparticles. The use of N-CNT as support provides stabilization of palladium (Pd ≥ 0.5 wt.%) in a more dispersed state. The Pd dispersion increases with an decrease in the reduction temperature of the catalyst, while the stability of Pd particles to sintering practically does not depend on the support composition. For both samples containing 2 wt.% Pd, when the reduction temperature increases from 100 to 300°C, palladium dispersion decreases by ~ 25%.

TEM data shows, that the active component of the catalysts is present in the form of Pd-particles (size 1-3 nm) and Pd-clusters (size less than 0.5 nm). As the content of Pd increases from 0.2 to 2 wt.% the average size of Pd particles slightly increases: from 1.1 to 1.5 nm for Pd/CNT, Fig. 2.

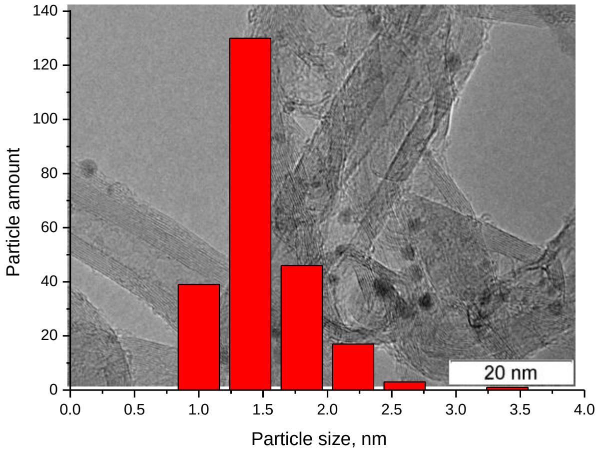

Figure 2. TEM images of 2Pd/CNT catalysts and particle size distribution. Reduction temperature is equal to 100^{o}C.

The tests of Pd catalysts in the reaction of nitrobenzene hydrogenation show that the process performance is enhanced with using the N-CNT as support and with increase of Pd content in the catalyst. The variation of the temperature of catalyst reduction has little effect on the catalyst activity.

The optimal catalyst composition is selected: 2Pd/N-CNT catalyst provides the 8 l H_2/gPd•min.

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Au/C CATALYSTS FOR 2,5-FURANDICARBOXYLIC ACID PRODUCTION

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The production of high added value chemicals from biomass sources have received recently a very special interest. One of the most important chemicals issue from the renewable sources is the 2,5-furandicarboxylic acid (FDCA) due to its high potential to substitute the terephthalic acid for polymers synthesis [1]. FDCA is frequently obtained by successive oxidation of 5-hydroxymethylfurfural (HMF). The HMF to FDCA oxidation have been studied over an important number of catalysts , being the noble metal based systems the more promising ones [2]. When using a gold metal for oxidation reaction it is generally considered that its activity is influenced either by the gold particles size or by the nature of the support. The support role in this reaction is not very well established but it is believed that the lixiviation of gold is negligible when using more hydrophobic supports. Within all usually employed supports those based on carbonaceous materials present the advantage of possibility to modulate its hydrophilicity. In general their hydrophobicity difficult the active phase lixiviation thus improving the activity/selectivity balance during catalyst use and recycling. On the other hand the above mentioned balance is also influenced by the active phase size and distribution.

In this context in this study the main objective is to study the activity/selectivity balance in the systems with different gold particle size and dispersion all supported over hydrophobic support where active phase lixiviation is not produced no matter the reaction parameters or duration.

Gold (2 wt.% nominal value) was deposited using the gold colloids method using polyvinyl alcohol (PVA) as surfactant and $NaBH_4$ as redactor and HAuCl4 as metal precursor. The necessary quantity of gold precursor was dissolved in distilled water to obtain a final concentration of 5.10-4M. After the corresponding quantity of PVA solution (1wt.% in water) were added and allowed to mix with gold during 20 min. In the last step, the corresponding volume of 0.1M $NaBH_4$ was used to reduce *in-situ* the precursor to corresponding nanoparticles. Once obtained and colloidal gold obtained the nanoparticles were immobilized on the support (DARCO active carbon). The catalyst were centrifuged, filtered, dried (100 ºC overnight and after calcined at 300ºC for 4 h.

The HMF oxidation reaction was carried out in autoclave batch reactor (Parr Instruments) of 250 mL, equipped with magnetic stirrer (0-600 rpm) and temperature and pressure control. Firstly the reactor is filled with aqueous solution of HMF, NaOH and catalyst in a HMF:Au:NaOH molar ratio of 1:0.01:2. The reactor is then purged twice with O_2 and pressurized at 10 bares. The system is then heated to 70°C, under constant stirring rate of 400 rpm during 4h. After this time, the reactor is cooled rapidly in ice bath and the simple is analyzed by HPLC, using 0.01M H_2SO_4 as mobile phase.

Using the knowledge from a previous work [3] where the influence of gold colloids preparation parameters over nanoparticles diameter was studied, four different preparations were made in order to achieve diversity of the finally obtained gold particles size. It was achieved only by the modification of the Au: PVA: $NaBH_4$ ratio employed in every sample. Table 1 summarizes the experimentally detected gold loadings and the estimated gold particle size for all samples. The experimental gold loading approximate the nominal value and the obtained particles sizes are very different. Exactly this effect was desired to evaluate the influence of gold particle size only on the reaction route, activity and selectivity.

Table 1. Gold particle size and loadings for the studied samples

Sample	% Au (ICP)	Au particle size (nm)
AuC I	2.3	5.2
AuC II	2.1	8.5
AuC III	1.7	15.6
AuC IV	2.1	34.9

The catalytic results for the studied systems are presented in Figure 1. It seems that the gold particle size do not influence the HMF conversion as complete conversion is observed in all cases. However, a negative effect of gold particles size increase is observed on both selectivity and C balance (the difference between the entering C moles and those analyzed after reaction). The selectivity to the final FDCA product decrease with the increase of the Au particles size in favor of the 5-hydroxymethyl-2-furancarboxylic acid (HMFCA) yield. In the same time the carbon balance decrease indicating either products adsorption or secondary reactions with the production of non-detectable products.

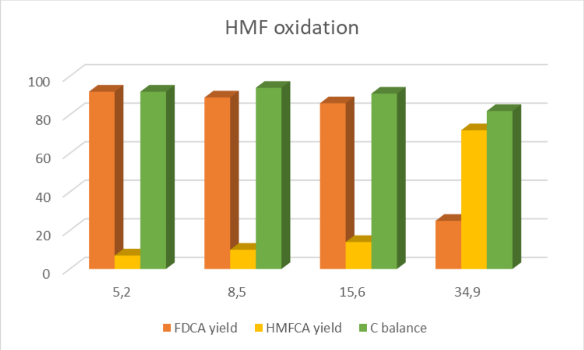

Figure 1. Catalytic activity as a function of gold particle size

Small Au particle size promote the formation of the final product. A yield superior to 90 % in FDCA is obtained at very low HMF/base ratio.

Acknowledgements

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SULFONATED HYDROTHERMAL CARBONS AS CATALYSTS FOR ORGANIC REACTIONS

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Hydrothermal carbons are prepared from renewable materials (saccharides) under mild conditions, leading to microspheres (Fig. 1a) with high density of oxygenated functional groups. The sulfonation with concentrated sulfuric acid leads to less oxygenated carbon materials bearing sulfonic and carboxylic groups, which confers to the surface a highly hydrophilic character. The sulfonated hydrothermal carbons present very low surface area and only ultramicropores, as shown by the comparison of the N_2 and CO_2 adsorption-desorption isotherms. However, their structure is not rigid, and the accessibility to the acid sites depends on the solvent, as demonstrated by the lack of adsorption of basic triethylphosphine oxide in non-polar solvents and the strong acidity shown in polar solvents [1]. The hydrothermal carbons can also be coated on the microfibers of graphite felt (GF), leading to a stable solid material that can be sulfonated in the same way as the bulk hydrothermal carbon to get SHTC@GF (Fig. 1b) [2].

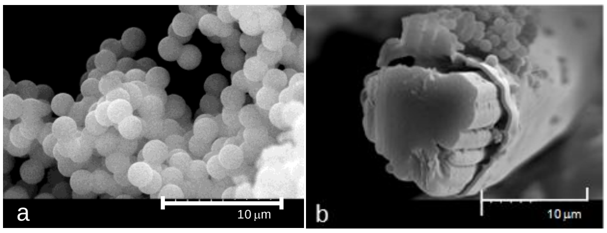

Figure 1. a) Microspheres of SHTC. b) SHTC@GF.

We have used this type of sulfonated hydrothermal carbons (SHTC) as heterogeneous Brønsted acids in catalytic processes (Fig. 2). In the **esterification** of palmitic acid with methanol, the comparison with other sulfonic solids, such as polystyrene based resins, propylsulfonic silica or siloxanes, and perfluorinated polymers, showed that SHTC was much more active than the rest of the sulfonic solids, even those with stronger acid sites. In addition, the SHTC were much tolerant to the presence of water in the reaction medium [3].

This improved catalytic activity has been also demonstrated in the case of the esterification of glycerol with different carboxylic acids. The reaction conditions can be tuned to obtain monoglycerides or triglycerides with high yield and selectivity [4]. It has been hypothesized that the enhanced catalytic activity is due to a synergetic effect of the acid groups, both carboxylic and sulfonic, in close proximity.

However, the main disadvantage of the SHTC is the easy deactivation, due to the covalent formation of esters by reaction of the surface acid groups with the alcohols [5].

The **acetalization** of glycerol with acetone, leading to solketal, or with other ketones is also catalyzed by SHTC with high efficiency under mild conditions. In this way, the deactivation by formation of esters does not take place. Even it is possible to perform the reaction in a continuous flow reactor using SHTC@GF, which possess excellent properties for microfluidics.

SHTC has been also used in the **dehydration** of sorbitol to isosorbide and in a **tandem** esterification to obtain isosorbide diesters [6], as well as in a tandem esterification-acetalization from quinic acid to obtain a precursor of the anti-influenza osetalmivir [7].

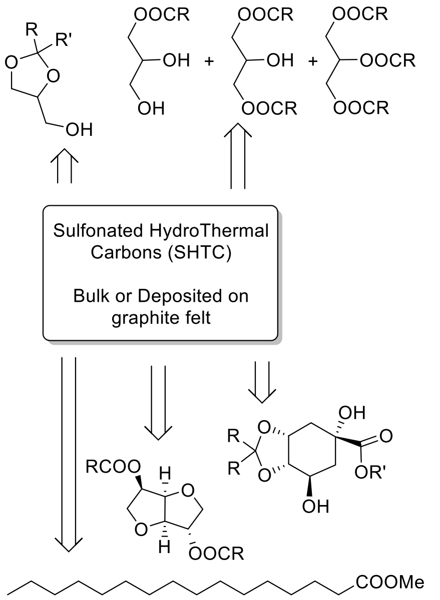

Figure 2. Products obtained in reactions of esterification, acetalization and dehydration catalyzed by SHTC.

In conclusion, SHTC (either bulk or coated on GF) is a versatile Brønsted acid catalyst, useful in different organic reactions. Further research is currently under development to get new applications and to solve the deactivation problems encountered in some cases.

Acknowledgements. This work was made possible by the financial support of the Spanish Ministerio de Economía y Competitividad (projects CTQ2014-52367-R and ENE2016-79282-C5-1-R) and the Gobierno de Aragón (E11 Group co-financed by the European Regional Development Funds).

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CARBON MATERIALS IN CYCLOHEXANE CATALYTIC OXIDATION

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Oxidation reactions play a vital role in industry, as the homogeneous catalytic oxidation of cyclohexane to cyclohexanol and cyclohexanone, raw materials for the manufacturing of adipic acid and caprolactam [1]. The current industrial process requires harsh conditions and leads to very low conversions, to assure a reasonable selectivity.

Homogeneous processes present as a major drawback the difficult separation of the relatively expensive catalysts. A strategy to overcome this limitation is to support the catalyst onto a solid matrix (silicas, zeolites or carbon materials). Carbon materials present great potential as versatile catalyst supports given their easily tailored physical and chemical surface properties [2].

The use of transition metal complexes bearing tris(pyrazolyl)methanes in oxidation catalysis has attracted much interest, given their ability to act as catalysts or catalyst precursors for relevant alkane oxidation reactions [3,4]. In this work, the C-scorpionate iron(II) complex [$FeCl_2(Tpm)$] [Tpm =κ^3-$HC(C_3H_3N_2)_3$] (**1**) was immobilized on four carbon supports to produce active, selective and recyclable catalysts for the oxidation of cyclohexane.

Experimental

- Different carbon materials were used as supports of the iron complex: a commercial carbon (GL-50, Norit), and an oxidized form (GL-50 oxi), a biomass-derived activated carbon (S) [5], and an ordered mesoporous carbon (CMK-3) [6].
- The iron complex was anchored onto the different carbon supports. The materials were characterized regarding their textural and surface chemistry properties through diverse techniques (N_2 adsorption isotherms, pH_{PZC}, SEM). The iron content was assessed by ICP-MS.
- Reactions under microwave (MW) irradiation were performed in a focused Anton Paar Monowave 300 reactor fitted with a rotational system and an IR temperature detector, using 10 mL capacity cylindrical Pyrex tubes.
- The products of the reaction, cyclohexanol and cyclohexanone were analyzed by gas chromatograph with a flame ionization detector, using Shul'pin's method [7].

Results

The heterogenization efficiency ranged from 0.45 to 1.55 % of Fe content in the prepared materials. The morphology of the carbon materials with the anchored complex was examined by SEM (Figure 1). The appearance of these materials is not very different from that of the pristine samples.

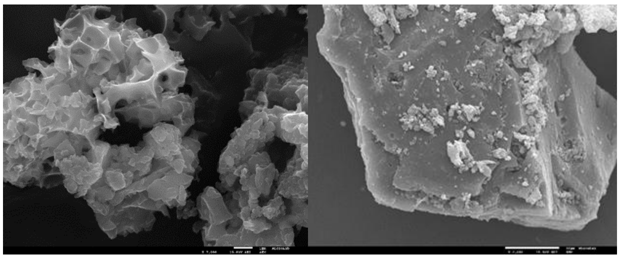

Figure 1. SEM images of: **1**@S (left), **1**@GL-50 oxi (rigth).

The results of the catalytic oxidation of cyclohexane are summarized in Table 1.

Table 1. MW-assisted oxidation of cyclohexane (2.5 mmol), in MeCN, with TBHP, 100 °C, catalyst amount (1-10 µmol), 1.5 h (selected data).

Catalyst	TON	Yield (%)
S	-	3.3
1@S	14	5.2
GL-50 oxi	-	5.6
1@GL-50 oxi	31	8.5
CMK-3	-	3.3
1@CMK-3	164	5.3
1	36	8.0

Although the total yields obtained are relatively low, on-going recycling studies point out the possibility of catalyst reuse up to, at least, five cycles, without significant loss of activity.

It is worth highlighting that the carbon nanomaterials have shown some catalytic activity in the MW-assisted oxidation of cyclohexane, that was not previously reported in the literature.

In light of these findings, complementary textural and surface chemistry analysis of the carbon materials will be performed, to gain some insights on the mechanism of cyclohexane oxidation by carbon materials.

Acknowledgements. Support for this work was provided by FCT through UID/QUI/00100/2013, PTDC/QEQ-ERQ/1648/2014 and PTDC/QEQ-QIN/3967/2014 projects. M.A. Andrade and A.S. Mestre acknowledge financial support from [BL/CQE-2017-022] and Post-doc grant (FCT) SFRH/BPD/86693/2012.

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EFFECT OF CARBON SUPPORT ON SELECTIVE HYDROGENATION BY CONCAVE PLATINUM NANOCUBES

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Wet chemical routes for the synthesis of metal nanocrystals are nowadays capable of fine controlling the nano-objects size, shape as well as chemical composition.[1,2] The possibility to control the size and shape of metal nanoparticles offers the opportunity to optimize their catalytic properties, and metal nano-objects exposing specific crystallographic facets are excellent candidates for the establishment of structure-property relationships in catalysis.[3,4]

Platinum based concave nanoparticles which possess a high density of low-coordinated atoms, steps, edges, and kinks, have recently attracted a lot of attention due to the fact that they exhibited much higher catalytic activity, selectivity, and stability mainly as fuel cell electrocatalysts.[5-7] While thermally catalysed reactions by concave nanoparticles is much less studied, recent research shows that concave nanostructures can be also interesting candidates.[8]

Here, we will present the synthesis and the catalytic performances in the selective hydrogenation of cinnamaldehyde of Pt concave nano-cubes exposing (110) facets, non-supported, and supported on silica and few layer graphene (FLG) support.

The nanocubes supported on FLG present superior activity, stability as well as selectivity towards cinnamyl alcohol.

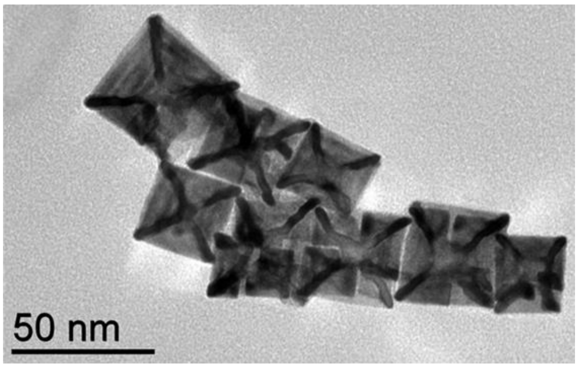

Figure 1. Non-supported concave Pt nanocubes.

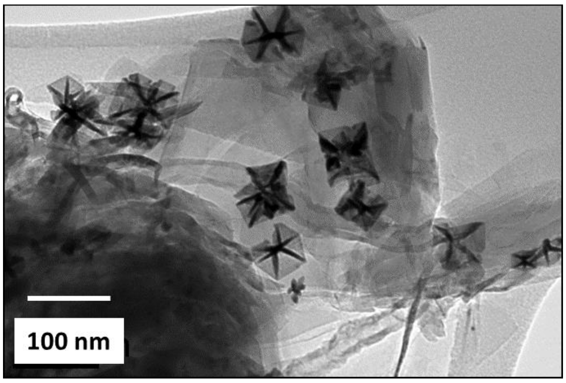

Figure 2. Concave Pt nanocubes immobilized on FLG support.

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SURFACE-MODIFIED NANOCARBONS AS METAL-FREE CATALYSTS FOR CATALYTIC OXIDATION

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Introduction

Worldwide attention was drawn to develop state-of-the-art technologies to process the toxic and hazardous organic compounds in industry wastewater. Among the techniques, advanced oxidation processes (AOPs) have been intensively investigated because the pollutants can be completely mineralized into CO_2, H_2O and harmless inorganic salts (e.g. CO_3^{2-}).[1] However, traditional Fenton reaction suffers from generation of excess sludge and strict pH requirement (~3). Moreover, metal leaching problems and the associated secondary contamination stubbornly existed in the recently reported metals/oxides and persulfates based heterogeneous systems.[2, 3]

We discovered that nanocarbons (such as active carbon, graphene, carbon nanotubes, and nanodiamond) could be employed as green catalysts for persulfate activation and pollutants degradation.[4-6] The metal-free system has presented a promising potential in practical environmental remediation. In this study, the nanocarbons will be further modified by chemical or physical approaches which would dramatically enhance the catalytic activities towards AOPs.

Methodology

The as-made carbon materials were characterized by XRD, Raman, HRTEM, XPS, etc. and evaluated in phenol, 2,4-dichlorophenol, and dyes solution by activation of peroxymonosulfate (PMS). Electron paramagnetic resonance (EPR) was employed to probe the radical revolution on nanocarbons and various scavengers were used to probe the occurrence of nonradical pathway. Besides, density functional theory (DFT) calculations was performed to investigate the electronic states of surface-tailored carbons and the catalytic processes.

Results and Discussions

We synthesized sulfur and nitrogen co-doped graphene (S-N-G) via a one-pot approach from green organic compounds as sulfur and nitrogen precursors and graphene oxide (GO) as carbon source.[7] As illustrated in **Figure 1**, the S- N- co-doping can impressively promote the catalytic activity than pristine graphene and S (or N) sole doped graphene for catalytic phenol decomposition. In situ EPR technology directly evidenced the generation of massive reactive oxygen species during the catalytic oxidation. Interestingly, increasing the sulfur amount in a certain range can improve the catalytic performance of phenol oxidative decomposition, yet the synergistic effect would be weakened when superabundant sulfur atoms were introduced into the N-graphene framework. This has been further verified by the theoretical calculations that the incorporating a sulfur atom into the carbon lattice of N-graphene leads to a larger positively charged areas with more catalytic sites to facilitate the adsorption of HSO_5^- and break up peroxide O-O bond in PMS activation.

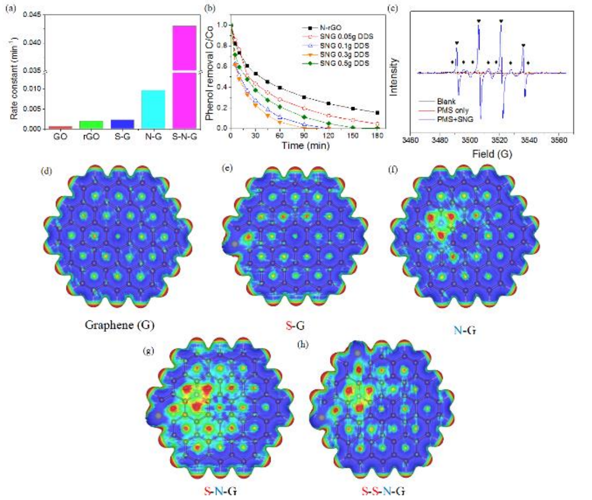

Figure 1. (a) Rate constants of phenol oxidation on different carbocatalysts; (b) impacts of sulfur precursor loading; (c) EPR spectra of SNG/PMS system; electrostatic potential distribution of (d) Graphene, (e) S-G, (f) N-G, (g) S-N-G, (h) S-S-N-G.

Conclusion

We developed an advanced strategy to utilize green precursors to synthesize S-, N- co-doped graphene. The surface modification with dual alien atoms of graphene can significantly enhance the catalytic activity for peroxymonosulfate activation and phenol oxidation. More importantly, the radical trapping and quenching tests illustrated that both sulfate and hydroxyl radicals were involved in the metal-free oxidation. This study deepens mechanisms into carbocatalysis and provides a promising system for green remediation of organic contaminants in water.

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MODIFIED CARBIDE-DERIVED CARBONS USED IN THE CATALYTIC WET PEROXIDE OXIDATION OF OILY WASTEWATERS

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Modified carbide-derived carbon (CDC) materials, prepared from TiC, were tested as catalysts in the decomposition of H_2O_2 and in the catalytic wet peroxide oxidation (CWPO) of 4-nitrophenol (4-NP), either in aqueous phase or in biphasic medium. The reactive extraction of Ti from the metal carbide (2 µm) was carried out to prepare the CDC materials, as described elsewhere [1]. Briefly, 0.03 $m\ s^{-1}$ Cl_2 gas was used (1.5 mol m^{-3} in He) as extraction agent during 5 h at 800, 1000 and 1200 ºC. Afterwards, H_2 was used for 0.5 h at the extraction temperature to remove residual chlorine, resulting in CDC-800, CDC-1000 and CDC-1200 materials, respectively. Additionally, CDC-800 was treated with a mixture of 98% H_2SO_4 and 30% w/v H_2O_2 (3:1) at room temperature for 3 h by two methods: (1) wetting the material in the oxidative solution and (2) oxidizing the material partially encapsulated with WAX paraffin, resulting in CDC-800-Ox and CDC-800-Wax, respectively. Firstly, the materials were tested in the decomposition of H_2O_2 and, then, in the adsorption and CWPO of 4-NP, adapting the experimental procedure described in previous works [2-3] at the following operating conditions: 25-50 ºC, $pH_0 = 3.0$, and concentrations of solid material, 4-NP and H_2O_2 of 2.5 g/L, 5.0 g/L and 17.8 g/L, respectively. Cyclohexane, *c*-C_6 (O/W volume ratio = 1:5) was used to simulate oily wastewater and study the influence of the oil phase presence in the medium.

The materials were characterized by temperature-programmed desorption and water contact angle measurements in order to determine the content of oxygen surface groups (OSGs) and the hydrophobic character. CDC-800, CDC-1000 and CDC-1200 materials showed a negligible oxygen content and a remarkable hydrophobic character (contact angle ca. 145º) when compared with other materials [3]. Functionalization of CDC-800 allows the incorporation of OSGs and the decrement of its hydrophobicity.

The results obtained for the decomposition of H_2O_2 in 4 h, adsorption and CWPO of 4-NP are depicted in Figure 1. Non-functionalized CDC materials showed a high catalytic activity in the decomposition of H_2O_2, when compared with other carbonaceous solids [2], and a significant increase of the H_2O_2 conversion was found when temperature was increased (Fig. 1-A). However, the presence of *c*-C_6 strongly affected the catalytic activity of the materials, decreasing substantially the conversion of H_2O_2 and restricting their use when an oil phase is present in effluents (oily wastewaters). That was ascribed to the hydrophobic character of the catalysts that lead to migration of the carbon materials to the oil phase (Fig. 1-B). The oxidized samples, CDC-800-Ox and CDC-800-Wax, showed lower catalytic activity in H_2O_2 decomposition and 4-NP adsorption (Fig. 1-C) when compared to non-functionalized samples. The negligible adsorption can be ascribed to the functionalization of the surface that can block the access to the pores of the material. However, the removal of 4-NP by CWPO was higher when using oxidized samples (subtracting adsorption contribution) and the efficiency of H_2O_2 consumption (measured as converted 4-NP moles per consumed H_2O_2 moles) obtained was increased by using those materials. In addition, the asymmetric functionalized sample prepared by selective superficial oxidation (CDC-800-Wax) is capable of stabilizing a Pickering emulsion of *c*-C6-water that is essential to maximize the interfacial area in the treatment of oily wastewaters.

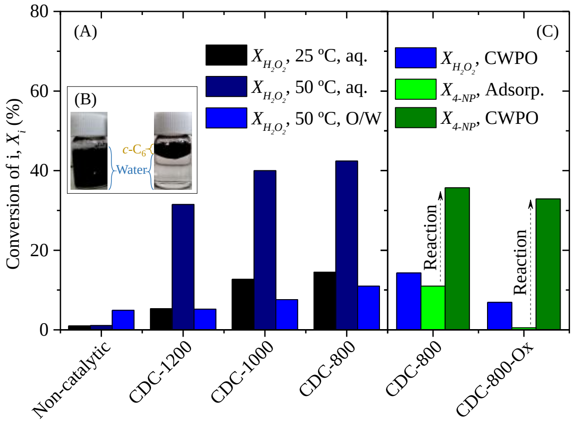

Figure 1. (A) Decomposition of H_2O_2 at 4 h, (B) photographs of CDC-800 dispersion in aqueous phase and in the water-*c*-C_6 mixture and (C) adsorption and CWPO of 4-NP at 50 ºC after 4 h.

Acknowledgements. This work is a result of project "AIProcMat@N2020 - Advanced Industrial Processes and Materials for a Sustainable Northern Region of Portugal 2020", with the reference NORTE-01-0145-FEDER-000006, supported by NORTE 2020, under the Portugal 2020 Partnership Agreement, through FEDER and of Project POCI-01-0145-FEDER-006984 – Associate Laboratory LSRE-LCM funded by FEDER through COMPETE2020 - POCI – and by national funds through FCT. M. Munoz thanks the Spanish MINECO for the Ramón y Cajal postdoctoral contract (RYC-2016-20648).

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HIGHLY NITROGEN-SELECTIVE Pt-In/C CATALYSTS IN THE REDUCTION OF NITRITES IN WATER

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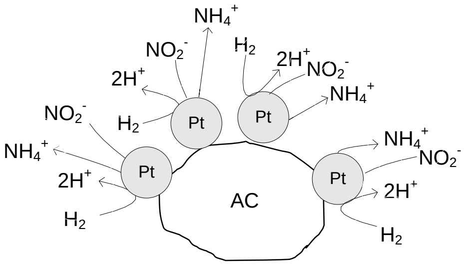
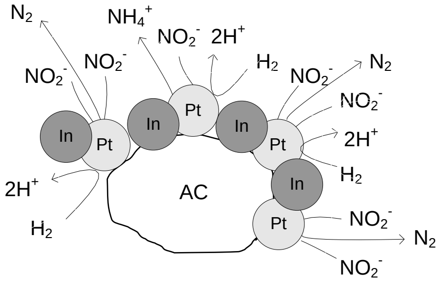
The removal of nitrate from drinking water is necessary in order to protect the environment and human health. The technologies for nitrate removal are usually more complex and more expensive than those required for microbial control. Nevertheless, the increasing pollution of natural sources of drinking water encourages the development of new emerging technologies and processes for water remediation. The catalytic reduction with hydrogen over a solid catalyst is a promising technique for the nitrate/nitrite removal. The main drawback of this process is the formation of ammonia as by-product, which is undesirable in drinking water. Nitrate reduction can be described by a series of consecutive and parallel reactions where nitrate is reduced to nitrite in the presence of hydrogen, which is then converted to nitrogen as main product and ammonia as undesired by-product. The nitrite reduction seems to play an important role in the process selectivity. Only a few research works have been published on the reduction of nitrite in water, and most of the work done in this area is related to nitrate reduction.

The catalytic reduction of nitrites over Pt-In catalysts supported on activated carbon has been studied in a semi-batch reactor, at room temperature and atmospheric pressure, and using hydrogen as the reducing agent. The influence of the indium content on the activity and selectivity was evaluated. Monometallic Pt catalysts are very active for nitrite reduction, but the addition of up to 1 wt.% of indium increases significantly the nitrogen selectivity from 0 to 96%.

We have characterized the materials by a large number of techniques, as XPS, TPR etc., and with all these results in hand we have found that the increase of the indium content up to 1 wt.% significantly increases the selectivity to nitrogen due to the decrease of the accessible surface noble metal atoms and the modification of the electronic properties of both the noble metal and the promoter. For higher In loadings the nitrite conversion significantly decreases. In the bimetallic catalysts, indium and platinum metal particles are interacting and forming alloy phases that favour the combination of nitrogen-containing intermediates to produce N_2 instead of being deeply hydrogenated into ammonium. The nitrogen selectivity increases with the decrease of the available hydrogen on the catalyst surface, which is achieved using high In loadings. The calcination and reduction temperatures play an important role in the activity, although they do not have an important effect on the nitrogen selectivity.



Scheme 1. Scheme of nitrite reduction over the monometallic Pt catalyst.



Scheme 2. Scheme of nitrite reduction over the bimetallic Pt-In catalysts.

Acknowledgments

This work is a result of project “AIProcMat@N2020 - Advanced Industrial Processes and Materials for a Sustainable Northern Region of Portugal 2020”, with the reference NORTE-01-0145-FEDER-000006, supported by Norte Portugal Regional Operational Programme (NORTE 2020), under the Portugal 2020 Partnership Agreement, through the European Regional Development Fund (ERDF) and of Project POCI-01-0145-FEDER-006984 – Associate Laboratory LSRE-LCM funded by ERDF through COMPETE2020 - Programa Operacional Competitividade e Internacionalização (POCI) – and by national funds through FCT - Fundação para a Ciência e a Tecnologia and Acção Integrada Luso-Espanhola n.º E31/08 – HP2007-0106.

Financial support from Generalitat Valenciana (project PROMETEOII/2014/004) and MINECO (Project MAT2016-80285-P) is gratefully acknowledged. EVRF also thanks MINECO for his Ramon y Cajal fellow RYC-2012-11427 and the following project MAT2016-81732-ERC.

SHORT ORAL COMMUNICATIONS

(SOC)

CONFINEMENT OF IRON AND PROMOTERS IN CARBON NANOTUBES FOR DIRECT SELECTIVE SYNTHESIS OF LOWER OLEFINS FROM SYNGAS OVER Bi AND Pb PROMOTED IRON CATALYSTS

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Lower olefins (C_2-$C_4^=$) are key building blocks in the chemical industry. Light olefins are mainly produced from steam cracking of naphtha or ethane cracking. Fischer-Tropsch to Olefins (FTO) is a key process for the direct transformation of renewable and alternative carbon feedstocks into lower olefins via syngas [1]. However, the selectivity of lower olefins remains a major challenge because of broad Anderson-Schulz-Flory (ASF) distribution of the hydrocarbons produced in Fischer-Tropsch synthesis [2].

Use of carbon nanotubes (CNT) as catalytic supports for iron Fischer-Tropsch catalysts has several important advantages. Different to commonly used oxide supports, carbon does not form inert mixed compounds between iron and supports (e.g. iron silicate or aluminate) which are difficult to reduce and to carbidize during the catalyst activation and reaction. Higher extent of iron carbidisation can obtained on CNTs compared to the oxide supports. Iron confinement in CNTs has been studied in low temperature Fischer-Tropsch synthesis, the iron inside the CNT tubes has higher reducibility and facile formation of the more active iron carbide phase compared with iron outside the CNT channels. The resulting catalysts showed enhanced activity in syngas conversion [3-4] towards the C_{5+} hydrocarbons. Very few papers focused on the confinement of iron and promoters for selective synthesis of lower olefins from syngas.

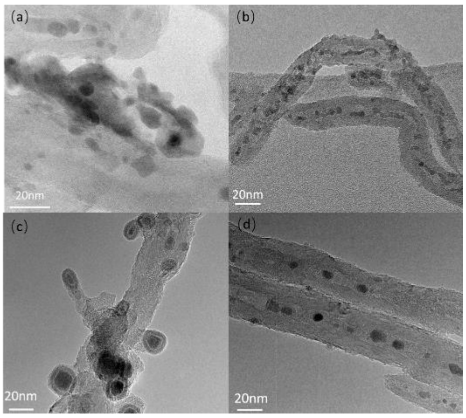

Figure 1. TEM figures of the fresh and used catalysts. (a) Fe/CNT-out-fresh, (b) Fe/CNT-in-fresh, (c) Fe/CNT-out-used, (d) Fe/CNT-in-used.

The present work focuses on the confinement effect in CNTs in the Bi and Pb promoted iron catalysts for direct lower olefin synthesis in high temperature Fischer-Tropsch synthesis. Recently a major effect of promotion with Bi and Pb was uncovered [2] for silica supported iron Fischer-Tropsch catalysts. Interestingly, the present work suggests that the promoting effect of Bi and Pb is much significant for the encapsulated iron catalysts. The iron time yield is as much high as $8.3*10^{-4}$ $mol_{CO}g^{-1}s^{-1}$ for the FePb/CNT-in catalysts which is one of the best results for the iron-based Fischer-Tropsch synthesis catalysts available so far in the literature. Importantly and differently to the previously studied catalysts, over the optimised catalysts, direct olefin synthesis from syngas occurs with a very high yield even at under atmospheric pressure. The best results have been obtained for the promoted encapsulated iron catalysts under atmosphere pressure with a major (>10 times compared with Fe/CNT-out) increase in FTO reaction rate (CO conversion at 25-40%) and selectivity to the C_2-C_4 olefins (up to 56%-65%). Moreover, the encapsulated iron catalysts showed significantly better stability compared to the conventional iron catalysts.

A combination of characterization techniques (TEM-EDX, XPS, XRD, TPR, SSITKA) reveals high extent of encapsulation of iron particles in CNTs, which reduces their sintering during the reaction and thus then improving stability. The iron species encapsulated inside CNTs tend to form more iron carbides under the reaction conditions. Higher extent of iron carbidisation is essential for higher Fischer-Tropsch activity. Iron encapsulation inside CNTs results a 10 times higher yield of lower olefins. The promoting effects and intimate contact of bismuth and lead inside the CNT channels are crucial for obtaining higher catalyst productivity. The lower melting points and high mobility of these two metal promoters during the catalyst activation result in their migration inside CNTs during catalysts activation and reaction. Isotope and transient kinetic experiments suggest that carbon monoxide dissociation on the promoted catalysts is facilitated by oxygen scavenging from iron carbide to the promoters.

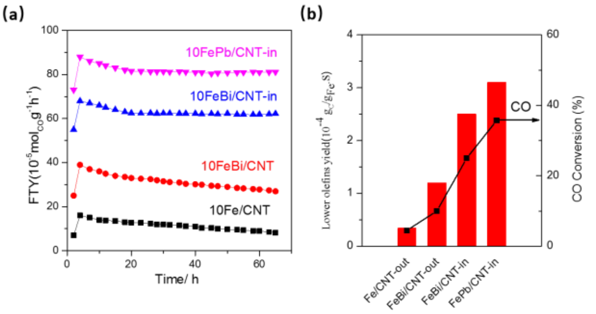

Figure 2. Iron time yield (FTY) vs time on stream of iron outside and inside CNT catalysts at 10bar, $H_2/CO = 1$, T = 350 ºC. (b) CO conversion and lower olefins yield at 1bar, $H_2/CO = 1$, T = 350 ºC.

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MANGANESE PROMOTER EFFECTS IN CARBON-SUPPORTED COPPER-BASED ESTER HYDROGENATION CATALYSIS

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Introduction

Catalytic ester hydrogenation is an important industrial process for the bulk production of various alcohols. Examples of particular current interest include the formation of ethylene glycol, methanol and ethanol as versatile platform chemicals. Copper-based catalysts are widely applied for these hydrogenation reactions. Addition of promoters is often crucial to enhance catalytic activity, selectivity and stability. Promoters may induce structural and electronic effects or create a new type of active sites.[1] Manganese oxide (MnO$_x$) is proposed as a more environmentally-friendly replacement for the widely used chromium promoter.[2] However, the MnO$_x$ promoter effects are not yet fully understood.

In this project, we study the MnO$_x$ promoter effects for Cu-based hydrogenation catalysis. A strong tool is the use of inert graphitic carbon supports, which have a tunable surface chemistry and a weak interaction with the active metals, facilitating characterization and fundamental studies.[3] We present the preparation of well-defined CuMnO$_x$ nanoparticles on carbon supports, with various amounts of promoter and are currently evaluating their performance in the catalyst hydrogenation of ethyl acetate to ethanol.

Experimental

CuMnO$_x$ nanoparticles were deposited using co-impregnation of the graphitic carbon support (~ 500 nm^2 g^{-1} BET surface area, ~ 0.7 mL g-1 total pore volume) with a mixed aqueous solution of Cu(NO$_3$)$_2$ and Mn(NO$_3$)$_2$, followed by drying and heat treatment under H$_2$-containing flow to 400 °C. Catalysts were mainly characterized by (scanning) transmission electron microscopy ((S)TEM), energy-dispersive X-ray spectroscopy (EDX) and temperature-programmed reduction (TPR). The performance of the CuMnO$_x$ catalysts is being investigated for the gas-phase hydrogenation of ethyl acetate to ethanol, at 30 barg reaction pressure and 180–210 °C reaction temperature.

Results and discussion

A method was developed to prepare highly dispersed, well-defined CuMnO$_x$ nanoparticles using facile and scalable co-impregnation of the graphitic carbon supports with the mixed metal precursor aqueous solution, followed by drying and thermal treatment to decompose the metal precursors (Fig. 1 A). With constant Cu loading and increasing Mn loadings, we achieved similar CuMnO$_x$ nanoparticle sizes over a wide range of Mn concentrations (Fig. 1 B). Analyses by TPR and STEM-EDX indicate close contact between Cu and MnO$_x$, essential to efficiently induce the promoter effects (Fig. 1C).

The influence of MnO$_x$ promoter concentrations is currently being investigated for the catalytic hydrogenation of ethyl acetate to ethanol. Preliminary results showed a strong effect of increasing Mn concentrations upon catalytic performance. The nature of the MnO$_x$ promotor effects for activity and stability over time for this important hydrogenation reaction will be presented at the conference.

Conclusions

Well-defined and highly dispersed carbon-supported CuMnO$_x$ nanoparticles were prepared via a facile impregnation method. The Mn loading could be varied over a wide range, for the same final CuMnO$_x$ particle size. The correlation between Mn concentration and catalytic activity is currently being studied. Using carbon as an inert support allows us to further study the promoter effects on the nanometre scale. These findings may contribute to implementing MnO$_x$ as an efficient promoter for a range of different hydrogenation reactions.

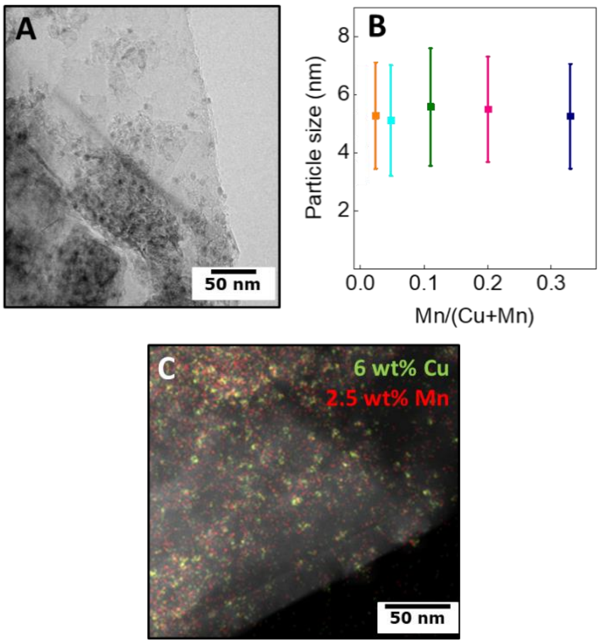

Figure 1. (**A**) TEM image of well-defined CuMnO$_x$ nanoparticles; (**B**) Particle size distribution from TEM analysis of Cu-based catalysts with increasing Mn promoter concentrations; (**C**) STEM-EDX image of Cu (green) and Mn (red) distributions on carbon.

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HIGHLY SELECTIVE CONVERSION OF METHANOL TO PROPYLENE: DESIGN OF A MFI ZEOLITE WITH SELECTIVE-BLOCKAGE OF (010) SURFACES

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Methanol-to-propylene (MTP) is one of the most important processes in modern chemical industry. ZSM-5 is widely used in MTP process, and its anisotropy of diffusion path lead to a varied product distribution. The diffusion of aromatics products results in a lower olefin selectivity. Herein, for the first time, we designed a surface-specific silica deposition method to selectively block straight channels. The surface-specific coated sample shows a significantly lower aromatic selectivity (3%) compared to non-specific coated counterpart (12%), and paraffin selectivity is also suppressed. This study provide new methodology for zeolite structure construction and will be greatly beneficial to industrial MTP process.

As one of a 10-membered ring zeolite, a larger pore opening of ZSM-5 can lead to a lower selectivity for ethylene and propylene, as well as a higher selectivity of aromatic species as compared to SAPO-34. According to the mass balance, as the formation of one aromatic molecule are accompanied by the formation of three alkane molecules, a high aromatics selectivity leads to a high of paraffin selectivity, resulting in a loss of olefin selectivity. Aromatics and paraffin, as by-products, are not only less-valuable but also influence the cycling of C4-C8 olefins.

The diffusion of aromatics products (benzene, toluene and para-xylene (PX)) out of MFI zeolite are not through sinusoidal channel, but through the straight channels.[1] So, blocking straight channels without affecting sinusoidal ones is speculated to prevent the generation of aromatics products, thereby improving the performance of the MTO reaction. In previous literature, much work has been done on surface modification of ZSM-5 to improve the product selectivity in relevant methanol conversion process. For example, in methanol-to-aromatics (MTA) reaction, by removing the surface acid sites, isomerization reaction of xylene can be effectively suppressed.[2] However, surface-selective modification can barely be achieved, facing difficulties in orientation. Recently, we found that during the MTA reaction, the (100) surfaces of spent Zn/ZSM-5 was covered with a thick coke layer, which blocked the sinusoidal channels of ZSM-5 and prevented the diffusion of paraffin and olefin out of zeolite channels, while the coke on (010) surfaces was much smaller, leading to ultrahigh aromatic selectivity (>98%).[3] Here, based on this interesting phenomenon, we designed a silica deposition process, which can block straight pores without affecting sinusoidal channels on ZSM-5 crystals. By trapping carbon catalysis species inside the zeolite channels, the selectivity of both aromatics and paraffin were significantly suppressed, and the olefin selectivity would be greatly benefited.

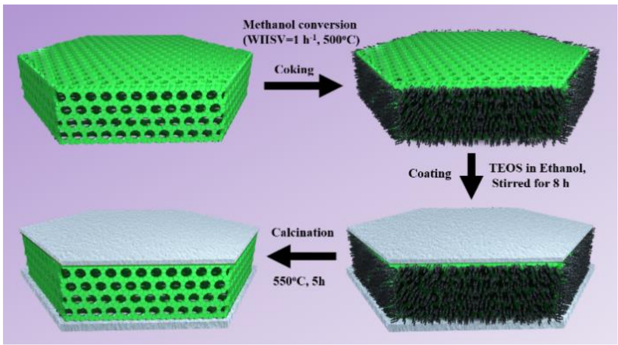

Figure 1. Designed scheme of silica deposition process.

Figure 1 gives the scheme of selective blockage. Figure 2 lists the catalysis performance. We can notice that by selective blockage of (010) surface of nano ZSM-5, the aromatics selectivity would be suppressed to less than 3%, comparing with 12% of pristine result.
The lifetime of as-synthesized catalyst keeps over 200 h, showing its possibility for industrial application.

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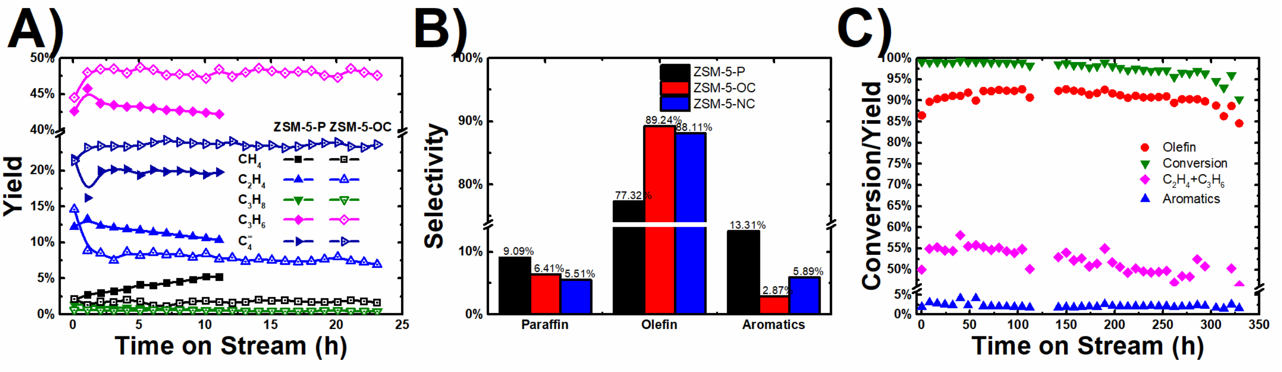

Figure 2. Comparison of catalytic performance of various ZSM-5 catalysts in the MTO reaction. A) Carbon-based yield of different species (methanol conversion keeps at 100%), B) olefins, aromatics and paraffin selectivity, (TOS=9 h) C) Lifetime test of ZSM-5-OC (WHSV=1 h^{-1}, reaction temperature: 500°C, N_2 flow rate is 30 SCCM).

HYDRODEOXYGENATION OF VANILLIN OVER CARBON SUPPORTED NOBLE METAL CATALYSTS

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Introduction

The production of hydrocarbon fuels from biomass is a next major challenge in the effort to develop advanced biofuels, and the thermolysis of lignocellulosic biomass has attracted significant attention in the last decade and appears to be a practical method to produce bio-oils. In order to produce petroleum-like hydrocarbon fuels, the oxygen atoms in bio-oils must be removed. For that purpose, the catalytic hydrodeoxygenation (HDO) reaction is a very promising route. Recently, special efforts have been focused on water-phase HDO reactions because bio-oil contains a large amount of water (15–30 wt%) and water soluble components. It has been reported that a wide range of biomass compounds such as phenol, sorbitol and anisole can be hydrodeoxygenated selectively in water over supported noble metal (e.g. Ru, Pt and Pd) catalysts, their catalytic performances depending on the nature of both the metal and the support. Due to the reaction is carried out in an aqueous phase, the hydrophilic character of the support plays a fundamental role. In the particular case of the aqueous phase HDO of vanillin, it has been reported that palladium-based catalysts supported on hydrophilic carbon present excellent activity and selectivity toward p-creosol **[1]**. In this work, we evaluate the effect of the nature of the noble metal (Ru, Pd, Au and Rh) dispersed on a commercial hydrophilic charcoal in the mentioned reaction.

Experimental

A hydrophilic charcoal DARCO® was used as a support. Catalysts were prepared by wetness impregnation with acetone and aqueous solutions of ruthenium (III) nitrosyl nitrate (Johnson Matthey; purity = 14.34%), rhodium (III) nitrate (Johnson Matthey; purity = 12.43%) and palladium (II) acetate (Johnson Matthey; purity = 47.14%). Because of a difficulty of obtaining small gold particle sizes by wetness impregnation, the gold catalyst was prepared by colloidal synthesis. Chloroauric acid, $HAuCl_4$ (Johnson Matthey, purity = 49.81%) was used as a gold precursor. In all cases, the catalysts were synthetized with a nominal value of the noble metal of 2% (wt.%).

All solids were characterized by means of nitrogen physisorption, XRD, SEM and TEM microscopies, ICP, Elemental analysis, XPS and DRIFTS.

Catalytic activity in HDO was tested in a Parr reactor at 30 bars and 100°C during 3 h, with 100 mL of 1 mg/mL vanillin solution and 50 mg of catalyst. Vanillin and products concentrations were determined by HPLC and the activity was expressed through vanillin conversion (%).

Results and discussions

In all cases, the catalysts exhibit an average noble metal particle size below 10 nm with a metal loading close to the nominal one (2%) (**Table 1**).

Table 1. Catalyst metal loading, mean particle size and dispersion.

Noble Metal	TEM particle size (nm)	% Metal [ICP]	Calculated Dispersion (%)
Gold	6.0 ± 1.1	1.96	22
Palladium	3.9 ± 1	2.94	34
Rhodium	7.9 ± 2.5	1.39	19
Ruthenium	2.6 ± 0.5	2.05	17

Dispersion of the active phase was calculated from TEM observations, assuming cuboctahedra particles and the metal loading determined by ICP analysis.

Similar textural properties were found for all catalyst, indicating that the synthesis method did not influence the textural properties of the commercial support. Isotherms of type IV characteristics of mesoporous catalysts were found, with an average pore diameter of 4 nm.

Evolution of vanillin conversion and the selectivity towards the target product (p-creosol) with reaction time at 100°C is shown in **Figure 1**. As the reaction proceeds, the content of vanillin alcohol begins to decrease with a corresponding increase in p-creosol, **Fig. 1b**. The concentration of p-creosol increases gradually, implying that vanillyl alcohol is an intermediate product and subsequently it is consumed by hydrogenolysis to form p-creosol **[2]**. Compared with vanillin alcohol, p-creosol is more valuable as a biofuel.

After 3 hours, vanillin was completely consumed for all catalysts tested (Ru, Pd, Au and Rh) and p-creosol selectivity of 40% was achieved for every catalyst except palladium which exhibitied selectivity higher than 90% at 100°C.

In conclusion, effective catalytic hydrodeoxygenation of vanillin to p-creosol under mild reaction conditions has been realized using catalysts based on different noble metal nanoparticles supported on activated commercial charcoal. According to the catalytic results, palladium is shown as the most active one. Moreover, palladium supported catalyst is also the most selective towards the p-creosol.

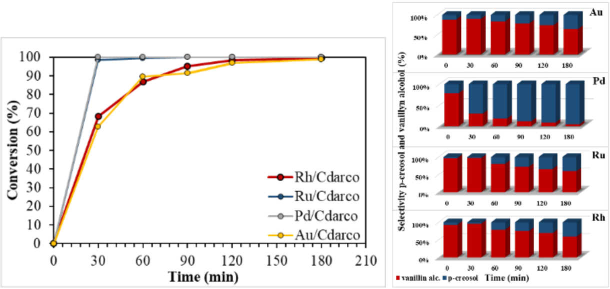

Figure 1. Conversion of vanillin **(a)** and p-creosol selectivity **(b)** for the catalysts evaluated (T=100°C, P=30 bar, 50 mg catalyst, 100 mL, 100 mg vanillin).

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TRACKING THE PATHS FOR THE SUCROSE TRANSFORMATIONS OVER BIFUNCTIONAL Ru-POM/AC CATALYSTS

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The application of heterogeneous catalysis in the synthesis of platform molecules from biomass raw materials is one of the most attention focus over last few years[1]. 1,2-propanediol (PDO) is one of the platform molecules with high added value in chemical industry, and in this way, recently, studies about propylene glycol or PDO synthesis have been reported[2]. Particularly, transformation of sugars into PDO has been studied using bifunctional catalytic sites[3]. Herein we report a study about transformation of sugars (sucrose, glucose and fructose) to PDO aiming to determine possible pathways for these reactions using a new bifunctional acid-metallic catalyst. The series of catalysts here presented were synthetized using a high purity activated carbon as support, and polyoxometalates (POMs) and ruthenium nanoparticles as active phases. Notice that these transformations involve different steps, first the sugar is hydrogenated to sorbitol or mannitol and secondly hydrogenolysis yielding glycerol and later PDO take place[4].

In the preparation of catalysts two POMs have been used: STA ($H_4[W_{12}SiO_{40}]$), TPA ($H_3PW_{12}O_{40}$). Once the activated carbon support is impregnated (incipient wetness method) with POMs and/or with the Ru precursor ($RuCl_3 \cdot xH_2O$) solutions, the material was dried at 373 K. Prior to the catalytic tests the catalysts were reduced at 623 K for 1 h under H_2 flow. Techniques such as, X-rays diffraction (XRD) and transmission electron microscopy (TEM-EDX) were used to characterize these bifunctional catalysts. The catalytic tests were carried out in a batch reactor at 140 ºC and 30 bar of H_2, using a mixture of ethanol and water (9:1) as solvent. A load with 15% of POM mass versus sugar mass and various percent of Ru mass were employed. Products were analyzed by liquid chromatography (Agilent, HPLC, Hi-plex H column, index refraction detector).

Table 1 shows some of the catalytic results. When sucrose is the reactant non interest products are obtained over the monofunctional STA/AC acid catalyst. However, some conversion is observed to dehydration products. Therefore a metallic ingredient over the catalyst surfaces is compulsory. Thus, monofunctional ruthenium (Ru/AC) and bifunctional (Ru-STA/AC) catalysts have been comparatively tested. If a load of 2% Ru and/or 15% STA mass versus sugar mass is in the reactor, sorbitol is the main product with the monometallic catalyst (Ru/AC) while hydrogenolysis products, glycerol and 1,2 PDO, are formed with the bifunctional catalyst. So, for obtaining 1,2 PDO is necessary the cooperative action of metallic and acid catalytic sites. From selectivity values reported in Table 1 is evident that other compounds (such as humic acids) have been also produced. Subsequently in order to understand the different reaction pathways we have studied fructose or glucose as reactants.

Table 1. Sucrose conversions and yields to interest products using different mono and bifunctional catalysts in EtOH/H_2O.

	Conv Glucose	**Conv. Fru.**	**Sorbitol/ Mannitol**	**Glycerol**	**PDO**
STA/AC	40	50	0	0	0
Ru/ AC	80	77	40	2	1
Ru-STA/AC	83	94	10	20	23
Ru-STA/AC[a]	-	96	5	28	52
Ru-STA/AC[b]	80	-	30	2	3

[a]: Fructose as reactant [b]: Glucose as reactant

In Table 1 we can also see for the bifunctional catalyst that if glucose is the reactant sorbitol is obtained while the fructose is transformed into PDO with a yield around 50% under our experimental conditions. Therefore, in the next sequence of experiments we have compared the fructose catalytic reactivity of the bifunctional catalyst and that of a physic mixture of the monofunctional catalysts (STA/AC and Ru/AC). In Figure 1 are shown all these results in terms of product yields. It is evident that the efficient catalyst has to contain acid surface sites and metallic particles in the close proximity at nanometric scale (as observed by TEM). The requirement of two catalytic functions to increase the PDO yield can be raised. Also two Ru-AC samples, with different metallic load (2% and 4%) were tested and the results presented in Figure 1. It is noteworthy the high mannitol selectivity obtained using monofuctional metallic catalyst. Moreover, mannitol selectivity goes up when the relation metal/fructose is increased, which means that over Ru-AC catalyst, the preferential path is fructose hydrogenation (1). Contrarily, only glycerol and PDO are observed using bifunctional catalysts (see scheme of Fig.1), so now the reaction follows the second possible path (2)

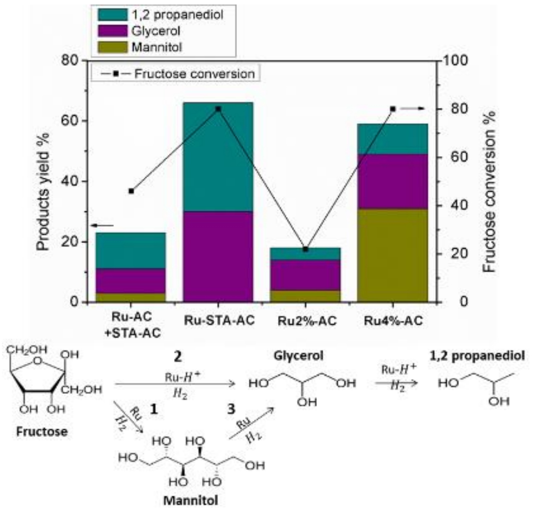

Figure 1. Products yields of each catalyst and its fructose conversion at 5h of reaction. Possible transformation pathways of fructose to glycerol and PDO.

In conclusion, using a new bifunctional metallic-acid catalyst (Ru-STA-AC) and fructose as reactant, the best results for 1,2 PDO synthesis are achieved. In addition, as it was mentioned above, the reaction needs a nanometric space between both functionalities of catalyst to follow a direct pathway from fructose to glycerol and PDO (2).

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TAILORING THE CATALYTIC PROPERTIES OF Mo_2C/CNF CATALYSTS FOR THE HDO OF GUAIACOL: INFLUENCE OF CARBURIZATION TIME

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The development of renewable resources to replace fossil fuels has focussed on the bio-oils obtained from lignocellulosic biomass pyrolysis. Nevertheless, bio-oils have some undesirable properties such as low heating value, low volatility and high viscosity derived from their high oxygen content, which should be improved. Catalytic Hydrodeoxygenation (HDO) allows to remove oxygenated groups from bio-oils in form of water under a high pressure H_2 atmosphere. Conventional catalysts used for the HDO reaction, based on CoMo and NiMo sulphides, have some disadvantages such as deactivation and product contamination with sulphur. On the other hand, noble metal catalysts show high activities and selectivities, although their high cost hampers their commercial use. Transition metal carbides catalysts, particularly Mo_2C, have recently received increased attention as they are effective catalysts in the HDO of lignin-derived molecules [1].

In this work, Mo_2C catalysts were synthetized by carburization of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ deposited over carbon nanofibers (CNF) by incipient wetness impregnation (Mo = 10 wt. %). The carburization process was performed in a fixed bed reactor using CNF as carbon source. The carburization temperature was raised up to 750 ºC (10 ºC/min), under a 100 ml/min H_2 flow, and then hold at this temperature for different carburization times (1, 2, 4 and 6 h). As-produced catalysts were characterized by XRD, XPS, ICP-OES and STEM. Subsequently, catalysts were evaluated in the guaiacol HDO using a batch autoclave reactor at mild conditions of temperature and pressure (300 ºC and 20 bar of H_2, respectively). After 2 hours of reaction, the liquid phase were identified and measured by gas chromatography (GC).

The characterization results of the fresh catalysts are summarized in Table 1. In all cases, XRD analysis showed the complete carburization of the Mo precursor into Mo_2C since no MoO_2 signal was detected. XRD patterns (Fig. not shown) clearly revealed the influence of the carburization time on the crystallinity of the catalysts; thus, larger Mo_2C crystal sizes and lower graphite peak intensities were obtained as the carburization time was increased. The latter is associated to the catalytic gasification of the CNF by the Mo_2C particles formed, which is more pronounced at longer carburization times. In line with this, Mo content measured by ICP increased as the carburization time did. In addition, XPS showed the same trend between the surface Mo content and carburization time.

Table 1. Characterization results and conversions in the HDO reaction of the catalyst carburized at different times

Carb. Time (h)	Mo_2C nm (XRD)	Mo at. % (XPS)	Mo wt. % (ICP)	Conv. % (GC)
1	6.50	2.01	11.5	34.5
2	10.32	2.76	14.0	72.0
4	12.35	3.32	17.0	56.7
6	14.72	10.35	27.0	72.3

Guaiacol conversion (Conv. in Table 1) increased from 34.5 % at 1 h to values ranging from 56.7 to 72.3 % at larger carburization times. However, when these values (and the corresponding yields to the different HDO products) are expressed as TOF (Figure 1), the catalyst carburized for 2 hours presented the best behaviour. The products obtained were classified according to the chemical transformation of guaiacol: HDO products (hydrodeoxygenation route: phenol, anisole and cyclohexane/benzene) and MET products (methylation route: xylenol, chatecol and cresol). Soluble higher molecular weight products that cannot be detected by GC were calculated by difference (labelled as "others").

Focusing on the catalysts carburized for 1 hour, low conversion was obtained in contrast to a high TOF to desired products, mainly phenol and cyclohexane/benzene. Xylenol was also identified as intermediate product in addition to a negligible amount of heavier compounds. For the catalyst carburized for 2 hours, an increase in conversion and higher TOF of HDO products, mainly cyclohexane/benzene, were observed. However, the amount of "Others" increased dramatically. Finally, the results of the catalysts carburized at 4 and 6 h showed lower TOF of HDO and MET products, and the amount of heavy compounds were also relevant.

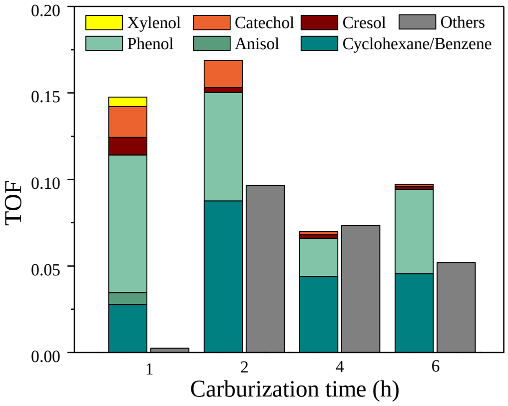

Figure 1. TOF of the main products in the HDO of guaiacol calculated as mmol of product/(h·mmol of Mo_2C).

In conclusion, larger Mo_2C crystal sizes and higher Mo contents were achieved after longer carburization times, as expenses of the gasification of the CNF support. In all cases, HDO products were obtained in higher proportions than MET products. The catalyst carburized during 1 hour showed phenol as the main product but relatively low conversion. 2 hours-carburized catalyst showed the best results in terms of conversion and TOF of cyclohexane and benzene, but also entailing high production of heavy compounds. This fact could be improved by either lowering the reaction time or increasing the reaction temperature. Longer carburization times (4 and 6 hours) showed much worse catalytic performance, evidencing the importance of the presence of the CNF support, as it will be evidenced by the STEM study.

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Au NANOPARTICLE SIZE CONTROL OVER FEW LAYER GRAPHENES

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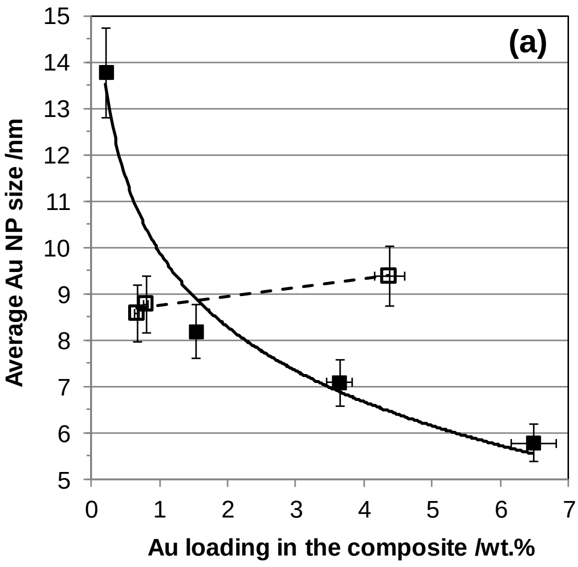
Gold exhibits the lowest melting point of all noble metals. As a result, gold nanoparticles (Au NPs) have a strong tendency towards growth, sintering and agglomeration. The reduction of a $HAuCl_4$/graphene oxide mixture typically leads to rGO-supported Au NPs with diameters above 10 nm [1]. Au NPs size can be drastically decreased by reacting $HAuCl_4$ with N-doped rGO which ensures reduction and Au NPs growth control down to 1.8 nm [2]. However, in the absence of a strong chemical interaction between the gold precursor and the graphene surface, huge Au aggregates (~300 nm) are produced [1]. Hence, the straight-forward decoration of unfunctionalized and undoped graphene surfaces with Au NPs is a scientific challenge.

In this communication, we report the direct synthesis of size-controlled Au NPs on pristine few layer graphenes (FLG). First, a high-quality FLG (O/C < 2at.%) is produced by surfactant-assisted, non-oxidative exfoliation of expanded graphite in the liquid phase, followed by annealing at 900°C, as confirmed by TGA, XRD, FTIR and Raman studies [3]. Then, Au NPs are loaded on the pristine graphene nanosheets by the controlled $NaBH_4$ reduction of Au (I) phosphine complexes within sonicated FLG suspensions in organic solvents. The resulting Au NPs size is unexpectedly found to *decrease with increasing Au content*, down to an average of 6 nm (Figure 1a), which is in marked contrast with the typical increase in Au NPs usually observed with increased loading [4]. We will further show how gold deposition and particle growth are affected by the solvent, gold complex, reduction time and drying conditions in particular, and how, by tuning these synthesis parameters, 1.2 ± 0.4 nm (TEM) Au NPs have been prepared (Figure 1b), yielding at high loadings (> 5 wt.%) easily processable Au/FLG powders which exhibit peculiar catalytic activity in the PROX reaction due to the hydrophobic nature of the composite (Figure 1c). These are, to our knowledge, the smallest Au NPs ever obtained by a surfactant-free chemical method over unfunctionalized graphene surfaces.



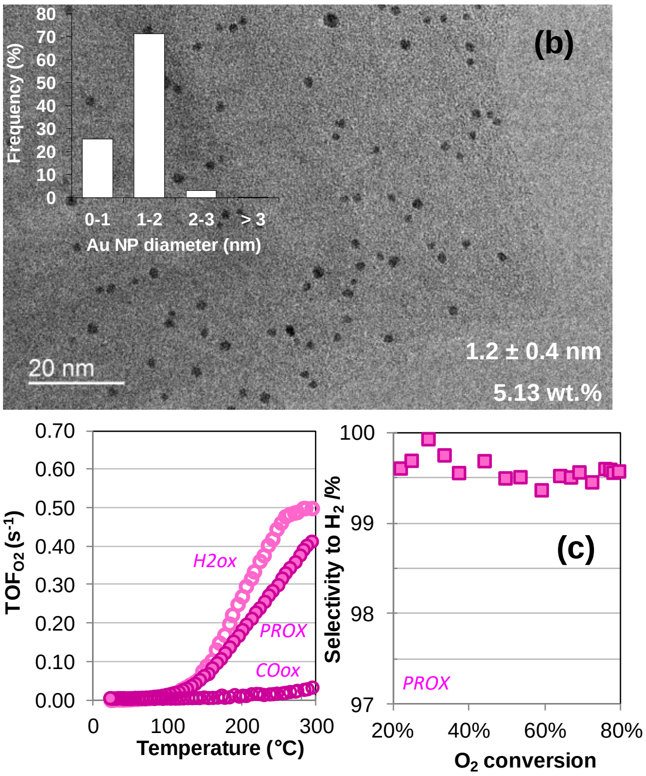


Figure 1. (a) Average XRD-derived Au NP size resulting from $NaBH_4$ reduction of $AuPPh_3Cl$ before (☐) or after (■) introduction of FLG in sonicated DMF suspensions. (b) TEM of an optimized Au/FLG composite. (c) Catalytic properties of a 5%Au(2.9±1.3 nm)/FLG in H2ox (1%O_2/24%H_2/He), PROX (1%CO/1%O_2/24%H_2/He) and COox (1%CO/1%O_2/He) at P=1 atm and GHSV=15000 h^{-1}.

Finally, we will discuss how their unique selectivity towards hydrogen makes them highly promising for partial hydrogenation processes containing traces of CO.

Acknowledgements. This work was funded by the IDEX Attractivité Program of the University of Strasbourg (GRAPHOGOLD project, W12RAT06).

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DEVELOPMENT OF MESOPOROUS, GRAPHITIC CARBONS AS FLEXIBLE CATALYST PLATFORM FOR METAL-FREE OXIDATIVE DEHYDROGENATION REACTIONS

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Introduction. Up to date on the topic of metal-free oxidation catalysis, carbon nanomaterials attracted the lion's share of research interest. Showing high activity and selectivity, a wide variety of carbon nanomaterials (e.g. carbon nanotubes, carbon nanofibers, onion-like carbon, nanodiamond) has been employed in the oxidative dehydrogenation (ODH) of lower alkanes and ethylbenzene.[1] However, because of intrinsic drawbacks such as the high pressure drop of fixed nanocarbon catalyst beds, a demanding scaling of synthesis and unclear health hazards nanocarbon materials are still awaiting industrial application. One possible alternative is provided by mesoporous, graphitic carbons, which have recently been shown to exhibit similar catalytic properties to carbon nanomaterials.[2,3] They are accessible via easily scalable synthetic pathways and average particle diameters exceed those of carbon nanomaterials usually by two to three orders of magnitude, thereby minimizing health risks and pressure drop in fixed catalyst beds.[4]

It is generally agreed upon that the catalytic properties of carbon materials are based on a complex interplay of texture and crystallinity on one hand, and surface chemistry on the other hand. Favorable textural properties have been reported to be high specific surface areas in combination with mesopores, leading to highly accessible surfaces and low mass transfer resistance. A certain degree of crystallinity is needed to ensure the necessary oxidation stability in oxygen-rich atmospheres. Furthermore, it has been postulated that the oxygen dissociation occurs at graphitic basal planes, whereby crystallinity plays a key-role in the reoxidation of the catalyst. Finally, the presence of oxygen surface groups, in particular carbonyl groups, was found to be responsible for the catalytic activity of carbon materials in general.[2,3]

However, up to date no significant effort has been made to understand the impact of the pore size distribution, degree of graphitization, surface functionalization and especially the interaction between those key-properties on the catalytic performance. This gap in knowledge occurs above all due to a lack of flexible synthetic pathways to mesoporous, graphitic carbons that enable an independent, wide range tuning of texture, crystallinity and surface chemistry.

Results. A new, flexible synthetic route for tailor-made mesoporous, graphitic carbons has been developed.

Phenol derivatives are polymerized in the presence of a soft template with formaldehyde.[4] Poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) triblock copolymers with different poly(ethylene oxide)/poly(propylene oxide) ratios and mixtures thereof serve as structure directing agents to tune the texture of the resulting carbon (Figure 1).

The phenol/formaldehyde/soft-template conjugates are then functionalized with carboxyl surface groups in order to enable a homogenous loading of a graphitization catalyst via ion exchange. Cobalt, Iron and Nickel are utilized as low temperature graphitization catalysts. Subsequent, the loaded polymer particles are pyrolyzed and graphitized simultaneously by heat treatment at temperatures between 700 and 1400 °C. The crystallinity and oxidation resistance of the resulting carbon can be tailored by the choice of graphitization catalyst (e.g. Co, Ni, Fe) and the pyrolysis temperature (Figure 2). After pyrolysis, the metal catalyst can be removed easily by washing with acid.

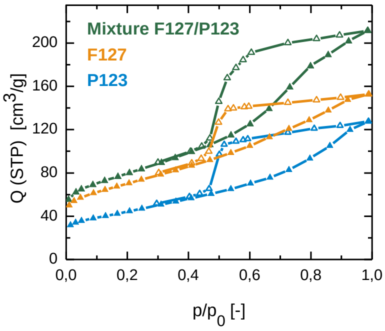

Figure 1. N_2-Sorption isotherms of graphitic carbons synthesized with the softtemplates Pluronic F127, Pluronic P123 and a 1:1 F127/P123 mixture.

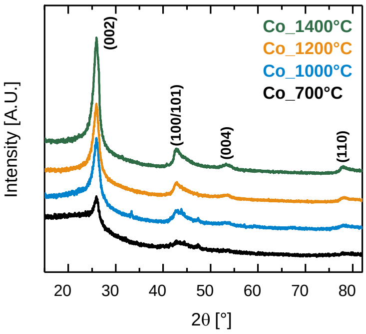

Figure 2. X-ray powder diffraction patterns of mesoporous carbon pyrolyzed in presence of 4 wt-% cobalt at different temperatures.

Finally, a treatment with an oxidizing agent (e.g. H_2O_2, HNO_3) introduces oxygen surface groups on the carbon surface.

Conclusion. A new, flexible synthetic route for mesoporous, graphitic carbons has been established. By combining softtemplate methods and catalytic graphitization, this pathway allows the individual tuning of key-properties like texture, crystallinity and surface functionalization.

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BAYER-VILLIGER OXIDATION AND ESTERIFICATION REACTION CATALYZED BY SAWDUST BIOCHAR

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In the last decade, synthetic carbon materials have driven the attention of the scientific community due to the fact that their properties, namely surface chemistry properties can also be tuned according to the application. For the catalytic point of view, an acidic surface is important, allowing that the carbon materials can work as catalyst supports, or as catalysts by their own. However, the surface functionalization processes of carbon materials require the manipulation of hazardous reagents, and so the development of synthetic procedures to obtain functionalized materials is currently an important research topic [1].

The aim of the present study is the synthesis of a functionalized biochar obtained by a two-step acid treatment of pine sawdust. Briefly, the acid liquor obtained after acid digestion at 50 ºC was refluxed for 6 h at 90 ºC. This synthesis is performed at low temperatures at atmospheric pressure in opposition to the most common methodology involving heat treatments under inert atmosphere at much higher temperature.

Two biochars were prepared using 13.5 M or concentrated (18 M) sulfuric acid, being the samples designated by S/13.5 and S/18, respectively. The use of less concentrated acid allowed a synthesis yield of 15.8 % while with the concentrated acid it attained 48.9 %. Both carbon materials have an acidic surface (pH_{pzc} of 2 for both synthetized materials) and the total of acid density groups at the surface of 0.45 and 0.96 mmol H^+/g_{carbon}, for S/13.5 and S/18, respectively. Considering the results for the surface characterization it is possible to conclude that a great amount of sulfonic acid groups must be present, so the as-synthesised biochars are functionalized materials.

The catalytic activity of the biochars was evaluated in an esterification model reaction (butyl acetate synthesis) due to the synthetized material have presented an acid surface. Esterifications are important reactions in organic synthesis, and, in the particular case of butyl acetate synthesis there are significant industrial applications (*e.g.*, flavouring in food industry or as solvents in pharmaceutical and textile industries).[2] The results obtained so far with the S/18 synthetized biochar can achieve 64 % yield in butyl acetate synthesis after 6 hours of reaction.

The second model reaction used to evaluate the catalytic activity of the biochars is the Baeyer-Villiger oxidation reaction of cyclohexanone, into ε-caprolactone using the method of sacrificial aldehyde with hydrogen peroxide as oxidant. Usually, this industrial process is catalysed by explosive peracetic acid which involves great risks.[3] Within the preliminary catalytic assays 23 % yield was obtained but optimization of the experimental conditions is ongoing.

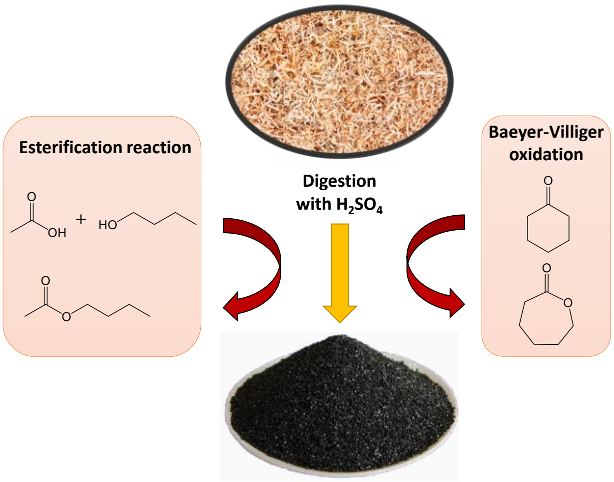

Figure 1. Representation of carbon material synthetized from sawdust and catalytic applications.

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NICKEL NANOPARTICLES DECORATED NITROGEN DOPED CARBON NANOTUBES AS AN EFFICIENT CATALYST FOR CO_2 METHANATION

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In order to reduce the CO_2 emissions, directives have been set to replace part of the fossil fuels by renewable energy (RE). However, the intermittent character of RE, calls for the development of sector coupling between electrical and gas/chemicals grids thus balancing the exceeding RE energy produced. The most developed chemical storage of RE relies on CO_2 methanation process. In the latter, CO_2 is reacted with hydrogen (issued in turn from RE resources by water electrolysis [1]), to generate methane that could be further injected into already existing natural gas pipelines, or it can be used as a fuel or raw material for the production of other chemicals. Here we report on the use of nitrogen-doped carbon nanotubes (N-CNTs) as basic support for nickel nanoparticles (Ni-NPs) in the CO_2 methanation process.

The low-magnification TEM micrograph evidences Ni-NPs as a roughly monodispersed metal phase at the surface of N-CNTs with an average particle size distribution of ca. 10 ± 3 nm determined from statistical TEM analysis on 200 particles (Figure 1). At the operative conditions (1 atm of H_2/CO_2 mixture with a H_2-to-CO_2 molar ratio = 4 and temp. = 360 °C), Ni/N-CNTs catalyst displays high CO_2 conversion along with high stability and CH_4 selectivity, *i.e*. CO_2 conversions up to 81% and 75% under GHSVs of 60.000 and 120.000 mL/g_{cat}/h, respectively, and CH_4 selectivity more than 94% at the highest GHSV value. The CO_2 conversion was also found to reach up to 96% for increasing H_2-to-CO_2 molar ratio to 6 (not shown). The catalyst displays no deactivation after about 50 h of test which indicates that metal sintering or leaching is unlikely to occur under these conditions. TEM analysis confirms that the Ni particle size distribution remains almost unchanged after a long-term test carried out for more than 70h. The outstanding performance of Ni/N-CNTs could be attributed to the presence of nitrogen functional groups on N-CNTs, which provides robust anchorage sites for the highly dispersed Ni-NPs and ultimately prevents sintering phenomena during the reaction process [2,3]. In addition, the presence of nitrogen sites on CNTs walls facilitates the adsorption/activation of CO_2 molecules and prevents the coke deposition for long time catalyst trials [3,4,5].

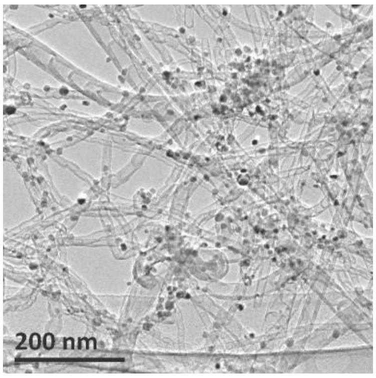

Figure 1. TEM analysis of Ni/N-CNTs showed the high and homogeneous dispersion of nickel nanoparticles on the CNTs walls.

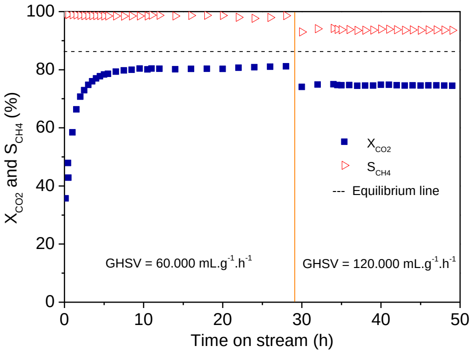

Figure 2. CO_2 conversion and CH_4 selectivity on Ni/N-CNTs catalyst as a function of the GHSV at 360°C, H_2-to-CO_2 molar ratio = 4 and pressure = 1 atm.

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PHOTOCATALYTIC BEHAVIOUR OF ZnO NANOPARTICLES AND THEIR COMPOSITES WITH GRAPHENE

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Graphene with its unique physical and chemical properties has attracted increasing interest in recent years[1]. Its transparency and electrical conductivity, as well as its easy processing when prepared from graphene oxide, position graphene as a good candidate for optoelectronic applications[2]. It has been observed that ZnO nanocrystalline semiconductor with different morphologies is a promising material for solar cells and photocatalytic applications due to its high electronic mobility, high photoactivity and transparency to visible light[3]. The combination of graphene properties and nanostructured ZnO would provide a unique platform for the development of nanostructured materials with improved photoactivity.

Herein, a novel method has been developed to prepare ZnO nanoparticles by microwave. The ZnO-GO hybrid materials were synthetised by ultrasound bath in order to improve the efficiency of the photocatalytic reaction of methylene blue degradation. The preparation protocol facilitated the establishment of interactions between ZnO and GO, which resulted in improved catalytic materials. Three types of GO with different degrees of oxidation (2, 4 and 16 hours) were analyzed, resulting the 4 hours-oxidized (GO2) in hybrids with greater activity. Also, hybrid materials with different ZnO:GO ratios (3:1, 10:1 and 20:1 w/w) were prepared using the optimum GO2 material. The ZnO-GO2 hybrid materials exhibited high conversions compared to ZnO alone (and even to TiO2 P25), whereby the hybrid synthesized at 10:1 (ZnO:GO) ratio exhibits the highest final conversion. Moreover, ZnO treated at 200ºC improves the pohotocatalytic activity of ZnO without heat treatment. The photoelectrochemistry, XRD, Raman and TEM of the prepared hybrid materials reveal important structural differences both in crystalline order and in the ZnO-GO interaction that could be the cause of the different catalytic efficiencies observed.

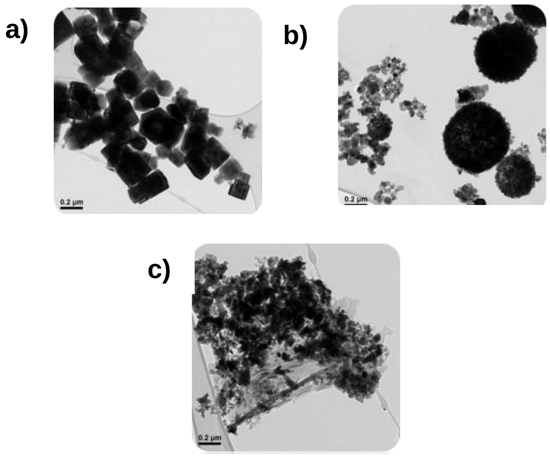

Figure 1. TEM images of a) ZnO as-synthetized, b) ZnO treated at 200ºC in air and c) ZnO-GO2 (3:1 w/w) composite.

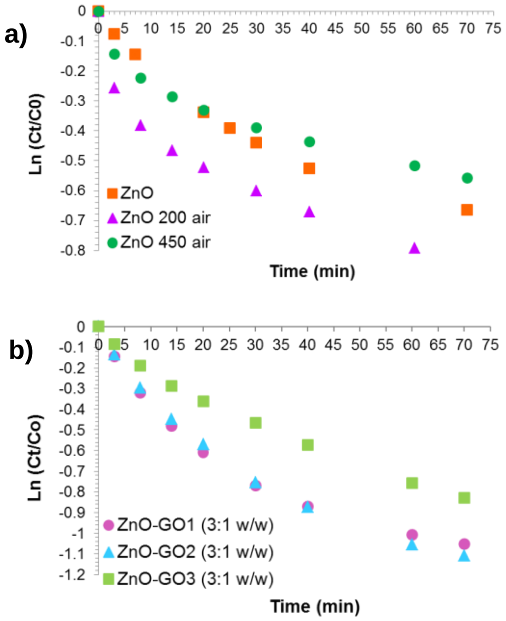

Figure 2. Photocatalytic behavior in the methylene blue degradation a) Influence of the heat-treatment of ZnO nanoparticles and b) influence of the oxidation degree of the GO in the composite

Acknowledgements. The financial support from Spanish Ministry MINECO and the European Regional Development Fund (project ENE2013-48816-C5-5-R), and Regional Government of Aragon (DGA-ESF-T66 Grupo Consolidado) are gratefully acknowledged

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CARBON-SUPPORTED Cu AND Cu_2O NANOPARTICLES FOR CO_2 ELECTROREDUCTION

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A strongly emerging topic is how we can use renewable energy sources to produce fuels and chemicals from H_2O and CO_2 using electroreduction. Energy efficiency and product selectivity of this conversion strongly depends on the electrocatalyst and the reaction medium utilized. The uniquely high activity of copper (Cu) catalysts to electroreduce CO_2 in aqueous solutions to hydrocarbons was reported by Hori almost 20 years ago [1], but has recently received much interest due to the possible relevance to convert solar electricity directly into fuels [2][3]. Cu oxide surfaces display intermediate hydrogen overpotentials and CO adsorption strength, which allows higher hydrocarbons such as ethylene and methanol to be produced in aqueous solutions[4]. Although mostly porous copper or copper oxide derived electrodes are used, alternatively the use of supported Cu_2O or Cu nanoparticles allows to tune in detail the catalyst properties [5] with the aim to improve the selectivity towards higher hydrocarbons. A very important factor in these supported catalysts is the high surface area support. Carbon-based materials provide an electrically conductive, high surface area support with a mesoporous structure, and allow by surface modification to tune the local conditions inside the pores. We report on the effect of carbon support properties and Cu($_2$O) nanoparticle properties on the electrocatalysed reduction of CO_2 and H_2O.

Cu-based nanoparticles (NPs) were supported on four different mesoporous carbon materials; Vulcan® CX72 conductive carbon black (VC), xGnP®500 graphene nanoplatelets (GNP), HSAG300 high surface area graphite (HSAG) and LITX200 conductive carbon black (LITX) via incipient wetness impregnation followed by two different reduction processes to achieve either a mixed Cu phase (Cu/Cu_2O) or metallic Cu [5]. X-ray diffraction measurements confirmed that the two crystal phases are present over the support (Fig. 1a). Raman spectroscopy (Fig 1b) revealed that the graphitic structure of carbon supports was not significantly altered upon deposition of Cu-based nanoparticles. Transmission electron microscopy demonstrated that Cu_2O/Cu nanoparticles were successfully deposited on the supports with a well dispersed and homogeneous particle size distribution. Figure 1c shows a representative TEM image of Cu/Cu_2O (Cu10wt.%) NPs supported on GNP (GNP-Cu/Cu_2O10) with a particle size distribution of 4.8±1.3 nm.

The electrocatalytic activity towards CO_2 reduction was evaluated by cyclic voltammetry in a CO_2-saturated 0.1M $KHCO_3$ pH 6.8 aqueous solution, and stability tests were performed using chronoamperometry. A well-defined plateau of diffusion limiting current is observed in the CO_2 reduction potential window, while at more negative potentials and exponentially increasing current can be attributed to hydrogen evolution reaction. The preliminary results shows that the nature of carbon as well as the crystal phase and the size of Cu derived nanoparticles, have a strong influence on the electrocatalytic activity. GNP-Cu/Cu_2O10 electrocatalysts exhibited lower negative onset potential at 0.12 V versus reversible hydrogen electrode (RHE), and the highest stability in current density over time, followed by HSAG-Cu/Cu_2O10 at 0.09 V vs. RHE (Fig 1d). We will discuss how the improved electrochemical performance can mainly be attributed to the differences in the physical and chemical properties of the carbon-based supports.

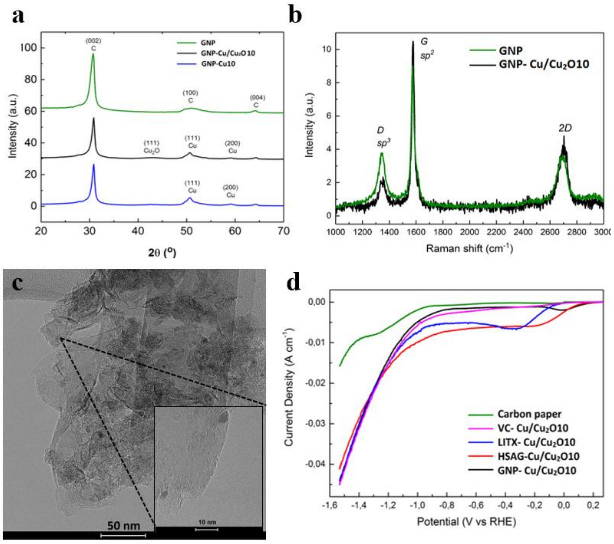

Figure 1. a) XRD patterns of the pristine GNP support, GNP-Cu10 and GNP-Cu_2O/Cu10 electrocatalysts, b) Raman spectra of pristine GNP support and GNP-Cu_2O/Cu10, c)Representative TEM images of GNP-Cu/Cu_2O10 electrocatalysts, and d) Voltammograms for Carbon paper, VC-Cu/Cu_2O10, LITX-Cu/Cu_2O10, HSAG-Cu/Cu_2O10 and GNP-Cu/Cu_2O10 electrocatalysts in CO_2 saturated 0.1M $KHCO_3$ pH 6.8 aqueous solution.

Acknowledgements. J.D. Meeldijk and J.E.S. van der Hoeven for the TEM imaging-training. Jan Willem de Rijk for his technical support.

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POSTER COMMUNICATIONS (PC)

MODIFIED ACTIVATED CARBON ADSORBENTS FOR SELECTIVE CO_2 ADSORPTION

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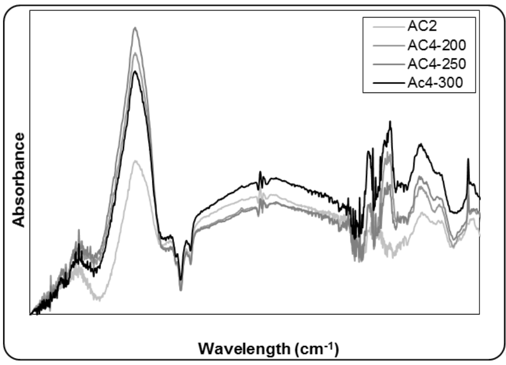
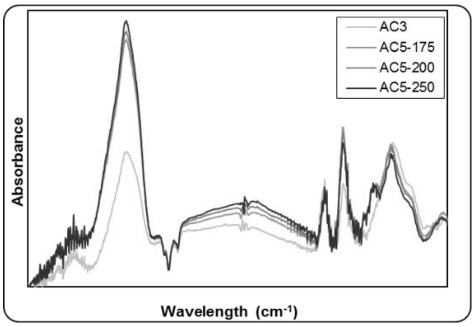
Adsorption has been considered as the most promising CO_2 capturing method owing to its low energy requirement led by the exothermicity of the process, cost advantage and ease of applicability over a relatively wide range of temperatures and CO_2 partial pressures [1]. Current potential adsorbent materials for CO_2 capture are carbon materials such as carbon molecular sieves, carbon nanotubes, and activated carbons (ACs), zeolites and metal organic frameworks. AC is the most preferred adsorbent in industries due to its low cost, high surface area, high porosity, and adequate mechanical strength after repeated adsorption and desorption cycles and high CO_2 adsorption capacity at ambient pressure and temperature [2].

CO_2 adsorption capacity of activated carbons at a given temperature and pressure depends the pore structure and the properties of functional groups introduced to the surface by certain pretreatments. CO_2 adsorption capacities of a commercial activated carbon subjected to different treatments such as HNO_3 oxidation, air oxidation, alkali impregnation (K_2CO_3, Na_2CO_3 and NaOH), ammonia modification and heat treatment under helium or air atmosphere were determined by gravimetric analyses for 25-200°C temperature and 0-20 bar pressure range with the purpose of developing AC-based adsorbents having both high and stable CO_2 adsorption capacity, and ability to adsorb CO_2 selectively from CO_2-CH_4 mixture. In this context, a new methodology for the determination of selective CO_2 adsorption capacity of the AC-based adsorbents under multicomponent gas mixture flow was developed and proposed. The adsorbent samples were characterized by SEM-EDX and FTIR-DRIFTS (Figure 1) in order to analyze their microstructural properties, alkali dispersion and surface oxygen species.

The adsorption and selective adsorption performance of air oxidized (AC2) and alkali impregnated samples were found superior to the performance of their HNO_3 oxidized (AC3) and alkali impregnated forms. The CO_2 and CH_4 mass uptake values of K_2CO_3 impregnated adsorbents are given as an example in Figure 2. An overall analysis of adsorption and selectivity data revealed that AC2K-200 having the highest CO_2 adsorption capacity, 197 mg/g adsorbent at 5000 mbar, has a very stable surface during adsorption tests at 25 °C regardless of pressure ranges used.



(a)



(b)

Figure 1. DRIFT spectra of the adsorbents under 50 ml/min He flow: spectra of (a) air oxidized Na_2CO_3-impregnated adsorbents and (c) HNO_3 oxidized Na_2CO_3-impregnated adsorbents.

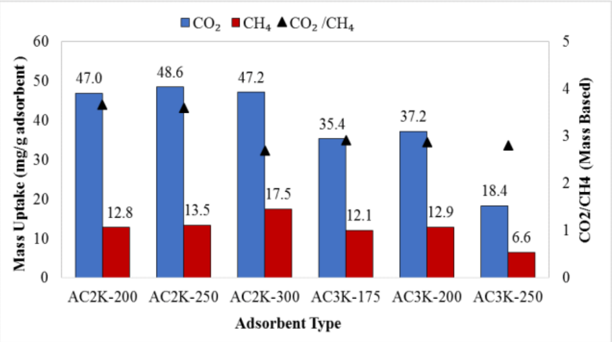


Figure 2. CO_2 and CH_4 mass uptake values of all samples at 1000 mbar and at 25 °C under 50% CO_2-50% CH_4 flow.

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N-DOPED CARBON-BASED CATALYSTS FOR GUAIACOL HDO USING H DONOR SOLVENTS

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Carbon materials have a large number of applications in heterogeneous catalysis, either as supports for the active phases or as catalyst by themselves due to the redox-active functional groups that are located at the surface. Recently, research has been focused on doping these carbons with nitrogen, thus increasing their stability, oxidation resistance and even their catalytic activity of these N-doped carbon materials. Melke *et al.* [1] have reported that Pt nanoparticles supported on N-doped carbons are more stable and bind more strongly to the support in regions with a high degree of N atoms. The Pt-N interaction provokes an exchange of electrons from Pt into the N-doped system increasing the electron density of the material. Also, N-groups act as nucleation centres for Pt nanoparticles what favours Pt dispersion. However, the benefits of the N-doped carbon materials not only depend on the presence of N, but also on the capability of the reactants to access to the catalytic sites, especially in reactions that involve large molecules. In this sense, mesoporous carbons favour the transport of the reactants and the products to and from the active centres. In this work, we have introduced N on an activated carbon, RGC-30, in two different ways. On one side we have used melamine as the N source, preparing an intimate solid-solid mixture (RGC-30+melanine) with a subsequent carbonization at 800ºC. On the other side, we have synthesized N-doped carbons polymerizing aniline and pyrrole on the carbon surface, and then pyrolysing the samples at 900ºC.

Carbons have been characterized by XPS and N_2 adsorption at -196ºC. The XPS results show the presence of four nitrogen species on the carbon surface. Pyridinic-type nitrogen gives rise to a peak at about 398.3 eV and pyrrolic-type nitrogen appears at about 400.8 eV. Also, the peak around 399.3 eV is assigned to amides and the small peak at 402 eV corresponds to quaternary nitrogen. The amount and type of carbon species is different for the different samples. Thus, we obtained 7 %N for RGC-30 + Melamine, 3.25% for PPy/RGC-30 and 3.75% for PANI/RGC-30. These differences can affect the catalytic properties and stability when they are used as catalytic supports. Mixed type I-type IV N_2 adsorption isotherms, typical of micro-mesoporous solids, were obtained for these N-doped carbon materials. However, the surface area and the porosity slightly decreased with the deposition of the polymer on the carbon surface, due to the partial blockage of the porous by the polymers.

Finally, these solids were tested as a supports for guaiacol hydrodeoxygenation reaction (HDO) catalysts.

Table 1. Adsorption properties of the synthesized carbons

Sample	Total Pore Volume (cc/g)	Mesoporous Volume (cc/g)	BET surface (m^2/g)
RGC-30 + Melamine	0.968	0.523	1207
PPy/RGC-30	0.665	0.342	860
PANI/RGC-30	0.618	0.334	755

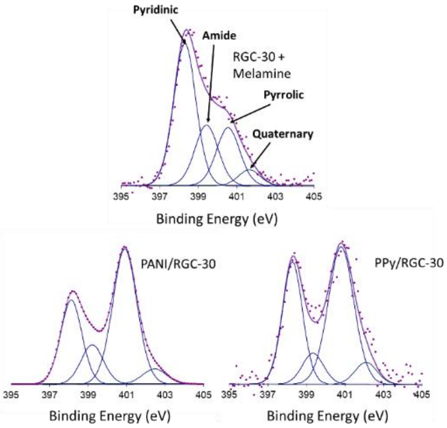

Figure 1. XPS N 1s spectra for supports.

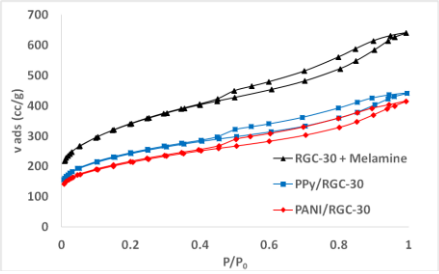

Figure 2. N_2 adsorption isotherms at -196ºC.

Catalytic HDO is a fundamental process for bio-oil upgrading, currently carried out with high H_2 pressures, in order to produce transportation fuels or high-valued chemicals. Due to the high cost of H_2 production and its potential risk in terms of transportation and storage, in this work we are replacing H_2 with a hydrogen donor molecule. Hydrogen released from a hydrogen donor solvent could be reacted with hydrogen acceptors on catalytic active sites. An efficient catalyst for deoxygenation reaction by using hydrogen donor solvent should have high potential for adsorption of both hydrogen donor and acceptor molecules. In this scenario our N-doped samples play an important role due to their enhance electron density.

Ni-based catalysts were synthetized using these supports, and were tested in the guaiacol HDO reaction. A deep analysis on the obtained results has been developed, trying to correlate the catalytic activity with the different properties of the N-doped carbon-supported catalysts.

Acknowledgements. Financial support from Ministerio de Economía y Competitividad, Spain (MAT2016-80285-P) is gratefully acknowledged. LPP thanks Comunitat Valenciana for her postdoctoral fellowship.

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FROM GRAPHENE NANORIBBONS TO GRAPHENE OXIDE NANORIBBONS: INFLUENCE OF OXIDATION CONDITIONS

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Graphitic nanorribons are said to be one-dimensional sp^2 hybridized carbon crystals. The fact that they possess high ratio of edges makes them suitable in various fields of application including catalysis. When suitably doped they could serve as metal free catalysts [1]. On the other hand, their exposed uncoordinated boundaries can be perfect anchoring sites for metallic nanoparticles [2,3]. The oxidation of these carbon nanostructures is sometimes a necessary step in the synthesis of highly dispersed catalytic nanoparticles [4].

In this communication we report a comparative study of the oxidation of graphene nanorribons (GNRs) employing two different well known graphene oxidation methods (Hummers and Brodie) varying synthesis conditions such as temperature and time. GNRs starting material (lab synthesized following a procedure reported elsewhere [5]) as well as the resulting graphene oxide nanoribbons (GONRs) were thoroughly characterized by XRD, FESEM, SEM-EDS, Raman, TGA, TPD, IR and XPS. We focus on the significant differences obtained within each series and also between both oxidation methods.

IR spectroscopy reveals the successful incorporation of oxygen groups on the pristine GNRs in all cases. In terms of disorder, the ratio of D to G band obtained from Raman spectroscopy is reduced after oxidation.

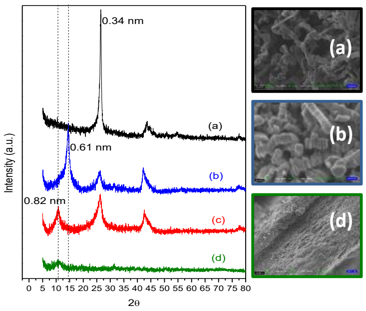

Figure 1. XRD patterns FESEM images of GNRs (a), GONRs-B oxidized at 0ºC during 9 h (b), GONRs-H oxidized at RT during 2 h (c) and GONRs-H oxidized at 60ºC during 9 h (d).

Crystallinity is also verified by XRD (Fig. 1). GNRs display a peak at about 26º corresponding to the graphitic 002 plane which is significantly reduced in GONRs-B (Brodie oxidation method) samples. A new peak at 15º appears due to a new interspace of about 0.61 nm. Similar effect is found throughout this series where increasing duration of oxidation (at 0ºC) time offered no further opening of the layers. As for the GONRs-H series (oxidation by Hummers method carried out at Rt, 35 and 60 ºC), those performed under mildest conditions partly maintained their crystallinity although not as much as for the GONRs-B series (Fig. 1 ratio of peaks) whereas the interlayer spacing is higher in this case (about 0.82 nm). On increasing the treatment temperature, peak intensities drastically decreased until practically disappeared for highest temperature and prolonged treatment time.

FESEM (Fig. 1) images confirm and clarify the reasons for XRD results. On one hand, the opening of the folds of GNRs gives rise to the accordion-like structure observed in the GONRs-B upon oxidation while crystalline structure of GONRs-H is completely altered. These differences are also highlighted on comparing TGA profiles of the pristine GNR with that of the corresponding oxidized materials. In Fig. 2 the results of the thermogravimetric analysis under air atmosphere are depicted for some of the studied samples. In general terms, oxidized materials possess lower decomposition temperatures and this is most accused for samples treated under more aggressive oxidation conditions.

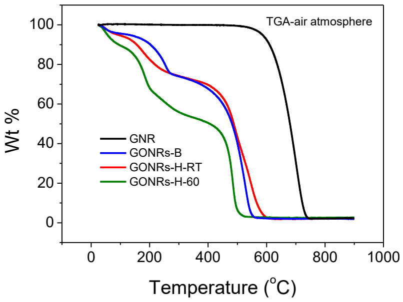

Figure 2. TGA profiles for four of the studied samples.

It was also found that the loss of surface groups commences at lower temperatures for the GONRs-H samples. This is in line with the results obtained from TPD experiments where apart from the difference in desorption temperatures between both series (Table 1); the nature of the species involved is also to be considered. On one hand, GONRs-H materials contain sulphur and the presence of this element is further confirmed by SEM-EDS and XPS. On the other hand, this series of carbon materials contain higher oxygen content with respect to the GONRs-B series.

Table 1. Summary of XPS and TPD results.

Samples	XPS at. %			Surface groups desorption temperature (ºC)	
	C 1s	O 1s	S 2p		
GONRs-B	72.0	28.0	0.0	203	250
GONRs-H	54.6	40.7	4.7	152	213

Acknowledgements. EAN is grateful to the UNED for a postdoctoral grant at The Pennsylvania State University.

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CONTROLLED GENERATION OF OXYGEN-CONTAINING SPECIES ON THE SURFACE OF UNDOPED AND N-DOPED CARBON NANOTUBES

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Heteroatom doped carbon materials represent today one of the most prominent families of materials. Doping modifies substantially the atomic scale structures, surface energy, chemical reactivity, and mechanical properties of carbon nanomaterials. The surface chemistry of nanocarbons is governed by the presence of heteroatoms (other than carbon) within the carbon matrix, and to the presence of carbene and carbyne structures at the edges of the graphene layer in $sp^2/sp^{2+\delta}$-hybridized materials. Moreover, the surface chemistry of these materials is also governed by basal carbon atoms, as well as by the presence of defects. Imperfections and defects along the edges of graphene layers are the most active sites due to a high density of unpaired electrons. There, heteroatoms such as oxygen, hydrogen, nitrogen, boron, sulfur, and phosphorous can be chemisorbed, leading to stable compounds, resulting in a complex surface chemistry with an acidic, basic, or neutral character [1]. Depending on the nature of the heteroatom(s) present, the surface can be tailored for specific applications.

Most pristine nanostructured carbon materials are chemically inert and functionalization or surface modification is crucial to render them chemically active. Carbon surface oxidation is the most popular way of modifying carbon surfaces. It can be done either from a gaseous (oxygen, ozone, air, and nitric oxides) or liquid phase (nitric acid, hydrogen peroxide, and sulfuric acid). Although conditions of gas-phase oxidation vary, it is usually carried out in an oven at elevated temperatures under a continuous oxidant flow. Oxidation in the liquid phase is much more complex and results in more severe changes to the carbon surface chemistry. The oxidations are usually carried out in open vessels with oxidants in a wide range of concentrations, depending on the desired effects. Another important factor in this type of oxidation is temperature; high temperatures and strong oxidants result in a higher degree of surface oxidation. In this context, the controlled functionalization of carbon-materials with dilute concentrations of oxidant could be potentially interesting [2]. In this work, we discuss the effect of different parameters such as oxidant concentration, treatment duration, carbon load, and temperature on the controlled formation of oxygen-containing species on both undoped and N-doped CNTs using a hydrothermal oxidation treatment.

The CNTs used in this study were produced by chemical vapor deposition at 650 ºC. Two different catalysts were used ($FeMo/Al_2O_3$ and $AlFeCoO_4$) in order to produce materials with different properties, namely the amount of N present in N-doped CNTs. Depending on the nature of the CNT (doped or undoped), ethylene (C) or acetonitrile (C/N) sources were used. The hydrothermal functionalization was carried out during 1−4 h at 393–473 K in a 125-mL Teflon-lined vessel, using 0.1−0.4 g of material and 75 mL of a HNO_3 solution (concentration < 0.3 M). The materials were characterized using elemental analysis, TGA, TPD, N_2 adsorption-desorption isotherms at 77K, TEM, IR spectroscopy, and XPS.

Preliminary results have shown that the concentration of oxygen-containing groups increased with increasing nitric acid concentration, and treatment temperature and duration; this effect was more significant for N-containing nanotubes, as higher concentration of oxygen groups were introduced on N-CNTs than on CNTs, under the same conditions. This was attributed to the fact that introduction of heteroatoms on the carbon surface is energetically more favorable on broken-symmetry sites (e.g., defects) than on the pristine/undoped surfaces. Moreover, similar samples (either undoped or N-doped) prepared using different catalysts behaved differently, with the nanotubes obtained from $FeMo/Al_2O_3$ being easier to oxidize than the ones obtained from $AlFeCoO_4$.

In addition to the introduction of surface groups, this functionalization treatment had a significant effect over the textural properties of the materials as well, namely over the specific surface area (Table 1).

Table 1. Evolution of the specific surface area ($m^2\ g^{-1}$) for the CNTs and N-CNTs with nitric acid concentration (M).

$[HNO_3]$ (M)	$FeMo/Al_2O_3$ CNTs	$FeMo/Al_2O_3$ N-CNTs	$AlCoFeO_4$ CNTs	$AlCoFeO_4$ N-CNTs
Orig.	278	258	201	263
0.10	312	308	244	234
0.30	486	333	262	226

The surface area of the materials increased significantly with increasing nitric acid concentration (Table 1). This increase can be interpreted in light of CNT tip opening, which could also explain the lower extent to which the area of N-CNTs increased, due to their bamboo-like structure. However, the N-CNTs synthesized from the $AlCoFeO_4$, revealed a small decrease in surface area. Since these nanotubes are more stable (lower functionalization), it is likely that this decrease might be associated to the disappearance of some amorphous carbon during the hydrothermal oxidation.

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PREPARATION OF FEW-LAYER GRAPHENE/CARBON NANOTUBE HYBRYDS BY CHEMICAL VAPOR DEPOSITION

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Graphene is an extremely versatile 2D material for nanotechnology applications in view of its excellent physical, chemical, and mechanical properties. Hybrids based on graphene take advantage of these properties to create functional 3D materials by anchoring other nanomaterials onto graphene; among the different additives, CNTs are the most studied. Their high aspect ratio in combination with electrical conductivity and mechanical properties implies that they can function as effective connector material between the graphene sheets, creating 3D nanostructures with improved functional properties. Indeed, a synergistic behavior has already been reported between CNTs and graphene or few-layered graphene (FLG) for application in energy, catalysis, and electronics [1].

Due to their chemical similarity, there is a strong interaction between CNTs and graphene; while such interaction is highly favorable to synergy in applications, it also means that properties of the hybrid depend significantly on the preparation method including the assembling technique used. Thus, for large-scale applications, the development of one-step production methods to achieve large volumes of hybrid material with controlled morphology and structure is highly desirable. Several methods have been used for the fabrication of graphene-CNT hybrids including physical mixing, chemical layer-by-layer assembly, and growing CNTs on graphene surfaces. Simultaneous graphene and CNT growth using a single-step CVD approach has also been reported, wherein CNT growth catalyst was deposited on the graphene growth catalyst. However, a control of the hybrid composition for large-scale production of these materials is still far from optimized. In this study, we report a single-step preparation of CNT/FLG hybrid materials by fluidized bed chemical vapor deposition (FB-CVD) process to prepare gram-scale quantities of CNT-FLG hybrids. Physical mixtures of two catalysts (FLG using $CoFe_2O_4$ and CNT using $AlCoFeO_4$) were also prepared for comparison purposes. This study is a follow up of a previous work on the large-scale process for the CVD of thickness-controlled few-layer graphene [2], where fine cobalt ferrite powders were used as catalysts to produce FG with controlled thickness.

Both cobalt ferrite oxide and Al-doped cobalt ferrite oxide catalysts ($Al_xCo_{1-x}Fe_2O_4$ with x = 0.025–0.10) were prepared using a previously reported citrate-nitrate gel combustion method [2]. The combustion and calcination steps were carried out in a muffle furnace at 200ºC for 2 h and 400ºC for 5 h, respectively. In order to prepare physically mixed catalysts, different amounts (25–75%) of both $CoFe_2O_4$ (FLG catalyst) and $AlFeCoO_4$ (CNT catalyst) were ball-milled for 30 min. The hybrids were produced by chemical vapor deposition at 650 ºC using ethylene as carbon source. The yield of the reactions was calculated using the parameter $\xi = g_{hybrid}/g_{cat}$. The carbon deposits containing reduced catalysts were immersed in 35% HCl at 20ºC overnight to dissolve the catalyst. The materials were characterized using TEM, XRD, Raman spectroscopy, TGA, and N_2 adsorption-desorption isotherms at −196 ºC.

The results have shown that Al doping of cobalt ferrite in the 0.01–0.025 mol range lead to the formation of a uniform hybrid (Figure 1a), where the FLG thickness and CNT diameter could be controlled by changing the reaction conditions. Only FLG was obtained when $CoFe_2O_4$ was used. However, the introduction of small amounts of Al induced the production of CNTs. For catalysts with higher Al content (e.g., $AlCoFeO_4$), CNTs were selectively produced. Hence, there is a small window (x < 0.05), where CNTs and FLG can be obtained simultaneously. Regarding the hybrids prepared by mixing $CoFe_2O_4$ and $AlCoFeO_4$ catalysts (Figure 1b), rather thick FLG (5-8 nm) and thin CNTs (less than 10 walls) were obtained. However, a control of thickness of FLG was not achieved in this method due to the different carbon diffusion kinetics of the two catalysts. It was observed that the FLG catalyst was highly active at the start of the reaction. However, CNT growth rate increased after the first few minutes and dominated thereafter. Thus, the final product was composed mainly of CNTs with few thick FLG domains.

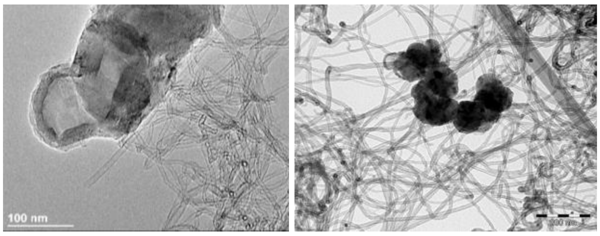

Figure 1. TEM micrograph from hybrids (a) single-catalyst ($Al_{0.025}Co_{0.975}Fe_2O_4$); (b) Mixed catalyst (25% $AlCoFeO_4$ + 75% $CoFe_2O_4$).

Raman spectra were used to confirm the formation of CNTs and FLG; all samples showed high D-bands, typical of CVD-synthesized CNTs and FLG. XRD results show a broad (002) diffraction peak for CNTs (low intensity), becoming thinner as FLG is added (hybrid; in addition there is a small shift between CNTs and FLG. Regarding the hybrid from single catalyst, the spectrum shows predominately the FLG phase with a small shoulder corresponding to CNTs, due to the low intensity of the CNTs compared to FLG. In this study, we show that by doping $CoFe_2O_4$ with Al in the 0.01−0.025 range, uniformly distributed CNTs and FLG hybrids are obtained. These materials could be a useful steppingstone for the single catalyst-based preparation of CNT/FLG hybrid materials.

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HSO_3-FUNCTIONALIZED CARBON-DERIVED INDUSTRIAL RESIDUES: SOLID ACID CATALYSTS FOR BUTYL-LEVULINATE PRODUCTION

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The depletion of fossil resources, increasing of greenhouse emissions and awareness for a sustainable development, makes the transformation of industrial wastes and biomass residues into valuable materials/products and renewable energy mandatory areas in fundamental research and technological applications in the context of future sustainable economy.

Coal fly ash (CFA) is the largest by-product of coal combustion in power plants and, in consequence, global recycling rate of CFA is still insufficient. Actually, the main application of its reuse is in cement manufacturing, but it has also been used in small scale for soil amelioration, zeolite synthesis and catalysis [1],[2].

Pulp and paper industry also generates considerable amount of by-products including bark. Bark is mainly reused as fuel; nevertheless, it can be managed in a sustainable manner to become a valuable raw material for other industrial applications. Bark residues can be submitted to hydrothermal liquefaction (HTL) treatment, leading to the formation of bio-oil (a potential biofuel) and biochar. Biochar is a carbonaceous material and due to its intrinsic properties can be easily tuned by appropriate activation or functionalization processes and has been increasingly used as a soil amendment for carbon sequestration or chemical adsorbent. [3],[4].

The potential of these two types of residues to be used as carbon-derived acid catalysts is not well explored, but it appears as an important method for industrial/biomass residues valorization and simultaneously reducing the negative impact of coal power plants on the environment and the huge amount of the non- processing bark in paper industry.

Sulfonic acid functionalization of solid materials is an interesting approach to improve the intrinsic acidity of these materials for esterification reactions[5] including levulinic acid (LA) esterification. Levulic acid is one of the top 12 platform molecules with high industrial interest due to the relevance of levulinate esters as alternaive to fossil fuel derivatives in emerging markets such as flavouring and fragrance industries and additives for gasoline and diesel fuels.

Herein we present, for the first time, the functionalization of CFA and Biochar with organosulfonic groups (Figure 1) in order to improve the acid capacity of these carbon-derived residues to enlarge their potential applications as solid acid catalysts for esterification of LA with butanol, to produce butyl levulinate.

The functionalized carbon-derived materials (denoted as CFAx-SO_3H and BIOCx-SO_3H) showed a significant increase on the acid capacity (up to 0.69 mmol H^+/g) measured by potentiometric titration. In the esterification reaction of levulinic acid with buthanol using CFA carbon derived materials as acid catalysts the CFA1-SO_3H presented higher catalytic activity with conversions upper 90% after 30 min of reaction. For sulfonic acid functionalized biochar, the best result was obtained for BIOC3-SO_3H, with 92 % of conversion in the first 30 min of reaction. We have also evaluated the stability and recyclability of all sulfonic acid functionalized carbon-derived materials for up to 10 catalytic cycles. BIOC3-SO_3H showed the highest stability and reusability with catalytic conversion upper 70% until 10 recycling cyles, for 2 hrs of reaction.

All the catalytic results will be presented and discuss as well as reusability tests and catalyst characterization, before and after catalysis, by XPS, EA, FTIR-ATR and XRF techniques.

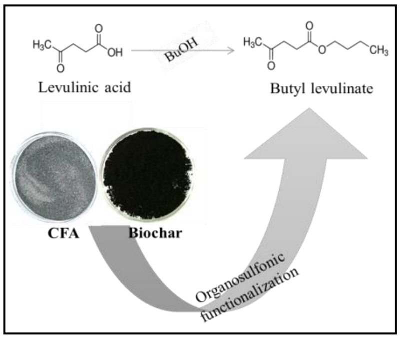

Figure 1. Schematic illustration of the HSO_3-functionalized carbon-derived industrial residues and catalytic LA esterification reaction.

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GASEOUS NITRIC ACID ACTIVATED MACROSCOPIC GRAPHITE FELTS AS HIERARCHICAL METAL-FREE CATALYST FOR SELECTIVE OXIDATION OF H_2S

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Nanocarbon-based metal-free catalysts consisted by nitrogen-doped carbon matrix have received an ever increasing scientific and industrial interest in the field of heterogeneous catalysis since the last decade for several potential processes. In this study, we reported on the influence of gaseous HNO_3 treatment on the formation of defects decorated with oxygenated functional groups on macroscopic commercial graphite felts (GFs). Such sample will be further used as all-carbon metal-free catalyst in the selective oxidation of H_2S into elemental sulfur to prevent the problem of air pollution. It is worthy to note that it is the first time that such results are reported as literature only reports metal-free catalysts based on nanocarbons, whose synthesis requires harsh reaction conditions along with problems linked with waste treatment.

The acid treatment, at 250°C for various durations up to 30h, leads to a significant increase of the sample specific surface area (SSA) from 10 to > 300 m^2/g which could be attributed to defects and porous network formation within the pristine sample (Fig. 1A). Such defects formation is also confirmed by Raman results where the I_D/I_G ratio continuously increases with increasing the treatment duration (Fig. 1B). The HNO_3 treated filamentous GFs was decorated with an evenly carbon nodules as evidenced by the SEM analysis (Fig. 2A and B). High magnification SEM micrograph (Fig. 2C) also evidences the formation of holes on the cross section of the OGFs sample (indicated by arrows). TEM analysis reveals the formation of a less dense graphite structure in the OGFs sample (Fig. 2E) compared to that observed for the pristine GFs (Fig. 2D). High resolution TEM micrographs (Fig. 2F) clearly evidence the porous structure of the treated sample.

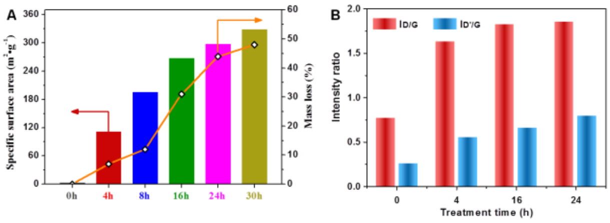

Figure 1. (A) Weight loss (open circles) and specific surface area (columns) and (B) Raman I_D/I_G and $I_{D'}/I_G$ ratios of the pristine GFs and the OGFs after acid treatment with various durations.

According to the catalytic results the defects created on the filamentous carbon wall and the formation of oxygenated functional groups during the gaseous acid treatment provide active sites for H_2S and oxygen adsorption, which contribute to the selective oxidation of H_2S into elemental sulfur. The catalyst displays a relatively high sulfur selectivity as well as high stability as a function of time-on-stream (Fig. 3) indicating that deactivation by surface fouling or oxygen groups removing is unlikely to occur. The high specific surface area as well as surface porous structure could be extremely helpful for developing new catalytic systems.

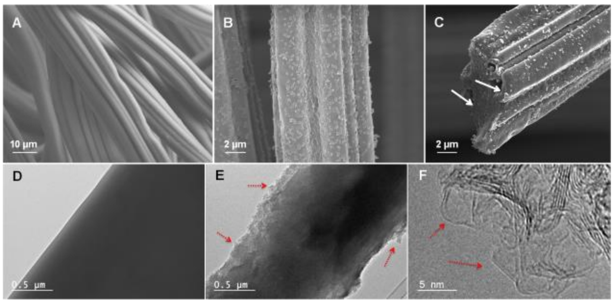

Figure 2. SEM micrographs of (A) pristine commercial GFs, and (B, C) the same after treatment under gaseous HNO_3 at 250°C for 24 h (OGFs-24). TEM images of GFs (D) and OGFs-24 (E, F).

Work is ongoing to evaluate such carbon-based materials as support for metal nanoparticles which is expected to be useful in other catalytic processes where high dispersion and strong anchorage of the active phase are required in order to prevent long term deactivation through catalyst sintering (gas-phase reaction) or leaching (liquid-phase reaction).

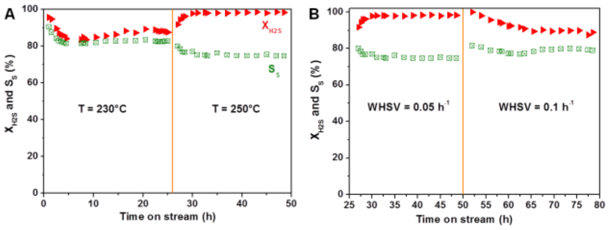

Figure 3. Desulfurization performance on the OGFs-24 catalyst (red) H_2S conversion, (green) sulphur selectivity. (A) Reaction conditions: $[H_2S]$ = 1vol. %, $[O_2]$ = 2.5 vol. %, $[H_2O]$ = 30 vol.%, WHSV= 0.05 h^{-1}.
(B) Reaction conditions: $[H_2S]$ = 1vol. %, $[O_2]$ = 2.5 vol. %, $[H_2O]$ = 30 vol. %, Reaction temperature = 250 °C.

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GOLD NANOPARTICLES SUPPORTED ON SIBUNIT CARBON MATERIALS

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Siberian carbon support, usually called «Sibunit», is a black/pyrolytic synthetic carbon composite produced by the pyrolysis of light hydrocarbons on a carbon black template, followed by the steam activation of the resulting composite [1,2] (Figure 1). The textural characteristics of the Sibunit carbon material, such as surface area, pore size distribution and agglomerate size and shape can be varied in a wide range by choosing the appropriate template and synthesis conditions. Therefore, a number of special properties, namely the development of specific surface area and large volume of pores, make possible to use this material effectively as a support for metal catalysts, due to the possibility of obtaining a high monodispersity of the supported metal.

Such Subunit supported metals can be used as catalysts in several different types of reactions. The metals supported on are usually platinum and palladium, as described in several publications [3-9].

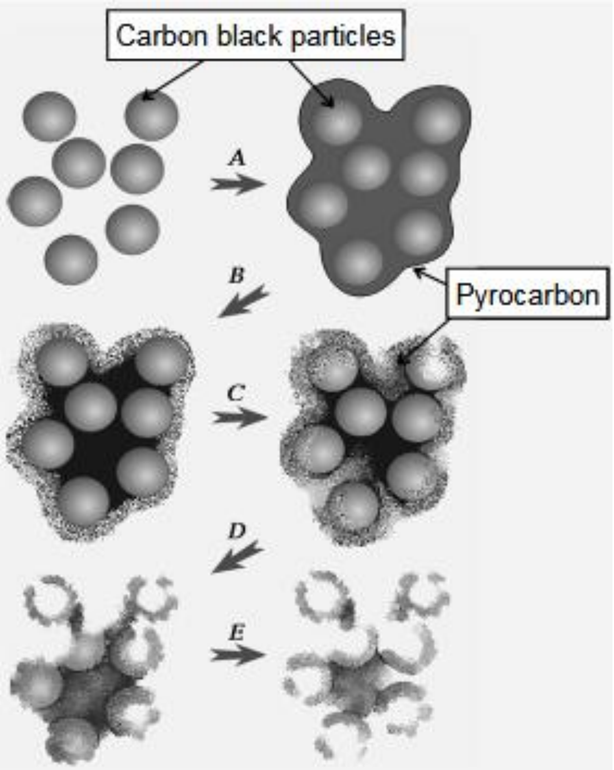

Figure 1. Synthesis and formation of the Sibunit texture. A: condensation (deposition of pyrocarbon onto carbon black particles), B,C,D,E – activation (oxidative gasification of the pyrocarbon/carbon black composite) [2].

Gold nanoparticles proved to be very efficient catalysts in different kinds of reactions [10-11], so we decided to also use gold on the Sibunit material. Therefore, in the present work, Au was loaded on the Sibunit with a nominal loading of 4 wt.% via incipient wetness impregnation with $[Au(NH_3)_4](NO_3)_3$ complex solution, followed by hydrogen reduction at 300 °C, for decomposition of the gold precursor and formation of an active surface.

Systematic and comparative studies of the structural, electronic and catalytic properties of the catalysts were carried out. The obtained catalysts are very promising for several reactions. The obtained results will be discussed.

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REDUCTIVE DEGRADATION OF 2,4-DICHLOROPHENOXYACETIC ACID BY ADSORPTION/CATALYSIS USING Pd/CARBON WITH BIFUNCTIONAL ROLES

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Emerging pollutants (EPs) are synthetic chemicals that have the potential to enter into the environment and can cause adverse ecological and/or human health effects, which are not commonly monitored, but hardly removed from aquatic media. Due to their low soil sorption and taking into account their high potential of leachability, these residues are often reported in surface and ground water. The consequent contamination caused by these EPs has attracted extensive attention due to their high toxicity and carcinogenicity. Chlorinated compounds are a group of these important chemical products, which are widely applied as end-products or intermediates in chemical and agrochemicals processes. Many techniques have been developed in order to remove these compounds, such as adsorption [1], oxidation [2], photocatalysis [3] and dechlorination methods [4].

Adsorption processes have been widely used as alternative to other techniques due to initial low cost, flexibility and simplicity of design and ease of operation. However, adsorption processes transfer the contaminants from water to another phase, and disposal in a landfill or further contaminant treatment is required. So its cost is still high due to the regeneration process of the spent adsorbents. Adsorption and posterior hydrodechlorination (HDC) processes are defined as some of the most effective methods to separate and eliminate contaminants from the liquid phase. While adsorption and HDC are well established technologies, their combination for EPs abatement purposes has been employed in fewer cases.

Therefore, the aim of this work was to combine physical adsorption and catalytic degradation by using Pd catalytic nanoparticles supported on carbon materials as an adsorption/catalysis bifunctional material. During the adsorption from polluted water, the carbon surface provides adsorption sites to concentrate the chlorinated compounds, such as chlorophenoxyacetic acid (2,4-D) in the present study. After the carbon is saturated with the 2,4-D molecules, these can be decomposed in H_2 atmosphere by the catalytic action of the Pd nanoparticles.

Two types of commercial carbon nanofibers (NF) were used in this study: Pyrograph III PR24-HHT and PR24-PS, both of them were provided by Applied Sciences Inc. The carbon materials used in this work were strategically chosen as supports, due to their reduced textural and chemical complexity. Catalysts were prepared by incipient wetness impregnation using an acetone solution of palladium nitrate $Pd(NO_3)_2$ and denoted as PdHHT and PdPS. Supports and catalysts were characterized by BET, TG, XPS and TEM. The HDC of 2,4-D was carried out in a flask reactor at atmospheric pressure after reduction of the catalysts with $NaBH_4$. The reaction temperature was maintained at 25 ºC. Prior to the catalysis, the adsorption experiments of 2,4-D were carried out for 1 h with stirring at atmospheric pressure in order to study the effect of adsorption. Subsequently H_2 was bubbled and the hydrogenation products analysed by HPLC.

TEM micrographs were obtained to determine dispersion, particle size and spatial location of Pd nanoparticles (NPs) in the catalysts after reaction. Some of these data are shown in Table and Figure 1. A similar range of particle sizes, but a different spatial localization of the Pd NPs were observed for the distinct catalysts.

As far as the HDC reactions are concerned, the PdHHT catalyst showed excellent activity to convert 2,4-D into phenoxyacetid acid (ultimate dechlorinated product). However, PdPS catalyst only showed the partial dechlorinated products. Considering the reasons for causing the difference in catalytic activity and selectivity between these catalysts, we should be aware that the properties of Pd such as, particle size or Pd species are relevant to catalytic activity and selectivity. Moreover, the NF structure seems to determine a different metal-support interaction. Notably, the 2,4-D adsorption over HHT was higher than that over PS indicating an adsorption-controlled mechanism that could favour the ultimate dechlorinated product. More details on the material properties, characterisation and catalytic reaction of these catalysts will be presented in this communication.

Table 1. Mean particle diameter of Pd NPs

	$d(\Sigma nd/\Sigma n)$	$d\ (\Sigma nd^3/\Sigma nd^2)$
PdHHT	3.2	3.7
PdPS	3.6	5.2

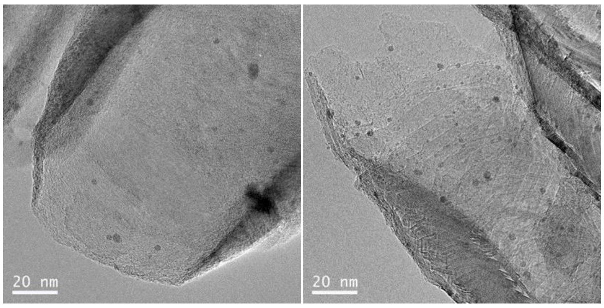

Figure 1. TEM images of PdPS and PdHHT catalysts.

Acknowledgements. We acknowledge financial support from the Spanish Government (CTQ2014-52956-C3-3-R) and Postdoctoral UNED program.

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HYBRID NANOCATALYSTS BASED ON CARBON NANOTUBES FOR THE ACTIVATION OF SMALL MOLECULES

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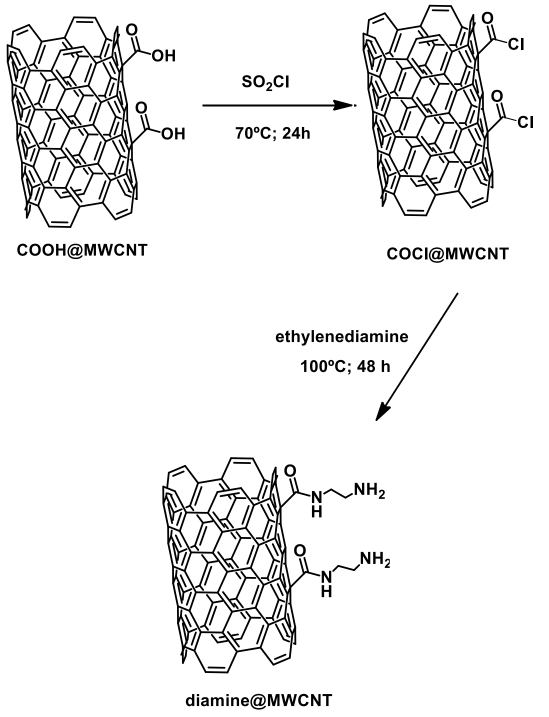
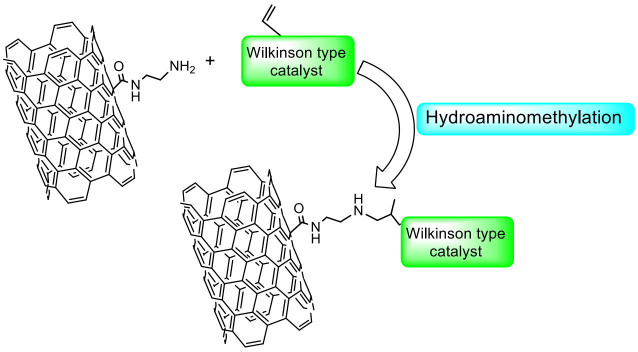
Nowadays, the development of sustainable catalytic processes for the activation of inexpensive and abundant small molecules (CO and H_2) is a major challenge for both academic and industrial purposes [1]. In biological systems, these molecules are paradigmatic entities, since they may act as reservoirs of chemical energy and also as crucial synthons for the assembly of more complex structures. However, they are thermodynamically stable and their successful utilization as reagents requires overcoming high kinetic barriers, where metal catalysts such as the enzyme's prosthetic groups play important roles [1,2]. Nevertheless, outside biological systems, their activation has been successfully achieved by the use of catalysts based on expensive and toxic transition metals [3].

To mimic enzymatic processes, the continuous search for active and selective bio-inspired catalysts using nontoxic and abundant metal complexes with easy reutilization is considered a major ambition for the future of catalysis [4, 5]. With this in mind, the use of carbon nanomaterials, such as carbon nanotubes (CNT), as supports for homogeneous ligands represents one of the most promising routes to obtain systems for heterogeneous catalysis, due to easy recovery with simple techniques as centrifugation or filtration [4, 6].

The hybrid material for the activation of CO and H_2 (hydroformylation reaction) was prepared through amine-functionalization of multiwalled carbon nanotubes (Scheme 1), followed by "one-pot" hydroaminomethylation, to achieve the selected Wilkinson type catalyst (Scheme 2). All the materials were characterized by XPS analysis.

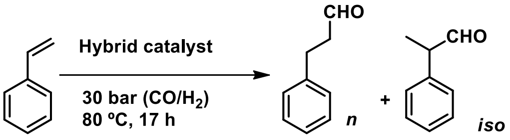


Scheme 1 - Synthesis of diamine@MWCNT materials.



Scheme 2 - Synthesis of the hybrid nanocatalyst.

The results of the use of the hybrid catalysts in hydroformylation of olefins (Scheme 3) will be presented and discussed.



Scheme 3 - Hydroformylation of styrene.

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IMMOBILIZATION OF TETRAPYRROLIC MACROCYCLES ONTO NANODIAMONDS

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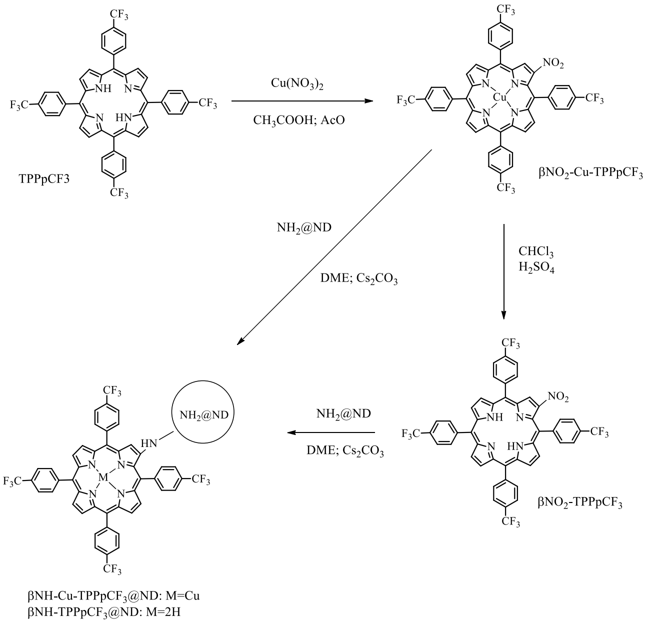
The development of sustainable catalytic processes is a major challenge for both academic and industrial purposes [1]. The continuous search for active and selective bio-inspired catalysts using nontoxic and abundant metal complexes with easy reutilization is considered a major ambition for the future of catalysis [2], as well as the development of sustainable catalytic processes for the activation of inexpensive and abundant small molecules (like O_2). The use of nanodiamonds (NDs) as supports for homogeneous ligands may provide an interesting alternative for heterogeneous catalysis, due to easy recovery with simple techniques, as centrifugation or filtration [2a-3].

Herein, we present innovative methodologies to promote the immobilization of tetrapyrrolic macrocycles on nanodiamonds (NDs), as shown in Scheme 1. 5,10,15,20 - tetra (4-trifluoromethylphenyl) porphyrin (TPPpCF3) was prepared by reacting pyrrole with the corresponding aldehyde. TPPpCF3 was added to a solution of copper nitrate trihydrate to obtain the copper (II) 2-nitro - 5,10,15,20 – tetra (4-trifluoromethylphenyl) porphyrin (βNO_2-Cu-TPPpCF3), with 84% yield.

Nanodiamonds (Sigma Aldrich) were functionalized with diamine (NH_2@)ND, according to a procedure already used for carbon nanotubes [3]. The tetrapyrrolic macrocycle was anchored on NH_2@ND to obtain βNH-Cu-TPPpCF3@ND and βNH-TPPpCF3@ND. Materials were analysed by X-ray photoelectron spectroscopy (XPS), ultraviolet–visible spectroscopy (UV-Vis) and fluorescence emission spectroscopy. Figures 1 and 2 show some results. Reusing the hybrid catalysts in the oxidation of olefins will be discussed.



Scheme 1. Immobilization of tetrapyrrolic macrocycles on NDs.

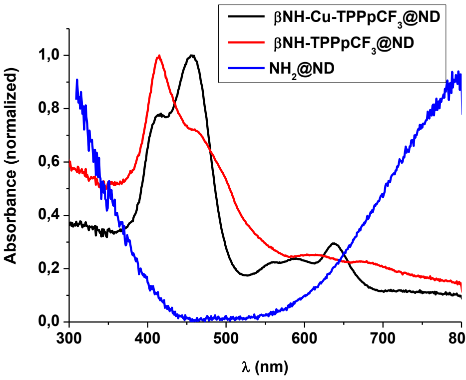


Figure 1. Solid state normalized UV-Vis spectra of nanomaterial βNH-TPPpCF3@ND (red line), NH_2@ND (blue line) and βNH-Cu-TPPpCF3@ND (black line).

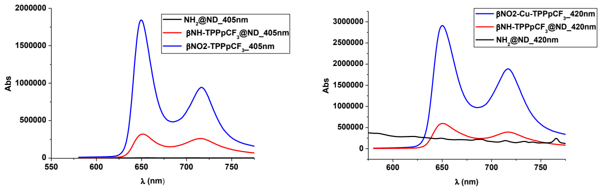


Figure 2. Fluorescence emission spectra of βNH-TPPpCF3@ND (blue line), NH_2@ND (red line) and βNO_2-Cu-TPPpCF3 (black line) in DMF with excitation at 420 nm (right).

Acknowledgements. FCT, for financial support to CQC, (PEst-OE/QUI/UI0313/2014; PTDC/QEQ-MED/3521/2014) and the project POCI-01-0145-FEDER-016387. F.M.S.R., C.A.H., M.J.F.C and S.A.C.C also thank FCT for the funding (PD/BD/114340/2016; TDC/QEQ-MED/3521/2014; SFRH/BPD/99698/2014; IF/01381/2013/CP1160/CT0007 respectively). Project "AIProcMat@N2020, with the reference NORTE-01-0145-FEDER-000006, supported by NORTE 2020, under the Portugal 2020 Partnership Agreement, through the ERD) and of Project POCI-01-0145-FEDER-006984 – Associate Laboratory LSRE-LCM funded by ERDF through COMPETE2020 – POCI – and by national funds through FCT.

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HETEROATOM DOPED POROUS CARBON CATALYSTS WITH SYSTEMATICALLY VARIED PROPERTIES OBTAINED BY TEMPLATE-ASSISTED SYNTHESIS

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Introduction. For decades porous carbon catalysts have been investigated regarding their structural, textural, compositional and catalytic properties. The resulting almost unmanageable amount of publications makes it difficult to compare the results of the literature. Hence it becomes difficult to predict correlations between the physical and chemical properties of the porous carbon materials with their catalytic activity in redox reactions with molecular oxygen, for example the oxidation of aqueous sulfurous acid to sulfuric acid and the electrochemical oxygen reduction reaction (ORR) [1]. For these reactions, which have in common the interaction of the corresponding reactant molecules with the carbon material, various catalytic active components are discussed. Especially, for the adsorption and activation of oxygen the graphitic structures with their high amount of edge carbon atoms and basal areas are important for the catalytic activity of the carbon. Furthermore, the incorporation of heteroatoms into the carbon matrix, for example nitrogen, which is supposed to increase the electron transfer from the carbon material to the adsorbed oxygen species, or sulfur, which is assumed to favor the adsorption and activation of oxygen by its spin density and lone pairs, are discussed in terms of their influence on the catalytic behavior of the carbon material. Furthermore, the internal surface area of the catalysts has to be considered since it correlates directly with the number of the active sites. For this reason, the development of a concept of a modular design of carbon catalysts to establish a “carbon catalyst library” would be useful to determine the influence of the systematic change of the properties of the carbon materials on their catalytic behavior. The template assisted synthesis route should be a useful tool for this purpose [2]. In this contribution, we report on the template assisted synthesis of porous carbon catalysts for the electrochemical reduction of oxygen and the oxidation of aqueous sulfurous acid to sulfuric acid. The catalytic activity is discussed with regard to the textural and the graphitic properties as well as the nitrogen and sulfur content in the carbon catalysts.

Experimental. Silica gel (CWK Bad Köstritz GmbH) was used as the template, which was infiltrated with aqueous solutions of sucrose, sucrose/urea and sucrose/*p*-toluenesulfonic acid as carbon precursors, respectively. Template and precursor were first carbonized (N_2, 600 °C) and after calcination (N_2, 900 °C) the template was removed by treatment with hydrofluoric acid (40 %). The resulting carbon material was subsequently washed with deionized water until neutrality and dried (120 °C). The catalytic behavior of the materials was correlated with their properties determined by means of nitrogen adsorption at -196 °C, elemental analysis (EA), temperature programmed oxidation (TPO), X-ray diffraction (XRD), Raman spectroscopy and X-ray photoelectron spectroscopy (XPS).

Results. Carbons with different surface areas, structures and content of modifiers (namely nitrogen or sulfur) were prepared by varying the number of the template loading cycles and the precursor composition, respectively. The activity of the catalysts correlates with their textural properties and the amount of nitrogen or sulfur incorporated into the carbon. As all investigated reactions involve an activation of oxygen it can be assumed, that nitrogen doping of the carbon material improves the electron transfer to the adsorbed oxygen species. In the oxidation of sulfurous acid the presence of incorporated sulfur species leads to a decrease of the catalytic activity compared to the undoped porous carbon catalyst, while in the ORR those speciess have no significant influence on the activity.

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FUNCTIONALIZATION OF ORDERED MESOPOROUS CARBON VIA HYDROTHERMAL AND SOLVENT EVAPORATION METHODS

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Mesoporous carbons have recently received enormous attention by a number of researchers around the world. The widespread interest in these materials results from their unusual properties such as electric conductivity, chemical inertness and thermal stability [1,2]. Due to the high surface area and ordered pore structure, they have found application in catalysis, adsorption, nanotechnology, energy storage, gas separation, water and air purification [1-3]. Synthesis of ordered mesoporous carbons with a large number of organic functional groups uniformly dispersed on pore walls has been intensely studied for many years [4,5]. The type and character of organic groups applied for functionalization as well as their dispersion affect the surface activity of carbon materials and accessibility of their pores to certain molecules. The most often applied and most effective method of mesoporous carbon modification, leading to generation of carboxyl, hydroxyl, lactone, carbonyl or ether groups which can serve as grafting points for other species (usually achieved via covalent bonding) is oxidation. Many functional groups can be covalently attached in this way to the surface of ordered mesoporous carbons, including basic and acid functionalities [4]. The correct choice of organic functional groups for modification of mesoporous carbon materials changes their neutral and hydrophobic surface into more hydrophilic one.

The main assumption of the presented research was to increase surface activity of mesoporous carbon via its functionalization with different organic groups, in order to enhance its applicability potential.

Mesoporous carbon (C_{SBA-15}) was prepared by hard template method with the use of ordered silica material SBA-15 (hexagonal structure) as template and sucrose as the carbon source. 1 g of SBA-15 was added to a solution obtained by dissolving 1.25 g of sucrose and 0.14 g of H_2SO_4 in 5 g of H_2O. The mixture was placed in a drying oven for 6 h at 100ºC, and subsequently the oven temperature was raised to 160ºC and maintained there for 6 h. The sample turned dark brown during the treatment in the oven. The silica sample, containing partially polymerized and carbonized sucrose at the present step, was treated again at 100ºC and 160ºC using the same drying oven after the addition of 0.8 g of sucrose, 0.09 g of H_2SO_4 and 5 g of H_2O. The carbonization was completed by pyrolysis with heating to typically 900ºC for 6 h in argon atmosphere. The carbon-silica composite obtained after pyrolysis was washed with 5 wt % hydrofluoric acid at room temperature, to remove the silica template. In the next step, mesoporous carbon was filtered, washed with ethanol, and dried at 105ºC.

The key element of the research concerned functionalization of carbon material with different modifiers among which urea, thiourea as well as hexadecyltrimethylammonium bromide (CTAB) can be mentioned. The modification was realized both via hydrothermal treatment of synthesized material (120ºC, 12 h) in the presence of a proper modifying agent as well as via solvent evaporation method. During experiments influence of a method, amount of modifier and type of solvent used (water, isopropyl alcohol) onto efficiency of carbon material functionalization was estimated. Materials obtained were thoroughly characterized with respect to morphology (SEM), structure (X-ray diffraction), characteristic functional groups (FT-IR), electrokinetic stability (LDV), acid-base nature of surface groups (Boehm titration), parameters of the porous structure (BET and BJH algorithm) and thermal stability (TG analysis).

According to preliminary collected experimental data it was proved that mesoporous carbon material of hexagonal structure was the most efficient modified with hexadecyltrimethylammonium bromide irrespective of the amount of organic modifier used. Less effective was application of urea and thiourea for this purpose. What is more important solvent evaporation method seems to be more appropriate for this kind of functionalization as compared to hydrothermal route. Additionally, application of two type of solvents also marked some important issues. All analyzed modifying agents exhibited very good solubility both in water and alcohol medium, but the second one enabled better deposition of urea, thiourea as well as CTAB onto the surface of carbon material.

Finally, based on the results of physicochemical evaluations of prepared materials it was possible to propose the mechanism of carbon/modifier interaction. It was confirmed that described methods have some advantages and disadvantages but are relatively good to functionalize carbon-based materials. This type of modification significantly affect the range of possible application of so-prepared carbon materials in different technological areas such as adsorption or catalysis.

Acknowledgements: This research was supported by the National Science Centre, Poland (project SONATA-12 no: 2016/23/D/NZ7/01347).

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MODIFICATION OF ORDERED MESOPOROUS CARBONS WITH SULFONIC GROUPS FOR GLYCEROL ACETYLATION

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Mesoporous carbons are important in many areas of modern science and technology, including water and air purification, gas separation, catalysis, chromatography, and energy storage [1]. The presence of a high surface area and large pore volume are the main advantages of these types of materials [2]. From the point of view of catalytic processes, modification of mesoporous carbons is very important. An interesting direction of studies is functionalization of carbon materials with sulfonic groups to generate acidic active sites. The acidity of catalyst has significant impact on the catalytic performance in the glycerol esterification. The esterification of glycerol with acetic acid to produce glycerol acetates as valuable bioadditives of biodiesel is one of the most promising approaches for glycerol utilization [3]. This route leads to the formation of glyceryl monoacetate (MAG), glyceryl diacetate (DAG) and glyceryl triacetate (TAG), which are widely applied in cryogenics, cosmetics and biodegradable polyester. Glyceryl diacetate and glyceryl triacetate have been identified as potentially high quality bioadditives for liquid fuels because they can enhance cold and viscosity properties, decrease fuel cloud point and reduce greenhouse gas emissions [3].

The aim of this study was to synthesize the mesoporous carbons functionalized with sulfonic groups and to establish their catalytic activity in the glycerol acetylation.

Ordered mesoporous carbons were prepared by hard template method using ordered silica of hexagonal structure (SBA-15) as template and sucrose as carbon precursor. After sucrose pyrolysis samples were washed with 5 wt % hydrofluoric acid at room temperature to remove the silica template.

Sulfonic groups were introduced on the surface of mesoporous carbon materials of hexagonal structure by two methods:

I. 3.5 g of mesoporous carbon were mixed with distilled water (175 ml), an equimolar amount of 4-aminobenzenesulfonic acid (5 g) and sodium nitrite (2 g), as well as concentrated hydrochloric acid (35 ml). The reaction was carried out at ambient temperature for 20 h under continuous stirring. Mesoporous carbon functionalized with sulfonic groups via *in situ* generated diazonium cation was denoted as OMC-DS.

II. 3.5 g of mesoporous carbon were mixed with concentrated sulfuric acid (90 ml) and heated at 140°C for 20 h under helium flow upon continuous stirring. Sample prepared was denoted as OMC-H_2SO_4.

A number of techniques, including low-temperature nitrogen sorption, X-ray diffraction, scanning and transmission electron microscopy, have been applied to characterize a series of mesoporous carbons modified with sulfonic groups. The content of the surface oxygen functional groups, both acidic and basic, was determined by standard neutralization – titration with HCl and NaOH, according to Boehm method.

The catalytic activity of the materials was subsequently investigated in the glycerol acetylation. The process was carried out at 80^{o}C for 24 h with the use of required amounts of glycerol (7.75 g), acetic acid (28.9 ml), and a catalyst (0.70 g). During this time 5 samples of reaction mixtures were collected (after 1, 2, 4, 6 and 24 h). Analysis of the composition of the reaction samples was performed using a GC chromatograph equipped with a FID detector.

The XRD patterns in small-angle range and transmission electron microscopy images revealed that functionalization of mesoporous carbons with sulfonic groups leads to decreased ordering of their structure. These samples were found to have smaller surface area and smaller pore volume than those of unmodified mesoporous carbons. The reduction of the surface area and total pore volume is attributed to a fairly larger extent by the micropores than the mesopores. It is hypothesized that the functionalization of the surface carbon species with sulfonic groups happens at the micropore/small mesopore openings.

Mesoporous carbons modified with sulfonic groups were found to be active in the glycerol esterification. The conversion of glycerol was up to 90% within only 2 h of reaction time for sample functionalized via *in situ* generated diazonium cation (OMC-DS). This catalyst exhibited selectivity to glyceryl diacetate and glyceryl triacetate of 57% and 23%, respectively (Fig. 1). Mesoporous carbon OMC-H_2SO_4 showed smaller catalytic activity in the reaction than sample OMC-DS.

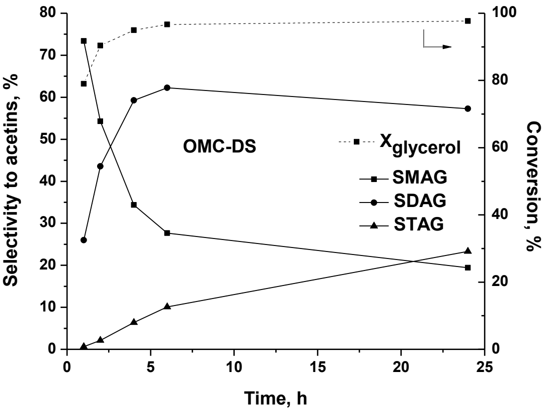

Figure 1. Catalytic performance of mesoporous carbon functionalized with sulfonic groups via *in situ* generated diazonium cation in the process of glycerol esterification.

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AMINO-FUNCTIONALIZED CARBON MATERIALS AS SOLID BASE CATALYSTS FOR KNOEVENAGEL REACTION

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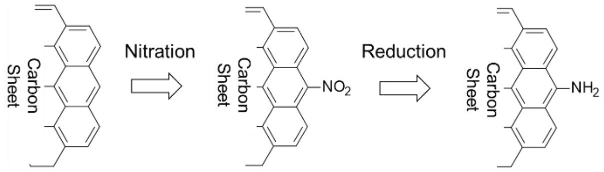
Introduction

Doping of heteroatoms into hexagonal network of carbon imparts catalytic activities to carbon materials for various reactions such as electrochemical and organic synthesis reactions. Previous studies revealed that nitrogen doping to carbon materials enhanced the catalytic activity for base-catalyzed reactions [1]. The nitrogen doping to carbon materials was performed via chemical vapour deposition (CVD) of nitrogen-containing organic compounds, carbonization of nitrogen-containing polymers, and ammoxidation of carbon materials, however, it is difficult to introduce specific nitrogen species possessing basic property such as pyridine-type and aniline-type nitrogen.

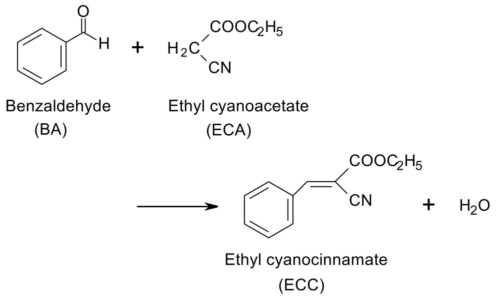
In this study, we selectively introduced aniline-like nitrogen to carbon sheets by amination of carbon materials. The influences of the amination on surface chemical states and catalytic activity for base-catalyzed reaction were investigated.

Experimental

Material. Amino-functionalized carbon materials were prepared by following two steps; 1) nitration of carbon materials, 2) reduction of nitro-functionalized carbons as shown in **Scheme 1**. Firstly, two types of carbon materials such as activated carbon (AC) and Ketjen Black EC600JD (KB) were treated with fuming nitric acid in acetic anhydride at room temperature for 5 h to introduce nitro-groups on the carbon surface. The nitro-groups were reduced by sodium hydrosulfite in NH_3 aq. for 24 h. The obtained amino-functionalized carbons were referred to as A-AC and A-KB.



Scheme 1. Amination of carbon sheet by nitration followed by reduction of carbon materials.



Scheme 2. Knoevenagel reaction of benzaldehyde and ethyl cyanoacetate.

Characterization. Surface elemental compositions of the carbons were analyzed by X-ray photoelectron spectroscopy (XPS). The base catalytic activities of the carbons were assessed by using Knoevenagel reactions as shown in **Scheme 2**. A carbon catalyst (100 mg) was put in a reactant mixture consisting of benzaldehyde (10 mmol) and ethyl cyanoacetate (10 mmol) diluted by n-butanol (4 mL). The reaction was conducted at 80°C for 1 h under a reflux condition. The reaction yields of was defined by the molar ratio of the product (ethyl cyanocinnamate (ECC)) to the initial amount of benzaldehyde.

Results and discussion

Figure 1 shows the N1s XPS spectra and N/C (atomic ratio of nitrogen to carbon) of A-AC and N-KB. There was a single peak at 399 eV in A-AC and A-KB, which was assigned to aniline-like nitrogen [2]. This result indicates that the amination of AC and KB selectively introduced aniline-like nitrogen.

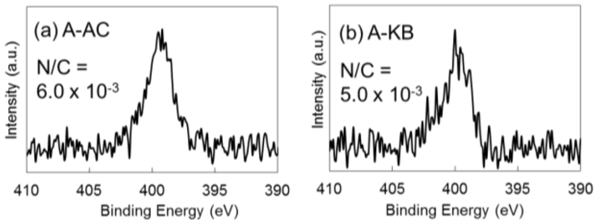


Figure 1. N 1s XPS spectra of (a) A-AC and (b) A-KB.

Table 1 shows the results of Knoevenagel reaction. The amination of AC increased both of the BA conversion from 16.0 % to 44.3 % and ECC yield from 6.30 to 39.0 %. This result indicates that the amination imparted basic property to AC. In the case of KB, the BA conversion was increased from 26.2 % to 52.7 % by the amination, while the ECC yield was not increased. The results of XPS and Knoevenagel reaction indicates that the amination of AC and KB selectively introduced aniline-like nitrogen, however the catalytic activity of amino-functionalized carbons for Knoevenagel reaction depended on the types of carbon matrix.

Table 1. Results of Knoevenagel reaction

Sample	BA conversion (%)	ECC yield (%)
AC	16.0	6.30
A-AC	44.3	39.0
KB	26.2	12.9
A-KB	52.7	3.00

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LIGNOCELLULOSE-BASED ACTIVATED CARBONS AS SUPPORT FOR NICKEL METAL CATALYST

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Introduction

Activated carbons are known to have large specific surface areas with high porosity and thermal stability. These qualities are important for the supported metal catalysts. Lignosellulosic waste and residual materials e.g. from saw or pulp industry can be used as a raw material for high quality activated carbon prepared by carbonization and activation. Activated carbon foams prepared by polymerization of tannins extracted from residual lignocellulosic materials is a possible support for heterogeneous catalysts.

Precious noble metals have been used widely in the catalytic applications. Replacement of noble metals with more abundant transitional metals e.g. nickel, iron, molybdenum or tungstate can be an option for more cost-effective catalysts.[1] Nickel, for example, is used widely in the catalytic reactions and biomass refining processes e.g. in the hydrogenation reactions.[2][3]

In the preparation of supported metal catalysts by impregnation method, the adsorption of metal ions from the impregnation solution is influenced by the physicochemical properties of the support, pH of the impregnating solution and nature of the solvent. Point of zero charge (PZC) of the support plays an important role in the adsorption of metal ions [4] and it differs for each support material depending on its preparation. If the interaction of the metal and support is too weak, deactivation of activated carbon supported metal catalyst can occur caused by agglomeration or leaching of metal particles. Because of these, optimizing the preparation method of the metal supported catalyst on activated carbon by selecting the proper pre-treatment for the support, a proper solvent for the impregnation and proper drying step are very important factors for the AC supported metal catalyst.

In this research, activated carbons based on lignosellulosic residual materials have been prepared and the preparation step of impregnated nickel catalyst on activated carbon have been optimized. This study has been done to have a knowledge how to prepare stable and effective nickel metal catalyst on activated carbon.

Preparation of activated carbon supports

- Sawdust based activated carbon

Activated carbon prepared from lignocellulosic residual material e.g. saw dust of birch was carbonized and steam activated at the one-step process at 800 °C in an inert atmosphere.

- Tannin-based catalyst support material

Synthesized activated carbon foam was prepared by addition of tannic acid to the mixture of furfuryl alcohol, water and a surfactant, before addition of blowing agent, n-pentane and a catalyst. The foam was allowed to rise followed by maturation in an oven for 24 h at 105 °C. Finally, the foam was carbonized and steam activated at the one-step process at 800 °C in an inert atmosphere.

Preparation of supported metal catalyst

In the preparation of AC supported metal catalyst nickel nitrate has been used as a precursor. Different washing techniques with water and acids have been used to prepare proper support, multiple solvents in the impregnation step have been used and finally drying step followed by calcination has been studied.

The properties of the prepared supported nickel metal catalyst have been characterized by multiple techniques including e.g. physisorption and chemisorption, field emission scanning electron microscopy, transmission electron microscopy, x-ray diffraction and x-ray spectroscopy.

Finally, the leaching of the metal has been studied by desorption method with multiple solvents e.g. water and organic solvents.

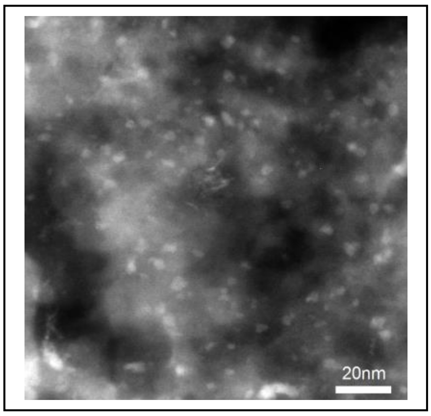

Figure 2. TEM-image from 3wt.% Nickel catalyst on sawdust based activated carbon (dark field image, white dots presenting nickel)

Conclusions

Optimizing the preparation method of nickel metal catalyst for the each activated carbon prepared by selecting the proper pre-treatment for the support, a proper solvent for the impregnation step and proper drying procedure are affecting to the catalyst characters e.g. metal particle size and distribution and to the stability of the catalyst.

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FUNCTIONALIZED METALLURGICAL COKE AS CATALYSTS SUPPORTS OF THE DIRECT COAL LIQUEFACTION

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Hydrogenation reactions are often carried out at high temperatures and pressures so thus demand a much stronger thermal strength of the carbon framework. Metallurgical coke has a high potential to be used as catalyst support for this type of reactions.

A Colombian metallurgical coke (CK) was functionalized with nitric acid and diluted oxygen and changes in textural properties and surface chemistry were determined. The catalysts were synthesized, using CK modified as support, by impregnation with an aqueous solution of iron/thiourea and subsequent thermal activation. The catalytic tests were performed by direct coal liquefaction (DCL) and it was evaluated the conversion and its relationship with the type of surface oxygenated groups generated in the support functionalization.

Table 1 shows the textural and surface chemistry characterization of the modified materials and the reference raw one. It is evident that different oxidative treatments produce dissimilar textural characteristics. Treatment with diluted oxygen affects the physical and chemical properties of the material by increasing the S_{BET} and V_{Total}, due to the formation of new pores and the opening of pores that before the treatment were not available [1]. The increase in the evolution of CO_2 y CO, in TPD-MS, indicate the formation of lactone and phenol type oxygenated groups. Treatment with HNO_3 slightly affects the textural properties of the coke, however at high concentrations of HNO_3 (12 M) a slight increase in the surface area and in the pore diameter is observed due to, that under these conditions, wear occurs on the walls of the pores [2]. The surface oxygenated groups generated under the HNO_3 treatment depends on the concentration used; at low concentrations, the lactone, carbonyl and quinone groups are majority, while and at high concentrations, anhydride and carboxylic acid groups increase.

Table 1. Characterization of surface and textural chemistry

Material	µmol totales CO_2/g	µmol totales CO/g	S_{BET} (m^2/g)	V_{Total} (cm^3/g)	D_p (nm)
CK	213,4	123,0	3,2	0,008	10,35
CK4M	289,0	196,3	3,2	0,008	10,13
CK12M	312,7	159,4	4,6	0,014	12,24
CKO18	444,0	937,3	59,0	0,036	2,43
CKO36	818,6	1854,6	164	0,107	2,61

Figure 1 shows the X-ray diffraction of the catalysts where the presence of different phases of iron sulphide is observed. In addition to those of pyrite, diffractions corresponding to greigite, marcasite as well as crystalline phases of α-Fe and Fe_4N are presented.

X-ray fluorescence analysis allows determining the amount of iron and sulfur incorporated during the impregnation of the supports. Nitric acid treatments improve the efficiency of the impregnation process, depositing iron sulphides with S/Fe molar ratio less than 2. This indicates that the predominant iron sulfide phases deposited are poor in sulfur. On the other hand, treatment with diluted oxygen favors the incorporation of an active phase enriched in sulfur. This result is in accordance with the X-ray diffraction ones.

Figure 2 shows the relation of µmol CO/µmol CO_2 as a function of the conversion in direct liquefaction of coal (LDC). The highest oil yield is obtained with the catalyst which the highest amount of surface oxygenated groups in the support, independently of the type of oxidant used and the nature of the incorporated groups. The functionalization of the metallurgical coke allowed a good interaction with the active phase improving its dispersion and the conversion of DCL.

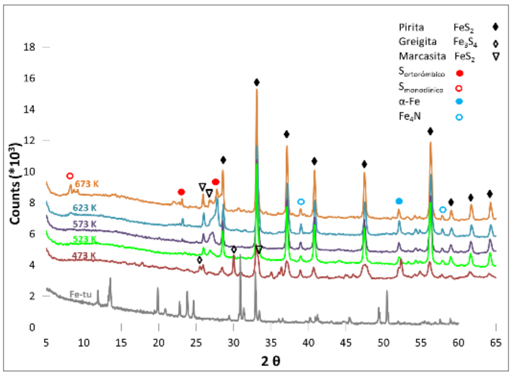

Figure 1. X-ray diffraction of the catalysts.

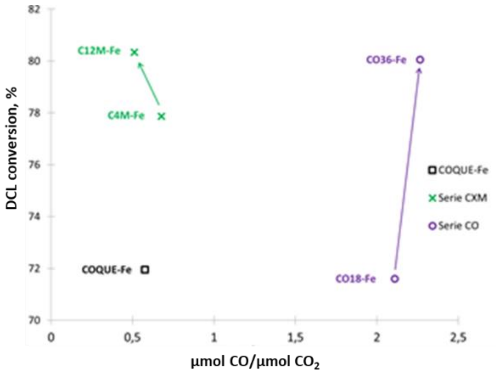

Figure 2. Conversion of the DCL versus CO/CO_2 ratio.

It is observed that oxygenated groups in the catalytic supports increases the efficiency in the impregnation and improves the conversion of the LDC. In addition, the highest yield to oils is obtained with the CO36-Fe catalyst, which has a greater surface area and relative dispersion.

Acknowledgements. The National University of Colombia and the Dirección de Investigación Sede Bogotá financially supported this research through the "student assistant" scholarship.

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STUDY OF CARBON SORBENTS BY RAMAN SPECTROSCOPY

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The Raman spectroscopy is an indispensable tool for studying amorphous structures. It is possible to carry to such objects as sorbents prepared on the basis of a fossil coal, the composition of which mainly consists of carbon with different types of hybridization.

The study was carried out on the Renishaw Invia Basis Raman spectrometer at 514.5 nm excitation wavelength, with the light spot diameter and using the 1800 l / mm grating. Calibration of the Raman shift was performed by the fundamental vibration of silicon at 520 cm^{-1}.

The objects of the study were the sapromixite type Barzas coal and the carbon sorbents prepared from it. The coal was washed with water from clay inclusions, dried, and crushed to particle size <0.5 mm, Sorbents were prepared by carbonization of coal in the presence of alkali (KOH or NaOH). The alkali solution was introduced with a weight ratio [carbon] / [alkali] = 1: 0.5, 1: 1, 1: 2. Then the mixture was heated to 800 ° C at a heating rate of 8 ° C / min and held at 800 ° C for 1 hour. The sintered carbonizate was ground and cleaned of alkali and dried at 105 ° C to constant weight.

Raman spectra of sorbents are two main scattering bands of the first order: ≈1350 cm^{-1} and ≈1600 cm^{-1}, and their overtones in the spectral range of 2700 cm^{-1} to 3200 cm^{-1}. The peak at 1600 cm^{-1} is related to the fully symmetric vibrations of sp^2-hybridized carbon atoms in the plane of the polycyclic aromatic rings. The peak at 1350 cm^{-1} is characteristic for amorphous carbon, or distortion of the graphite plane by sp^3-hybridized carbon atoms. Such atoms are mainly located at the crystallites grains edges, of which the sorbent consists. By the ratio of the intensities of these bands, one can judge the degree of disorder of the system as a whole. A rather intense second-order spectrum indicates a good crystallinity of the sample because of the low probability of a two-photon process in an amorphous body.

Analysis of the spectra was carried out with the decomposition of the bands into composite vibrations using a function combining the Gaussian and Loretz functions with a Lorentz fraction of at least 0.85. Samples of carbonizates prepared by using NaOH (1: 2) have in their composition smaller crystallites than samples prepared under the same conditions from KOH. This can be judged from the shifts of the main peaks to the blue region (from 1352 cm^{-1} to 1364 cm^{-1} and from 1597 cm^{-1} to 1605 cm^{-1}) and an increase in the peak half-width of the sp^3-carbon oscillation from 136 cm^{-1} to 172 cm $^{-1}$, when using caustic soda. The "disorder / order" ratio of the system with NaOH (1.27), in which the CH-groups of the sp^3-state are located along the boundaries of individual clusters, in contrast to the more ordered structure after treatment with KOH (0.92), also speaks in favor of this. Also, a sample of NaOH has a minimal surface area compared to the other carbonizates.

Sorbents prepared under various synthesis conditions (the size of the carbon particles, the alkali content) using KOH form similar structures, the «disorder / order» ratio of which for samples practically does not change 1.14 ± 0.04.

When the Raman excitation is excited in the samples of naturally oxidized Barzas coal, intense luminescence is observed with 10 time’s higher intensity than the intensity of the Raman signal of the sorbents. This indicates a significant difference in the structure of the initial coal between carbonizates prepared on their basis.

The report will give a detailed analysis of the Raman spectra of sorbents.

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CARBON DOTS WITH DUAL ROLE IN CATALYSIS

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The aim of this work is to demonstrate the potential of carbon dots [1] in the determination and quantification of metal leaching in catalysis. Carbon quantum dots (CQDs) are small carbon nanoparticles of less than 10 nm in size. Due to their unique properties, like size-dependent fluorescence (Figure 1), non-toxicity and biocompatibility, carbon quantum dots have garnered much interest due to their promising application in fields such as, chemical sensing or catalysis and drug delivery [2,3]. We will address the synthetic process for ~~producing~~ carbon dots, namely parameters such as the power or the reaction time and how these affect CQDs fluorescence. Tests using catalytic samples will be performed and discussion regarding the influence of the size of the carbon dot in the concentration of the metal detected will be presented.

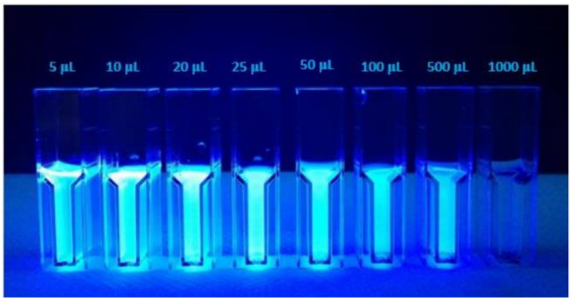

Figure 1 - The influence of [CQDs] in fluorescence.

In this work we will show the difference in several important parameters, such as:

- [CQDs] and pH;
- Different metals and compounds
- UV studies (Figure 2) of their behaviour

We also will present how this parameters change a catalytic process.

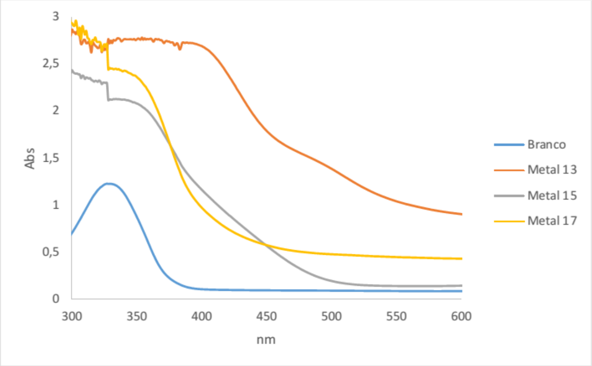

Figure 2 - UV spectra shows the difference between the blank (only CQDs) and the solutions were the fluorescence disappeared.

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STRUCTURE AND PROPERTIES OF COALS AND SORBENTS

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The Raman spectroscopy is a non-destructive analysis method, which in combination with SEM makes it possible to study the fine structure of fossil coals and sorbent derived from them. Carbon is the basis of a coal substance representing natural coal. An in-depth study of the structure of coal matter by the Raman method, using coal from the Kuznetsk basin (their crystallinity and defectiveness), depending on the yield of volatile substances and the stage of metamorphism, is an urgent task of this study.

The Coal of Kuzbass of grades "D", "DG", "GZO", "F", "K", "KS" and "OS", which represent a practically complete series of metamorphism of coal matter, were investigated by the Raman method. Due to the selected series of samples, it is possible to trace the changes in the fine vibrational structure of the coals. The samples of the coals were ground on a ball mill to grain sizes <1 mm and dried at room temperature to an air-dry state. The Raman spectra were recorded on a Renishaw inVia Basis spectrometer with an excitation wavelength of 514.5 nm and a beam diameter focused on a plane-parallel plate not exceeding 2 μm. The obtained Raman spectra were analyzed by decomposing the peaks into oscillation components using a combination of the Gaussian and Lorentz functions.

The Raman spectra of coal can be characterized by two broad peaks, the position of the maxima of which coincides with the vibrations of the C-C bonds (E_g mode): in case of sp^3- (D-band ~1365 cm^{-1}) and sp^2- hybridized carbon (G-band~1590 cm^{-1}). The position of the D-band is slightly dependent on the degree of metamorphism - 1368 cm^{-1} for coal of mark «D» and 1366 cm^{-1} or coal of mark «OS». In this case, the G-band shifts significantly to the blue region from 1574 cm^{-1} to 1592 cm^{-1}. The band shift characterizing the presence of graphite planes can be caused by a decrease in the size of the crystallites that make up the coal. The intensity of the G-band increases, which indicates the formation of a stable graphite phase.

As the coal matures, the oscillation attributed to the violation of the graphite plane (D ~ 1610 cm^{-1}) [3] shifts to the red area, and subsequently disappears. There is a decrease in the half-width of the D-band from 230 cm^{-1} for coal of mark «D» to 193 cm^{-1} for coal of mark «OS». This may indicate that the structure is simplified and the oscillations contributing to the D-band either degenerate or disappear due to a change in the internal structure. It can also be associated with the redistribution of aromatic and aliphatic groups.

Mature coals have a higher degree of crystallinity and a lower content of organic molecules than younger ones. This is evidenced by the presence of a second order of scattering and a sharp decrease in the background of fluorescence in the blue region of the spectrum.

Thus, the Raman method, in comparison with other physicochemical methods, in particular, methods SEM, NMR and IR-spectroscopy, will allow us to establish the structural features of coals and sorbents derived from them in the series of metamorphism.

The work was carried out with the financial support of the Ministry of Education and Science of Russia within the framework of the agreement RFMEFI61317X0079.

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CATALYTIC VALORIZATION OF CELLULOSE DIRECTLY INTO ETHYLENE GLYCOL

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Being the primary building block components of lignocellulosic biomass, carbohydrates have the potential to supplement petroleum-derived hydrocarbons and other high-added value chemicals [1]. Lignocellulose can be fractionated to its constituents (cellulose, hemicelluloses and lignin), which can be further transformed into platform chemicals. The one-pot hydrolytic hydrogenation of cellulose into valuable chemicals (e.g. ethylene glycol) over heterogeneous catalysts is one of the most efficient pathways for a future sustainable society based on cellulosic biomass, due to its greenness and energy efficiency compared to other primary conversion processes. Ethylene glycol (EG) is an important chemical used as energy platform for the production of hydrogen and liquid alkane fuels via the aqueous reforming process or as precursor for plastics and polymers, being considered a high-value market product [2]. Therefore, this work focused on the design of efficient and selective catalysts for the direct production of EG from cellulose.

A 0.4 wt.% Ru and a 30 wt.% W monometallic catalysts supported on carbon nanotubes (CNT_0) were prepared by the incipient wetness impregnation method and denoted as Ru/CNT_0 and W/CNT_0, respectively. A 0.4%Ru-30%W bimetallic catalyst was also synthesized by impregnation of Ru into the already prepared W/CNT_0 catalyst and denoted as Ru-W/CNT_0. Also, the original carbon nanotubes were modified by chemical treatment with HNO_3 (CNT_1) and a 0.4 wt.% Ru catalyst was prepared on this modified material (Ru/CNT_1). The catalysts were characterized by different techniques (N_2 adsorption, microscopy, TPD, TPR, XRD, XPS, ICP) and tested in the one-pot conversion of cellulose, which was previously ball-milled for 4 h at 20 s^{-1}. In standard tests, 300 mL of water, 750 mg of ball-milled cellulose and 300 mg of catalyst were placed into a 1000 mL reactor under stirring (150 rpm). After heating under N_2 to 205 ºC, the reaction was started by switching from inert gas to H_2 (50 bar), and samples were periodically withdrawn for analysis by HPLC and TOC.

The textural and chemical properties of the supports and the metallic catalysts were determined by N_2 adsorption isotherms and temperature programmed desorption (TPD), respectively. The supports presented type II isotherms, characteristic of non-microporous materials. A decrease of the surface area (S_{BET}) of the catalysts was noticed comparing to the starting supports due to the introduction of the metallic phases. The oxidative treatment led to an increase of the surface area of CNT_1 (Table 1), since it opened up the endcaps of CNT_0 and created sidewall defects. The larger amounts of CO and CO_2 released during the TPD analysis of CNT_1 evidence the increase of the amount of surface oxygenated groups by the oxidation treatment.

The catalysts were evaluated in the one-pot reaction and conversions of cellulose around 100 % were reached after 5 h in all cases. Ru/CNT_0 and Ru/CNT_1 favoured the formation of sorbitol (> 50 % yield) over EG, but the presence of the acidic groups showed no important differences (Figure 1). However, W/CNT_0 did not favour the formation of sorbitol neither EG, but other unknown products. Ru-W/CNT_0 was then tested and the addition of W to the Ru catalyst shifted the reaction from the production of sorbitol to EG (35 % yield). Subsequently, a combination of the Ru/CNT_1 and W/CNT_0 was evaluated, in order to see if the presence of acidic groups would have any influence on the reaction. Indeed, a significant increase of the EG yield to over 40 % was observed with this physical mixture of catalysts. This result indicates that a combination of ruthenium and tungsten species, together with acidic groups, is essential to maximize the production of ethylene glycol.

Table 1. Textural and chemical properties of the materials.

Sample	S_{BET} ($m^2·g^{-1}$)	CO (μmol·g^{-1})	CO_2 (μmol·g^{-1})
CNT_0	267	415	92
CNT_1	315	2169	737
Ru/CNT_0	245	-	-
Ru/CNT_1	305	-	-
W/CNT_0	170	-	-
Ru-W/CNT_0	162	-	-

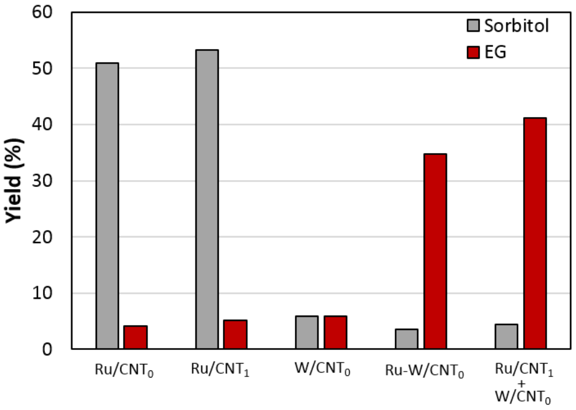

Figure 1. Yields of sorbitol and EG after 5 h of reaction.

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Ru NANOPARTICLES SUPPORTED ON N-DOPED REDUCED GRAPHENE OXIDE AS VALUABLE CATALYST FOR THE SELECTIVE AEROBIC OXIDATION OF BENZYL ALCOHOL

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Selective oxidation of benzyl alcohol to benzaldehyde is one of the most relevant transformations in chemical synthesis. Benzaldehyde is widely employed as precursor and intermediate in the agrochemical, pharmaceutical and perfumery industries.[1] The use of noble metals such as Au, Pd and Pt[2,3] has been extensively studied, and in some cases carbonaceous materials have been used as support for these metallic nanoparticles. However, due to the lack of economically attractive and stable heterogeneous catalyst systems, we propose the development of more efficient Ru based heterogeneous catalysts. In particular, we aim to investigate the effect of two graphenic materials, with and without nitrogen adatoms, on the catalytic behavior of Ru nanoparticles catalysts in the oxidation of benzyl alcohol to yield benzaldehyde.

Ru supported catalysts, with a Ru loading of 4 wt.% were prepared by wetness impregnation with $Ru_3(CO)_{12}$ (serie denoted with "CO"), $RuCl_3$ (denoted as "Cl") or $Ru(NO)(NO_3)_3$ (labelled with "NN") as precursors.[4] Two graphenic materials were prepared via thermal treatment of graphite oxide (GO). When exfoliation of GO is carried out under inert gas (N_2) a reduced graphene oxide (rGO) is obtained, while if reactive atmospheres (NH_3 +N_2) is used a nitrogen doped reduced graphene oxide (NrGO) is obtained. An incorporation of 5% of nitrogen atoms is achieved with this procedure. Also two commercial carbon materials were employed as supports: activated carbon (AC) and high surface area graphite (HSAG). A multi-technique approach was applied to c characterize the supports and catalytic samples. Previous to the reaction tests the catalyst materials were activated at 350°C for 2 h under flowing H_2.

The oxidation tests were carried out using a Radleys Starfish carousel batch reactor at 90ºC with oxygen bubbled through the reaction solution (5 ml min^{-1} at 1 bar) under magnetic stirring (700 rpm). 25 mg of catalyst was added to a reaction mixture of 8.4 mmol benzyl alcohol, 0.1ml of mesitylene as internal standard, and 10 ml of toluene as solvent. Aliquots of 0.25 ml of the reactor liquids were collected periodically, filtered and diluted with 1.75 ml of toluene. The reaction product mixture was analysed on a Varian 3900GC with CP-8400 autosampler (CP-Sil5 CB column, (15 m × 0.25 mm × 0.25 µm). Carbon mass balances were higher than 95% in all the catalytic determinations.

In Table 1 the main catalytic findings are reported. Interestingly, under our experimental reaction conditions, all the tested catalysts provide 100% of selectivity to benzaldehyde. Apparently the catalysts prepared with Ru chloride as precursor gives are less active, this effect is not correlated with the Ru particles sizes. Additionally catalysts supported on commercial supports (AC and HSAG) are inferior in terms of catalytic activities.

Systematically Ru catalysts supported on NrGO produce higher conversions when compared with Ru supported on rGO. In Figure 1 are shown the evolution of catalytic conversion values with the time in the reactor, obtained with the Ru(CO)/NrGO and Ru(CO)/rGO catalysts. Thus the nitrogen-doped graphenic support material seems to be acting cooperatively with the Ru nanoparticles. As a tentative explanation to these findings, the interaction of surface nitrogen groups exposed at the NrGO support with the product of the reaction should be considered. In order to understand such interaction, a comparative study by immersion calorimetry in toluene, in benzyl alcohol and in benzaldehyde, of both rGO and NrGO materials is currently in progress.

Table 1. Mean Ru particle sizes obtained by TEM and catalytic activity (benzyl alcohol conversion) after 24 hr in reaction the Ru catalysts.

Catalyst	d_{TEM} (nm)	Conv (%)
NrGO	-	0.3
Ru(CO)/rGO	1.4	35.5
Ru(CO)/NrGO	1.8	46.2
Ru(NN)/rGO	1.4	30.7
Ru(NN)/NrGO	1.7	31.9
Ru(Cl)/rGO	1.5	13.6
Ru(Cl)/NrGO	2.1	16.0
Ru(CO)/AC	2.3	16.0
Ru(CO)/HSAG	2.4	18.0

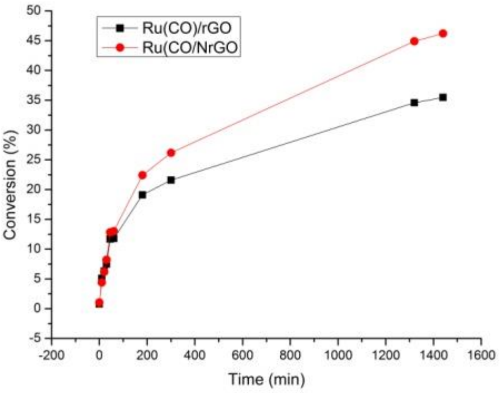

Figure 1. Time course of conversion over Ru(CO)/NrGO and Ru(CO)/rGO catalysts.

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EFFECT OF THE TEXTURAL PROPERTIES OF BIOMASS-DERIVED CARBON SUPPORTS ON THE CATALYTIC CONVERSION OF CELLULOSE TO SORBITOL

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The use of biomass for the production of chemical compounds is an essential issue to achieve a more sustainable and green economy. The formation of platform molecules from biomass through low temperature processes is a widely used strategy to obtain high added value chemical products. Sorbitol is one of the most promising platform molecules included in the list of the twelve base products of maximum potentiality derived from biomass, specifically from cellulose. The most common way to obtain sorbitol is the catalytic conversion of cellulose by using supported ruthenium catalysts. Among the different supports that have been studied, carbon materials, such as carbon nanotubes and activated carbons, are the most promising, the former offering the best catalytic performance [1]. However, it is necessary to carry out further research to try to match or surpass the results obtained with carbon nanotubes using a cheaper carbon support. Accordingly, the aim of the present work is to use glucose, one of the main fractions of biomass, as precursor of the carbon supports. As a result, lower costs can be achieved, and two of the most important fractions of the biomass are valorized: glucose for the preparation of the catalyst, and cellulose as the main raw material for the reaction.

Carbon supports were prepared by hydrothermal polymerization of glucose and subsequent physical activation at 900 ºC under CO_2 atmosphere for 2, 4 and 6 h, in order to obtain materials with different surface areas. Catalysts were prepared by incipient wetness impregnation of the carbon supports with a solution of ruthenium (III) chloride. The amount of the metal precursor was calculated to achieve a metal loading of 0.4 wt. % Ru. Catalysts were then heated under nitrogen flow at 250 ºC for 3 h and subsequently reduced under hydrogen flow at 250 ºC for 3 h. The catalysts were denoted as Ru/AG in reference to activated glucose, followed by the value of the surface area determined by nitrogen adsorption. Carbon nanotubes were also used as support under the same experimental conditions, for comparison. Supports and catalysts were characterized by nitrogen adsorption, scanning electron microscopy, thermogravimetric analysis, elemental analysis, temperature programmed desorption and X-ray photoelectron spectroscopy. The conversion of cellulose into sorbitol was tested by one-pot catalytic reaction. In standard tests, 300 mL of water, 750 mg of ball-milled cellulose and 300 mg of catalyst were placed into a 1000 mL reactor under stirring (150 rpm). After heating under N_2 to 205 ºC, the reaction was started by switching from inert gas to H_2 (50 bar), and samples were periodically withdrawn for analysis by HPLC and TOC.

Glucose-derived supports presented type I isotherms, characteristic of microporous materials. As expected, an increase in activation temperature led to higher microporosity (Table 1). Besides, isotherms obtained from catalysts remained virtually unchanged although BET surface areas slightly decreased due to the incorporation of the metal. The catalysts were evaluated in the one-pot reaction, cellulose conversions of around 100 % being reached after just 3 h of reaction. As shown in Figure 1, the microporosity favoured the formation of higher amounts of sorbitol throughout the reaction. In addition, 50 % yield was obtained within the first hour for sample Ru/AG_2200. This result may be due to the higher surface area and micropore volume.

Table 1. Textural and chemical properties of the materials.

Sample	S_{BET} $(m^2\cdot g^{-1})$	Yield (%, 2 h)	Conversion (%, 5 h)
Ru/CNT	282	47	83
Ru/AG_600	569	33	100
Ru/AG_900	936	46	100
Ru/AG_2200	1852	60	100

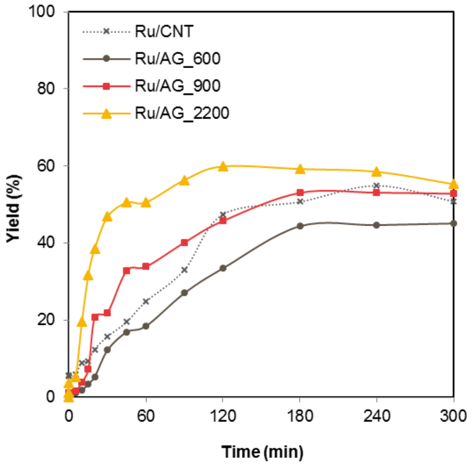

Figure 1. Effect of textural properties on the production of sorbitol.

In the present study, yields and conversions higher than those of the reference catalyst (Ru/CNT) were obtained for samples Ru/AG_900 and Ru/AG_2200 (Figure 1). These results indicate that carbon nanotubes can be successfully replaced by a cheaper support derived from biomass.

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OPTIMIZATION OF Mn PROMOTED Cu-Ni CATALYSTS FOR THE CONVERSION OF ETHANOL TO BUTANOL

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The interest in the production of 1-butanol has grown due to its application as a raw material of chemical products in the paint and solvent industry, and to its optimal properties that make it a promising alternative to ethanol as a substitute for fossil fuels.[1] 1-Butanol can be produced by ethanol condensation through the Guerbet reaction, which implies dehydrogenation of ethanol to acetaldehyde, aldol condensation of acetaldehyde to crotonaldehyde and hydrogenation of crotonaldehyde to 1-butanol. Guerbet industrial process employs homogeneous catalysts, although recent research focuses on its heterogeneization[2]. While hydrogenation /dehydrogenation reactions require easily heterogenizable metal catalysts, aldol condensation is more difficult to apply on solid metal oxides. Manganese based catalysts have been studied for the condensation of ethanol into 1-butanol, most studies being homogeneous catalyzed.[3] Copper has been studied as a metallic component to catalyze the Guerbet reaction since its presence reduces the reaction temperature.[1, 4] In this study, an inert and non-porous carbonaceous support has been used, high surface area graphite (HSAG), to disperse the active phases (Mn oxide and reduced metallic precursors) maximizing the number of surface centers exposed and favoring their interaction. So we pretend to improve the formation of alloy phases among Cu and Ni, as well as to maximize the surface metal-promoter sites.

Catalysts 2.5Mn-HSAG, 5Cu/HSAG, 5Ni/HSAG, 5Cu/Mn-HSAG, 5Ni/Mn-HSAG, 4Cu1Ni/Mn-HSAG and 2.5Cu2.5Ni/Mn-HSAG (numbers are indicating the metal loading in wt%) were prepared by wetness impregnation with aqueous solutions of the corresponding metal nitrate. The 2.5Mn-HSAG sample was thermally treated at 673K for 3 h in helium atmosphere prior to the metal precursor addition. The catalysts were characterized by X-ray diffraction (XRD), temperature-programmed reduction (TPR), CO_2 chemisorption, NH_3 temperature-programmed desorption and transmission electron microscopy (TEM). The catalytic condensation of ethanol was carried out in a fixed-bed reactor in gas phase at 503 K and 50 bar in a continuous flow. The catalysts (0.5 g) were reduced in situ with hydrogen at 573K for 1 h before reaction, except Ni/HSAG and Ni/Mn-HSAG which were reduced at 723K. For all experiments, the feed mixture consisted of 50 mL_{STP}/min of He and 0.02 mL/min of ethanol introduced with an HPLC pump. The condensed products were collected and analyzed by gas chromatography (GC), while the gaseous products were analyzed by on-line GC.

The results obtained in the catalytic tests with the different samples are shown in Table 1. Preliminary tests with the HSAG support and with 2.5Mn-HSAG show that these are practically inactive under our reaction conditions. 5Cu/HSAG shows high activity for the conversion of ethanol but not high selectivity to butanol. However, the bimetallic Cu-Ni catalysts doped with Mn showed an improvement in the selectivity toward 1-butanol. Figure 1 compares in terms of 1-butanol yield the different Mn promoted Cu-Ni catalysts. It can be observed that the 2.5wt.% Cu and 2.5wt.% Ni is the optimal Cu-Ni load. For all experiments the catalysts reach the steady state after 2 h in reaction, subsequently conversion and selectivity are practically constant throughout the reaction time, with acetaldehyde, methane, propane, carbon monoxide and 1-hexanol being formed as main by-products.

Table 1. Ethanol condensation at 503K and 50 bar after 24 hr on stream.

	Ethanol Conv. (%)	1-Butanol Select. (%)
2.5Mn-HSAG	0.3	0
5Cu/HSAG	38.0	1.7
5Ni/HSAG	-	-
5Cu/Mn-HSAG	27.4	32.4
5Ni/Mn-HSAG	47.4	22.6
4Cu1Ni/Mn-HSAG	37.8	35.0
2.5Cu2.5Ni/Mn-HSAG	39.9	35.4

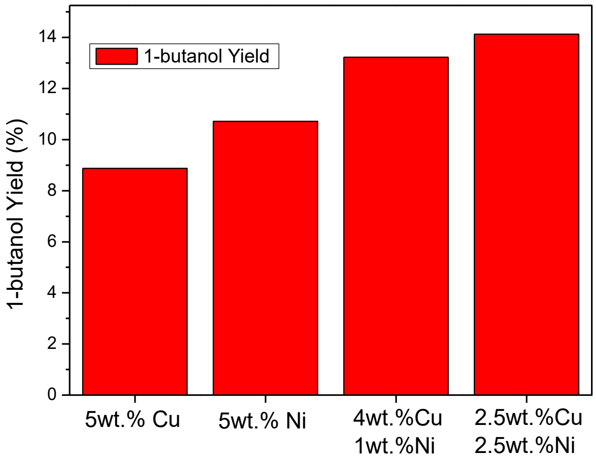

Figure 1. Variation of 1-butanol yield as a function of Cu and Ni wt.% load over Mn promoted catalysts.

In conclusion, the presence of manganese as promoter and its combination with metallic components (Cu and/or Ni) dispersed over high surface area graphite material gives place to an improved catalyst, in terms of high 1-butanol yields, when applied in the Guerbet process. Remarkably the 2.5Cu2.5Ni/Mn-HSAG sample shows good stability and very low deactivation during 24 h of catalytic tests.

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BIOMASS-BASED FREESTANDING ELECTRODE FOR ENERGY CONVERSION DEVICES

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Carbon and transition metals have emerged as promising candidates for many energy storage and conversion devices. They facilitate charge transfer reactions whilst showing a good stability. These materials, fabricated as freestanding electrodes pose the potential of simplified electrode manufacturing procedures whilst demonstrating excellent electrocatalytic, mechanical, and structural properties, resulting from interconnected network structures. In such freestanding configuration, the lack of a binder leads to a better conductivity, ease in the manufacturing processing and allow a lower catalyst mass loading, all of which lead to obvious benefits.[1]

Figure 1. Synthesis route for freestanding electrode.

In this work, a new electrocatalytic electrode has been introduced, which is synthesized by firstly converting biomass into carbonaceous materials via hydrothermal process followed by pelleting process with nitrogen precursor, and further carbonization to obtain a (heteroatom doped) freestanding and conductive carbon electrode (**Figure 1**). A 3D freestanding structure with preferred pore structure, nitrogen content and conductivity for oxygen reduction reaction application has been fabricated. The obtained freestanding structure shows superior oxygen reduction reaction performance and superior long-term stability than powdered catalyst. This freestanding electrode can be extended to other gas-involved electrocatalytic applications by simply loading metal ion via immersion method which thus implies the possible application on both electrocatalytic anode and cathode of energy conversion devices (**Figure 2**). Moreover, testing freestanding materials on rotating disk electrode with special designed tip which screw the working electrode on rotating disk shows a facile way to evaluate the oxygen reduction reaction performance of freestanding materials.

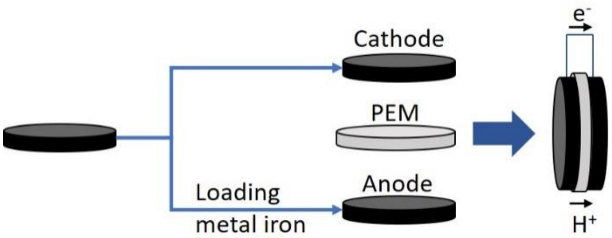

Figure 2. Schematic of assembling PEM fuel cell based on freestanding cathode and anode.

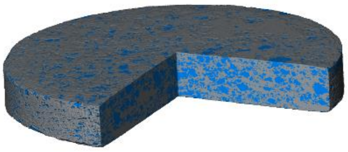

Figure 3. Computed tomography of freestanding electrode. (grey part is the carbon while blue part is pores connected to the air)

The 3D model of pellet has been established through computed tomography (**Figure 3**), 40% porosity can be seen in the structure (blue part), whilst very little amount of isolated dead pores (2.8% of the total pore volume) exist. The N_2 adsorption has also been conducted (**Figure 4a**), larger surface area has been obtained in pellet (414 m^2/g for pellet and 300 m^2/g for powder), which indicates the formation of mesopores in pellet due to decomposition of melamine in the limited space.

Electrochemical performance of pellet and powder is showed in the **Figure 4b**. Instead of using conventional RDE tips, pellet is loaded into a freestanding tip which can apply rotation. As can be seen in Figure 4b, after extracting LSV under N2 and O2 conditions, similar LSV curves obtained for both pellet and powder. And prolonged electrochemical stability has been obtained in pellet, which indicates the advantageous performance of N-doped freestanding pellet.

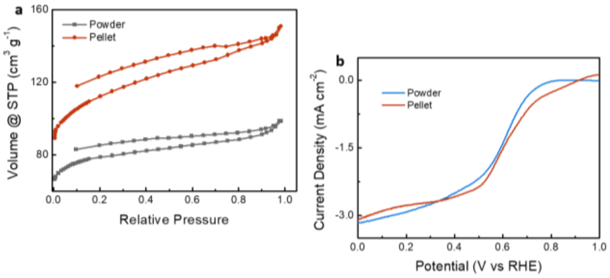

Figure 4. a) N_2 sorption isothermal of the N-doped carbon pellet (red line) and N-doped carbon powder (grey line). b) Polarization curve of powder and pellet used as the ORR electrode operating in 0.1M KOH, the scan rate is 1mV/s with 1600rpm rotating speed.

In conclusion, a N-doped hierarchical freestanding electrode has been prepared. This freestanding electrode shows increased ORR performance and stability than powder formed catalyst. Significantly, we proposed a convenient method to evaluate ORR performance of freestanding electrode while keeping its 3D structure with using binder.

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CARBONACEOUS MICROSPHERES AS HETEROGENEOUS CATALYSTS FOR BIOMASS CONVERSION

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Hydrothermal carbonization is regarded as a highly effective method to convert biomass into a source of chemicals and carbon materials. The various products of hydrothermal treatment on biomass can be divided in two classes: water soluble organic compounds and insoluble, amorphous carbonaceous materials.

The reaction paths which lead to the formation of these two kinds of products run in parallel; so, depending on which one is the product of interest, the other is regarded as a by-product and vice versa.

5-hydroxymethyl furfural and levulinic acid are two of the several soluble organic compounds which result from dehydration of cellulosic biomass under hydrothermal conditions; their use as building blocks for the synthesis of a vast number of chemicals has been demonstrated [1], [2].

Hydrothermal carbon results from the polymerization and condensation of the aforementioned molecules. Its high amount of carboxylic groups has been successfully employed to build acid carbon catalysts that are reported to be effective in catalyzing synthesis of HMF and biodiesel[3], [4].

The aim of this work is to prove that hydrothermal carbon can be effectively employed, in a closed cycle, as a catalyst for the synthesis of 5-HMF and levulinic acid.

In this preliminary work we report the synthesis of hydrothermal carbon (HTC) via hydrothermal carbonization of glucose and fructose, used as model molecules to mimic cellulose behaviour. Effect of residence time, initial pH and acid catalyst on HTC yield of an aqueous solution of sugar 10% w/w has been evaluated.

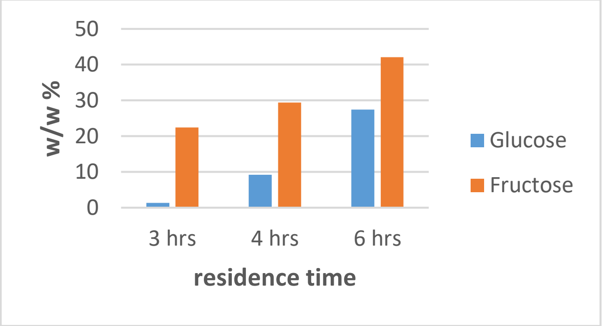

Figure 1. HTC yields from glucose and fructose after different reaction times at neutral pH.

Figure 1 shows that HTC yield increases with residence time. Moreover, fructose reactivity is significantly higher than glucose and the trend is constant throughout the reaction time range considered. Figure 2 shows that HTC yield from glucose in initial acidic conditions is roughly 9- to 10-fold that in uncatalyzed conditions.

SEM micrographs of HTC (Figure 3) show that reaction parameters also affect morphology of the carbon spheres. Fructose, in neutral conditions, produces bigger spheres than glucose. Lower initial pH also produces bigger spheres when compared to those obtained in neutral condition.

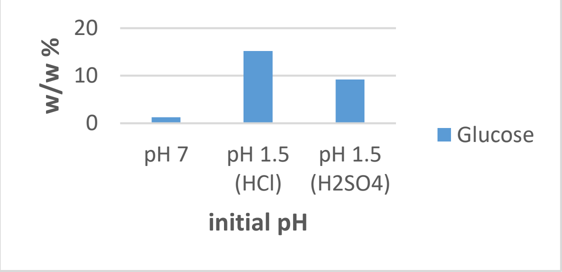

Figure 2. HTC yields from glucose at different initial pH and acid catalysts.

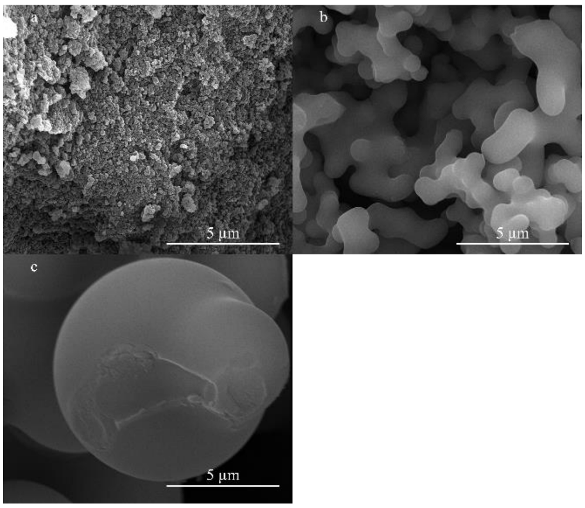

Figure 3. SEM micrographs of HTC derived from: a) glucose, pH 7, 3 hrs; b) fructose, pH 7, 3 hrs; c) glucose, pH 1.5 HCl, 3 hrs.

In conclusion, this preliminary study proves that more severe reaction conditions (longer residence time, lower pH) effect both the yield and the morphology of HTC from sugars. Future studies are needed to furtherly optimize the reaction conditions for the synthesis of HTC and evaluate its catalytic performances in the conversion of cellulose to HMF and levulinic acid.

Acknowledgements. This research is supported by European Union in the framework of the H2020 Marie Skłodowska Curie Actions – Innovative Training Networks.

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CO_2 CAPTURE AND CONVERSION USING CARBON BASED MATERIALS FROM BIOMASS RESOURCES

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Global warming and climate changes are matters of great concern around the globe. With an increase of about 40% in the atmospheric concentration, since the industrial revolution, CO_2 represents the primary cause of the greenhouse effect. The main sources of this high emission are represented by human activities, contributing with more than 80% of the atmospheric CO_2 in urban areas [1]. Over the time, several technologies have been developed in order to decrease the CO_2 concertation, such as absorption using alkaline solvents, separation via membranes, conversion and adsorption using a wide range of adsorbents, like zeolites, metal organic frameworks, calcium oxide and activated carbons [2]. But despite all the efforts devoted to minimize its emission, recent studies reported an increase of CO_2 atmospheric concentration from 280ppm, in 1750, up to 406 ppm in 2017. Therefore, finding new ways to diminish the CO_2 content in the atmosphere is still a topic of great interest.

Porous carbon materials have attracted a lot of attention, due to their multiple applications, such as catalysis, adsorption processes for water and air depollution, energy storage (supercapacitors and Li-ion batteries) and energy production. In particular, CO_2 capture via physical adsorption represents an eco-friendly alternative to the traditional amine-based adsorption processes [3]. Also, a lot of attention has been recently devoted to CO_2 electrochemical reduction (CO_2RR) using carbon based catalysts, as a complementary tool for the adsorption process. In this way, CO_2 can be converted in more valuable products, including acids, alcohols and aldehydes [4].

Herein we report the synthesis of porous carbon materials, starting from d-glucose and d-fructose, via hydrothermal carbonization (HTC), for CO_2 capture and conversion. To ensure good textural properties different templates, such as Pluronic® F127 triblock copolymer (Mw = 12 600, EO106-PO70-EO106), Pluronic® P123 (Mw=5 800, PEG-PPG-PEG), and eutectic mixture of $LiCl/ZnCl_2$, have been used during the HTC. The pristine carbons have been further activated in high temperature tubular furnace at 900˚C, in N_2 atmosphere. To confirm the textural properties of the materials, different characterization techniques have been used (N_2 adsorption – desorption isotherms, SEM, TEM). The obtained materials have been tested as potential CO_2 adsorbents, at 1 bar and 0˚C.

The N_2 adsorption-desorption isotherms revealed the presence of mesoporous carbon materials (figure 1), with surface areas in between 259 m^2/g and 1398 m^2/g, depending on the type of template and its concentration.

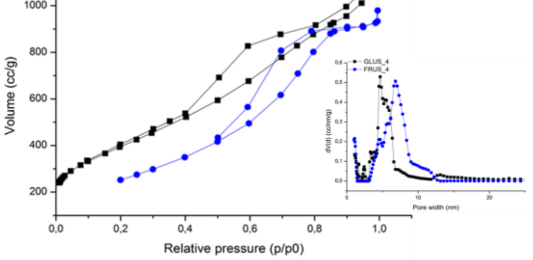

Figure1. N_2 adsorption-desorption isotherm and pore size distribution for carbon materials derived from glucose and fructose using $LiCl/ZnCl_2$ as template.

These are in agreement with the SEM and TEM results, which show the formation of spherical carbon particles and pores orientation. Also, from SEM micrographs we may see that a variation of the synthesis parameters is influencing both homogeneity and pores orientation in the final structure. For example figure 2 shows that by changing the precursor from d-glucose (a,b) to d-fructose (c,d) the particle size is increasing and the homogeneity tends to decrease.

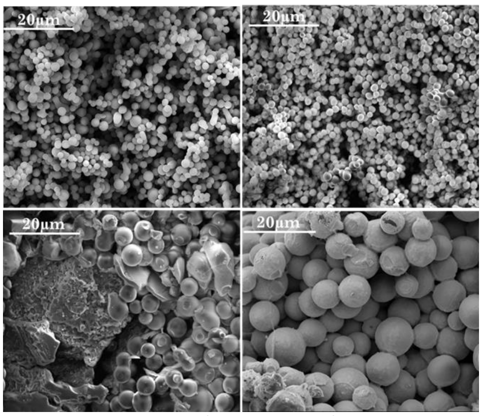

Figure 2. SEM micrographs of glucose and fructose carbon materials templated with Pluronic F127 and P123: a.GF127, b.GP123, c.FF127 and d.FP12

The adsorption capacity for CO_2 has been measured and the experimental results indicate that the materials having high surface area and micro-mesoporous structure perform best. The values for adsorption capacities are in between 3 and 4.4 mmol/g.

Overall, our preliminary results show that carbon materials derived from renewable resources perform well for adsorption experiments of CO_2. Future studies are mainly focused on testing the materials as potential electrocatalysts for CO_2RR and on improving their adsorbent properties.

Acknowledgements. This research is supported by European Union in the framework of the H2020 Marie Skłodowska Curie Actions – Innovative Training Networks.

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RUTHENIUM CATALYSTS FOR THE SELECTIVE HYDROGENATION OF 5-HYDROXYMETHYL FURFURAL (HMF)

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Introduction

Over the last years, the world is passing through a crucial moment concerning the dependence on oil as its main source of chemicals and energy. The diminishing of the reserves combined with the increasing of the world demand has led to the necessity to find new sustainable resources in order to gradually replace oil in both chemical and energetic field. Biomass represents nowadays the most attractive carbon feedstock, since it is abundant, widespread and inexpensive.[1] One of the most important products directly derived from lignocellulosic biomass is 5-hydroxymethylfurfural (HMF). HMF can be found in nature in different plants and foods[2]. The attractiveness of this “sleeping giant”, is due to the simultaneous presence of a carbonyl and alcoholic group and an aromatic furan ring. Moreover, HMF can be produced with high selectivity by dehydration or isomerization of fructose, but recently new routes have been reported using cellulose directly as starting material[2,3]. Currently, a wide range of HMF derivatives are reported to be potentially suitable to use in several sector of chemical industries and as biofuels. Among all these, the HMF hydrogenation products are of particular interest. The hydrogenation reaction of HMF involves numerous intermediate products and the mechanism for their formation is rather complex. The dominant pathways are the hydrogenation and hydrogenolysis reactions (Figure 1), but other secondary reactions can happen, such as decarboxylation[4], ring opening[5] and etherification when using alcohol as solvent[6].

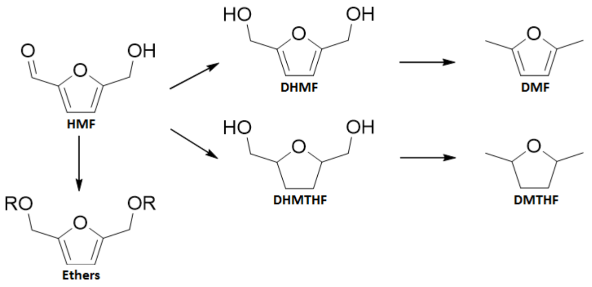

Figure 1. Support effect on the HMF hydrogenation reaction.

In this work, a Ru on activated carbon catalyst (x40s) was synthesised and tested in the HMF hydrogenation reaction. Various parameters were optimised, such as reaction temperature, hydrogen pressure and reaction time. Subsequently, Ru was deposited onto different carbon supports, namely VulcanXC72R (graphitized carbon) and carbon nanofibers. Differences in activity and selectivity were correlated to variation in surface properties and morphology of the support.

Experimental

The metal loading of all the catalysts was 1 wt%. Ru was deposited on different carbonaceous supports: x40s, Vulcan and nanofiber. All the catalysts were activated for 1 hour in H_2 atmosphere at 200 °C before use. ICP-OES, TPR, XPS and TEM analysis were performed on the catalysts. The hydrogenation reactions were carried out in a 75 ml steel autoclave, using 2-butanol as solvent. The reaction products were analysed by GC and GC-MS.

Results

The carbon supported catalysts were analysed with TEM, revealing the presence of small and uniformly distributed Ru nanoparticles. A representative TEM image of Ru/X40s is reported in Figure 2a. XPS analysis showed that Ru, despite an activation step in H_2 atmosphere, was partially oxidised to Ru^{4+}, with a calculated Ru/Ru^{4+} ratio of 6:4. This is in contrast to TPR analysis that indicate that full Ru reduction takes place at temperatures lower than 200 °C. This discrepancy was ascribed to partial reoxidation phenomena that can occur during the storing of the catalyst in air before XPS analysis.

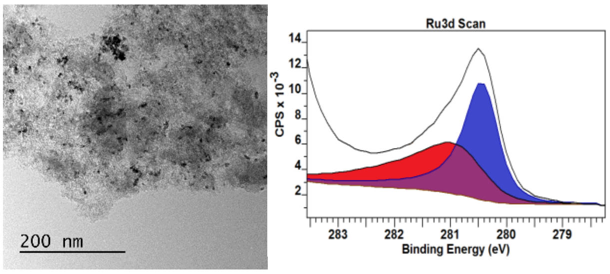

Figure 2. Representative a) TEM image and b) XPS analysis of the Ru/x40s catalyst.

The temperature effect was investigated from 80 to 230 °C. It was observed that the selectivity turned to more hydrogenated compounds as the temperature increased. In particular, at 80 °C only the hydrogenation of the aldehydic group took place, while increasing the temperature to 130 °C and further to 180 °C the rate of both hydrogenolysis and ring-hydrogenation processes increased. Indeed, only traces of DHMTHF were present at 80 °C (DHMF selectivity 81 %), while at 130 °C DHMTHF and DMTHF were present with a combined selectivity of up to 80 %. A further increase to 230 °C had the only effect of increase the formation of humin.

The hydrogen pressure effect was evaluated in a 5 – 60 bar range. The ring hydrogenation starts to become important only at high pressure (≥ 20 bar): at 5 bar, in fact, the main product was DMF (73 %). Interestingly, the hydrogenolysis mechanism seemed to be less favoured at higher pressure. Indeed, the selectivity to DMTHF and DHMTHF increased to 58 and 15 % respectively increasing the pressure from 5 to 40 bar. A further increase to 60 bar led only to an increase in humin formation.

Tests for the support effect are still ongoing and the results will be presented at the conference.

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CARBON ANODE IN CARBON HISTORY

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At the start of things, that is more than 15 Gy ago, all the matter and energy that we can observe was concentrated in a volume element about the size of a small coin (~100mm3). Later, within resultant stars, at temperatures of about 1015K, hydrogen atoms were stripped of their nuclei and fused to form helium nuclei. As stars cooled, collision of helium nuclei led to beryllium, of fleeting stability but of sufficient stability to allow a further collision with a helium nuclei, to give us carbon. And, a continuing collision of carbon with a helium nuclei gave us oxygen. And so our story has started.

Some 5 Gy ago, from of the cosmic dust out there, an event occurred leading to the formation of the solar system, with the sun, planets and moons. Only one planet (earth) was of the correct size and at an optimal distance from the sun to create and maintain oceans and an atmosphere. The atmosphere was first made up by volcanic activity, of carbon dioxide and water vapour, two greenhouse gases. Eventually, nitrogen was added to the atmosphere. The oceans were created and carbon dioxide was established within the carbon cycle with formation of carbonates. These greenhouse gases kept the atmospheric and oceanic temperatures compatible with chemical reactions leading to molecules evolution, i.e. the creation of life. The oceanic plant forms took out the carbon dioxide from the atmosphere and replace it with oxygen (photosynthesis). These early plants became entrapped within the rocks and their remains are now identified as kerogens, and petroleum deposits and methane reservoirs. As the continents of earth moved over its surface there were established the great rain forests, which provided the organic material, which, after being chemically degraded and fossilised, is now recognizable as coal. Nature in the process of maturation of kerogen and coal, had, as the end product, graphitic material, which is the basis of all carbon forms, with the exception of crystalline diamond. About 15,000 years ago, petroleum and coal appeared making life very easy for modern man. The waste products of the petroleum industry (the distillation of the barrel), and the waste products of the coal carbonization industry (the manufacture of metallurgical coke) as coal-tar and coal-tar pitch, are used to create the carbon artefacts (matrix and binder) of the carbon electrode industry [1].

During the first half of the last century, it had become obvious that the route to aluminium production was via the Hall-Héroult cell, i.e. the electrochemical reduction of alumina, by carbon, in a molten bath of cryolite. Developments of the carbon anode had pointed the way to the use of a coke bonded with coal-tar pitch. At the same time as the aluminium industry was expanding, so the petroleum and steel making industries were providing the necessary ingredients of anode manufacture. Clearly, this exploitation and hence continuous quality control of cocke and pitch for the anode is a necessity.

Carbon blacks associated with printing inks, are an essential ingredient of the automobile tyre, of plastics in the modern car, and in the paint, which covers the modern car. Aircraft use braking systems of carbon composite, made up of carbon fibre matrices bonded with carbon from coal-tar pitch. And the steel industry makes its steels in the furnace heated using the graphite electrode, made from premium quality delayed coke (needle coke) and coal-tar pitch. In the present century sophisticated carbon electrodes have been manufactured for many applications, namely in the area of electrochemical energy devices [2].

Light metals meetings and many other meetings involving several industries using carbon electrodes, continue to show that there are many factors that need to be considered and improved to obtain efficient anodes. Restricting to the aluminium electowinning we really do not understand very well what happens within the green anode when we pyrolyse and bake it, namely we do not know exactly how to modulate optimum relationships between coke particle (shape and size), butt particle and mixing extent with coke particles, and the shape and size of the binder coke bridges [3].

We are at a Carbon Meeting, and we must finalise stressing that not all days are black. We saw the development of synthetic diamonds, of the diamond and diamond-like film, we saw the emergence of the carbon fibre, and the explanation for the formation of anisotropic graphitizable carbons via the intermediate phase of mesophase, that nematic, aromatic, discotic liquid crystal system. The most intriguing discovery has been the fullerene systems and the nanotubes. Who says that the carbon scientist has a dull life?

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BIOMASS-DERIVED NANOPOROUS CARBONS AS ELECTROCATALYSTS FOR OXYGEN REDUCTION REACTION

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Introduction

Improving renewable energy production processes is a key to face energy crises and it is essential that these new approaches follow sustainability principles, namely by attaining high performance avoiding the use of non-renewable and expensive chemicals. For example, nowadays the development of carbon-based metal-free electrocatalysts for the oxygen reduction reaction (ORR) this is one of the most attractive topics in fuel cell field. Thus, in the present work sisal residues (biomass) were used as precursors in the synthesis of novel metal-free nanoporous carbons that were further successfully tested as electrocatalysts for ORR.

Experimental

Nanoporous carbons were prepared from sisal (S) rejects of rope industry, by a two-step methodology: sisal saccharic units extraction by H_2SO_4 digestion at 50 ºC followed by polycondensation reaction at 90 ºC. The acid-chars obtained were activated with K_2CO_3 or KOH (weight ratio of 1:3, heating at 800 ºC for 1h under N_2 flow of 5 cm^3s^{-1}). Labels: S/$[H_2SO_4,M]_{digestion}$/$[H_2SO_4,M]_{polycondensation}$/$K_2CO_3$(C3) or KOH(H3). Solution impregnation is labelled with "(s)", impregnation with K_2CO_3 without previous drying is labelled with "wet", and variations in temperature are also indicated. Characterization of the carbon materials was made by SEM, N_2 and CO_2 adsorption at, respectively, -196 and 0 ºC, thermogravimetric, elemental analysis, ash content, pH_{PZC} and apparent density determination, DRIFT and DRX. The electrochemical characterization was made through cyclic voltammetry with $K_3[Fe(CN)_6]$ (1.0×10^{-3} M in KCl 1.0 M). The electroactive surface areas were determined using the Randles–Sevcik eq.

Electrochemical tests were carried out in N_2- or O_2-saturated KOH (0.1 M). To achieve this, the electrolyte was degassed for 30 min with the selected gas. CV measurements were performed at 0.005 V s^{-1} and the LSV ones at 0.005 V s^{-1} with rotation speeds in the range 400 - 3000 rpm. Onset potential (E_{onset}) was calculated as described in literature and is defined as the potential at which the reduction of O_2 begins. The Koutecky-Levich equation was used to analyse the LSV data and the number of electrons transferred *per* O_2 molecule in the ORR was determined by K-L plot slopes. Tafel plots were obtained after the measured LSV currents were rectified for diffusion to yield the corresponding kinetic current values.

Results and Discussion

Nanoporous materials obtained present high apparent surface areas and distinct pore networks (microporous or micro+mesoporous materials) (Table 1). The materials have an acidic surface chemistry and their morphology and density depend on the H_2SO_4 concentration and activation method.

In alkaline medium, all the materials presented electrocatalytic properties towards the ORR. All the nanoporous carbons presented similar onset potentials (0.80 – 0.84 V *vs.* RHE), which are close to that observed for Pt/C (0.91 V *vs.* RHE). The diffusion-limiting current densities (j_L, 0.26V, 1600 rpm) were also comparable between the AC studied with AC_2 presenting the higher value. Still, these values are somewhat lower than that obtained for Pt/C electrode (-4.7 mA cm^{-2}).

Table 1. Textural parameters (apparent surface area – A_{BET}, meso – V_{meso} and micropore - V_{micro} volumes) and electroactive surface area (A) determined using the Randles-Sevcik equation.

Sample	**Full name**	A_{BET} m^2g^{-1}	V_{meso} cm^3g^{-1}	V_{micro} cm^3g^{-1}	A cm^2
GCE	Glassy carbon electrode	-	-	-	0.039
AC_1	S13.3/13.5/C3(s)	1419	0.45	0.44	0.053
AC_2	S13.3/13.5/C3(s/wet)	1373	0.33	0.44	0.040
AC_3	S13.5/13.5/H3(s)	2309	0.07	0.96	0.052
AC_4	S13.5/13.5/H3(s/700)	1906	0.07	0.75	0.057
AC_5	S12/9/C3	1391	0.09	0.54	0.053
AC_6	S9/9/C3	1938	0.13	0.87	0.060

The AC_1 and AC_4 showed selectivity towards direct O_2 reduction to water, with n_{O2} close to 4 electrons, while the other activated carbons showed a mixture of the 2- and 4-electron mechanisms. The Tafel slopes obtained varied between 47 – 250 mV dec^{-1}. In a previous work sucrose-derived nanoporous carbons were studied as electrocatalysts and were not selective for either the 2 or 4 electron processes [1].

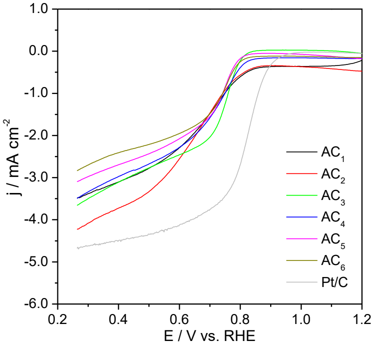

Figure 1. LSVs for different electrocatalysts in 0.1 $moldm^{-3}$ KOH at a $\nu = 0.005$ V^{-1}. .

Acknowledgements. Authors thank Cordex for the supply of sisal wastes and Catarina Marranita from EPS. Financial support is also acknowledged through projects UID/MULTI/00612/2013 (CQB) and UID/QUI/50006/2013-POCI/01/0145/FEDER/007265 (REQUIMTE). ASM (SFRH/BPD/86693/2012) thanks FCT her grant. DF also thanks Project UNIRCELL - POCI-01-0145-FEDER-016422.

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GRAPHENE-BASED ELECTROCATALYSTS FOR EMERGING POLLUTANTS DETERMINATION

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Taking advantage of the electroactivity of some drugs and biomolecules, the application of electrochemical sensors for biological analysis has been growing rapidly, mainly due to the simplicity, accuracy, precision, low cost and rapidity of the electrochemical techniques [1]. In order to develop electrochemical sensors with higher selectivity and sensitivity, the chemical modification of electrode surfaces has been a major focus of research. Nanostructured materials, in particular, carbon-based nanomaterials such as carbon nanotubes and graphene, have attracted considerable interest in this field, owing to their unique physical, chemical and electrochemical properties. They present low residual current, readily renewable surfaces and wide potential windows, providing an important and feasible platform for electroanalysis [1-3].

Graphene, in particular, emerged as a "superstar" material in the last years. Its properties, such as fast electron transportation, high thermal conductivity, excellent mechanical strength and high surface area, suggest its ability to detect analyte molecules and to promote a fast electron transfer between the electrode and the analyte, which make it a promising electrocatalyst [1,4]. In the last decade, advances in graphene research showed that the chemical doping with heteroatoms can be an effective strategy to modulate their electronic properties and surface chemistry [5,6].

This work reports the preparation of novel graphene-based nanomaterials and explores their application as electrocatalysts towards the detection of different emerging pollutants. Graphene was initially doped with nitrogen and sulphur through a mechanochemical synthesis followed by carbonization under nitrogen atmosphere. Then, the pristine and doped graphene were modified with metal oxides (polyoxometalates (POMs) and Co_3O_4 and Mn_3O_4). All prepared nanomaterials were fully characterized by FTIR, XPS, Raman and XRD.

The electrochemical characterization was initially conducted by cyclic voltammetry with two redox probes: $K_3[Fe(CN)_6]$ (1.0×10^{-3} M in KCl 1.0 M) and $[Ru(NH_3)_6]Cl_3$ (1.0×10^{-3} M in KCl 1.0 M). The electroactive surface areas were determined using the Randles–Sevcik equation. Electrocatalytic tests were performed using cyclic voltammetry (CV) and square wave voltammetry (SWV).

FTIR spectra of the $Co_4(PW_9)_2$@GF nanocomposite (**Figure 1**) confirms the immobilization of $Co_4(PW_9)_2$ onto GF as verified from the presence of bands due to GF between 1140 and 1631 cm^{-1}, and the characteristic ones from POM between 798 and 1081 cm^{-1}. The same behaviour was observed for the other prepared nanocomposites. XPS, Raman and XRD results also confirmed not only the N and S-doping of graphene as well as the immobilization of the metal oxides.

Electrochemical characterization with the redox probes showed that pristine and N and S-doped graphene were highly permeable to the positively charged $[Ru(NH_3)_6]^{3+}$ and almost impermeable to the negatively charged $[Fe(CN)_6]^{3-}$. However, the introduction of the POM and metal oxides onto graphene nanomaterials lead to an increase of $[Fe(CN)_6]^{3-}$ peak currents suggesting that their immobilization provides a more conductive pathway for the electron-transfer of $[Fe(CN)6]^{3-/4-}$.

Taking into account these findings, the prepared nanocomposites were applied for the electrocatalytic determination of different emerging pollutants (carbamazepine, citalopram and trazadone) and promising results have been obtained.

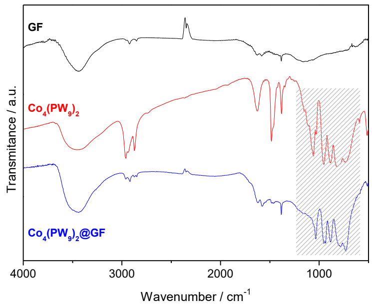

Figure 1. FTIR spectra in the range 4000 – 500 cm^{-1} for GF (black), $Co_4(PW_9)_2$ (red) and $Co_4(PW_9)_2$@GF (blue).

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MESOPOROUS GRAPHITIC CARBON NITRIDE AS METAL NANOPARTICLE SUPPORT FOR DESIGN OF NOVEL ELECTROCATALYSTS

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The production of highly active and low-cost catalysts is the key to solve the commercialisation problem of electrochemical energy conversion devices, such as fuel cells and water electrolysers. The anodic borohydride oxidation reaction (BOR) in fuel cells or the cathodic hydrogen evolution reaction (HER) in water electrolysers are just some of the electrode processes occurring in the mentioned devices. Hence, it is necessary to develop catalysts with high performance for these reactions and, simultaneously, with lower amounts of precious metals, like platinum (Pt) and, thus, with lower cost [1,2].

The electrode material normally contains not only the catalytically active metal, but also a support. The support is typically a material with high surface area and good electrical conductivity, which has the function to accommodate the metal particles and to enhance the catalyst activity by increasing its electrochemically active surface area. Among the mostly used support materials are the carbon-based supports, namely carbon black, graphite materials, carbon nanotubes, and mesoporous carbons. Different support materials lead to different behaviours of the electrocatalysts [3,4].

Mesoporous carbon-supported materials have been studied as catalysts for typical fuel cell reactions, such as the oxygen reduction and methanol oxidation reactions, demonstrating higher metal dispersion and higher catalytic activity than carbon black-supported electrocatalysts in similar conditions [4,5]. Considering that, in this work electrocatalysts composed of Pt and Pt alloys nanoparticles supported on mesoporous graphitic carbon nitride (mpg-C_3N_4) were tested for both HER and BOR. These materials, containing low metal amounts (<10 wt.%) are promising, since it has been recently reported [6] that metal-free mesoporous nitrogen-rich carbon catalysts show activity for BOR. Their performance can be further improved by doping the support with metal nanoparticles.

Thus, Pt/mpg-C_3N_4, PtNi/mpg-C_3N_4, PtCu/mpg-C_3N_4 and PtCo/mpg-C_3N_4 were synthesised and characterised by Fourier-transform infrared spectroscopy, X-ray photoelectron spectroscopy, scanning electron microscopy and transmission electron microscopy. Electrodes were prepared by depositing 10 μL of the corresponding catalytic ink, containing each of the four electrocatalysts, onto a glassy carbon (GC) disc electrode with an area of 0.1256 cm^2 and leaving it to dry at 80 ºC overnight.

The performance of the four prepared electrocatalysts for BOR in alkaline media (2 M NaOH) was assessed using cyclic voltammetry (CV) and linear scan voltammetry (LSV) using a rotating disc electrode system. Influence of different parameters, such as polarisation and rotation rate, temperature and borohydride concentration was explored within the study. Kinetic parameters of BOR, including charge transfer coefficients, number of exchanged electrons, order of reaction and activation energies were calculated.

Evaluation of the electrocatalysts' activity for HER was performed in an 8 M KOH electrolyte solution. The LSV technique at low scan rate (1 mV s^{-1}) was used to determine the HER kinetic parameters, namely the charge transfer coefficients, exchange current densities, Tafel slopes and activation energies.

The catalysts showed good activity for both HER and BOR with the obtained results being comparable to those reported in the literature.

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FUNCTIONALIZED DIAMOND THIN FILMS AND NANODIAMOND PARTICLES FOR (ELECTRO)CATALYTIC AND BIOSENSING APPLICATIONS

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Out of the many carbon-based materials available, diamond holds a special position in electrochemistry/-catalysis. Boron-doped diamond (BDD) offers mechanical robustness, a wide working potential window, low background current, biocompatibility, and self-cleaning features [1]. BDD electrodes are arguably the most versatile of all the different carbon electrode materials and generally show superior properties over conventional *sp2* carbon electrodes in terms of limit of detection, stability of response, and linear dynamic range [1]. BDD electrodes have therefore attracted large interest from researchers and industry, and nowadays find extensive use in electroanalysis, chemical/biological sensing, and water treatment. Additionally, the huge potential of diamond in photocatalysis [2] and as corrosion-resistant catalyst support (both in thin-film form and as nanoparticles) is rapidly gaining traction these days.

In our group, we are currently developing micro- and nanostructured diamond electrodes using conventional growth and cleanroom processing techniques as well as novel, low-cost fabrication and functionalization methods. Among others, we use liquid dispensing techniques for the selective seeding of nanodiamond particles, template-based bottom-up growth of thin-film diamond microstructures, and femtosecond laser scribing for the nanostructuring of the diamond thin-film electrode surfaces [3]. *We seek collaboration with surface chemists and catalysis experts to further extend our research activities. To this aim, we here present several examples of functionalized BDD and nanodiamond particle supports for electrocatalytic (bio)sensing and heterogeneous catalysis.*

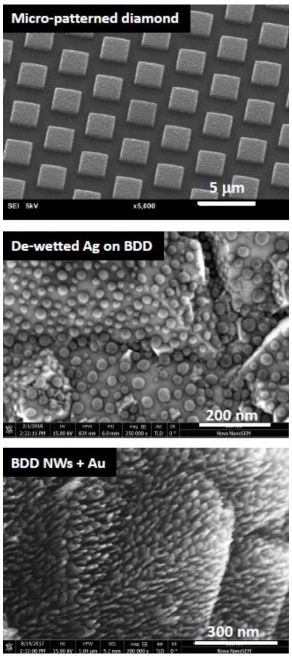

Figure 1. SEM images of micro-patterned diamond (top), and surface-modified BDD, i.e. Ag-NPs on BDD (middle) and Au-decorated BDD nanowires (bottom). Materials were obtained by template-assisted CVD growth, and e-beam evaporation, de-wetting (7 min, 800 °C in H_2/Ar), and reactive ion etching in O_2 (50 sccm, 8 min at 100 W), resp.

Figure 1 shows SEM images of different micro- and nanostructured diamond surfaces produced by either bottom-up or top-down approaches. Hot-filament chemical vapor deposition was used for the diamond synthesis in all cases, and e-beam evaporation of few-nm thick Ag and Au layers, thermal de-wetting and reactive ion etching were explored for the modification and functionalization of the as-grown polycrystalline diamond surfaces. In particular, tailoring of nanowire-textured BDD surfaces with nano-sized Au particles (bottom image) enables the electrocatalytic detection of biomolecules such as glucose [4]. For example, Figure 2 shows the oxidation and reduction peaks recorded by cyclic voltammetry in aqueous solutions of glucose with various concentrations in the mM range. Different metal-decorated and unmodified BDD electrode surfaces have been studied for other (electro)catalytic oxidation and reduction processes and main results of these studies will be presented as well.

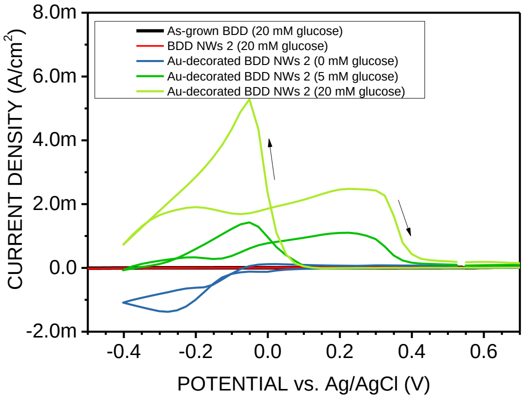

Figure 2. Au-mediated catalytic detection of glucose with surface-modified BDD (adapted from [4]).

Acknowledgements. We would like to thank the following people for their specific contributions: Thijs Boehme, Thomas Hantschel, and Wilfried Vandervorst from Imec/KU Leuven (Leuven, Belgium) for the supply of BDD base material and Stefano Orlando, Alessandro Bellucci, and Daniele Trucchi from Istituto di Struttura della Materia (Rome, Italy) for the laser texturing of BDD.

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CARBON NANOTUBE SUPPORTED CATALYSTS FOR THE ELECTROCHEMICAL OXIDATION OF AMOXICILLIN IN AQUEOUS MEDIUM

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The increasing amounts of emerging organic pollutants in water bodies, especially antibiotics, are of great concern and their removal from the surrounding environment has become a crucial issue [1]. Electrochemical oxidation, among other existing methodologies, plays an important role in this context, by providing efficient conversion in mild conditions, replacing harmful redox agent by electricity.

Thanks to their peculiar characteristics, like high active surface and electrical conductivity, the use of multiwalled carbon nanotubes (CNTs) as a heterogeneous catalyst or support material has attracted growing attention [2,3]. In this context, the electroreactivity of amoxicillin (AMX) (Figure 1) and the kinetic parameters of the reactions for different CNT supported metal catalysts (M/CNT) were studied using cyclic voltammetry [4]. Two oxidation peaks were noticed in the presence of amoxicillin, corresponding to the dehydrogenative adsorption and further oxidation of AMX and to the oxidation of primary products on a surface covered by oxygenated species, respectively. The oxidation of AMX on Ru/CNT starts at lower potentials than those observed for the Pt/CNT and Pd/CNT electrocatalysts. This can be explained by the relative ease of oxidation of adsorbed CO on Ru, at lower potentials with comparison to the other noble metals, since this species can be considered as the main responsible for catalyst deactivation.

The electrolysis of AMX was carried out at different pH media using different electrocatalysts in a two compartment electrochemical cell.

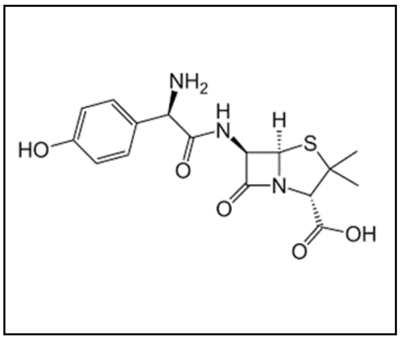

Figure 1. Molecular structure of amoxicillin.

The reaction products were identified and quantified using HPLC-UV, HPLC-MS and GC-MS techniques. The mineralization rate was calculated from TOC and IC analyses. Besides phenyl hydroxypyrazine and C9-dicarboxylic acid, which are mentioned in the literature as main degradation products, some low molecular weight mono and dicarboxylic acids were determined. Product distribution depends on the metal electrocatalyst and pH medium. The relationship between electrode material and oxidation products was established by principal component analysis (PCA). The identification of primary products and reaction intermediates allows proposing reaction pathways for different pH media. An interaction between the carbon atom of carbonyl group in hydrated or non-hydrated forms and oxygen species on the electrode surface can be foreseen as the initial step of AMX oxidative degradation. Full factorial experimental design and response surface methodology were used in order to determine the importance of experimental parameters and to optimize the experimental conditions like electrode material, pH, applied potential or current intensity.

Acknowledgements. This work has been developed under the scope of the projects: BioTecNorte (operation NORTE-01-0145-FEDER-000004) and "AIProcMat@N2020 - Advanced Industrial Processes and Materials for a Sustainable Northern Region of Portugal 2020", NORTE-01-0145-FEDER-000006, supported by the Northern Portugal Regional Operational Programme (NORTE 2020), under the Portugal 2020 Partnership Agreement, through the European Regional Development Fund (ERDF). This work also has been funded by national funds (FCT, Fundação para a Ciência e a Tecnologia), through the projects: PTDC/AAGTEC/5269/2014, Centre of Chemistry (UID-QUI/00686/2013 and UID/QUI/0686/2016) and LSRE-LCM (POCI-01-0145-FEDER-006984).

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ELECTROCATALYTIC EFFICIENCY OF MANGANESE-BASED/CNT COMPOSITE ON HYDROGEN EVOLUTION REACTION: THE ROLE OF MANGANESE

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Abstract.

Carbon materials constitute a promising class of electrodes due to their versatility combined with low cost and availability. These materials present high surface area, excellent mechanical, chemical and thermal properties, high electron conductivity, high porosity and good chemical inertness. They can be easily functionalized and/or decorated with metallic nanoparticles to improve the catalytic performance [1]. Despite these promising features there are still several issues to be overcome such as the eventual oxidation to carbon dioxide and carbon monoxide in aqueous media [2]. Due to this fragility, research in the field of carbon materials has been conducted mainly in alkaline media, to decrease the corrosion rates of carbon. However, alkaline media imply higher energy consumption due to the low kinetics of water dissociation [3], when compared with electrolysis in acid media [4]. Additionally, the acidic nature of the electrolyte in the polymer electrolyte membrane, usually Nafion, justifies the search for less acidic membranes, as well as pursuing the efforts in acid medium [5]. The optimal material should be chemically inert and therefore, the optimal electrocatalyst should also protect carbon from corrosion, without compromising its electrical properties, which would greatly increase its lifetime. In this context, non-noble metals with affinity for carbon, could be the solution. Previous results point to a promising electrocatalytic performance of cryptomelane/carbon nanotubes (CNT) composites towards hydrogen evolution reaction (HER) and to a synergic effect between cryptomelane and CNTs that prevents carbon corrosion, besides favoring HER [6].

In this work the electrochemical characterization of manganese oxide/carbon nanotube (CNT) composites with different properties, such as different oxidation states of manganese, and CNT functionalized with different heteroatoms like O (CNToxid) and N (CNT_N), was performed in acid and alkaline media at room temperature. A commercial catalyst with 20 % platinum on carbon black (Pt/C) was used as standard material. The techniques used were open circuit potential measurements, cyclic voltammetry, linear sweep voltammetry, electrochemical impedance spectroscopy (EIS) and square wave voltammetry (SWV). Results show the better electrocatalytic effect of cryptomelane manganese oxide for HER, when compared with other manganese oxides, pointing to the important role played by the one-dimensional tunnel structure, helping electrolyte penetration and facilitating bubble release. In addition, similar synergic effects of cryptomelane with N-doped and oxidized CNTs are suggested, although in lesser extension, reinforcing the role of cryptomelane on both electrocatalytic and corrosion protection effects, more pronounced in acid medium.

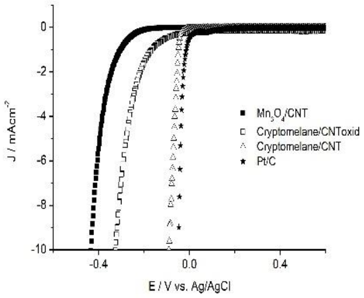

Figure 1. Linear sweep voltammetry of the studied electrocatalysts performed at room temperature under nitrogen atmosphere at 5mVs^{-1} sweep rate and 1600 rpm.

Acknowledgements. This work is a result of the projects "UniRCell", with the reference POCI-01-0145-FEDER-016422 and project "AIProcMat@N2020+, Advanced Industrial Processes and Materials for a Sustainable Northern Region of Portugal 2020", with the reference NORTE-01-0145-FEDER-000006, supported by Norte Portugal Regional Operational Programme (NORTE 2020), under the Portugal 2020 Partnership Agreement, through the European Regional Development Fund (ERDF) and of Project POCI-01-0145-FEDER-006984 – Associate Laboratory LSRE-LCM funded by ERDF through COMPETE2020 - Programa Operacional Competitividade e Internacionalização (POCI) – and by national funds through FCT - Fundação para a Ciência e a Tecnologia.

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BIOMASS-DERIVED ACTIVATED CARBONS FOR OXYGEN REDUCTION REACTION

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Nowadays, an efficient way to convert chemical energy to electrical energy is required to face the global growing energy demands and to reduce the environmental impact of fossil fuels [1]. Currently, polymer electrolyte membrane fuel cells (PEMFCs) are outstanding conversion devices, drawn back by their high cost due to the use of platinum-based electrocatalysts [2]. Replacement of Pt by new low cost materials is mandatory for the widespread use of this type of devices. The oxygen reduction reaction (ORR), which takes places at the cathode of a fuel cell, plays a key role since it is a slow process that limits the overall reaction kinetics [3]. It is therefore essential to design materials with the appropriate properties that could enhance the performance of fuel cells. Carbon nanotubes (CNTs), graphene-based materials and activated carbons have been widely studied as electrocatalysts in the ORR. Moreover, chemical functionalization of the carbon structures has become an interesting methodology to improve their performance for this reaction. A recent publication has demonstrated that N-doped CNTs can be easily prepared by ball milling, which resulted in materials with high catalytic activity [4]. Therefore, the objective of the present study is to prepare hybrid carbon materials by the hydrothermal polymerization of glucose, one of the main fractions of biomass (low cost and abundant), in the presence of carbon nanotubes, and to optimize their properties to improve their catalytic activity in the ORR.

Glucose and CNTs were dispersed in deionized water under sonication. The mixture was introduced into a Teflon-lined autoclave, sealed and heated at 180 ºC for 12 h. The resulting polymerized material was then washed with distilled water and dried at 80 ºC overnight. One of the samples was carbonized at 700 ºC in a nitrogen atmosphere for 2 h (CG_CNT), while the other three were physically activated at 900 ºC in a CO_2 atmosphere for 4 h (AG_CNT). Two of the activated samples were then mixed with melamine: one by one-pot method ($AG\_CNT\_M_{mix}$) and the other by ball-milling ($AG\_CNT\_M_{BM}$). Finally, both samples were treated at 700 ºC in a nitrogen atmosphere for 2 h. The synthetized carbon materials were characterised by nitrogen adsorption at -196 ºC and used as electrocatalysts in the ORR. Electrocatalysts were prepared by dispersing the carbon materials in a mixture of water, ethanol and nafion, and then deposited on a glassy carbon electrode. The ORR performance was evaluated in a three-electrode cell immersed in 0.1 M KOH electrolyte solution. The catalytic efficiency, reproducibility and stability of the samples on the ORR were evaluated through cyclic voltammetry and linear sweep voltammetry using an Autolab PGSTAT 302N potentiostat/galvanostat.

As expected, activation led to materials with higher microporosity (Table 1). N_2 isotherms obtained from doped materials remained almost unchanged although BET surface areas slightly increased probably due to changes in the structure during the doping process that could open some blocked pores. Activation of glucose-derived carbons shifts the onset potential to more positive values and increases the kinetic current density. However, as shown in Figure 1, the LSV response still exhibits two reduction processes, characteristic of the two-electron pathway. N-doped materials shift the ORR reaction from two to four electron mechanism. In addition, functionalization by ball-milling results in materials with higher catalytic activity, probably due to differences in the amounts and types of the functional groups. The results obtained in the present study show the potential of glucose-derived activated carbons as electrocatalysts for the oxygen reduction reaction.

Table 1. Textural properties and onset potencial calculated at 5 % absolute maximum current intensity.

Sample	S_{BET} (m^2/g)	V_p (cm^3)	V_{DR} (cm^3)	E_{on} (V vs RHE)
CG_CNT	535	0.26	0.20	0.62
AG_CNT	1489	0.64	0.56	0.76
$AG\_CNT\_M_{mix}$	1669	0.77	0.65	0.74
$AG\_CNT\_M_{BM}$	1517	0.71	0.55	0.76

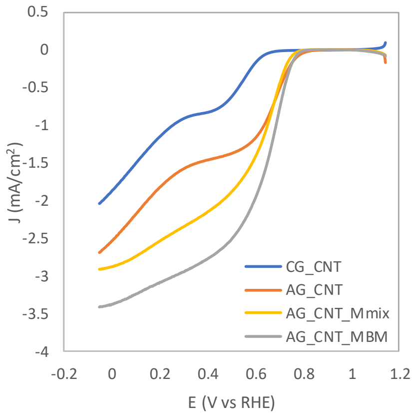

Figure 1. LSV curves for ORR in O_2 saturated 0.1 mol dm^{-1} KOH solution (at 5 mV s^{-1}) at 1600 rpm.

Acknowledgements. Projects "UniRCell", with the reference POCI-01-0145-FEDER-016422, Project "AIProcMat@N2020 - Advanced Industrial Processes and Materials for a Sustainable Northern Region of Portugal 2020", with the reference NORTE-01-0145-FEDER-000006, supported by Norte Portugal Regional Operational Programme (NORTE 2020), under the PORTUGAL 2020 Partnership Agreement, through the European Regional Development Fund (ERDF), and Project POCI-01-0145-FEDER-006984 – Associate Laboratory LSRE-LCM funded by ERDF through COMPETE2020 - Programa Operacional Competitividade e Internacionalização (POCI) – and by national funds through FCT - Fundação para a Ciência e a Tecnologia.

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LIGNOSULFONATE DERIVED MACRO/MESOPOROUS ACIDIC CARBOCATALYSTS: PREPARATION AND APPLICATIONS

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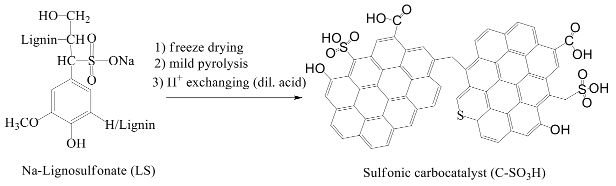
The authors wish to highlight the application of industrially available and low cost sulphur/sulfate rich materials {Lignosulfonate (LS), polystyrene sulfonate (PS)} as efficient single precursors for the direct synthesis of macro/mesoporous acidic carbocatalysts [1,2].



Scheme 1. Method for preparing sulfonic acid functionalized carbon materials from LS.

The desired synthesis could be achieved in three simple steps involving ice-templating, mild pyrolysis (350-450 °C) and ion/H+ exchanging (Scheme 1). Extensive characterization by FT-IR, Raman, XRD, XPS, ^{13}C-MAS NMR, TGA, FE-SEM, TEM and N_2-physisorption methods showed that the surface chemistry of these materials to be closely related to the well-known sulfonated carbons [3]. In other words, the LS/PS derived materials exhibited a macro/mesoporous and highly functionalized heteroatom doped (O, S) carbon structure with large amounts of surface –OH, –COOH and $-SO_3H$ groups.

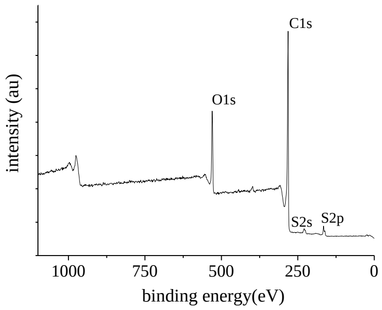


Figure 1. XPS spectra (survey) of a representative carbocatalyst

The textural and acidic properties were mainly dependent on the pyrolysis step: *temperatures 400 °C and above favoured porosity; however, temperatures above 450 °C were found to have an adverse effect on the density of* $-SO_3H$ *sites* [1].

Table 1. Textural and acidic properties of representative carbocatalysts

Catalyst	Surface area (m^2/g)	Pore size (nm)	Acidity (mmol/g)
80LS20PS450H$^+$	122	14.5	3.49
60LS40PS350H$^+$	3	26	6.4
Amberlyst®70	<1	-	2.5
Amberlite®IR120	<1	-	1.8

In terms of catalytic performance these materials outperformed sulfonic acid resins (Amberlyst®70, Amberlite®IR120 and LF resin), zeolites and liquid acids (H_2SO_4, *p*-toluenesulfonic acid) upon acetalization of glycerol and hydroxyalkylation/alkylation of biomass derived furanics (reaction leading to biofuel additives and renewable Jet-fuel precursors). The exceptional catalytic activity and reusability (stability) of these carbocatalysts were attributed to the presence of strongly Brønsted acidic $-SO_3H$ sites, covalently incorporated into the structural framework (Ar-SO_3H and CH_2-SO_3H linkages) of the carbocatalyst and the promotional effects of hydrophilic surface functional groups (-COOH and -OH) present on material surface, favouring the adsorption of oxygenated reactant molecules. If fact, upon continuous glycerol acetalization with acetone, the materials showed no signs of deactivation upto 90 h TOS. Moreover the materials also presented a superior thermal stability ($T_{max}\geq230$ °C) in comparison to the acidic resins ($T_{max}\geq190$ °C).

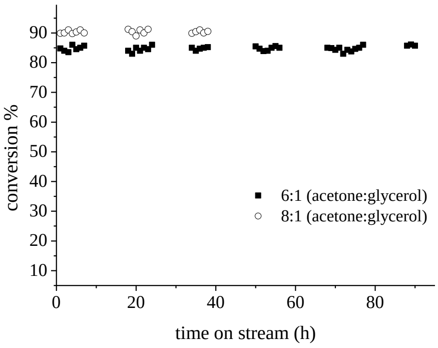


Figure 2. Glycerol conversion over 80LS20PS450H$^+$ as function of time on stream at 50 °C and feed (glycerol acetone mixture) flow rate of 0.1 ml/min); desired product (solketal) selectivity was ≥99.5% in all cases

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PALLADIUM SUPPORTED ON CARBON NANOGLOBULES AS A PROMISING CATALYST FOR SELECTIVE HYDROGENATION OF ETHYL 4-NITROBENZOATE TO BENZOCAINE

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Local anesthetics of the ester type, such as novocaine, tetracaine, and benzocaine, are commercially synthesized by the reduction of 4-nitrobenzoic acid derivatives. For this purpose, two well-known methods are used: the reduction of nitro compound by iron in acidic medium and the hydrogenation over Raney Ni. In view of the disadvantages of these techniques (non-recyclable wastes, significant amount of by-products, pyrophoricity of Raney Ni), the development of catalysts that are highly active and selective in hydrogenation of 4-nitrobenzoic acid derivatives to the corresponding amines is a topical task [1]. The Pd/C catalysts, in the presence of which up to 75% of hydrogenation reactions are currently carried out [2], can be considered as promising ones.

For the first time, we found that palladium supported on carbon nanoglobules (CNGs) is a highly selective catalyst for hydrogenation of ethyl 4-nitrobenzoate (**1**) to ethyl 4-aminobenzoate, i.e. benzocaine (**2**). We used different kinds of CNGs prepared by the thermal decomposition of hydrocarbons in the gas phase. The variation of process conditions and composition of feedstock allowed us to obtain the samples of CNGs (Figure 1) with different size of globules, shape of aggregates and pore structure. The CNGs-1 and CNGs-2 supports were prepared by oxidative pyrolysis of a mixed hydrocarbon feedstock at 1773 K, whereas CNGs-3 was obtained by non-oxidative pyrolysis of methane at 1373 K.

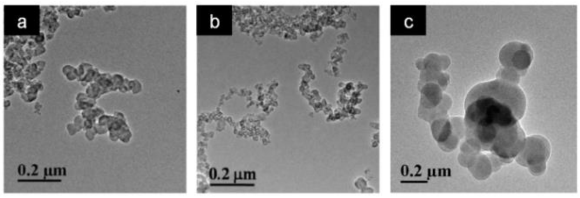


Figure 1. TEM images of the supports: CNGs-1 (a), CNGs-2 (b), CNGs-3 (c).

The CNGs-supported catalysts containing only 1 or 2 wt.% Pd were synthesized by two techniques: (i) impregnation of CNGs by chloride complexes (CC) of Pd with subsequent drying and reduction by H_2 at 573 K, (ii) deposition of polynuclear hydroxy complexes (PHC) of Pd on CNGs and subsequent reduction by sodium formate at 363 K. Dispersion of Pd particles in the catalysts was determined by CO chemisorption and TEM.

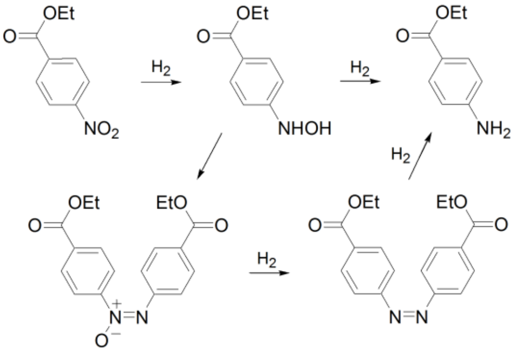
The hydrogenation of **1** with H_2 over Pd/CNGs catalysts was performed in the periodic reactor at a temperature of 323 K and pressure of 0.5 MPa in ethanol. The reaction products were identified by GC-MS and ^{1}H NMR. The quantitative composition of the reaction mixtures was determined by GC.

As can be seen from Table 1, the catalysts based on CNGs-3 are very active in the hydrogenation of **1** and allow to reach almost complete conversion of substrate and 100% selectivity for **2**. At the same time, the activity of the catalysts supported on CNGs-1 and CNGs-2 depends on the conditions of the catalyst preparation. So, the hydrogenation over the catalysts synthesized by using Pd PHC always proceeds with a high rate, leads to nearly full conversion of substrate and gives **2** in 100% yield. The catalysts prepared by impregnation of CNGs-1 and CNGs-2 with Pd CC are less active and the selectivity does not reach 100%. In the case of least active 1%Pd-CC/CNGs-2 catalyst, such by-products as ethyl 4-(hydroxyamino)benzoate, diethyl 4,4'-azoxydibenzoate and diethyl 4,4'-azodibenzoate were detected in the reaction mixture (see Scheme 1).

Table 1. Catalytic properties of the 1%Pd/CNGs samples in the hydrogenation of **1** (ethanol, 323 K, 0.5 MPa, 1 h)

Catalyst	TOF (mol H_2 · mol Pd_s^{-1} · min^{-1})	*X* (%)[a]	*S* (%)[b]
1%Pd-CC/CNGs-1	undefined	> 99	95
1%Pd-PHC/CNGs-1	153.4	> 99	100
1%Pd-CC/CNGs-2	< 80	97	78
1%Pd-PHC/CNGs-2	328.1	> 99	100
1%Pd-CC/CNGs-3	252.7	> 99	100
1%Pd-PHC/CNGs-3	397.8	> 99	100
1%Pd-CC/CNTs	91.7	> 99	100

[a] Conversion of **1** according to GC. [b] Selectivity for **2** according to GC.



Scheme 1. Reaction pathways of the hydrogenation of **1** over Pd/CNGs catalysts.

For comparison, we carried out the hydrogenation of **1** in the presence of a catalyst based on commercial carbon nanotubes (CNTs) purchased from Bayer AG. As you can see (Table 1), the most of Pd/CNGs catalysts are not inferior to Pd/CNTs in yield of **2**, but exceed in rate of hydrogenation. As an important advantage of CNGs-based catalysts, it can be pointed out that CNGs is a low cost nanostructured carbon material produced commercially in a large scale as carbon black.

Acknowledgements. The authors thank A.V. Romanenko for the supply of ethyl 4-nitrobenzoate. The study was financially supported by the Russian Foundation for Basic Research (Project No. 16-29-10742).

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BIFUNCTIONAL CARBON XEROGELS FOR PRODUCTION OF 5-HYDROXYMETHYLFURFURAL (5-HMF) FROM CARBOHYDRATES

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Biomass is one of the sustainable alternative sources of carbon for production of energy and chemicals [1]. The dehydration of carbohydrates to produce 5-Hydroxymethylfurfural (5-HMF) has attracted great attention in both academia and industry, mainly due to its possible application in the production of 2,5 dimethylfuran (DMF) - a second generation biofuel or fuel additive [1]. HMF is also a versatile key intermediate for production of a wide range of fine chemicals and polymers [2]. The conversion of glucose to HMF involves two steps, which are typically catalysed by two types of acids, respectively: A) isomerisation of glucose to fructose mediated by Lewis acids, and B) dehydration of fructose to HMF facilitated by Brønsted acids. In addition, side reactions that reduce the yield and selectivity of HMF occur simultaneously, which mostly include rehydration of HMF to levulinic and formic acids and production of insoluble humins.

Water is the green solvent of choice for biomass valorisation reactions. However, in such a highly protic medium, very few solid acid catalysts can maintain the desirable characteristics of activity and stability. Thus, the development of insoluble water-tolerant solid acids is of great industrial interest, to make biomass conversion technologies commercially more attractive.

Carbon xerogels are among the best candidates as catalysts for biomass conversion, due to their high stability under hydrothermal conditions, easy control of structure and/or surface chemistry, high surface area and low cost. Additionally, phosphorylated carbons have been reported to be effective catalysts in fructose dehydration to HMF [3] [4].

In the present work, novel, multifunctional catalysts were synthesized containing strong and weak acidic sites from P-(OH), -SO_3H and Nb-(OH) groups and Lewis acid sites from Nb^{5+}. Phosphorous and sulphur groups were introduced by hydrothermal post-functionalization of carbon xerogels (average pore diameter 50 nm) with 8M phosphoric acid, or a mixture of 8M phosphoric acid with 2M sulphuric or 2M nitric acid, at 200°C, for 4h. Subsequently, Lewis acid sites were introduced by dispersion of Nb_2O_5 (Sigma Aldrich, 99% trace metal) with functionalized CX supports (with varied CX/Nb_2O_5 ratios) in 2-propanol, followed by ultrasonication for 30 min. Selected samples were thermally treated in static air at 350 °C for 2h in order to control the type of the P species. The treatment led to formation of more stable C–P functionalities.

The prepared materials were applied in the conversion of glucose and fructose to 5 -HMF in water, at 160°C and in various atmospheres (O_2, N_2, air) and pressures (1-5 bar), in a batch reactor, for 2h. The effects of acid/base site density, total acidity, reaction time, and the addition of a second solvent to water (i.e. acetonitrile/water, acetone/water) were studied.

IR and XPS studies showed that Nb_2O_5 was preferably attached to the oxygen functionalities introduced by hydrothermal acid treatment. The amount and nature of P groups were the key parameters affecting the catalytic performances of these functionalized materials. The yield of HMF depended on the ratio between P: Nb sites. It was revealed that both the type and strength of the acidic sites, as well as the total acidity of the catalysts, influence the conversion of sugars in water. Blank test (without catalyst) using glucose as substrate showed only 11.5 % conversion with 22 % selectivity to HMF in water. All studied catalysts containing P and S functional groups showed enhanced activity, as compared to the pristine CX. Moreover, deposition of Nb_2O_5 on CX further improved the catalyst performance in glucose dehydration to HMF. Surprisingly, higher yields of HMF were observed under 1 bar of air as compared to nitrogen atmosphere. In all cases, HMF was the main product of the reaction, apart from formic acid, levulinic acid and some insoluble dark humins. In addition, the selectivity to HMF was found to be higher in a water: acetone mixture than in pure water, which can be explained by the higher concentration of the furanoid form of fructose in acetone. The production of humins was more pronounced in the catalyst containing sulfonic groups, which apparently favoured condensation reactions.

Acknowledgements. This work was financially supported by: Project POCI-01-0145-FEDER-006984 – Associate Laboratory LSRE-LCM funded by FEDER through COMPETE2020 - Programa Operacional Competitividade e Internacionalização (POCI) – and by national funds through FCT - Fundação para a Ciência e a Tecnologia Project “AIProcMat@N2020 - Advanced Industrial Processes and Materials for a Sustainable Northern Region of Portugal 2020”, ref. NORTE-01-0145-FEDER-000006, supported by Norte Portugal Regional Operational Programme (NORTE 2020), under the Portugal 2020 Partnership Agreement, through the European Regional Development Fund (ERDF)” . K. Morawa Eblagon is grateful to FCT for the post-doctoral grant with reference number SFRH/BPD/110474/2015.

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POLYMER BASED SPHERICAL ACTIVATED CARBONS (PBSAC) AS CATALYST SUPPORT FOR FINE CHEMICALS AND PHARMACEUTICAL PRODUCTS

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Polymer based spherical activated carbons (PBSAC) are in large scale commercial available products which are used in gas and liquid sorption application. Due to their unique properties PBSAC can be also used as catalyst support. For the synthesis of many fine chemical and pharmaceutical products carbons and activated carbons are the catalyst support material of choice. The particle size and pore structure of the PBSAC can be adjusted to fit the reaction system best [8]. Smaller particles and a hierarchically structured pore system, for instance, enhance pore diffusion and mass transport of reactant molecules between catalytically active sites and bulk solution. Nowadays the application of powdered activated carbon catalysts in chemical reactions makes product separation time consuming, due to the fraction of abraded fines. The particulate nature of spherical carbon in combination with high mechanical stability (up to 4 kg per sphere) and negligible dust formation allows for easy catalyst filtration and efficient product separation. Thus, post processing times are minimized. Catalyst recycling is possible, as well. In flow chemistry applications, the low pressure drop of the spherical catalyst beds is of great advantage. Fluids can pass the bed of spherical catalyst material with low resistance, thus enlarging the window of operation. Additionally, spherical shape and particulate character improve material handling during reactor loading and catalyst preparation.

As known from activated carbon supported catalysts, a broad variety of active sites can be dispersed on PBSAC supports as i) metals (Co, Ni, Pd, Pt, Ru, Rh), ii) metal oxides (CeO2, TiO2), or performing iii) N- and S-doping.

The reliably high purity of polymer-based carbon evidenced by the very low ash content is ideal for pharmaceutical and fine chemical processes. Chemical reactions such as hydrogenations, dehydrogenations, oxidations, hydrogenolysis reactions and hydrodehalogenations are effectively and selectively promoted by carbon supported noble metal catalysts [1-3]. For instance, the hydrogenation of alkynes and alkenes is catalyzed by palladium on carbon. Rhodium and ruthenium on carbon are generally the most active catalysts in the hydrogenation of carbocyclic rings. Technical applications of carbon supported noble metal catalysts are, for example, the hydrogenation of thymol and menthone to produce menthol [4, 5], the hydrogenation of cinnamaldehyde and crotonaldehyde [3], and the hydrogenation and dehydrogenation of liquid hydrogen carriers [7].

Several unique features render activated carbons a very suitable catalyst support material. Their large specific area (up to 1800 m^2 g-1) allows for large dispersion of noble metals. Large dispersions are usually desired for good catalytic activities, i.e. many noble metal atoms are accessible to reactants.

Figure1 shows the synthesis route of enantionmerene pure (R)-(-)-linalool. The catalytic hydrogenation of the +α-pinene to pinane using PBSAC based palladium catalyst shows high activity and selectivity.

The hydrogenation of cinnamaldehyde on spherical and pulverized activated carbons modified with platinum [8]. All prepared platinum catalysts were active in the hydrogenation of cinnamaldehyde. Normalized to the platinum loading the 0.5 wt.-% platinum spherical performed best. Cinnamaldehyde hydrogenation quickly approached full conversion. The catalysts with 5 and 8.4 wt.-% platinum loading on spherical carbon materials showed lower catalytic activities. The commercial platinum catalyst was less active than the equally loaded spherical carbon system. In case of spherical catalysts final selectivity at full conversion varied between 49 and 65%. The 5 wt.-% platinum spherical catalyst exhibited a lower selectivity towards hydrocinnamic alcohol than the two other spherical materials. With 43%, the commercial catalyst had the lowest final selectivity. The concentration of cinnamic alcohol increased in the beginning of the reaction and decreased towards full conversion. A depletion of hydrocinnamic aldehyde was not observed. While the spherical catalyst did not show signs of poisoning in this experimental series, the commercial catalyst exhibited deactivation. Possibly the deactivation arise from different support interactions [8].

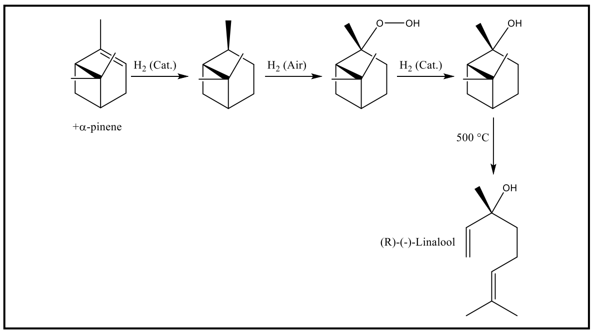

Figure 1. Reaction mechanism of (R)-(-)-Linalool via catalytic hydrogenation of α-pinene to α-pinan.

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DIRECT SYNTHESIS OF CYCLIC CARBONATES FROM EPOXIDES AND CO_2 OVER N-DOPED ACTIVE CARBONS

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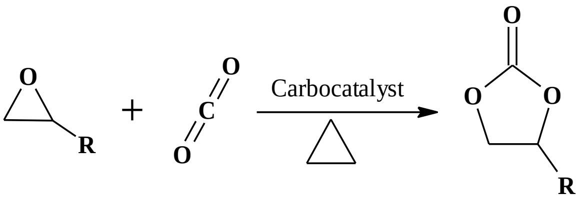
In the recent years, an extensive effort has been taken especially by the European countries to fight against the climate change and global warming. In the context of eradicating the dependency of fossils for fuels and other commodity chemicals (that leads CO_2 emission), much attention has given on the growth of renewable energy technologies such as solar, wind and fuel from biomass as considered to be important driving forces in reducing the greenhouse gas emissions. On the other hand, Europe sets a long-term goal on the utilisation of carbon dioxide (emitted) as a feedstock for new products through chemical and biochemical conversion processes. Innovations in the effective utilisation and conversion of CO_2 into value added products could create new opportunities, supply products to the rest of the world and that could strengthen the European economy.

In this context, various methodologies have been developed for converting CO_2 into value added products such as methanol, methane, dimethyl ether, formic acid, urea, methanol, formamidine derivatives, cyclic carbonates and polycarbonates as well as pharmaceutical products. Out of these, synthesis of cyclic carbonates and polycarbonates is currently considered as one of the most effective means of chemical CO_2 utilisation (Scheme 1). These carbonates are of significant industrial interest as solvents, electrolytes, monomers for polymer synthesis, synthetic building blocks, fine chemicals, and industrial lubricants.



Scheme 1. Green route for direct carbonation of epoxide with CO_2

In the spirit of green chemistry and greenhouse gas mitigation, we explore herein the chemical utilization of CO_2 upon synthesis of cyclic carbonates over N-doped active carbons. The novel N-doped carbocatalysts were obtained from inexpensive biowaste precursors through simple chemical activation method. Physico-chemical characteristics of the catalytic materials such as surface morphology, pore architecture, chemical composition, basicity and surface functionalities were extensively characterized by means of XRD, N_2 physisorption, XPS, SEM, TEM, FT-IR and Micro-Raman spectroscopy techniques. The prepared carbocatalysts were studied over the direct carbonation of different epoxides with CO_2 under solvent free conditions at ambient temperature and low CO_2 pressure (15 bar). The obtained GC results revealed that the materials exhibited excellent catalytic activity on the epoxide conversion and selectively produced cyclic carbonates. (Table 1). The observed catalytic activity of the N-doped carbocatalysts was attributed to the pyridinic and quaternary N sites activating the CO_2 molecule. Control experiments with MWCNT, active carbon and oxidized-active carbon failed to produce any product. In terms of the catalytic performance, the N-doped carbocatalysts presenting the high porosity and high levels of pyridinic and quaternary N-doping exhibited the highest activity (TOF and cyclic carbonate yields upto 99% in 5-15 h). Most importantly, these materials demonstrated exceptional operational stability and reusability (recycled for multiple times without any noticeable loss of activity or change of structural features). In conclusion, excellent catalytic activity of bio-waste derived N-doped activated carbon materials were demonstrated as a catalyst for one step direct carbonisation of epoxides with CO_2 and the reaction selectively produced cyclic carbonates at ambient reaction conditions.

Table 1. Results of preliminary catalytic tests conducted with the different catalysts upon carbonation of epichlorohydrin with CO_2

Catalyst	Initial rate (h^{-1})	Turnover frequency (h^{-1})	[a] Conversion (%)		[a] Cyclic carbonate selectivity (%)	
			5h	15 h	5h	15 h
Blank	0.001	-	0	2	0	0
Pyridine*	2.76	242	99	-	99	-
Activated carbon	0.013	0.5	0	18	0	0
MWCNT	0.0013	-	0	2.5	0	0
JA500	0.32	12.1	72	99	90	93
MA500	1.55 (1.31)	136 (115)	88	99	99 (93.5)	98.5 (97)

[a] Conditions: 100 mg catalyst (*equivalent to amount of N-sites in MA500), 20 mmol epichlorohydrin, 15 bar CO_2, 150 °C, 400 rpm stirring rate.
Figures in parentheses () represent values for spent catalyst

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MODIFIED CARBONACEOUS SPHERES AS HIGHLY EFFECTIVE CATALYSTS FOR THE PRODUCTION OF FUEL ADDITIVES VIA GLYCEROL ACETYLATION

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Although biodiesel is not free from controversy, its global production still remains huge. Taking this into account and bearing in mind that in the process of biodiesel synthesis (i.e., transesterification of oils or fats) also glycerol as a by-product is formed, it is not surprising that there is a large supply of glycerol on the market. Furthermore, the glycerol supply exceeds currently its demand.

Various methods of glycerol valorization have been proposed so far. Among them are the processes of glycerol dehydration, etherification, esterification, dehydrogenation, or acetalization. All of these reactions allowed obtaining products of great importance for different branches of industry.

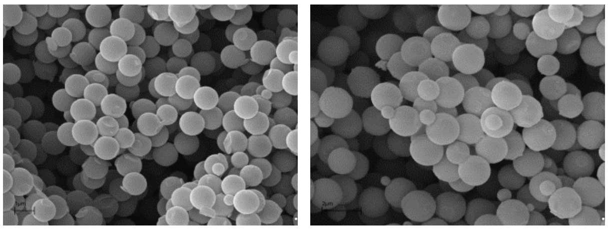
One of the most promising technologies to deal with surplus of glycerol is esterification of this compound with acetic acid. The products formed in the process, so-called acetins, are used as raw materials for the manufacture of polyesters, tanning agents, explosives, also as food additives, plasticizers, solvents, softening agents, or environmentally friendly fuel bio-additives.

The glycerol esterification reaction is traditionally carried out in the presence of mineral acids, such as H_2SO_4, HCl, or p-toluenosulfonic acid (PTSA). However, because of some difficulties related to the use of these homogeneous catalysts, the current research is rather focused on the use of heterogeneous systems in this process. The most frequently explored are sulfonated resins of different types, such as Amberlyst 15, 35, or 36. However, low thermal stability of these materials should be taken into consideration when conducting the experiments. Other catalysts that have been tested in the glycerol esterification are among others HPA-based catalysts [1] or modified SBA-15 systems [2]. On the other hand, there are only scarce data on the use of carbon catalysts in this process. Our studies seem to fill this gap.

In this project, high quality polymeric and carbon spheres (PSs and CSs, respectively) were produced with high yields, based on the procedure presented by [3]. PSs were obtained from a glucose solution under hydrothermal conditions with the assistance of phosphotungstic acid ($H_3PW_{12}O_{40} \cdot xH_2O$) as a catalyst. The process was performed at 180°C for 8 h. The product obtained was collected, washed with distilled water, and ethanol, and dried overnight at 110°C. To obtain CSs, PSs were subjected to pyrolysis at 500°C for 2.5 h (heating rate of 2°C/min was applied). The samples obtained were then modified for example with conc. sulfuric acid to endow their surface with acidic properties.

The glycerol esterification reaction was performed in a batch system equipped with a magnetic stirrer and a reflux condenser. The process was carried out at 80°C for 24 h, using a glycerol to acetic acid molar ratio of 1:6. In a typical experiment, 0.7 g of a carbon catalyst was tested. For the sake of comparison, the blank test (without a catalyst) was performed. For the best sample, also recycle experiments were conducted.

Figure 1 presents SEM micrographs of the samples produced. Well-developed structure of polymeric spheres is clearly visible in Figure 1A. The pyrolysis of PSs does not affect the morphology of the starting material (Figure 1B). The structure of CSs remains intact. The conversion yield of PSs was about 28-30% (mass of PSs/mass of glucose), whereas the carbonization yield was equal to about 65%.



A) B)

Figure 1. The structure of polymeric (A) and carbon (B) spheres obtained

As can be seen in Figure 2, all the catalysts produced show high catalytic activity in the reaction, giving very high glycerol conversion just after 6 h of the process. After that time, a combined selectivity to DAG and TAG can achieve about 72% (60% and 12%, respectively, PS-H_2SO_4 sample).

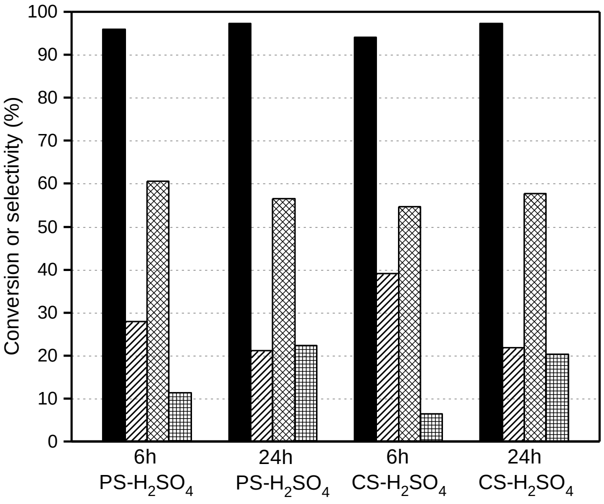


Figure 2. Catalytic performance of modified polymeric and carbon spheres in the process of glycerol acetylation after 6 or 24 h (■ glycerol conversion, ▨ selectivity to monoacetins, ▩ selectivity to diacetins, ▦ selectivity to triacetin)

The catalytic performance of the modified samples results from the presence of strongly acidic sulfonic groups present on their surface. The results of reusability tests were also promising.

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IN-SITU PREPARED FEW LAYER GRAPHENE- POROUS CARBON COMPOSITE ELECTRODES FOR ENERGY STORAGE

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The accelerated requirements of the society for "green" energy production and storage have recently induced intensive research in the related fields and, among others, in the development of supercapacitors. In view of sustainable development, the choice of high performance materials and of their synthesis is an important aspect under consideration. One of the crucial materials include carbon-based materials, where usually either highly conductive graphene or porous non-graphitic carbons are studied.

We present the studies of supercapacitance of the composites including few layer graphene (FLG) and porous non-graphitc carbon in aqua electrolytes. The precursors of the composites have been prepared "*in*-situ" by modified green method consisting of FLG preparation, exfoliation of graphite in water [1] covering both, the production of FLG and their coupling with carbon precursors (protein, polysaccharide), in water. The following carbonization steps allow to get final FLG-porous carbon composites. The studies include different FLG-C ratio and various C functionalities introduced by modification of carbonization conditions. Fig. 1 demonstrates the representative SEM micrograph and one of the CV curve obtained for FLG-C composite (with average supercapacitance of 102 F/g at 1 mA/g in 0.5 M H_2SO_4).

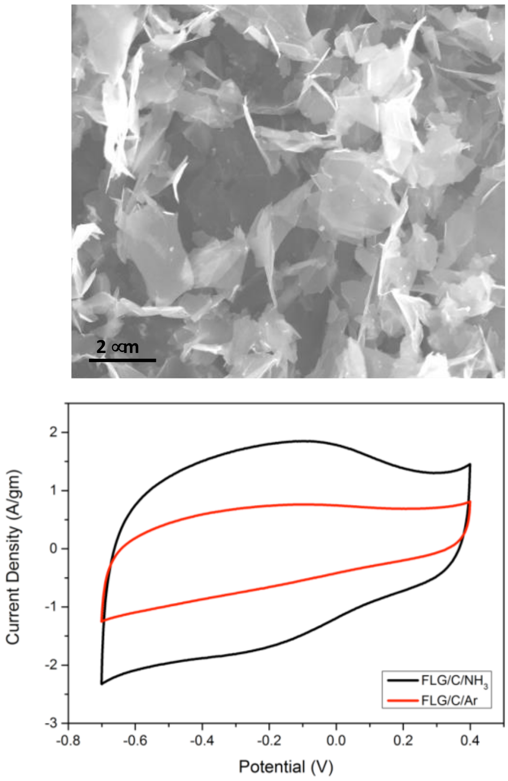

Figure 1. The exemplary SEM micrograph and CV curve of FLG-C composite

Acknowledgements. FRC-Solvay foundation is greatly acknowledged for A. Mohanty's PhD fellowship support.

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GOLD(I) AND GOLD(III) COMPOUNDS SUPPORTED ON FUNCIONALISED CARBON MATERIALS FOR CYCLOHEXANE HYDROCARBOXYLATION

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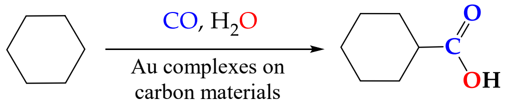
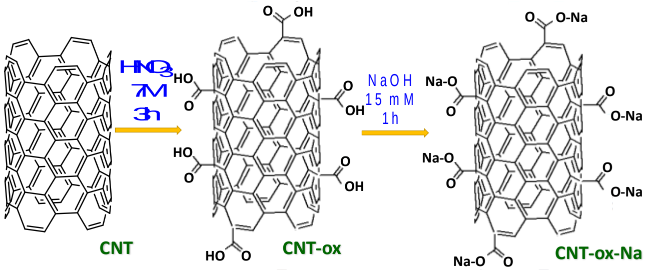
The single-pot carboxylation by CO of C_n alkanes to C_{n+1} carboxylic acids is a particularly attractive alkane functionalization procedure [1,2], in view of the increasing industrial demand of carboxylic acids and of the drawbacks of the current synthetic methods. However, catalytic carboxylation of saturated hydrocarbons, requiring C-H activation, is a chemical challenge, in particular for the least reactive lower alkanes.

Recently, we reported on cyclohexane hydrocarboxylation to cyclohexanecarboxylic acid (Scheme 1), in the presence of CO and water, with Au nanoparticles deposited on carbon nanotubes, carbon xerogels and activated carbon, with three different surface chemistries: in their original forms (CNT, CX or AC, respectively), oxidized with HNO_3 (-ox) or oxidized with HNO_3 and subsequently treated with NaOH (-ox-Na) [1,2]. Scheme 2 shows how the carbon supports were functionalised, using CNT as an example.



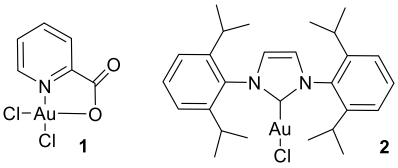
Scheme 1. Hydrocarboxylation of cyclohexane to cyclohexanecarboxylic acid.



Scheme 2. Functionalisation of CNT.

In the present work, the commercial Au(I or III) nitrogen containing complexes shown in Scheme 3, dichloro(2-pyridinecarboxylato)gold(III) (**1**), from Aldrich, and 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidenegold(I) chloride (**2**) from Strem Chemicals, were anchored on original, -oxi and-oxi-Na functionalised CNT, CX and AC materials (9 supports in total). These hybrid materials proved to be efficient in the oxidation of cyclohexane and alcohols [3]. It is well known that anchored complexes have advantages over their soluble analogues, such as, higher activity, easier separation from the products and possibility of catalyst recycling [4]. This was confirmed in previous works of ours for other catalysts and reactions [5-7].

The homogenous and heterogenised gold-nitrogen compounds **1** and **2** were tested in hydrocarboxylation of cyclohexane to cyclohexanecarboxylic acid. The results were compared with those previously reported for gold nanoparticles deposited on carbon materials for the same reaction [1,2].



Scheme 3. Gold-nitrogen complexes.

Acknowledgements. Financial support from Fundação para a Ciência e a Tecnologia (FCT), Portugal, for fellowship SFRH/BPD/90883/2012 to APCR and for UID/QUI/00100/2013, UID/NAN/50024/2013, PTDC/QEQ-ERQ/1648/2014 and PTDC/QEQ-QIN/3967/2014 projects is gratefully acknowledged. Project “AIProcMat@N2020 - Advanced Industrial Processes and Materials for a Sustainable Northern Region of Portugal 2020” (NORTE-01-0145-FEDER-000006), supported by NORTE 2020, under the Portugal 2020 Partnership Agreement, through the European Regional Development Fund (ERDF) and Project POCI-01-0145-FEDER-006984 – Associate Laboratory LSRE-LCM funded by ERDF through COMPETE2020 – POCI – and by national funds through FCT, are also acknowledged. SACC is thankful to FCT for Investigador FCT program (IF/01381/2013/CP1160/CT0007). E. Pakrieva is grateful for the “Scholarship of the President of the Russian Federation for training abroad in 2017/18 years”.

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UNRAVELLING SURFACE BASICITY AND BULK MORPHOLOGY ON METAL-FREE C-BASED CATALYSTS WITH UNIQUE DEHYDROGENATION PERFORMANCE

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The high chemical versatility together with the unique chemico-physical properties of carbon-based nanomaterials (CNMs) have opened wide horizons in key sectors of functional materials basic research and heterogeneous catalysis. In particular, CNMs doped with light-heteroelements and featured by hierarchical porous architectures have been studied as unique catalytic materials for promoting a number of key industrial transformations. On this ground, the steam- and oxygen-free direct dehydrogenation (DDH) of Ethylbenzene (EB) to Styrene (ST) represents one of the most important industrial processes at the heart of polymer synthesis[1] where activity and selectivity represent two significant features. The catalyst stability under harsh operative conditions, the reduction of leaching of its active sites and their resistance to deactivation phenomena on stream are key parameters to be kept in mind while designing and synthesizing new catalytic materials for the process. The current industrial technology for ST production is a highly energy-demanding process typically promoted by a K-Fe_2O_3 catalyst (K-Fe) at temperatures between 580 and 630 °C with the use of a large amount of steam. Despite the general process feasibility, K-Fe lists the classical disadvantages of metal-based heterogeneous catalysts: a drastic deactivation/passivation due to the rapid generation of "coke" deposits and metal leaching or structural collapse occurring under severe operative conditions. Carbon-based catalysts have recently emerged as valuable metal-free catalysts for DDH, offering superior performance in terms of activity and selectivity compared to the K-Fe system.[2-4] However, from the viewpoint of developing effective and sustainable metal-free catalysts for the DDH process, some key issues related to the complex puzzle of physicochemical and morphological properties of CNMs still remain to be addressed.[5] In particular, the role of the surface basicity in N-doped carbons on the DDH selectivity and catalyst stability on stream, remains a matter of debate among the scientific community. This contribution sheds light on this tricky matter revealing complex structure-reactivity relationships of a class of highly microporous, N-rich Covalent Triazine Frameworks (Figure 1) with superior activity and stability in DDH compared to the benchmark metal-based and metal-free systems of the *state-of-the-art*, particularly at harsh operative conditions close to those used in industrial plants.[6]

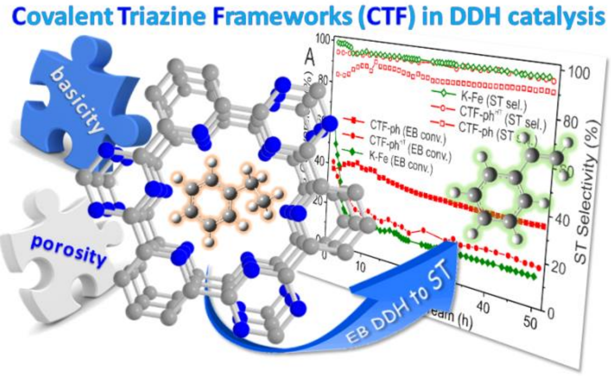

Figure 1. CTF-based catalyst in Direct Dehydrogenation of Ethylbenzene to Styrene.

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EFFECT OF Mo PROMOTION ON THE ACTIVITY AND SELECTIVITY OF Ru/GRAPHITE CATALYSTS FOR FISCHER-TROPSCH SYNTHESIS

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Fischer–Tropsch synthesis (FT) is an attractive reaction path to produce liquid fuels and chemicals from syngas (mixture of H_2 and CO) avoiding the use of petroleum resources, and leading the utilization of alternative row materials such as natural gas, coal or biomass. The most active catalytic metals in FT reaction are Ru, Co, Fe and Ni. One of the principal requirements for FTS processes, to be economically viable, is to achieve a high activity, maximizing selectivity toward C5+ hydrocarbons together with a low selectivity to byproducts such as methane. In order to accomplish this purpose as well as increase the olefin productivity, FT catalysts often contain chemical promoters such as alkali metals, noble metals or transition metal oxides to attain the optimal catalytic performance.[1] A promoter of particular interest for FTS catalysts is Mo. It has been reported that Mo promotion increases catalyst activity, decreases C_1 formation and increases the olefin to paraffin (O/P) ratio of the C_2-C_4 fraction.[2] Preparation methods of catalysts should be designed which lead to interaction of metal and promoter with each other, rather than separately with the support. Alternatively an inert support such as a graphitic material can be used to foster the metal-promoter interaction. Here, we present a comprehensive study aimed at investigating the influence of Mo promotion on the activity and selectivity of Ru catalysts supported on high surface area graphite (G) for the FT process.

The support of the catalysts, HSAG, was obtained from Timcal (surface area around 400 m^2/g). First, the support was impregnated with molybdenum by incipient wetness impregnation method, using ammonium molybdate tetrahydrate ($H_{24}Mo_7N_6O_{24}$.$4H_2O$, Aldrich) in H_2O solution as precursor, in the adequate concentration to incorporate the desired Mo wt% to the support. After the impregnation, the catalyst was kept at room temperature over the night and later heated at 393 K during 24 h. Triruthenium dodecarbonyl ($Ru_3(CO)_{12}$, Aldrich) was employed as ruthenium precursor. It was dissolved in 50 cm^3 of acetone and introduced in a rotavapor at 50 rpm during 30 min together with the previous impregnated support. After that, acetone was evaporated at 323 K. After reduction in hydrogen at 673 K the samples were characterized by CO chemisorption coupled with microcalorimetry, transmission electron microscopy (TEM) and X-ray Photoelectron Spectroscopy (XPS). The catalytic tests were performed in a continuous flow reactor at 3.5 bar of pressure and at 523 K. The analysis of the effluent gases from the reactor was carried out with an on line connected gas chromatograph (Bruker 450) equipped with three columns, two TCD detectors and one FID detector.

Characterization of the reduced catalysts reveals that the addition of Mo does not significantly affect the mean diameters of the Ru nanoparticles as measured from TEM images or from the CO uptakes (Table 1). The results obtained in the FT reaction shown that ruthenium catalytic properties are severely affected by the addition of Mo, even with very low loadings. So the presence of molybdenum in a bimetallic Ru-Mo catalyst improves the catalytic behavior of ruthenium in terms of catalytic activity, long-chain hydrocarbon selectivity and the olefin-to-paraffin ratio. Specifically, when the site time yield (STY) to C5+ ruthenium is considered (Figure 1), the 2Ru0.1Mo/G sample shows the best performance. Calorimetric CO adsorption profiles reveal an important increase of CO adsorption heats for the Mo promoted samples with respect to Ru monometallic catalyst, particularly when the Mo/Ru atomic ratios are in the range 0.02 to 0.26. This fact can be explained because CO molecules might bind to MoO_x surfaces through the O atom, while being simultaneously bound to the Ru metal through the C atom, giving place to bridged species, which correspond to higher adsorption heats. By XPS performed to 2Ru0.5Mo/G sample, after in-situ H_2 reduction treatment, were evidenced the presence of MoO_3, MoO_2, Mo_2C and Mo^0 species on the catalyst surface.

Table 1. Main characteristics of the Ru catalysts.

Catalyst	Ru (wt%)	Mo* (wt%)	d_{TEM} (nm)	CO uptake (μmol/gCat)
2Ru/G	1.98	-	3.4	22
2Ru0.05Mo/G	2.04	0.05	3.4	28
2Ru0.1Mo/G	2.03	0.10	3.0	35
2Ru0.5Mo/G	2.02	0.50	3.3	27
2Ru1Mo/G	2.05	1.00	3.0	22
2Ru5Mo/G	2.01	5.00	3.6	20

*Nominal content of Mo wt%.

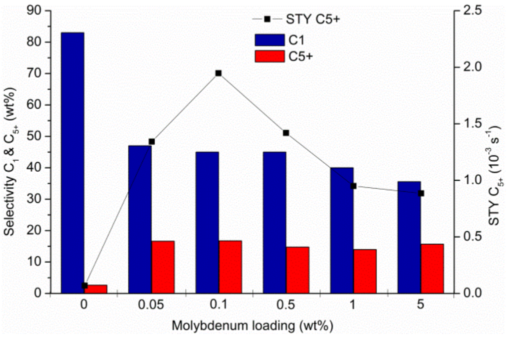

Figure 1. Influence of Mo loading on selectivity and site time yield to C5+ of 2 wt% Ru/G, measured at 523 K, 3.5 bar, $H_2/CO = 2$, GHSV = 5.4 m^3STP kg^{-1}cat h^{-1}. Reported data are for stable performance after 550 min of operation.

In conclusion, in this work we show that graphitic material (G) provides a suitable support for studying the molybdenum promotion effect in Ru based FT catalysts. The influence of the promoter species may be explained by assuming that the MoO_x particles are located surrounding the Ru particles, thus affecting the dissociation rate of CO by weakening the internal CO bond.

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HIERARCHICALLY STRUCTURED CARBON COMPOSITE BY ELECTROSPINNING PROCESS FOR HETEROGENEOUS CATALYTIC APPLICATIONS

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Nanocarbons with unique physicochemical properties have been considered as typical sustainable materials for use as catalyst support and directly as catalyst. Unfortunately, the powder form of nanocarbons renders it difficult to be used in the industrial process due to the high pressure drop, the difficulty for handling as well as health injuries caused to human beings. Recently, nanocarbon materials fabricated through electrospinning process with hierarchical and continuous structure have also been reported as high performance electrodes in the electrochemical energy storage processes[1], but the hierarchical structured monolith, usually used in heterogeneous catalysis field, has not been prepared till now through electrospinning process. In general, the porosity of carbon fibers (CF) obtained from electrospinning is mostly generated through the conversion of the polymer precursor into CF during the annealing process under inert gas at high temperature. It is though that such CF composite could find interest in the field of catalysis where the high open porous structure provides high accessibility of the reactant to the active sites along with improved escaping of the intermediate products leading to an improvement of the process selectivity.[2] However, the as-synthesized carbon fibers material from polymer(s) mixture only displays a relatively low specific surface area with moderate catalytic activity. It is thus of interest to develop new synthesis process to improve the overall specific surface area of the material while keeping the initial high porous structure as well as the control of the macroscopic shape for subsequent potential processes in the field of nanofiltration, wastewater treatment and catalysis.

Herein, hierarchical carbon fibers/carbon nanofibers (CF/CNF) composites with high effective surface area and controlled macroscopic shape were successfully synthesized through a combination of electrospinning (ES) and chemical vapour deposition (CVD) processes. A web of poly(acrylonitrile)/ poly(vinyl pyrrolidone) (PAN/PVP) composite fibers embedding a nickel salt was firstly produced by electrospinning (ES). After a carbonization step, the polymeric material was converted into porous carbon embedding nickel nanoparticles available on the fiber surface. Then, the catalytic growth of CNFs was carried out from the nickel nanoparticles by CVD leading finally to the formation of a hierarchical carbon web of hairy fibers with high effective surface area (Figure 1). The density, diameter and length of CNFs attached on the surface of the CFs could be finely tuned by adjusting the CVD conditions.[3] The specific surface area of the CF/CNF monolith was amounted to more than 200 m^2/g along with a high accessibility due to they small dimension. The hierarchical CF/CNF composite has been used as metal-free catalyst for the steam- and oxygen-free catalytic dehydrogenation of ethylbenzene to styrene.

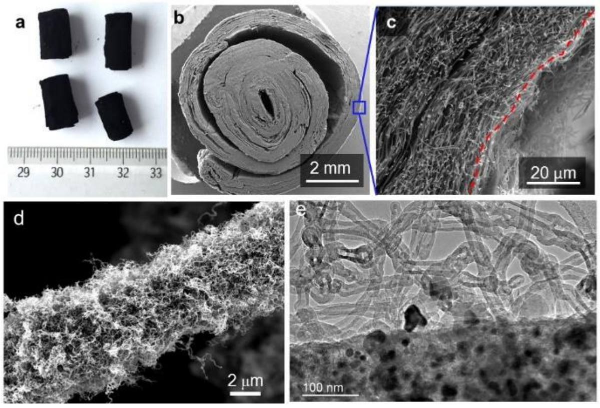

Figure 1. Digital photos of macroscopic shaping electrospun Ni/CF monolith after CVD process (b, c) SEM images on a cross-section of the macroscopic shaped Ni/CF material in scroll pellet after carbonization. (d) An isolated hairy carbon fiber of a CF/CNF composite. (e) TEM micrograph of the same sample showing the CNF network formed at the CF surface. The Ni NPs growth catalyst can be visualized as dark dots inside the composite

The catalytic results have pointed out that such monolith can be efficiently used as a material platform for different applications going from catalysis to wastewater treatment thanks to the high effective surface area and reactivity of the CNF with prismatic planes. The high accessibility and the effective surface area of the composite could also represent a net advantage for they use in the field of the electrochemical energy storage.

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CATALYTIC CARBON GASIFICATION: UNDERSTANDING CATALYST-CARBON CONTACT AND RATE JUMP BEHAVIOR

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Understanding mechanisms are an important key to optimize reactions. Catalytic carbon gasification is an area of industrial importance nowadays. The mechanism based on C bulk diffusion has been recently updated[1]. The relevance of the Tammann temperature to get efficient catalyst nanoparticle contact is now better understood. Interaction between kinetics and thermodynamics needs some clarification.

It was reported in the 1980's that there is a deviation of the temperature at which the particle movement starts (ΔT), when gasification of graphite is observed under in-situ TEM or SEM. In the case of gasification by O_2 (exothermic process) the particles start moving apparently 160 ºC below the Tammann temperature. In our opinion, this indicates that the active contact (CASA) front becomes operative, because the temperature of the particle rises to that level, despite the prevailing lower temperature of the operating cell.

In order to understand and model the rise of temperature of the particles, the following 3 factors must be considered: 1) The heat capacity of the particles; 2) The thermal conductivity of the solid; 3) The size of the particle. Fig. 2 shows the geometries and catalyst-carbon contacts involved in graphite gasification, observed by in-situ electron microscopy (in graphite gasification, Fig. 1A) or assumed (in coke gasification, Fig. 1 B, based on the kinetic behavior) [1].

Rate jumps are kinetic phenomena observed in some cases in catalytic carbon gasification by air or oxygen following a minor increase in temperature (*v.g.* ΔT = 5 ºC). Their occurrence has been reported but the phenomenon is not well understood. The rate jumps can be consistently explained by the "carbon-worm" mechanism, due to a jump in the temperature of the moving nanocatalyst particles. The carbon bulk diffusion step is then much faster and the external film mass transfer becomes the rate-limiting step. The reaction order changes from zero to one. The nature and role of catalyst-carbon contact in catalytic carbon gasification is discussed.

Rate jumps dealing with catalytic carbon gasification by air can be observed in several systems. The rate jumps observed by Devi and Kannan, in the air oxidation of carbon methyl cellulose (CMC) based carbon, using Cu as catalyst, were a 350 fold, following an increase of temperature of just 5 ºC [2]. These *rate jumps* should rather be understood as *temperature jumps of the particle, with the external mass transfer becoming the rate determining step*, as shown in the Arrhenius plot of Fig. 1.

In fact, the preliminary heat treatment temperature (HTT) studies, reported by Devi, showed that an important increase in the average size of Fe, Co, Ni and Cu catalyst particles/crystallites may take place at higher temperatures. The enlargement was estimated based on the XRD diffraction spectra using the Scherrer formula. In the case of Ni, the average size of the particles increases about 25 times, when HTT is raised from 500 to 800 ºC [8]. With Cu, an average particle size increase of 4 times was observed, comparing XRD diffraction observations at 400 and 800 ºC. However, this information must be regarded as merely indicative: solid-state reactions are slow and more time resolved studies of the changes are needed (v.g. using operando XRD).

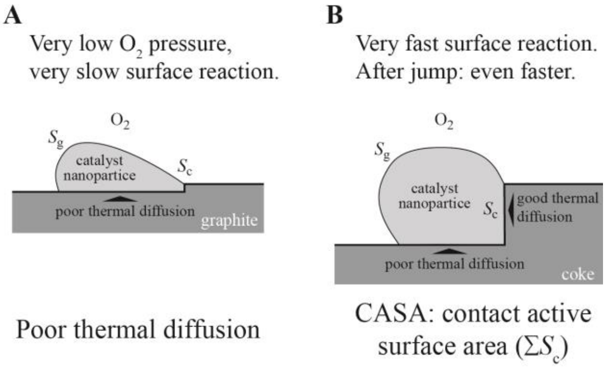

Fig. 1. Schematic representation of contact between catalyst particles and: A) Graphite; B) Coke. *Graphite is very anisotropic. The conduction in the crystallographic c direction is negligible, compared with the other perpendicular directions (parallel to graphene plans) exhibiting conductivity similar to copper.*

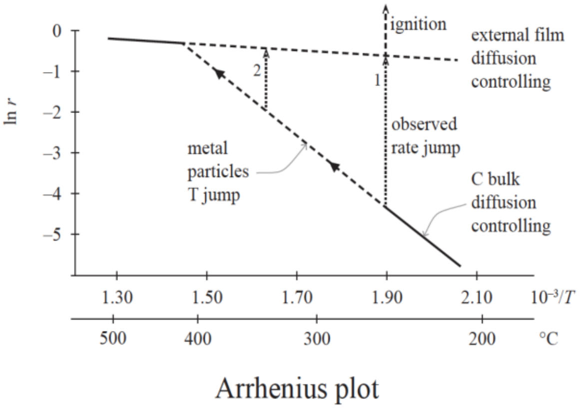

Figure 2. Rate jumps explained using an Arrhenius plot. A jump in the temperature of the catalyst particles corresponds to a much faster carbon bulk diffusion step. The external film mass transfer becomes the slower and rate determining step. The jump is observed at lower temperatures with smaller particles (case 1) and at higher temperatures with larger ones (case 2).

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KINETICS OF CATALYTIC COKE GASIFICATION BY AIR AND BY CO_2

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Introduction. Char gasification is of great industrial importance nowadays due to its use in energy generation and Fisher-Tropsch. Diesel soot reduction is also an urgent priority in major cities in Europe. The study of the kinetics of these processes is the best key to understand its mechanism and so to prepare better catalysts and improve working conditions. An Arrhenius plot of the rates shows the controlling steps (Fig.1)

Experimental. A TG-DSC apparatus was used to follow simultaneously kinetics (gasification rates) and thermodynamics (heat transfer). Both V and Cu were used as catalysts. The catalysts were deposited by incipient wetness from NH_4VO_3 and $(CH_3COO)_2Cu.H_2O$. Dispersion on carbon black and size of catalyst particles of V and Cu alone and combined as observed by in-situ XRD at 500 ºC under argon, as well as the nature of the solid phases present during reaction. The average diameter of the particles was estimated using the Scherrer formula.

Results. A record of active carbon doped with 1% V reacting with air at 450 ºC showed an initial period of heating up associated with solid-sate changes (30 min) but a steady-state gasification followed. The loss of weight was approximately linear and heat flux (HF) is then constant. After 20 min the gasification is almost complete, rate slows down quickly and the HF drops to zero. The steady-state rates observed are plotted in an Arrhenius plot (Fig. 2). V is a better catalyst than Cu. Mass transfer limitations are observed at high temperatures – the rate is leveled independently of the catalyst. An apparent reaction order of 1 is observed, corresponding to the mass transfer through the external gas film at catalyst particle level. The corresponding HF is also leveled. An important observation was the evolution of the gas product – mostly CO at low and high temperatures, mostly CO_2 at 650 ºC.

Role of solid-state. There are only atoms and ions in the solid-state. Fick's Laws rule. The phase diagram for Cu and V shows a very low solubility (Savinstzky, 1984). The interfacial mixing of the two metals at nano-level has been studied in some detail (Sauvage, 2009). We found by in-situ XRD that the Cu-V phases that reveal a strong interaction between Cu and V. We found by in-situ XRD that the Cu-V phases that reveal a strong interaction between Cu and V. A way to get more information about the phases present (stable or metastable) during reaction is to allow complete C gasification under operando XRD, as done by Shen et al. 2015. They were using Ni as catalyst to gasify rice husk char by CO_2. Ni was apparently the catalyst but once char was consumed Ni turned to NiO.

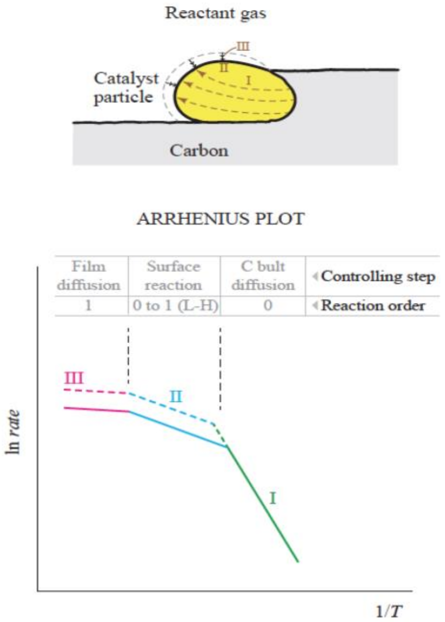

Figure 1. Arrhenius plot showing the temperature dependence and the change of rate determining step.

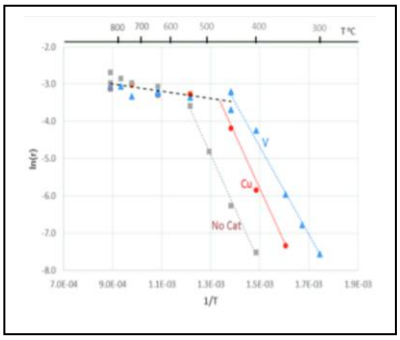

Figure 2. Arrhenius plot of the rates of charcoal gasification by O_2 uncatalized and catalyzed by Cu and by V. The activation energies observed were 14.6, 14.1 and 11.7 kcal/mole, respectively.

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EFFECTIVE CONVERSION OF RAPESEED OIL TO BIODIESEL FUEL IN THE PRESENCE OF BASIC ACTIVATED CARBON CATALYSTS

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Growing environmental awareness together with increasingly restrictive regulations regarding air pollution as well as global shortage of fossil fuels and increasing demand for energy have resulted in intensive development of research work focused on biodiesel, which is recognized as one of the most promising non-conventional renewable energy sources [1]. The most important method of producing fatty acids methyl esters (FAME), the main components of biodiesel, is the acid-catalyzed or base-catalyzed transesterification of vegetable oils or animal fats in the presence of alcohol. In industry, the preferred catalysts of this reaction are different bases, e.g., NaOH, KOH or alcoholates of alkali metals [2]. Recently, various heterogeneous catalysts have also been tested in the transesterification process [3], which is justified from the practical and economical point of view. In general, heterogeneous catalysts are usually a bit less effective than homogeneous ones, but it is easier and cheaper to separate them from the products and they can be used many times.

There are only scarce data on the use of carbon materials as independent catalysts of transesterification processes. Meanwhile, according to many authors, well-tailored carbons can be effective catalysts of various acid-base reactions. The ease of modification, thermal and mechanical stability or relatively low production costs can be mentioned as other advantages of these materials [4].

In view of the above, the aim of our study was to design relatively cheap and effective heterogeneous basic catalysts of the reaction of biodiesel formation. A number of activated carbon catalysts have been obtained and tested. Most of these materials were novel catalysts not used in the transesterification reaction until now.

The initial activated carbon (AW) was prepared from ash wood. The starting material was impregnated with a 7% aqueous solution of $CaCl_2$. The impregnated sample was carbonized at 800ºC for 1 h and activated with CO_2 at the same temperature for 0.5 h. Subsequently, AW was modified with different N-containing agents (such as gaseous ammonia, aniline, melamine, benzene-1,4-diamine, aminosilane, or guanidine derivatives) in order to introduce basic functional groups on its surface.

The transesterification of rapeseed oil with methanol was performed in a batch autoclave at the temperature of 130°C and a pressure of 1.3 MPa for 24 h upon continuous stirring. The experiments were typically conducted using 50 cm^3 of rapeseed oil, 24.4 cm^3 of methanol and 0.89 g of a catalyst (a methanol to oil molar ratio was 12:1, a catalyst loading was equal to 2% vs the oil mass). The samples of the reaction mixture were collected after 1, 3, 6 and 24 h, and they were analyzed using a GC technique. For the best materials, the reusability tests were also conducted.

Fig. 1 presents the results of biodiesel formation obtained for selected N-containing activated carbon catalysts. For the sake of comparison, the same figure also gives the results attained in the reaction carried out in the presence of unmodified activated carbon and a commercial homogeneous catalyst – NaOH. As follows from the data presented in the graph, the unmodified activated carbon showed only negligible catalytic activity in the process, with the FAME yield of about 1% after 24 h of the reaction.

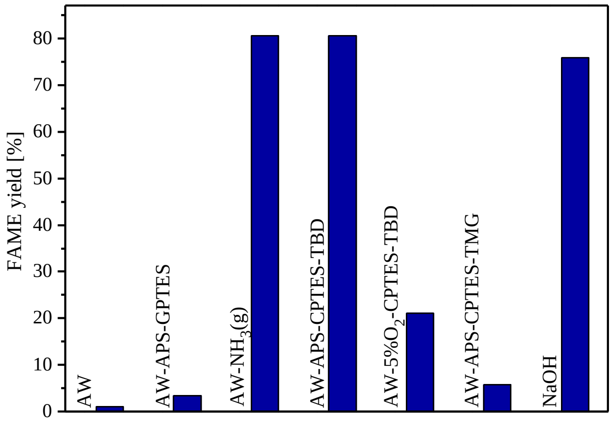

Figure 1. Catalytic activity of selected samples after 24 h of the reaction
APS - ammonium persulfate,
TBD - 1,5,7-triazabicyclo[4.4.0]dec-5-ene,
CPTES - (3-chloropropyl)triethoxysilane,
TMG - 1,1,3,3-tetramethylguanidine,
GPTES - 3-(N,N'-dicyclohexylguanidine)propyltrimethoxysilane

The modifications applied led to the improvement in catalytic performance of the catalyst obtained. Some of them were particularly effective. The best results were obtained for the transesterification reaction carried out in the presence of AW treated with gaseous ammonia at high temperature and AW oxidized by APS and then modified with TBD. After 24 h of the process, the yield of FAME in the presence of these two samples was almost the same and close to 80%. However, it should be mentioned that the use of AW-APS-CPTES-TBD resulted in a higher yield of FAME in the first 6 h of the reaction (not shown). After 24 h of the process, the yields of FAME obtained with the use of the best samples were higher than that achieved in the presence of sodium hydroxide, however, the presence of the latter permitted faster reaching a steady state of the reaction.

On the basis of the results presented it can be supposed that the modified carbons prepared might be also promising solid base catalysts for other base-catalyzed reactions.

Acknowledgements. This work was partially supported by the National Science Center, Poland (grant number 2012/05/N/ST5/00093).

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MECHANISTIC AND KINETIC INSIGHTS INTO THE Pt-Ru SYNERGY IN HYDROLYTIC DEHYDROGENATION OF AMMONIA BORANE

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Pt catalyst is one of the most investigated and industrially relevant catalysts, and increasing its utilization efficiency is of considerable scientific and industrial importance. Exemplified with Pt-catalyzed hydrolytic dehydrogenation of ammonia borane (AB) for room-temperature hydrogen generation, we have proposed one strategy for development of highly efficient and cost-effective Pt catalysts by engineering the size and shape of Pt nanoparticles and surface properties of support toward more Pt active sites and/or targeted Pt electronic properties[1,2].

Recently, another strategy to obtain highly efficient and cost-effective Pt catalysts has been proposed to make full use of the synergy in the Pt-based bimetallic catalysts by partial substitution of Pt with over 11 times less expensive Ru [3]. PtRu/CNT catalysts with different Pt to Ru ratios were prepared and used to catalyze hydrolytic dehydrogenation of ammonia borane. The volcano-shape of activity between catalytic compositions (Fig. 1a) strongly indicates a remarkable Pt-Ru synergy for this reaction, and $Pt_{0.5}Ru_{0.5}$/CNT shows almost 1.8 times higher activation to pure Pt catalyst. The opposite trend of activation energy (E_a) and the pre-exponential factor (A) for the five catalysts suggests a trade-off between the activation energy and pre-exponential factor, which gives rise to the highest hydrogen generation rate of the $Pt_{0.5}Ru_{0.5}$/CNT catalyst (Fig. 1b). Isotopic experiments, using D_2O instead of H_2O as the reactant, is employed to gain more mechanistic insights into the Pt-Ru synergy (Fig. 1c). A much lower kinetic isotopic effect of $Pt_{0.5}Ru_{0.5}$/CNT and $Pt_{0.75}Ru_{0.25}$/CNT catalysts compared with their monometallic counterparts indicates the Pt-Ru synergy in these bimetallic catalysts could promote the activation of water.

The appropriate activation energy and entropy of activation for the reaction are mainly responsible for the highly active $Pt_{0.5}Ru_{0.5}$/CNT catalyst, and a volcano-shaped relationship for the reactivity of these five catalysts as a function of entropy of activation is proposed. Based on the transition state theory, the turnover frequency (TOF) can be expressed in the Eyring form:

$$TOF = \frac{k_B T}{h}\exp(\frac{\Delta S^{0^*}}{R})\exp(-\frac{\Delta H^{0^*}}{RT}) \qquad (1)$$

where k_B, T, h, ΔS^{0*}, R and ΔH^{0*} are the Boltzmann constant, absolute temperature, Planck constant, entropy of activation, universal gas constant and enthalpy of activation, respectively. On the other hand, the turnover frequency (TOF) can be also described as:

$$TOF = \frac{k}{\tau} \qquad (2)$$

where τ is the dispersion of metal nanoparticles.

The activation energy (E_a) could be related to ΔH^{0*} by the Temkin equation:

$$E_a = \Delta H^{0^*} + \sum n_i \Delta H_i \qquad (3)$$

where ΔH_i and n_i are the adsorption enthalpies and reaction order of reactant i, respectively. Taking into account the characteristic of zero-order reaction (i.e., $n_i = 0$), E_a is equal to the ΔH^{0*}. Combining Eqs. (1), (2), (3) and the Arrhenius equation gives:

$$\Delta S^0 = R\ln(\frac{Ah}{k_B T\tau}) \qquad (4)$$

The insights revealed here might guide the rational design of catalysts for this reaction, and the methodology could be extended to unravel the nature of other bi- or multi-metallic catalysts.

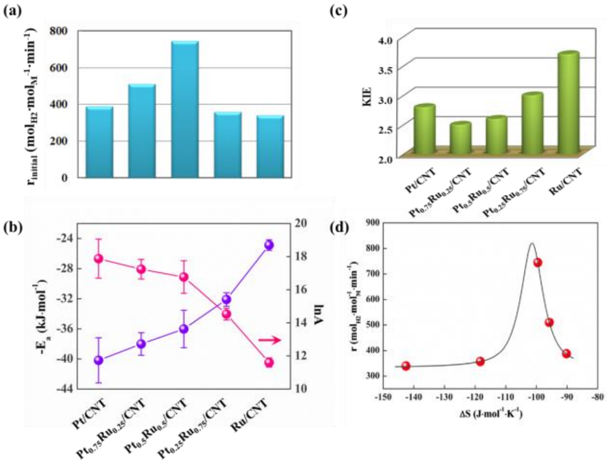

Figure 1. (a) Initial hydrogen generation rate ($r_{initial}$), (b) Activation energy (E_a) and the logarithm of pre-exponential factor (lnA), (c) Kinetic isotope effect (KIE) values of Pt/CNT, $Pt_{0.75}Ru_{0.25}$/CNT, $Pt_{0.5}Ru_{0.5}$/CNT, $Pt_{0.25}Ru_{0.75}$/CNT and Ru/CNT catalysts, and (f) Schematic illustration of the relationship between the catalytic activity and entropy of activation for PtRu-based catalysts, where the solid line is the trend line.

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OXIDIZED MULTI-WALLED CARBON NANOTUBES AND ACTIVE CARBON CATALYZED DEHYDROGENATIVE C-C ARYL COUPLINGS

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Oxidized carbon materials have well-known ability to catalyse various reactions, in particular, dehydrogenations and oxidations, e.g. ethylbenzene styrene conversion, a range of aromatizations and oxidative functional group conversions.[1] In contrast to this, apart from some acid catalysed C-C coupling reactions,[1] there are only a few examples of dehydrogenative couplings carried out by oxidized carbon material.[2]

We have shown recently that oxidized active carbon (oAC) or multi-walled carbon nanotubes (oMWCNT) can dehydrogenatively couple indoles, benzofurans and benzothiophenes to the corresponding 3,3'-derivates with oxygen as a terminal oxidant.[3] Originally, the coupling was observed as a serendipitous discovery, when we studied heterogenous gold catalyst supported on active carbon for 2-alkynylaniline cycloisomerization to indoles, some electron rich indoles tend to oxidatively homocouple as a side reaction.[4]

Later, we identified that the catalytic activity is specifically associated with the oxidized carbon material used as support. To convert active carbon to catalytically active oAC, we studied and optimized the effect of different oxidative treatments to catalyse the dehydrogenative couplings. The XPS analysis of various oAC materials showed that the activity correlates strongly with the amount of carbonyl groups. For a further evidence, chemical blocking and model compound studies indicated similarly the likelihood of carbonyl/quinone functionalities as the catalytically active site of oAC. Guided by the reactivity of homogeneous quinone, DDQ, we discovered that the oxidative power of both carbocatalysts could be raised with a suitable acid additive to perform more difficult coupling reactions (Figure 1).

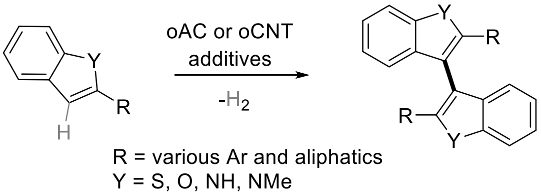

Figure 1. Various oxidized carbon materials are capable for dehydrogenative couplings of benzofused heterocycles. Oxidative power can be adjusted by acid additive.

Importantly, the use of carbocatalysts for oxidative couplings permits the use of sensitive indoles as substrates that are incompatible with some homogeneous quinones and other oxidants. It has, for example, been reported that indole and DDQ form a covalent adduct [5] and also in our studies we have witnessed the incompatibility of harsh homogeneous oxidants and indoles. Thus, carbocatalysis can oxidize indoles in relatively mild conditions and as a very unique example, we have accomplished the synthesis of unforeseen tetraindole cyclooctatetraenes (COTs) directly from 2,2'-indole dimer in one pot (Figure 2). We are currently extending this strategy for other benzofused heterocycles.

We have also observed that electron-rich aromatics undergo couplings similarly than the indoles, benzofurans and benzothiophenes with oxidized carbon materials either intra- or intermolecularly (Figure 3). In these studies, we discovered that HNO_3-oxidized active carbon could perform better in more difficult oxidations than air-oxidized active carbon and HNO_3:H_2SO_4-treated MWCNTs. At the present, we are exploring the origin of these varying activities.[6]

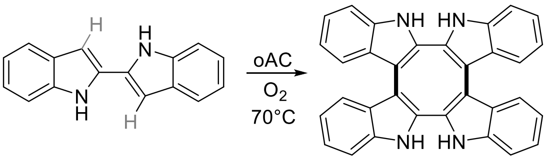

Figure 2. The oAc catalyzed one pot synthesis of C2-symmetric cyclooctatetraene tetraindole.

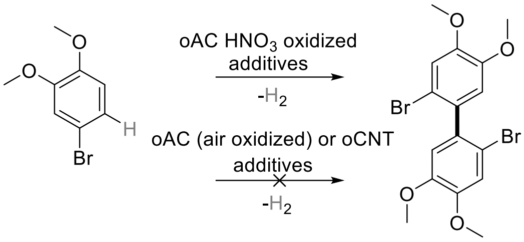

Figure 3. Different oxidized carbon materials have slightly different oxidization powers.

The oxidized carbon catalyst offers a competitive heterogeneous catalyst alternative for homogeneous quinone type oxidants, due to the ability of carbon material to exploit O_2 as terminal oxidant and being benigner oxidant for fragile substrates and products.

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SINGLE STEP TRANSFORMATION OF SYNGAS TO TETRAMETHYLBENZENE WITH HIGH SELECTIVITY

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Controlling the selectivity in a single step conversion to single aromatic hydrocarbon to enhance the CO utilization is the largest challenge in syngas chemistry [1-5]. Fischer-Tropsch synthesis (FTS) is limited by equal probability chain growth Anderson-Schulz-Flory (ASF) distribution with chain growth factor less than one [6-7]. Here, we achieved a remarkable formation of aromatics with exponential growth of carbon chain reaction of every increase in aromatic carbon number results up to 8 fold of next high aromatics carbon number gain. The benzene ring acts as self-catalysis catalyst in the formation of aromatics carbon chain bursting all the way toward the maximum selectivity of Tetra-methyl-benzene(TMB). The selectivity of TMB as high as 70 % at total CO conversion of 37 % under H_2 deficient syngas environment with temperature as low as 350°C and remained stable for up to 600 hrs. This burst aromatics chain reaction will open new pathways of understanding the syngas chemistry and have significant impact in upscaling of selective synthesis of valuable chemical products.

TUNING THE PROPERTIES OF g-C_3N_4 FOR ENHANCED PHOTOCATALYTIC PRODUCTION OF HYDROGEN FROM WATER

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Harvest, conversion and storage of renewable solar energy for the production of sustainable and green fuels (H_2) can become technologically relevant through the development of the heterogeneous photocatalysis field. Among several photocatalysts, the polymeric metal-free graphitic carbon nitride (g-C_3N_4, Figure 1) [1-3] is considered as one of the most attractive materials to design economic, clean and chemical stable visible light photocatalysts for the production of renewable solar fuels. This is due to its appealing features, including unique optical, structure, electric and physiochemical properties, which makes it a versatile material with application in several areas, mostly in solar energy conversion and environmental remediation [2-4]. However, g-C_3N_4 presents some drawbacks, and the major limiting factors affecting the efficiency of solar fuel application include; (i) light absorption, (ii) charge separation and transport and (iii) surface chemical reaction [2,3]. Hence, engineering g-C_3N_4 properties to overcome these disadvantages is of great significance.

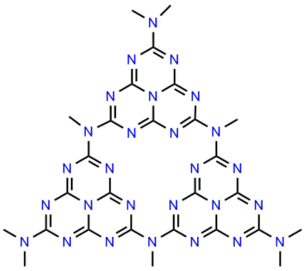

Figure 1. Chemical structure of tri-*s*-triazine unit, considered the tectonic structures of g-C_3N_4.

Herein we report synthesis strategies to prepare g-C_3N_4 (CN) materials with tuned optical, electronic and textural properties which contribute to improve the photocatalytic activity for hydrogen production from water. Several types of CN were prepared by polymerization using different precursors, particularly dicyandiamide (D-CN), urea (U-CN) and the mixture of both (DU1-CN and DU2-CN, in which 1 and 2 represent different D/U ratio). Furthermore, D-CN material was further modified by thermal (TD-CN) and liquid (LD-CN) exfoliation. The materials have been characterized by several techniques, including UV-vis diffuse reflectance, steady-state and time-resolved photoluminescence, scan electron microscopy (SEM), infrared spectroscopy, N_2 adsorption/desorption isotherms, elemental analysis and powder X-ray diffraction (XRD).

The photocatalytic performance of the *as*-prepared catalysts was assessed by measuring the amount of hydrogen evolved after 3h of UV-vis light irradiation in the presence of EDTA as sacrificial electron donor and Pt as co-catalyst. As shown in Figure 2, the photocatalytic activity of the materials is highly dependent on the type of precursor and of the post treatment process. The highest amount of H_2 was produced using dicyandiamide and thermal exfoliation (TD-CN, 199 μmol H_2), followed by the material prepared with a mixture of dicyandiamide/urea, without any post treatment (DU2-CN, 177 μmol H_2). The enhanced activity of both materials in relation to bare D-CN and U-CN results from increased surface area (143 $m^2\ g^{-1}$ *vs.* e10 $m^2\ g^{-1}$), efficient separation of charge carriers and textural modification. Further detailed information concerning the relationship between synthesis, structure properties and photocatalytic performance will be presented.

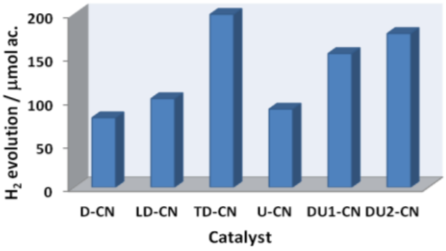

Figure 2. Photocatalytic H_2 production in function of catalyst upon 3h of UV-vis light (≥ 365 nm) irradiation in the presence of EDTA and Pt.

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VISIBLE-LIGHT DEGRADATION OF AROMATIC POLLUTANTS USING EXFOLIATED GRAPHITIC CARBON NITRIDE AS PHOTOCATALYST

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Advanced oxidation processes are conceptually based on the production of highly reactive species, such as hydroxyl radicals ($HO^{\bullet}$), capable to promote the degradation of organic molecules. Among them, heterogeneous photocatalysis employs UV and/or visible radiation as driving force. Graphitic carbon nitride, g-C_3N_4 (gCN), has recently attracted a huge interest as photocatalyst, since it can be synthesized easily using relatively cheap precursors, is active under visible light radiation and is able to efficiently remove organic compounds from water; however, most of reported studies have employed dyes as model compounds [1-3].

Some research articles dealing with the decomposition of aromatic molecules using this photocatalyst have shown that hydrogen peroxide (H_2O_2) is simultaneously produced via a two-electron oxygen reduction [4-6]. This is an important additional advantage for the photocatalytic process, since H_2O_2 is a clean and strong oxidizing agent which could produce hydroxyl radicals that aid in the decomposition of the organic pollutants.

The main aim of the present study was to gain knowledge on the mechanism involved in this photocatalytic system. To this end, a thermally-exfoliated gCN material [7] was tested under varying operating conditions for the degradation of different aromatic compounds in aqueous solutions, using light emitting diodes (LEDs) as irradiation source (maximum absorption wavelength of 417 nm). The pollutant and H_2O_2 concentrations, as well as the total organic carbon (TOC) content, were determined during the experiments.

The micrographs of exfoliated gCN are shown in Figures 1a and 1b, which were respectively obtained by scanning (SEM) and transmission (TEM) electron microscopies. It is possible to observe that gCN consists of well-dispersed thin layers, surrounded by a few aggregates of non-exfoliated gCN.

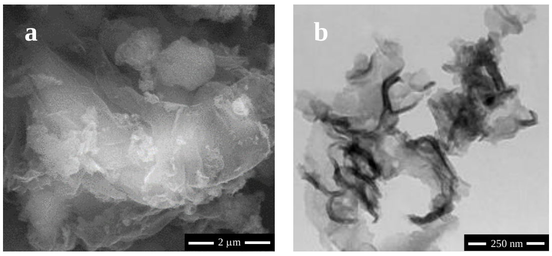

Figure 1. SEM (a) and TEM (b) micrographs of the exfoliated gCN.

The photocatalytic experiments demonstrated that gCN can degrade some of the target organic pollutants with simultaneous production of H_2O_2, as shown in Figure 2 when testing phenol (60 mg L^{-1}) as model compound. In fact, ca. 92 % and 100 % of phenol is photocatalytically removed in 60 and 90 min, respectively. Correspondingly, the highest H_2O_2 concentration (ca. 2.0 mmol L^{-1}) is reached in the system. Moreover, nearly 80% of TOC abatement was achieved after 180 min. The remaining TOC may be explained by the presence of aliphatic organic acids, which are the final oxidation products.

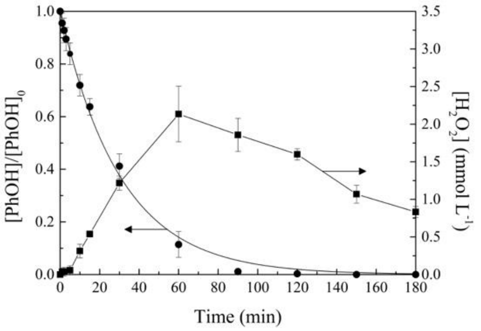

Figure 2. Normalized concentration of phenol ($[PhOH]/[PhOH]_0$) and H_2O_2 concentration profile during the photocatalytic degradation of phenol ($[PhOH]_0 = 60$ mg L^{-1}; photocatalyst load = 0.5 mg L^{-1}).

The other tested aromatic compounds were selected by considering the order, nature and position of the substituent on the aromatic ring (benzoic acid, gallic acid, protocatechuic acid, 4-hydroxybenzoic acid, tyrosol, *p*-methoxyphenol, *o*-cresol, *p*-cresol, among others) and the given pK_a values (4.2 to 10.4). The results obtained, under different operating conditions, will be presented in this communication.

Acknowledgements. This work is a result of project ‘‘AIProcMat@N2020 – Advanced Industrial Processes and Materials for a Sustainable Northern Region of Portugal 2020” (NORTE-01-0145- FEDER-000006), supported by NORTE 2020, under the Portugal 2020 Partnership Agreement, through the European Regional Development Fund (ERDF) and of Project POCI-01-0145-FEDER-006984 – Associate Laboratory LSRE-LCM funded by ERDF through COMPETE2020 - Programa Operacional Competitividade e Internacionalização (POCI) – and by national funds through FCT - Fundação para a Ciência e a Tecnologia. C.G.S. acknowledges the FCT Investigator Programme (IF/00514/2014) with financing from the European Social Fund (ESF) and the Human Potential Operational Programme.

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SYNTHESIS OF C-DOTS/TITANATE NANOTUBE COMPOSITES AND THEIR PHOTOCATALYTIC ABILITY FOR THE DEGRADATION OF POLLUTANTS

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Aiming to develop advanced materials with enhanced optical and photocatalytic properties for the photodegradation of organic pollutants, in particular pharmaceuticals and personal care products (PPCPs), titanate nanotubes (TNTs) modified by assembling carbon dots (C-dots) onto the TNTs' structures were successfully prepared by a swift synthesis method taking advantage of the hydrothermal process developed by our group [1,2] and using cork industry wastewaters as carbon source [3].

The structural, microstructural, morphological, and optical properties of the new hybrid nanomaterials were studied by XRD, TEM, HRTEM, FTIR and UV-Vis diffuse reflectance spectroscopy. Specific surface areas were obtained by the B.E.T. method. A TEM micrograph of a sample obtained is shown in figure 1. In particular, a strong increase on the visible light absorption was observed for the C-dots/TNT mesoporous nanocomposites in comparison to the TNTs' light absorption.

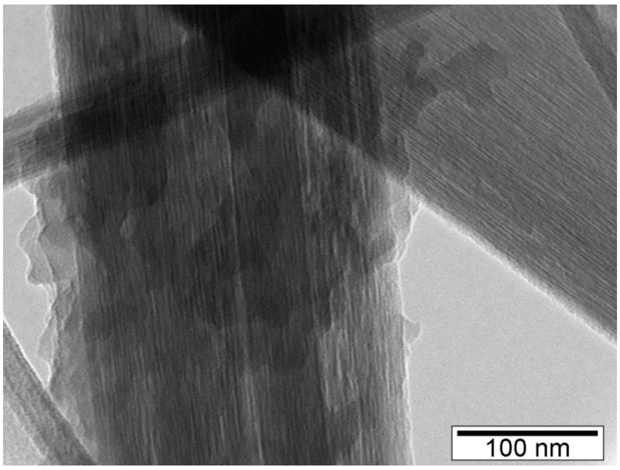

Figure 1. TEM micrograph of a C-dots/TNT nanocomposite sample.

The catalytic ability of C-dots/TNT samples for pollutant photodegradation was investigated. The samples' photocatalytic performance was first evaluated throughout the production of the OH radical using terephthalic acid as probe molecule. After, the photocatalytic ability of the C-dots/TNT nanocomposites for the degradation of PPCPs was investigated using caffeine as a pollutant model.

Acknowledgements. This work has been founded by Instituto Politécnico de Lisboa (IPL) under the IPL/2017/C-dots/TNT/ISEL research project and partially supported by the Portuguese Foundation for Science and Technology (FCT), under the UID/QUI/00616/2013, UID/MULTI/00612/2013, IF/01210/2014 and UID/CTM/04540/2013 projects.

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PHOTOCATALYTIC REFORMING OF BENZYL ALCOHOL OVER METAL-LOADED g-C_3N_4 FOR THE PRODUCTION OF HYDROGEN AND BENZALDEHYDE

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Our global economy is highly correlated with energy sources, particularly with the access of fossil fuels. Lately, to decrease our dependence on fossil fuels, researches have focused on new sources and forms of energy, such as hydrogen. Hydrogen is an interesting form of energy, since it's clean, being attractive from the environmental and economic points of view [1]. One route towards the production of hydrogen is the photocatalytic reforming of organic compounds, which generates hydrogen and value-added chemicals. Not of lesser importance, photocatalysis allows us to work at mild conditions of temperature and pressure [2]. In photocatalysis, solar energy promotes the migration of electrons, within an optical semiconductor, from the valence to the conduction band, leaving positive holes in the former. The electrons act as reducing agents, while the holes act as oxidizing agents. However, in these semiconductors the high recombination ratio (of the charge carriers) reduces the overall charge separation and breaks down their performance as photocatalysts. To overcome these limitations, we have been using specific carbon materials, such as graphitic carbon-nitride and applied them to the reforming of biomass [3].

In the present work, various photocatalysts based on graphitic carbon nitride (g-C_3N_4) were synthetized and applied to the photocatalytic reforming of benzyl alcohol (BA), in the absence of oxygen, into hydrogen and benzaldehyde (BAL). BAL is an organic compound, in which two of its major applications include cosmetics and safe food additives. The main targets of this study were the influence of a thermal treatment to g-C_3N_4 (T500) and the deposition of different metals on the surface of the material (Au, Pd, Pt, Ru).

The photocatalytic runs were carried out in a glass reactor, using a LEDs box emitting at 412-417 nm as the irradiation source. The solution of BA was 2 mM with a catalyst load of 1g.L^{-1} H_2 was quantified by gas chromatography (GC) analysis. BA conversion and BAL formation were followed by high pressure liquid chromatography (HPLC).

The graphitic carbon-nitride was prepared by thermal decomposition of dicyandiamide in a muffle. A post-thermal treatment was performed at 500ºC. All metals were deposited by incipient wetness impregnation, with a 1 wt.% of metal.

From the TEM images (not shown) it is visible that in the thermal treatment of the material, the average particle size decreases, leading to a higher activity. The photoluminescence spectra of the materials shows that the intensity of the emitted light is increased upon the thermal treatment, due to a higher surface area of the material and to the decrease of defects on the structure of the material.

On the other hand, the deposition of a metal on the surface of g-C_3N_4 also enhanced the photoactivity of the materials as a result of a synergistic interaction between the two constituent phases and a lower recombination of the charge carriers. Platinum performed better that the other metals for the production of hydrogen, while gold is more selective towards the production of BAL (Figure 1).

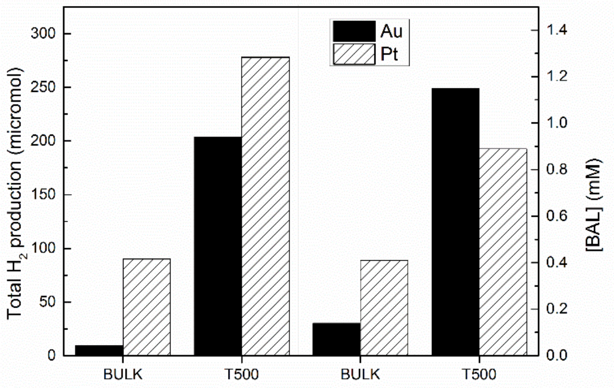

Figure 1. Total H_2 production and BAL concentration at a reaction time of 2h, for the best two metals, Au and Pt.

The conclusions to be taken from this study can be summarized as follows:

The thermal treatment to the material increased the production of BAL and hydrogen, which is due to a more pronounced separation of the layers of the material, resulting in a higher surface area.

The performance of the metals could be related to their dispersion over the carbon phase, these obtained results being explained by a lower particle size of gold over the T500.

Acknowledgements. This work was financially supported by Project POCI-01-0145-FEDER-006984 – Associate Laboratory LSRE-LCM funded by FEDER through COMPETE2020 - Programa Operacional Competitividade e Internacionalização (POCI) – and by national funds through FCT - Fundação para a Ciência e a Tecnologia. RAF acknowledges the PhD fellowship funded by Project NORTE-08-5369-FSE-000028, supported by Norte Portugal Regional Operational Programme (NORTE 2020), under the PORTUGAL 2020 Partnership Agreement, through the European Social Fund (ESF). MJL acknowledges FCT for the research grant PD/BD/52623/2014, while CGS acknowledges the FCT Investigator Programme (IF/00514/2014, respectively) with financing from the European Social Fund and the Human Potential Operational Programme.

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PLATINUM DOPED CARBON DOTS AND ITS HYBRIDIZATION WITH TiO_2 FOR ENHANCED VISIBLE LIGHT PHOTOCATALYTIC PERFORMANCE

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In order to address the challenge of pushing forward sustainable energy technologies to achieve low-cost solar fuels derived from abundant materials, it is essential to explore new types of materials to find those with desirable properties that meet these criteria. Due to the unique photoluminescence behavior, photo-induced electron transfer property, electron donor and acceptor role in hybridizing with other photoactive materials, carbon dots (CDs) are potentially considered to be an efficient component in the construction of high-performance photocatalysts, as well as a photosensitizer or a spectral converter along with other semiconductor materials in the photocatalytic processes. [1,2]

Here we report that nitrogen-doped carbon dots (NCDs) produced via hydrothermal carbonization can act as photocatalyst. Structural and optical characterizations such as TEM, XRD, XPS, FTIR and photoluminescence were conducted (Figure 1), which revealed that the NCDs show a mixture of crystalline and amorphous structure with a topological disorder, with N atoms exist on the surface as well as in the core structure. The heteroatom doping brings remarkable improvement to optoelectronic property. [3] Their photoactivity increases after hybridization with the well-known semiconductor material, TiO_2.

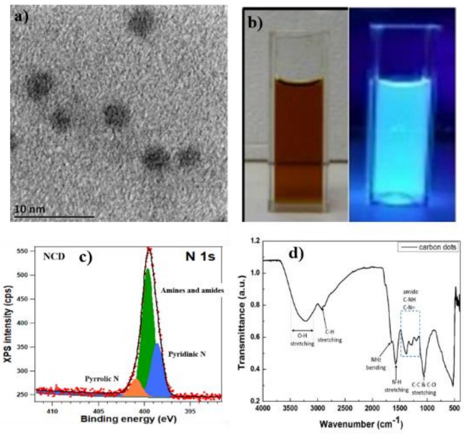

Figure 1 (a) TEM image of the NCDs; (b) photograph of NCDs in ethanol with 365 nm excitation; (c) XPS of N 1s spectra; (d) FTIR.

Techniques such as UV-Vis DRS, EIS, EPR, Mott-Schottky Plots, EPR and femtosecond TAS were employed to develop a fundamental understanding of the intimate relationships governing the interactions between CDs and TiO_2, and further improve the photocatalytic performance in terms of efficiency and selectivity.

The aim is to divulge how the excited states can affect the parameters that are critical for a photoelectrochemical reaction, such as carriers/radicals generation, recombination paths and carriers' lifetimes, Fermi levels, band gap values and type of conduction.

Furthermore, plasmonic metal is reduced onto the CDs surface to tune their optoelectronic properties, [4] and its hybridization with TiO_2 showed a significant improvement in photoelectrochemical performance compared to bare TiO_2 under visible light irradiation (Figure 2).

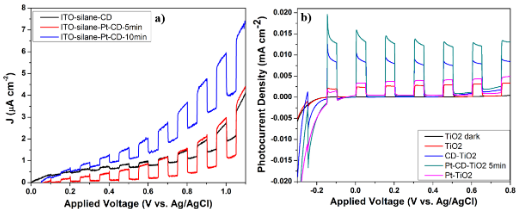

Figure 2 Photoelectrochemical performance of carbon dots, Pt-doped carbon dots (a) and carbon dots hybridized with TiO_2 (b).

Ultimately, the as prepared N-CDs, metal doped CDs and the CD-TiO2 system will be put into application for water splitting in the near future.

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PHOTOCATALYTIC OXIDATION OF PHENOL USING ZnO-DECORATED VERTICALLY ALIGNED CARBON NANOTUBES

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Vertically aligned carbon nanotubes (VACNTs) and N-doped VACNTs were prepared by thermal chemical vapor deposition (TCVD) process. The metal catalyst used was iron (Fe), which was deposited on the substrate by physical vapor deposition. The N-VACNTs were grown in a furnace reactor at 825 °C during 15 min. The precursor gases used in the growth of N-VACNTs were argon (Ar), hydrogen (H_2), acetylene (C_2H_2) and ammonia (NH_3), the latter being used as nitrogen source. Then, N-VACNTs were tested as catalysts in the photocatalytic oxidation of phenol. In order to improve the photocatalytic activity of the VACNTs, the latter were decorated with ZnO by atomic layer deposition (ALD), with 50 and 100 cycles.

The resulting nanomaterials were characterized by scanning and transmission electron microscopies (SEM and TEM) as well as Raman dispersion spectroscopy. The concentration of phenol during the photo-irradiation experiments was evaluated by high performance liquid chromatography (HPLC) analysis.

SEM images show densely packed, homogeneous in a large area on the substrate and well aligned CNT forests. The height of the N-doped VACNTs is approximately 22 µm. Figure 1 shows a line scan spectrum of nanocomposite with 50 cycles of ZnO by ALD and their image to the analyzed location. It is possible to observe the presence of C, Zn and N along the nanotubes. Figure 1 also present bright field TEM images of N-VACNTs with 100 cycles of ZnO. N-VACNTs composites decorated with 100 cycles of ZnO are almost totally decorated, unlike the nanocomposite with 50 cycles, which are partially decorated with the oxide semiconductor.

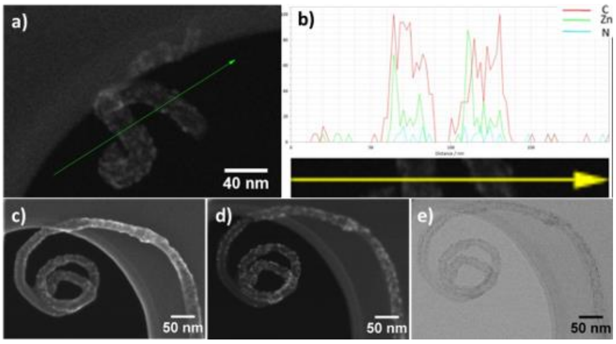

Figure 1. N-VACNTs/ZnO 50 cycles: a) TEM image indicating the analyzed location with an arrow in green; b) respective line scan spectrum; N-VACNTs/ZnO 100 cycles: c) bright field TEM images of secondary electrons (SE); d) atomic number contrast (ZC); e) transmission electrons (TE).

The undoped VACNTs did not present a clear relevant photocatalytic activity (Fig. 2). N-VACNTs degraded 25% of phenol at the end of 240 min of irradiation with a 392 nm LED, with catechol being found as the main reaction intermediate. The nanocomposites of N-VACNTs decorated with ZnO (100 cycles) led to a 38% of phenol degradation after 240 min of irradiation (Fig. 2). Again, catechol was the main intermediate.

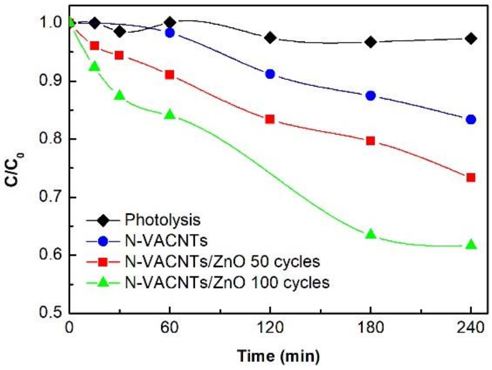

Figure 2. Evolution of the normalized concentration (C/C_0) of phenol during photolysis and photocatalytic reactions using N-VACNTs and N-VACNTs/ZnO nanocomposites under UV(392 nm)-LED irradiation.

After the photocatalytic tests, it was verified that there are some areas where the VACNTs forests collapse, which may be mostly attributed to the nanotubes hydrophobic character.

Tailoring these nanocomposites with higher degree of ZnO decoration is envisioned as a potential approach to improve their photocatalytic activity towards the degradation of phenolic compounds.

Acknowledgements.

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PHOTOCATALYTIC SYNTHESIS OF AROMATIC ALDEHYDES USING g-C$_3$N$_4$ UNDER UV-LED IRRADIATION

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Heterogeneous photocatalytic technology has been attracted worldwide researcher's attention, since reactions can be carried out at mild conditions of temperature and pressure, and using water as solvent. Currently, works reporting the use of semiconductor photocatalysis are mainly focused on the oxidation of organic pollutants, reduction of carbon, hydrogen production and selective oxidation of alcohols. Among, these applications, selective oxidation of alcohols to the corresponding aldehydes has become a hot-topic.

The traditional methods used in organic synthesis and fine chemical industry generally involve the use of strong oxidants or reductants and the presence of metal catalysts, which increase the process costs and lead to the production of toxic wastes. In this view, heterogeneous photocatalysis appear as a promising technology. Additionally, graphitic carbon nitride (g-C$_3$N$_4$) has been used in several photocatalytic applications. This material shows some advantages compared to conventional metal oxide semiconductors including narrow band gap energy (2.7 eV), easy and relative low-cost preparation, and thermal and chemical stability [1,2].

In this work, g-C$_3$N$_4$ was synthesized by thermal decomposition of dicyandiamide followed by a thermal post-treatment at 500 ºC, as described elsewhere [1]. The photocatalytic performance was evaluated on the selective oxidation of different aromatic alcohols, including anysil, benzyl, 4-methylbenzyl, vanillyl and piperonyl alcohols, into the corresponding aldehydes: anysaldehyde (AAD), benzaldehyde (BAD), tolualdehyde (TAD), vanillin (VAD) and piperonal (PAD). The initial concentration of the aqueous solutions of the aromatic alcohols was 1.5 mM and the catalyst load was fixed at 1 g L^{-1}. The suspensions were magnetically stirred and continuously saturated with air. Ultraviolet light emitting diodes (UV-LEDs) were used as radiation sources due to their high energy efficiency, high life expectancy, low cost and design flexibility.

In Figure 1 are shown the concentration profiles during the photocatalytic synthesis of the various aromatic aldehydes using g-C$_3$N$_4$.

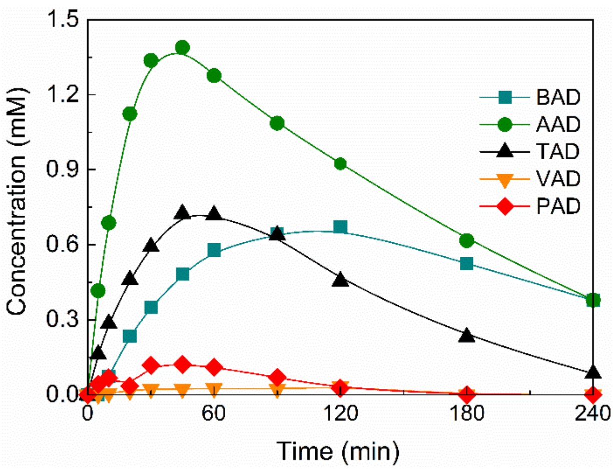

Figure 1. Concentration profiles of aromatic aldehydes during the photocatalytic reactions .

Results show good efficiency of the g-C$_3$N$_4$ material for the selective synthesis of AAD, TAD and BAD, being mostly inactive for the production of PAD and VAD.

Among all the aldehydes, the best results were obtained for the production of AAD, 100% selectivity (S) being achieved after merely 10 min of reaction, followed by BAD and TAD with S higher than 90% being reached after 90 min and 45 min of reaction, respectively (Fig. 2).

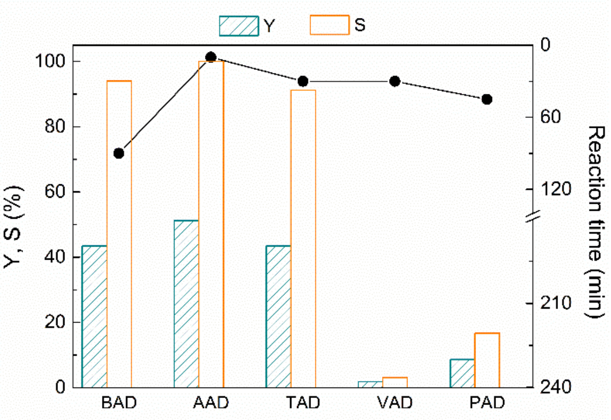

Figure 2. Maximum selectivity (S) and corresponding reaction time and yield (Y) obtained in the photocatalytic synthesis of the various aldehydes.

The different results can be rationalized in terms of the molecular structure of the different precursor molecules. Thus, the effect of the number of substituent groups, their electronic nature and position in the aromatic ring in the reactivity of the aromatic alcohols will be discussed.

Acknowledgements. This work is a result of project ''AIProcMat@N2020 – Advanced Industrial Processes and Materials for a Sustainable Northern Region of Portugal 2020" (NORTE-01-0145- FEDER-000006), supported by NORTE 2020, under the Portugal 2020 Partnership Agreement, through the European Regional Development Fund (ERDF) and of Project POCI-01-0145-FEDER-006984 – Associate Laboratory LSRE-LCM funded by ERDF through COMPETE2020 - Programa Operacional Competitividade e Internacionalização (POCI) – and by national funds through FCT - Fundação para a Ciência e a Tecnologia. C.G.S. acknowledge the FCT Investigator Programme (IF/00514/2014) with financing from the European Social Fund (ESF) and the Human Potential Operational Programme.

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PHOTOCATALYTIC SYNTHESIS OF BENZALDEHYDE DRIVEN BY MAGNETICALLY RECOVERABLE Fe_3O_4/g-C_3N_4 CATALYST

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Selective photocatalysis is an environmentally friendly alternative to conventional catalytic industrial processes since it uses light for catalyst activation and, therefore, diminishes the harsh industrial conditions of typical organic synthesis (homogeneous catalysts, organic solvents, severe conditions of temperature and pressure). Benzaldehyde (BAL) is the simplest aromatic aldehyde, but widely employed in industry as building block for several chemical processes, like in fragrances and pharmaceuticals production. Recently, our group reported the use of graphitic carbon nitride (g-C_3N_4) as highly-efficient metal-free photocatalyst for the synthesis of BAL from benzyl alcohol (BA) [1].

The g-C_3N_4 catalyst attracted much attention of the scientific community since it can be effectively activated by UV and visible light, keeping the advantage of its benign chemical composition (mostly composed by C and N, and a minor percentage of H) and easy chemical and physical modification [2].

Still, one of the major issues regarding the industrial application of heterogeneous catalysts is the difficulty of their recovery from the reaction medium. Immobilization of catalyst and the use of magnetic particles are alternatives to overcome those limitations [3, 4].

In the present work, thermally exfoliated g-C_3N_4 (CN_T) was magnetized by coupling of an optimized amount of Fe_3O_4 nanoparticles. The prepared materials were used for the selective photocatalytic conversion of BA into BAL in aqueous medium, natural pH, ambient temperature and pressure, and using light emitting diodes (UV-LEDs) as highly-efficient and low-cost radiation sources.

Different amounts of Fe_3O_4 (5, 10 and 20 *wt.*%) were loaded on the CN_T catalyst, the 20% Fe_3O_4/CNT catalyst being the only presenting magnetic response (Fig. 1).

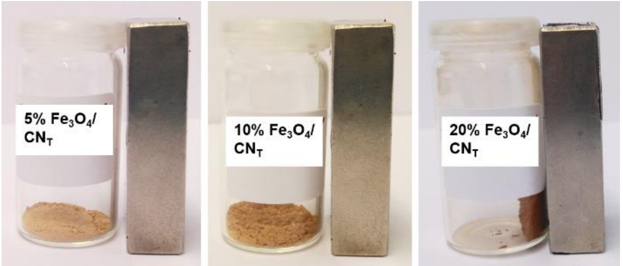

Figure 1. Magnetic response of Fe_3O_4/CN_T composites containing different amounts of Fe_3O_4.

The photocatalytic activity of 20% Fe_3O_4/CN_T magnetic catalyst was tested for comparison with the bare CN_T catalyst (Fig. 2). Reutilization runs were also performed to assess the stability of the magnetic material.

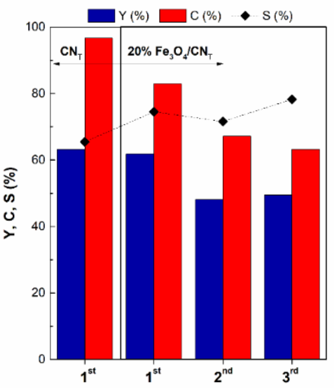

Figure 2. Conversion (C) of BA, yield (Y) and selectivity (S) to BAL using CN_T (1st use) and 20 % Fe_3O_4/CN_T catalyst (3 consecutive runs) after 240 min of irradiation.

Results revealed that fresh 20% Fe_3O_4/CN_T and CN_T catalysts performed similarly relative to BAL yield (c.a. 62%), the composite material presenting higher selectivity towards BAL production (75% contasting with 65% obtained with CN_T).

Reutilization runs using the magnetic catalyst showed a decrease of BAL yield from the 1st to the 2nd use (from 62 to 48%, respectively), which stabilized in the 3rd utilization.

In conclusion, we describe the use of 20% Fe_3O_4/CN_T catalyst capable to be applied and reused in the selective photocatalytic oxidation of BA to BAL. The prepared catalyst presents the advantage of easy magnetic separation with minor iron lixiviation to the reaction medium (maximum of 0.17 mg L^{-1}).

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FUNCTIONALIZATION OF TEXTILES WITH CARBON NANOSTRUCTURES FOR PHOTOCATALYTIC SELF-CLEANING APPLICATIONS

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The development of functionalized textiles with self-cleaning and antimicrobial properties has been drastically increasing in the recent years. New concepts have been investigated based on the incorporation of biocidal agents (including metals oxide particles, metal salts such as those of silver or copper, organic compounds, chitosan, among others that are available in the market) [1, 2], which are very useful for a wide variety of applications. However, there is still some controverse on the incorporation of these functional additives due to their side effects caused either by the contact with the human skin as well their spread into the environment.

Currently, the core research topic in textile industry is the development of eco-friendly, non-toxic, metal-free and antimicrobial and biocompatible materials. Carbon-based nanomaterials have been applied as innovative antimicrobial agents due to their unique physical and chemical properties, and therefore attracting wide attention in the heterogeneous photocatalysis field [3].

Graphitic carbon nitride (g-C_3N_4) has received wide interest among researchers in a variety of (photo)catalytic applications due to its narrow bandgap (2.7 eV), relative low-cost synthesis and non-toxicity. In addition, reports have been showing that coupling graphene oxide (GO) with g-C_3N_4 may improve the efficiency of the photocatalytic disinfection process [3].

In the present work, g-C_3N_4 was prepared by thermal decomposition of dicyandiamide, followed by a second thermal post-treatment. Then, few-layer g-C_3N_4 aqueous dispersions were obtained by ultrasonic exfoliation. GO was synthetized by oxidation of graphite through a modified Hummers' method. The hybrid GO/g-C_3N_4 material was prepared using the g-C_3N_4 aqueous dispersions and a certain amount of GO. The cotton textile (5 cm × 5 cm) was introduced into the dispersions containing g-C_3N_4 or GO/g-C_3N_4 materials for 3 h at 40 ºC, and finally dried.

The photocatalytic efficiency of the coated cotton fabrics was tested in a borosilicate glass petri dish filled with 50 mL of a 10 mg L^{-1} caffeine aqueous solution under LED irradiation (λ_{max} = 392 nm). A control experiment using uncoated cotton was also performed. Samples were withdrawn regularly and analyzed by high-performance liquid chromatography (HPLC).

The optical properties of the coated fabrics were investigated by photoluminescence (PL) analysis (Fig. 1).

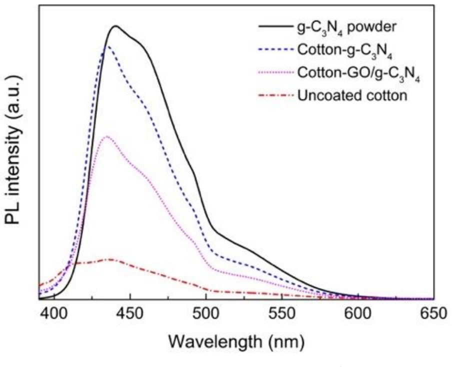

Figure 1. Photoluminescence (PL) spectra of uncoated cotton, g-C_3N_4 powder and cotton textile coated g-C_3N_4 based materials.

Results show a similar spectrum of the g-C_3N_4 coated cotton fabric compared with that of the g-C_3N_4 powder form, confirming the presence of the material on the cotton surface. Moreover, the incorporation of GO in the g-C_3N_4 leads to a quenching of the luminescence, which may indicate that GO inhibits the recombination of photoexcited electrons and holes. Preliminary results on the photocatalytic activity of the coated materials show that the introduction of GO leads to an increase in the efficiency of caffeine degradation in comparison to neat g-C_3N_4 (Fig. 2).

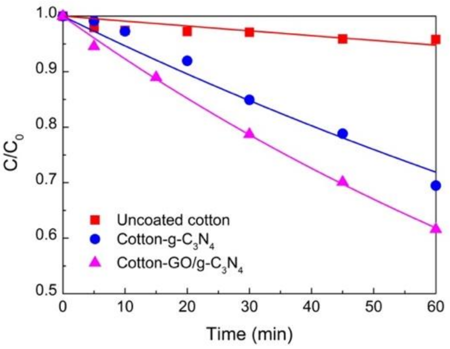

Figure 2. Normalized concentration of caffeine during the reactions using cotton textile uncoated and coated g-C_3N_4 based materials.

Ongoing work is being carried out to study the stability of the coating after several utilization cycles and efficient methods to attach the photocatalyst to the fabrics for further antimicrobial studies.

Acknowledgments: This work is a result of project ‘‘AIProcMat@N2020 – Advanced Industrial Processes and Materials for a Sustainable Northern Region of Portugal 2020” (NORTE-01-0145- FEDER-000006), supported by NORTE 2020, under the Portugal 2020 Partnership Agreement, through the European Regional Development Fund (ERDF) and of Project POCI-01-0145-FEDER-006984 – Associate Laboratory LSRE-LCM funded by ERDF through COMPETE2020 - Programa Operacional Competitividade e Internacionalização (POCI) – and by national funds through FCT - Fundação para a Ciência e a Tecnologia. C.G.S. acknowledges the FCT Investigator Programme (IF/00514/2014) with financing from the European Social Fund (ESF) and the Human Potential Operational Programme. M.P. gratefully acknowledges FCT for her scholarship SFRH/BD/102086/2014. We thank CeNTI (Portugal) for supplying the fabrics.

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SELECTIVE PHOTOCATALYTIC SYNTHESIS OF ANISALDEHYDE USING STRUCTURED g-C_3N_4 CATALYSTS

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Anisaldehyde is an aromatic aldehyde widely used in food, cosmetics and pharmaceuticals. Its industrial production requires harsh conditions of temperature and pressure and the use of organic solvents and metal-based catalysts to reach satisfactory yields. Heterogenous photocatalysis provides a greener alternative to conventional methods, by admitting the use of more eco-friendly conditions such as metal-free catalysts, water as solvent and moderate temperature and pressure [1].

Graphitic carbon nitride (g-C_3N_4) is a metal-free semiconductor that has been gaining relevance in photocatalysis, due to its easy and relative low-cost preparation and its ability to absorb visible light. However, it presents some limitations, as the low surface area and the fast recombination of electrons and holes [2].

In the present work, structured g-C_3N_4 catalysts were prepared and applied in the selective photocatalytic synthesis of anisaldehyde (AAD) through the oxidation of anisyl alcohol (AA), under room temperature and atmospheric pressure using UV-LEDs as light source. The structure of g-C_3N_4 was modified by incorporation of different silica templates during the preparation of the catalyst. The catalysts were denoted as UL-, MP- and 3D-g-C_3N_4 according to their morphology (urchin-like (UL), mesoporous (MP) and 3 dimensional (3D), respectively).

The efficiency of the catalysts was evaluated through the determination of conversion (*C*) of AA, and selectivity (*S*) and yield (*Y*) towards AAD production at 4 hours of irradiation (Fig. 1). The results obtained using bare and structured g-C_3N_4 catalysts were compared with those found with the benchmark photocatalyst, titanium dioxide (TiO_2).

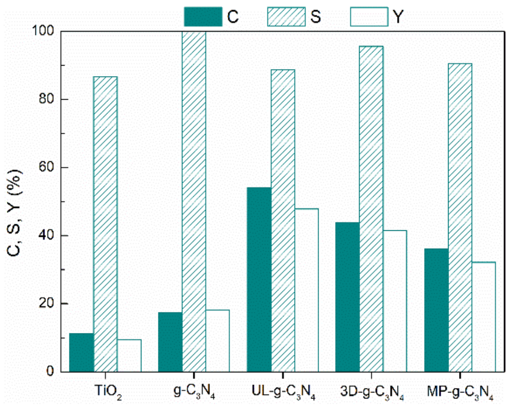

Figure 1. *C*, *S* and *Y* determined at 4 hours of irradiation for the photocatalytic synthesis of AAD, using TiO_2, g-C_3N_4, UL-, 3D- and MP-g-C_3N_4.

g-C_3N_4 proved to be more efficient than TiO_2, resulting in higher *S* and *Y*. Comparing with the bare g-C3N4, the structured material led to an increase in *Y* towards AAD production, while maintaining *S* above 90%. Among the structured materials, UL g-C_3N_4 presented the best performance, with 55% of *C*, 90% of *S* and 48% of *Y*. These results represent an increase in photocatalytic efficiency of about 28% and 38% in terms of *Y*, comparing with g-C_3N_4 and TiO_2, respectively.

The characterization of materials allowed to establish a relation between the materials photocatalytic performance and their morphology and electronic properties.

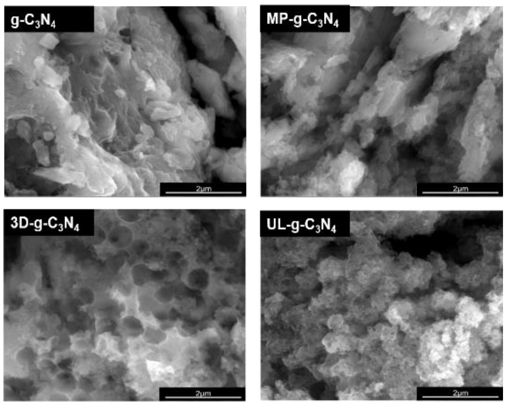

Figure 2. SEM images of g-C_3N_4, MP-, 3D- and UL-g-C_3N_4.

The introduction of silica templates induced different morphologies in g-C_3N_4 (Fig. 2). In general, materials presented a more intricate structure, whose defects may act as active sites for AA oxidation. Regarding electronic properties, it was verified a significantly decrease in the luminescence intensity of the modified materials comparing with bulk g-C_3N_4, which suggests a decrease in the electron/hole recombination, which may explain their photoefficiency enhancement.

Acknowledgements. This work is a result of project ‘‘AIProcMat@N2020 – Advanced Industrial Processes and Materials for a Sustainable Northern Region of Portugal 2020” (NORTE-01-0145- FEDER-000006), supported by NORTE 2020, under the Portugal 2020 Partnership Agreement, through the European Regional Development Fund (ERDF) and of Project POCI-01-0145-FEDER-006984 – Associate Laboratory LSRE-LCM funded by ERDF through COMPETE2020 - Programa Operacional Competitividade e Internacionalização (POCI) – and by national funds through FCT - Fundação para a Ciência e a Tecnologia. C.G.S. acknowledge the FCT Investigator Programme (IF/00514/2014) with financing from the European Social Fund (ESF) and the Human Potential Operational Programme. R.A.F. acknowledge the PhD fellowship funded by Project NORTE-08-5369-FSE-000028, supported by NORTE 2020, under the PORTUGAL 2020 Partnership Agreement, through the ESF.

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PHOTOCATALYTIC OZONATION IN THE PRESENCE OF MULTI-WALLED CARBON NANOTUBES

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Today's challenge is to treat efficiently water and wastewater, optimizing costs and energy. It is important to develop treatment strategies that are well-adjusted and will permit to treat water to the level required for its reuse or recycle. As individual treatments might present some limitations in the removal of certain pollutants, the combination of two or more advanced oxidation processes (AOPs) was also performed to overcome these drawbacks. Photocatalytic ozonation results from the combination of two different techniques and consequently the potential of pollutant abatement increases, since generation of hydroxyl radicals is promoted [1]. Analysing the papers published in the last years, most of studies reported the use of AEROXIDE© TiO_2 P25 (Evonik), the "gold standard" in photocatalysis [2], during photocatalytic ozonation. The present study describes our recently results obtained with multi-walled carbon nanotubes (MWCNT) as catalyst for photocatalytic ozonation. The carbon material was purchased from Nanocyl (ref. NC3100). Since carbon materials as an adsorbent media are able to remove a wide range of contaminants, adsorption on MWCNT was carried out in order to evaluate the contribution of this process during the treatment. With the aim of evaluating the effect of O_3 and radiation together, the non-catalytic run was also performed.

From the results presented in Figure 1 on the degradation of oxamic acid (OMA), a compound normally generated from the oxidation of pollutants containing nitrogen functional groups [3], is clear that adding MWCNT to O_3 and light is very advantageous; leading to nearly total OMA degradation after 120 min of reaction.

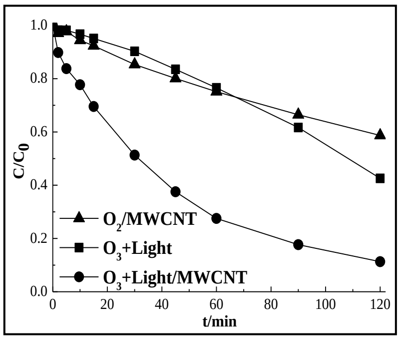

Figure 1. OMA removal by adsorption on MWCNT, photo-ozonation and photocatalytic ozonation in the presence of MWCNT ($C_{0,OMA}$ = 1mmol L^{-1}, $C_{cat.}$ = 0.5 g L^{-1}).

Adsorption on MWCNT led to an OMA removal of less than 40 % after 60 min of reaction. Is clear that interactions between O_3, light and MWCNT and the consequently improvement of highly oxidative species in aqueous media clearly contribute to the fast OMA degradation rate verified during photocatalytic ozonation.

Aniline (ANL), an aromatic amine used as raw material in many industrial processes, was totally degraded by the presence of only O_3 in a short reaction time due to the high reactivity of O_3 with this type of molecules [4]. However, the advantage of combining light and an appropriate catalyst is clear for the total organic carbon (TOC) removal. Figure 2 depicts the values of organic matter removal obtained after 60 min of reaction.

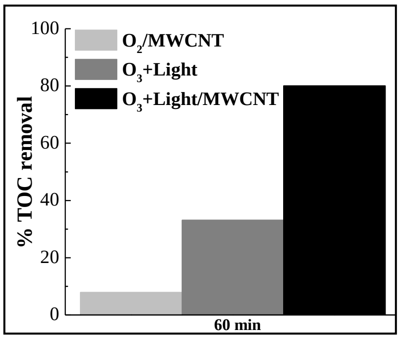

Figure 2. TOC removal during ANL degradation by adsorption on MWCNT, photo-ozonation and photocatalytic ozonation in the presence of MWCNT ($C_{0,ANL}$= 1mmol L^{-1}, $C_{cat.}$ = 0.5 g L^{-1}).

Photocatalytic ozonation in the presence of MWCNT allowed a mineralization degree of approximately 80 % after 60 min of reaction, in contrast with the non-catalytic run that only achieved 30 %. The TOC removal by adsorption on MWCNT is negligible in this case. Consequently, the process involves most likely a homogeneous (bulk) conversion, initiated by the heterogeneous formation of oxidative agents from reactions between O_3 and radiation on the MWCNT surface. Thus, in addition to ANL, considerable amounts of oxidation by-products were also degraded in the presence of MWCNT with O_3 and light. The concentration of final intermediates as oxalic acid (OXA) and OMA was analyzed during ANL degradation. In the case of photocatalytic ozonation in the presence of MWCNT, the concentration of OXA reached a maximum at 30 min and it disappeared from the solution at 60 min of reaction. The concentration of OMA increased reaching a maximum at 90 min, decreasing thereafter.

Acknowledgements

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CATALYTIC OXIDATION OF ORGANIC COUNPOUNDS OVER N-DOPED CARBON NANOTUBES: BATCH vs. CONTINUOUS PROCESS

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Catalytic wet oxidation (CWO) is a process applied to treat wastewaters contaminated with high amounts of recalcitrant and bio-toxic organic compounds. This process employs relatively high temperature and pressure, as well as a catalyst to form highly active radicals that will oxidize the organic compounds. Noble metals and, to a less extent, metal oxides are the most used catalysts for this reaction. However, the high cost of noble metals, as well as the typical deactivation observed due to the formation of carbonaceous deposits and/or leaching of the active phase, are limitations to the use of this type of catalysts [1]. The application of carbon materials as catalysts for CWO reactions can be an attractive alternative due to their lower cost, stability at typical reaction conditions and chemical and textural properties easily modifiable. Most studies of the CWO process over carbon materials are performed in batch mode; however, the reaction may proceed differently when performed in a batch or in a continuous reactor due to different phenomena, such as mass and heat transfer and liquid to solid ratio [2]. As such, the study of both reaction modes is important for the successful application of this technology.

In this work, commercial multi-walled carbon nanotubes (CNT-O) were milled without (CNT-BM) and with a nitrogen precursor (CNT-BM-M), in order to increase the surface area and incorporate nitrogen functionalities, respectively. These materials were tested in the CWO of oxalic acid and phenol in both batch and continuous mode. The influence of several reaction parameters (temperature, dissolved oxygen concentration and initial phenol concentration) was studied for the oxidation of phenol in both reaction modes over the most active catalyst. The deactivation and regeneration was also investigated.

Catalyst screening experiments were performed in batch mode for both contaminants. In both cases, the presence of nitrogen functional groups significantly improves the activity of the CNTs. For example, the N-doped catalyst (CNT-BM-M) presented over 90 % phenol removal after 1 h of reaction at 160 ºC, while the commercial CNT presented only 20 % removal in the same conditions.

Among all the reaction parameters tested, temperature was the most relevant, with 160 ºC being determined as the optimal temperature. Higher amount of dissolved oxygen slightly increased the phenol removal, while higher initial phenol concentrations improved the efficiency of the process, especially in terms of total organic carbon (TOC) removal.

A notorious deactivation of the N-doped catalyst was observed in the continuous oxidation of phenol. This was ascribed to the decrease of pyridine groups during the reaction, as well as the formation of carbonaceous deposits [3]. Significant regeneration of the catalyst was achieved by thermal treatment at 600 ºC under nitrogen atmosphere.

An experiment under intensified conditions (considerably higher phenol concentration) in continuous mode was also performed (Figure 1). Once again, the N-doped catalyst presented higher activity, 80 % phenol removal in the steady state at 160 ºC while the original catalyst only achieved 64 %.

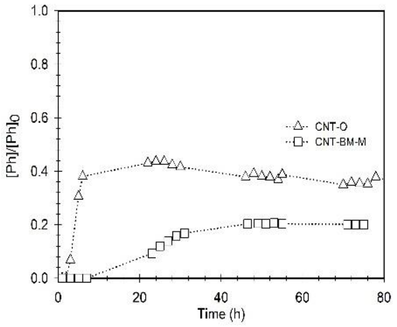

Figure 1. Normalized phenol concentration (Ph/Ph_0) in the intensified experiment.

It should be highlighted that complete phenol removal was observed with the N-doped catalyst in the first 7 h of reaction, and maleic acid was the only by-product identified (at low concentrations). Short regeneration cycles (ex. after every 7 h of reaction) can be applied to maximize the degradation of phenol.

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DESIGNING “NANOGOLD-ON-CARBON” CATALYSTS FOR GREEN PRODUCTION OF GLUCONATES AND GLYPHOSATE

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It is well known that gold particles with a size of several nanometers exhibit a very high catalytic activity and/or unusual selectivity in numerous redox reactions.[1] Different procedures have been developed for producing the catalysts containing Au nanoparticles on *oxide supports*, their catalytic properties being tested in detail.[2] For many potential applications of gold catalysts *carbons* would be preferable support materials because of low cost, excellent sorption properties, chemical inertness in different media *etc*. However, easy-to-use methods for synthesis of uniform-sized small Au particles on carbon materials are still lacking. Those techniques which commonly applied for depositing gold in a finely dispersed state onto oxides mainly yield coarse crystallites when carbon material is used as a support. It happens because anionic Au(III) complexes used as precursors are readily reduced by carbon to metallic gold which deposits on the external surface of the support granules. In order to avoid this undesirable phenomenon, carbon materials are impregnated with pre-reduced sols containing Au particles of the required size,[2] but it is not very suitable for practical application. Besides, residues of a reducing agent and a polymer stabilizer, which are used for sol preparation, may remain on the catalyst surface even after its thermal treatment and suppress the catalyst activity. The aim of our work was to develop a more practical technique based on the use of a cationic Au(III) complex as a precursor, which are hardly reducible by a carbon matrix but capable to ionic exchange reaction or electrostatic interaction with the surface functional groups. Herein, we present the results of applying this approach for preparation of the “gold-on-carbon” catalysts, as well as the data of their testing for the aqueous-phase aerobic oxidation of glucose (Glu) to gluconates, which are widely used biocompatible and biodegradable chemicals, and for oxidative dealkylation of N–isopropyl phosphonomethyl glycine (N-IPMG). The latter represents the final stage of the eco-friendly (“atom-efficient”) method for production of N-phosphono-methyl glycine (N-PMG or glyphosate) which is the most-used systemic herbicide in the world.

As the supports, we used mesoporous carbon-carbonaceous materials of the Sibunit (Sib) family with graphite-like structure and free of micropores (S_{BET} = 80 and 320 $m^2\ g^{-1}$) taken both as prepared and after oxidizing with 15% HNO_3 at 100°C in order to increase the content of the surface O-containing groups. The carbon granules were added with the solution of a Au(III) ammine complex, filtered after stirring with it for 8 h, washed with pure H_2O to remove the complexes that are not chemically anchored to the support surface, dried *in vacuo* and treated with flowing H_2 at 300°C. The samples taken before and/or after contact with H_2 were characterized by X-Ray Fluorescense, XRD, TEM, XPS and XAFS. It enabled us to prove the Au(III) precursor complexes are not reduced by carbon to metallic gold during the deposition step but are anchored onto the carbon surface, interacting with its phenolic and carboxyl groups to form molecular dispersed phase of ionic gold complexes. Subsequent treatment with H_2 leads to the formation of uniform-sized small particles of metallic gold mainly below 4 nm in diameter with an ”egg-shell” type of distribution through the grains of a carbon support and free of N-containing inclusions. The pre-oxidation of the carbon surface increases the share of gold extracted from a precursor solution (up to 100%) and the fraction of small Au particles (d_i = 1-3 nm) in the final material indicating their origin from the anchored ionic gold species.

Study of the Au/Sib catalysts in aerobic oxidation of Glu in the presence of NaOH/H_2O at 60°C and pH *ca.* 9 showed their outstanding catalytic performance that allows producing Na gluconate with 96-97% selectivity at ca. 95% conversion. At the high Glu:Au molar ratios the apparent reaction rate is affected by internal diffusion (the effectiveness factor of a catalyst grain is *ca.* 70%), while the interface gas–liquid–solid oxygen transfer influences the overall reaction kinetics as well. At a low Glu:Au molar ratio the reaction rate was limited by O_2 dissolution in the aqueous phase. In this mass transfer regime the rate of Glu oxidation over the Au/Sib catalysts exceeds the reaction rate over the Au/Al_2O_3 catalysts, which is attributed to a higher adhesion of the hydrophobic carbon support to the gas–liquid interface facilitating the oxygen mass transfer towards catalytic sites. Addition of palladium by impregnation of the Au/Sib composites with $Pd(NO_3)_2$ solution to atomic ratio of Pd:Au = 1:4 followed by calcination in air at 250°C and reduction with H_2 at the same temperature provides a further increase in the catalytic activity and selectivity due to formation of the alloyed Pd-Au nanoparticles and possibility of “concerted” reaction mechanism.

Finally, with the Au/Sib composites prepared as described above we found that the Au/Sib catalysts prepared as described above possess good catalytic activity and selectivity for aqueous-phase oxidative dealkylation of N-IPMG to glyphosate at 70 °C and atmospheric pressure with H_2O_2 as the oxidizing agent (93.1% selectivity at 98.1% conversion in 120 min after the beginning of the catalytic run) [3]. The catalyst efficiency for glyphosate production was highly dependent on the functional groups present on the carbon surface, nanogold deposited onto the pre-oxidized carbons providing the highest yield of glyphosate. Testing several other *N*-substituted glyphosates under the same conditions reveals that the nature of greatly influences both the substrate reactivity and selectivity for glyphosate increase with the electron-donating effect of the substituent at the N atom. The mechanism of N-IPMG dealkylation with H_2O_2 over the carbon-supported gold catalysts explaining this relationship and the reason for the promoting effect of acidic groups on the carbon surface will be presented, as well.

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CATALYTIC ACTIVITY OF CARBON BASED MATERIALS DEVELOPED FROM COMPOST DERIVED FROM MUNICIPAL SOLID WASTE

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In waste processing facilities equipped with mechanical biological treatment (MTB) systems, the municipal solid waste (MSW) is typically separated in organic residues, recyclable waste and rejects. The organic fraction is then treated by anaerobic digestion, obtaining biogas and a compost that can be used in agriculture. However, the current waste management legislation in Europe and the expected developments regarding the coming directives on the application of the "End-of-waste" criteria, are leading to barriers on the use of fertilizers resulting from waste [1]. Within this context, the current work proposes an alternative strategy to the valorisation of compost, through the production of high-added value materials to be used in catalytic processes. To this aim, a compost obtained from a MTB plant for MSW was considered in the formulation of carbonaceous materials prepared from glycerol, a low-cost by-product obtained in biodiesel production [2]. The composition of the compost used is summarized in Table 1. As can be observed, the content in organic matter is roughly 50%.

Table 1. Indicative composition of compost

Species	Mass composition
Moisture	29.6%
Organic matter	48.8%
Alkaline	7.1%
Iron	*ca.* 1%

In a first step, the compost was mixed with water (1 litter of water per 100 g of compost) and washed at room temperature, in order to homogenize the material and remove suspended solids. Then, carbon materials were prepared by partial carbonization of a mixture of carbon precursors (glycerol and compost), adapting the experimental procedure described elsewhere [2]. Mixtures of glycerol (99 wt.%) and compost (3:1, 1:1, 1:3) were contacted with H_2SO_4 (96-98 wt.%) in the ratio 80 g per 20 g of carbon precursors, at 180 ºC for 20 min. The resulting materials were calcined under nitrogen flow (100 $cm^3\ min^{-1}$) at 120, 400 and 600 ºC during 60 min at each temperature, and then at 800 ºC for 240 min, obtaining the G3C1, G1C1 and G1C3 samples according with the glycerol:compost mass ratio considered. In addition, another sample was prepared using only compost as precursor, following the same procedure, resulting in the C1 sample. The synthesized materials were assessed as catalysts in the decomposition of H_2O_2 (17.8 g/L) at room temperature by using a catalyst load of 2.5 g/L in aqueous phase (initial pH = 3).

The burn-off of the samples was found to be in the range 70.2-76.3% (measured as weight loss from the sum of compost and glycerol masses). The conversion of H_2O_2 obtained in the H_2O_2 decomposition experiments, using the carbon-based materials as catalysts, are depicted in Figure 1.

As can be observed, the materials prepared are catalytically active for H_2O_2 decomposition. When compared to the non-catalytic run, a visible increase in the conversion of H_2O_2 is seen. In addition, this conversion is increased when using simultaneously compost and glycerol precursors in the synthesis of the materials, when compared to the synthesis with only compost (Figure 1) or only glycerol [2], as precursors.

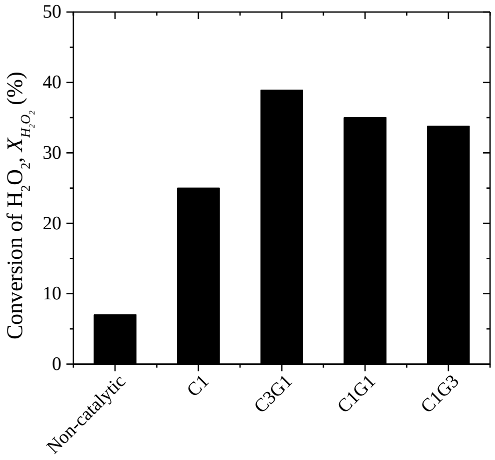

Figure 1. Hydrogen peroxide conversions at 24 h under the following conditions: room temperature, pH_0 = 3, $[H_2O_2]_0$ = 17.8 g/L and [catalyst] = 2.5 g/L.

Acknowledgements. This work is a result of projects: VALORCOMP, funded by FEDER through Programme INTERREG V A Spain - Portugal (POCTEP) 2014–2020; "AIProcMat@N2020 - Advanced Industrial Processes and Materials for a Sustainable Northern Region of Portugal 2020", with the reference NORTE-01-0145-FEDER-000006, supported by NORTE 2020, under the Portugal 2020 Partnership Agreement, through FEDER; and POCI-01-0145-FEDER-006984 – Associate Laboratory LSRE-LCM funded by FEDER through COMPETE2020 - POCI – and by national funds through FCT.

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CATALYTIC WET PEROXIDE OXIDATION WITH MODIFIED CARBON NANOTUBES

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Catalytic wet peroxide oxidation (CWPO) uses H_2O_2 as a source of hydroxyl radicals ($HO^\bullet$) for the oxidation of organic species. This process is regarded as a potential solution for the treatment of aqueous effluents containing recalcitrant and toxic organic pollutants, difficult to remove by conventional biological processes, mainly if present at high concentrations (1-10 g L^{-1}) [1]. In a recent study, three magnetic carbon nanotube (CNT) samples, named A30 (N-doped), E30 (undoped) and E10A20 (partially N-doped), were synthesized by chemical vapor deposition and tested in the CWPO process [2]. It was revealed that N-doped hydrophilic surfaces promoted a fast decomposition of H_2O_2 into non-reactive species (H_2O and O_2), limiting the CWPO performance.

In the present study, the surface of the CNTs was modified by introducing oxygenated surface groups (oxidation with HNO_3, samples CNT-N), and by heat treatment at 800 °C for the removal of surface functionalities (samples CNT-HT). The effect of these modifications was analysed during 24-hours-CWPO-experiments of highly concentrated 4-nitrophenol solutions (4-NP, 5 g L^{-1}), at atmospheric pressure and 50 °C, adjusting the initial pH to 3, using a catalyst load of 2.5 g L^{-1} and the stoichiometric amount of H_2O_2 needed for the complete mineralization of 4-NP. Given the magnetic properties of the Fe nanoparticles encapsulated inside the CNTs (formed during the CVD synthesis), catalyst separation after the catalytic reaction was easily achieved using a magnet.

The catalysts were characterized by elemental analysis, N_2 adsorption-desorption at –196 °C, transmission electron microscopy, X-ray photoelectron spectroscopy (XPS), temperature programmed desorption (TPD), pH of the point of zero charge (pH_{PZC}) and water contact angle.

Both treatments led to higher apparent surface areas, which could be related to CNT endcaps opening during the treatments, and a thinning effect of the nanotube walls, especially visible in the CNT-N samples. The oxidation was more effective on the N-doped surfaces, finding double the amount of oxygen by XPS in A30N than in E30N. Increasing concentrations of released CO and CO_2 were detected during TPDs as well. Both, XPS and TPD results, showed that heat treatment leads to neutral or basic surfaces, with pH_{PZC} values around 8, while oxidation treatment results in materials with a more acidic surface ($pH_{PZC} \approx 2$). The incorporation of O- and N-containing functionalities onto the CNTs after oxidation modified their hydrophilic properties, finding that the CNT-HT samples were less hydrophilic than the CNT-N ones (Figure 1).

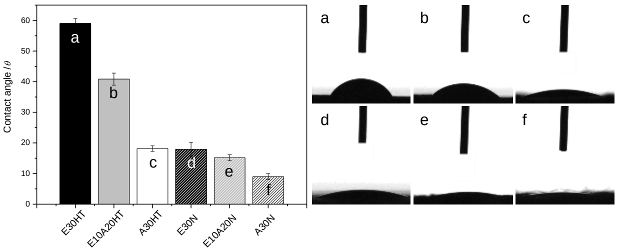

Figure 1. Contact angle measurements.

The high temperature treatment favoured the interaction between the 4-NP molecules and the CNT surface, enhancing significantly the activity of the CNTs towards CWPO, evaluated in terms of 4-NP and total organic carbon (TOC) conversion (Table 1). Among the CNT-HT samples, the more hydrophobic materials (E30HT and E10A20HT) promoted a controllable H_2O_2 decomposition into $HO^\bullet$ radicals, being able to remove *ca.* 100% of 4-NP after 8 h of operation. On the contrary, the hydrophilic A30HT promoted the fast H_2O_2 decomposition into non-reactive species, resulting in a poor pollutant removal. On the other hand, the treatment of the CNTs with HNO_3 produced hydrophilic samples with opened ends, in which the decomposition of H_2O_2 was fast, hindering the CWPO due radical’s recombination. Nevertheless, the reactivity generated inside the opened nanotubes favoured the reaction between the $HO^\bullet$ radicals and the 4-NP molecules in the internal cylindrical tubes (confinement effect), allowing the reaction to occur before they disappear by scavenging effects. The highly efficient decomposition of H_2O_2 into $HO^\bullet$ with E30HT results in a TOC conversion of *ca.* 60%, with ~3 mgC L^{-1} of aromatic byproducts and 1 gC L^{-1} of organic acids being detected after 24 h. The concentrations of the aromatic byproducts identified during the CWPO with E30HT follow the sequence: 4-nitrocatechol > hydroquinone > 1,4-benzoquinone > catechol. These intermediates almost disappear after 24 h, increasing the concentration of low-molecular-weight carboxylic acids (mainly malonic and malic acids).

Table 1. Removal of 4-NP by adsorption (Ads) and CWPO ($X_{4\text{-}NP}$); TOC removal, H_2O_2 decomposition and consumption efficiency (η).

	Ads. (%)	$X_{4\text{-}NP}$ (%)	$X_{H_2O_2}$ (%)	X_{TOC} (%)	$\eta_{H_2O_2}$
E30HT	8	100	59	59	100
E10A20HT	7	99	99	48	48
A30HT	4	35	99	22	22
E30N	14	99	90	54	60
E10A20N	7	60	42	43	31
A30N	8	48	100	2	2

Acknowledgements. This work was financially supported by Projects NORTE-01-0145-FEDER-000006 (NORTE 2020, ERDF) and POCI-01-0145-FEDER-006984–Associate Laboratory LSRE-LCM (COMPETE2020, ERDF). M. Martín Martínez and B.F. Machado acknowledge the FCT Postdoc grant SFRH/BPD/108510/2015 and the FCT Investigator 2015 Programme IF/00301/2015, respectively.

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KINETIC MODELLING OF WET PEROXIDE OXIDATION WITH N-DOPED CARBON NANOTUBES

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Carbon nanotubes (CNT) were tested as catalysts in the removal of 2-nitrophenol (2-NP) by catalytic wet peroxide oxidation (CWPO). The CNT materials were synthesized by catalytic chemical vapour deposition in a fluidized-bed reactor, as described elsewhere [1,2]. In order to synthesize a CNT with different characteristics, ethylene and acetylene were feeding as follows: 1) ethylene for 30 min (resulting in catalyst E30); 2) acetonitrile for 20 min, followed by ethylene for 20 min (A20E20); 3) acetonitrile for 20 min, followed by ethylene for 10 min (A20E10); 4) ethylene for 10 min, followed by acetonitrile for 20 min (E10A20); or 5) acetonitrile alone for 30 min (A30). These CNT were tested in CWPO adopting the experimental procedures reported in our previous studies [2-3] and at the following operating conditions: 50 ºC, $pH_0 = 3.0$, 0.25 g L^{-1} of catalyst, 0.5 g L^{-1} 2-NP and 1.78 g L^{-1} of added hydrogen peroxide (H_2O_2). Power-law kinetic equations were fitted to experimental data, following a similar statistical regression described elsewhere [4]. Results are depicted in Figure 1.

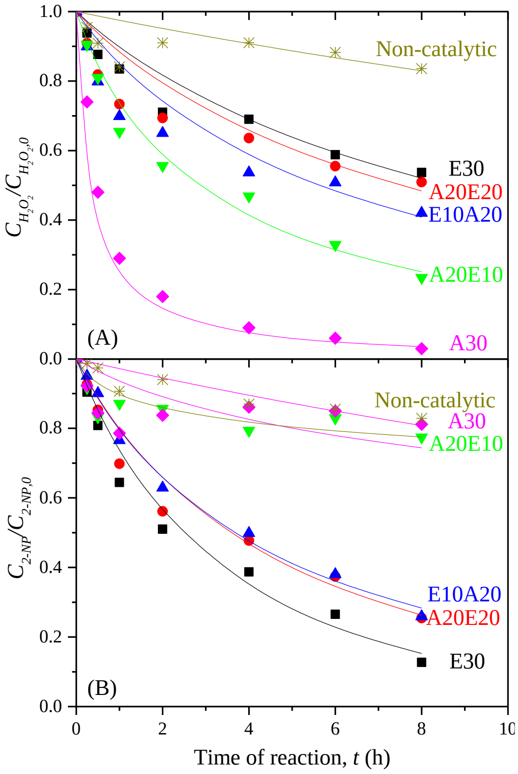

Figure 1. Experimental (symbols) and predicted (curves) evolution of (A) hydrogen peroxide and (B) 2-nitrophenol removals.

As can be observed, E30 was the most active catalyst for the degradation of 2-NP in CWPO. In addition, the H_2O_2 conversion obtained with this catalyst was the lowest, revealing a high efficiency in the H_2O_2 consumption (determined as converted 2-NP moles per consumed H_2O_2 moles). The power-law kinetic model predicts reasonably well the experimental data for all CNT samples. The equations of the model and the value of kinetic coefficients for each material are shown in Figure 2.

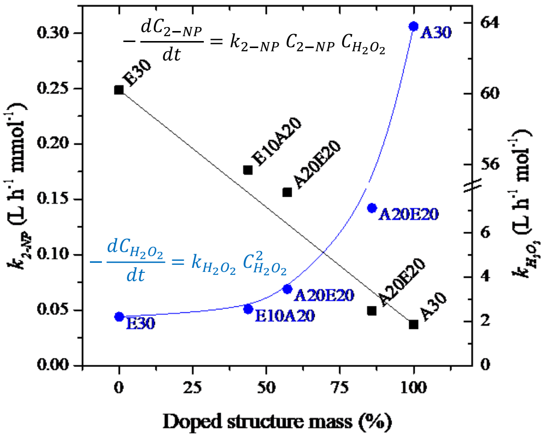

Figure 2. Kinetic constants as a function of the doped structure mass percentage in CNT catalysts.

As can be seen, coefficients were found to be related to the percentage of the doped structure in the CNT catalysts (determined by thermogravimetric analysis).

Acknowledgements. Project "AIProcMat@N2020 - Advanced Industrial Processes and Materials for a Sustainable Northern Region of Portugal 2020", reference NORTE-01-0145-FEDER-000006, supported by NORTE 2020, under the Portugal 2020 Partnership Agreement, through FEDER, and of Project POCI-01-0145-FEDER-006984 – Associate Laboratory LSRE-LCM funded by FEDER through COMPETE2020 - POCI – and by national funds through FCT. B.F. Machado (IF/00301/2015) acknowledges the FCT Investigator Programme, with financing from the European Social Fund and the Human Potential Operational Programme.

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CARBON-COATED METALLIC MAGNETIC NANOPARTICLES FOR THE REMOVAL OF BROMATE IN WATER

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Over the last years, there has been a growing interest in studying superparamagnetic nanoparticles (SMNPs). Magnetic metal nanoparticles (MNPs) can be coated with a layer of different materials to improve their stability and to introduce new surface properties and functionalities. Carbon materials are widely used as catalyst supports, but their use as a catalyst is attracting a great deal of attention [1].

Bromate in water has been associated with a significant risk of cancer, becoming one of the pollutants frequently detected in drinking water and wastewater, especially in processes involving ozonation. Catalytic reduction has been recognized as an effective treatment technique to remove ions by reducing them on metal catalysts (usually noble metals) in the presence of a reducing agent, usually hydrogen [2]. Therefore, the aim of this study is the synthesis and characterization of metallic magnetic nanoparticles coated with carbon (C-MNP) to be applied as catalyst in the removal of bromate in water. The use of magnetic nanoparticles coated with carbon will enable the catalyst recovery by magnetic separation and also taking advantage of the catalytic properties of the carbon materials.

In this work, the metallic (Fe, Co or Mn) MNP were based on FeO cores coated with carbon by chemical vapor deposition process (CVD) using ethane as carbon source. The catalytic reduction of bromate in water (10 mg L^{-1}) was carried out in a semi-batch reactor in the presence of hydrogen at ambient temperature and atmospheric pressure.

The carbon content of the materials was determined from the TG weight loss (Table 1). The presence of carbon was observed in all the materials prepared by CVD. It was also observed that the deposition of carbon decreases the surface area of the starting material. In addition, the characteristic reduction peaks of Fe_2O_3 observed in the TPR profiles, between 300 and 400 ºC due to its reduction to Fe_3O_4 and between 400 and 700 ºC related to the sequential reduction of Fe_3O_4 to FeO and Fe^e [3], were not observed in the materials prepared by CVD.

Table 1. Carbon and metal content of the C-MNP materials.

Sample	% Carbon	% Metal
FeO	-	98
CFeO@CVD 750	16	84
MnFeO	-	98
CMnFeO@CVD750	22	78
CoFeO	-	96
CCoFeO@CVD750	34	66
CuFeO	-	99
CuFeO@CVD750	57	43

The results show that the MNPs exhibit catalytic activity for the reduction of bromate in water, although they do not present any noble metal in their constitution. Higher bromate removals were observed in the presence of carbon-coated MNP (Figure 1).

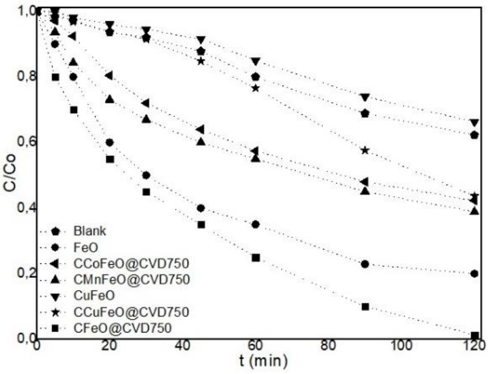

Figure 1. Reduction of the bromate after 2 h of reaction under hydrogen in the presence of the MNP.

The highest removal was obtained with the CFeO@CVD750 sample, resulting in a 99 % conversion at 2 h of reaction. The iron particles proved to be the most promising catalysts for the conversion of bromate to bromide. Due to their magnetic character, at the end of the first cycle, the materials were removed and applied in another 3 cycles without losing their catalytic properties.

Acknowledgements. This work is a result of project "AIProcMat@N2020 - Advanced Industrial Processes and Materials for a Sustainable Northern Region of Portugal 2020", with the reference NORTE-01-0145-FEDER-000006, supported by Norte Portugal Regional Operational Programme (NORTE 2020), under the Portugal 2020 Partnership Agreement, through the European Regional Development Fund (ERDF) and of Project POCI-01-0145-FEDER-006984 – Associate Laboratory LSRE-LCM funded by ERDF through COMPETE2020 - Program Operacional Competitividade e Internationalizes (POCI) – and by national funds through FCT - Fundação para a Ciência e a Tecnologia.

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METAL-FREE CATALYTIC WET AIR OXIDATION USING DOPED CARBON NANOTUBES PREPARED BY A DRY-BALL MILLING APPROACH

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The increasing role assumed by carbon materials as catalysts or catalyst supports in the fields of renewable energy and environmental technologies is attracting a great deal of attention in the scientific community. The ability to tune their physicochemical properties by suitable thermal or chemical post-treatments provides a major asset for these applications [1].

The surface of carbon materials can be modified by doping with heteroatoms such as oxygen, nitrogen, sulfur, boron or phosphorus, extending the application of carbon nanomaterials to a wide range of processes [2]. Ball milling is a promising method for modifying CNTs, by adjusting tube lengths, opening closed end caps or doping with heteroatoms.

In the present work, we extend a recently developed solvent-free post-doping methodology involving a mechanical treatment under ball-milling followed by a thermal treatment under inert atmosphere (N_2) [3] to the incorporation of B, N, P or S onto CNT surfaces, using different precursors: melamine (M), urea (U), thiourea (TU), sodium thiosulfate (TS), sodium sulphite (S), sodium dihydrogen phosphate (P) and boric acid (B).

N_2 adsorption was used to assess the changes in the textural properties induced by the applied treatments, while the nature and amounts of the surface groups incorporated on the CNT structures were determined by suitable methods, such as X-ray photoelectron spectroscopy (XPS), temperature programmed desorption (TPD), elemental analysis and thermogravimetry.

Table 1 highlights the extent of functionalization achieved using each precursor, with respect to the heteroatom in study, and the changes on the accessible surface area (S_{BET}) of the resulting doped carbon samples.

Table 1. Textural properties and heteroatom doping degree of CNT samples prepared by ball milling with different precursors.

Sample	S_{BET}	N	S	P	B
	(m^2 g^{-1})	(% wt.)^{XPS}			
CNT-O	291	-	-	-	-
CNT-BM	391	-	-	-	-
CNT-M	355	4.8	-	-	-
CNT-U	353	0.8	-	-	-
CNT-TU	350	1.0	0.6	-	-
CNT-TS	172	-	5.0	-	-
CNT-S	38		7.0		
CNT-P	93	-	-	5.4	-
CNT-B	45	-	-	-	18.7

The performance of these metal-free heteroatom-doped CNT catalysts was evaluated in the oxidation of organic compounds by Catalytic Wet Air Oxidation (CWAO), as an alternative to the noble metal and metal oxide catalysts traditionally used in this process. This technology is used in the treatment of contaminated wastewater with high organic loads, operating at high pressures (20-200 bar) and temperatures (200-300 °C) in the absence of a catalyst. However, the introduction of a homogeneous or heterogeneous catalyst can increase the efficiency of the process under less severe conditions (130-250 °C, 5-50 bar) [4].

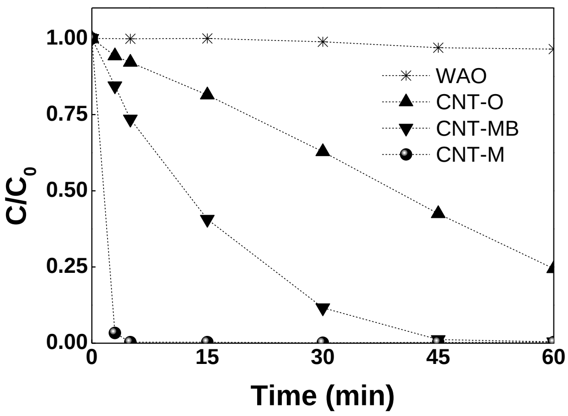

Figure 1. Dimensionless concentration of oxalic acid during CWAO.

Figure 1 illustrates the catalytic results of oxalic acid oxidation by CWAO obtained using selected samples: pristine carbon nanotubes (CNT-O), ball-milled carbon nanotubes (CNT-BM) and carbon nanotubes functionalized with melamine during ball-milling (CNT-BM-M). Enhanced catalytic activity was observed in the presence of N-functionalities, which seems to result from the interaction of oxygen with the carbon surface.

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TAILORED CARBON MATERIALS FOR *p*-NITROPHENOL REMOVAL FROM WASTEWATERS VIA ADSORPTION AND ADVANCED OXIDATION PROCESSES

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P-nitrofenol (PNP) is commonly present in several industrial wastewaters such as manufacturing of drugs, dyes, fungicides and explosives [1]. PNP has been listed as a priority pollutant by the U.S. EPA due to its toxicity [2]. In order to minimize its effects on public health and in the environment, it is crucial to reduce its concentration (or eliminate it) from effluents before their discharge into water bodies. Biological degradation is not suitable for PNP, because is inefficient or presents slow degradation rates [2,3]; so, the use of adsorption and/or advanced oxidation processes (AOPs) are good alternatives.

In this work, PNP and total organic carbon (TOC) removals were evaluated by adsorption and catalytic wet peroxidation (CWPO) using activated carbon (AC), carbon nanotubes (CNT) and carbon xerogels (XG) with or without nitrogen functionalities, and by the heterogeneous Fenton process with iron supported carbon-based catalysts (obtained by the incipient wetness impregnation method with 2 wt.% of iron). The supports/catalysts were characterized by several techniques: N_2 adsorption at -196 ºC, elemental analysis (EA) and pH at the point of zero charge (pH_{PZC}).

The efficiency of all processes was influenced by the textural properties of the materials. It was verified that the carbon material with the highest BET surface area (AC) provided the maximum PNP removal by adsorption; on the other hand, the support (XG) and catalyst (Fe/XG) with the highest mesoporisity led to the highest performance of CWPO and Fenton, respectively.

The chemical properties also play an important role in the performance of all processes, given that the degradation of PNP and TOC reduction increased in the presence of N-doped materials. In addition, it was also observed that the performance of the processes is enhanced in the presence of carbon materials with higher nitrogen content. The highest PNP (80.5 %) and TOC (64.4 %) removals were achieved in the Fenton process using carbon xerogel doped with melamine and impregnated with iron (Fe/XGM) as catalyst (see Figure 1).

For the Fenton process the catalysts were stable, there was no iron leaching and the PNP and TOC removals were constant during three consecutive cycles. In contrast, the deactivation of carbon materials by hydrogen peroxide was observed, considering that PNP and TOC removals decrease along the reutilization cycles.

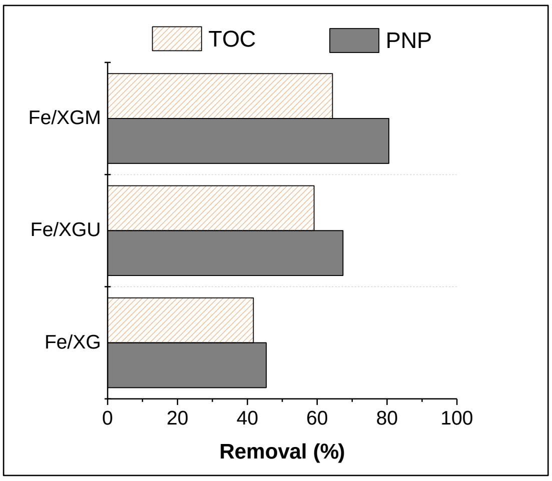

Figure 1. PNP and TOC removals after 2 h of Fenton reaction with N-doped xerogels: U - urea and M – melamine (pH= 3.0, T= 30 ºC, [catalyst] = 0.25 g L^{-1}, [H_2O_2] = 1.0 g L^{-1}, [PNP] = 500 mg L^{-1}).

This work allows to conclude that the chemical and textural properties of the carbon materials have an important role during PNP removal. High mesoporosity combined with high surface area and nitrogen functionalities improve their catalytic performance. Therefore, the Fenton reaction can be enhanced by tailoring the carbon materials.

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STUDIES OF HYDROGEN PEROXIDE FOR THERANOSTIC MEDICINE

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Nanomedicine formulations aim to improve the distribution and accumulation of substances used during therapeutic treatments, such as chemotherapy, and is also being employed in imaging applications. Additionally, during the last decade, advances in areas such as biology, chemistry, nanotechnology, pharmacy, medicine and imaging, allowed the development of different systems in order to combine disease diagnosis and therapy, known as theranostics. It is expected that these theranostics can be addressed for several goals as they contain both an imaging agent and a drug within a single formulation [1].

Stimuli-responsive theranostic nanomedicine, as hydrogen peroxide (H_2O_2)-responsive modality, is able to reach specific and high-performance diagnosis and therapy of various diseases. Interest on H_2O_2-responsive theranostic nanomedicine is emerging because several kinds of human diseases are related to H_2O_2, as it is the most stable and abundant reactive oxygen species (ROS) in human body [2]. In fact, conversion of H_2O_2 leads to hydroxyl radical (OH·), which is more toxic than the other ROS and has a short half-time of only 10^{-9} s. However, H_2O_2 is also produced in vivo through catalysis. Thus, H_2O_2 is a key factor in balancing the free radicals in physiological conditions [3]. As a result, important physiological and biological information for diagnosis of diseases can be provided by ROS detection, especially H_2O_2 [4].

Generation of oxygen by catalysing H_2O_2 with catalase is viewed as a reliable method for tumour hypoxia modulation and for photodynamic therapy (PDT) and chemo/radiotherapy (CRT) efficiency improvements [4-6] The tumour hypoxia [7] (the imbalance between the intake oxygen and the consumption of oxygen) is one of the specific features of solid tumours, which is induced by the rapid proliferation of cancer cells and the abnormal angiogenesis. However, the therapeutic efficiency of PDT/CRT would be significantly lowered due to the inadequate oxygen supply in hypoxic solid tumours. As a result, using catalase or catalase-mimic metallic oxide supported on carbon black (e.g., MnO_2, Mn_2O_3 and CeO_2) to catalyse H_2O_2 and generate oxygen can be developed to improve the therapeutic efficiency/outcome of PDT/CRT [6].

Thus, it is clear that H_2O_2 is an extremely important compound in many diseases, namely lung inflammation, cystic fibrosis, Parkinson’s disease, atherosclerosis, diabetes, tumours, Alzheimer’s disease, etc. Therefore, appropriate knowledge of H_2O_2, its related species, its oxidation and reduction behaviour, its attenuating and enhancing effects, among others, require a sound knowledge of its chemical and biochemical behaviour, particularly in the domain of its reduction on MnO_2, Mn_2O_3, and carbon-based electrodes [8-11]. These studies gave us basic knowledge to extend this experience to the domain of H_2O_2 in theranostic medicine. In this context, we are studying the electrochemical behaviour of H_2O_2 in blood, plasma, serum, urine and other biological fluids using cyclic voltammetry, chronoamperometry, chronopotentiometry, rotating disc and rotating ring-disc electrode measurements, complemented by physicochemical techniques, in order to properly detect H_2O_2, its redox behaviour and decomposition, among other key information. In this work, we discuss the recent developments of H_2O_2-responsive theranostic nanoplatforms for versatile biomedical applications [12]. In particular, attention is given to the mechanisms of oxidation and anti-oxidation of Pt, bimetallic alloys, MnO_2 and CeO_2 nanoparticles with H_2O_2, in mild microenvironments at 25 ºC. This is a novel study of catalysts and H_2O_2 interactions in nanomedicine.

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