



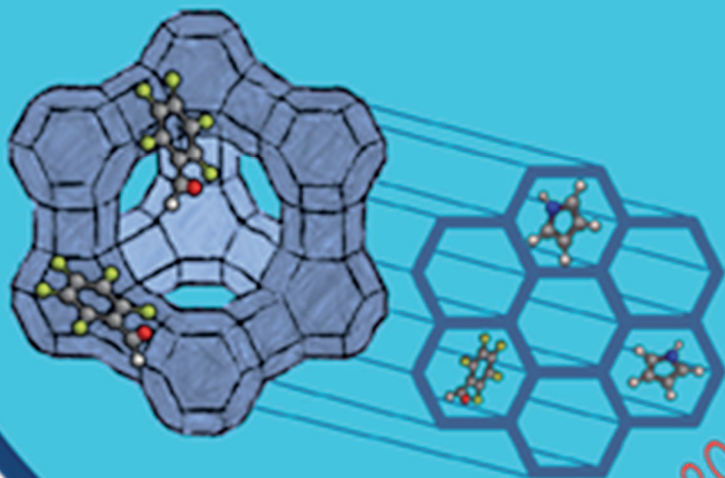
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SOCIEDADE PORTUGUESA DE QUÍMICA

10^o ENCMP

Encontro Nacional de Catálise
e Materiais Porosos



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Boas Vindas ao X ENCMP - 2016

A Comissão Organizadora dá as boas vindas e agradece a todos os que participam no 10º Encontro Nacional de Catálise e Materiais Porosos (10º ENCMP).

Este Encontro foi organizado conjuntamente pelo Instituto Superior Técnico e pela Divisão de Catálise e Materiais Porosos (DCMP) da Sociedade Portuguesa de Química (SPQ).

Estamos mais uma vez reunidos para mostrar alguns dos trabalhos que a comunidade portuguesa de catálise e materiais porosos tem vindo a realizar desde 2013, quando ocorreu no Porto o último ENCMP. Foram submetidos setenta e sete resumos, diversificados pelas áreas da catálise heterogénea, homogénea, fotocátalise; síntese, preparação e fabrico de novos materiais porosos; métodos de caracterização de materiais catalíticos e porosos; materiais porosos para energia e ambiente e aplicações medicinais e farmacológicas. Destes trabalhos, vinte serão apresentados oralmente e os restantes em duas sessões de posters que terão lugar no Museu Décio Thadeu (Pavilhão de Minas), integrado nos Museus de Geociências do IST. Durante este Encontro serão ainda apresentadas duas lições plenárias, cinco orais convidadas e uma oral apresentada pelo vencedor do Prémio Ramôa Ribeiro. Este prémio foi instituído este ano e passará a ser atribuído a cada Encontro da DCMP. Neste Encontro contaremos igualmente com a sessão de entrega do Prémio Luso-Espanhol de Química que no ano 2015 foi atribuído ex-equo a dois cientistas espanhóis, um deles da área da catálise heterogénea e materiais.

Mais uma vez contamos com uma elevada participação de investigadores e jovens estudantes, o que realça bem o carácter aglutinador dos encontros da DCMP e o papel que estes eventos poderão ter para promover o intercâmbio de conhecimento entre investigadores, formar os jovens estudantes, e ainda potenciar novas colaborações. Desejamos igualmente que estejam criadas condições para que se discutam novos projetos de colaboração e sejam criadas plataformas para submissão de projetos conjuntos nos próximos concursos nacionais e internacionais.

Durante a assembleia da DCMP que se irá realizar durante este Encontro, será eleita a nova direção da DCMP e decididas as representações nacionais nas diversas sociedades de catálise: Iberoamericana (FISOCAT), Europeia (EFCATS) e Federação Europeia de Zeólitos (FEZA). Iremos discutir a candidatura de Portugal para organizar o XXVI Congresso Iberoamericano de Catálise em 2018. Esperamos igualmente que seja possível num futuro próximo organizar em Portugal conferências internacionais como EUROPACAT e as Summer Schools in Catalysis.

Desejamos que todos os participantes disfrutem do 10º ECMP e que os membros da comunidade portuguesa de catálise e materiais porosos tenham cada vez mais possibilidades de desenvolver as suas actividades científicas a nível nacional mantendo vivo o espírito destes Encontros.

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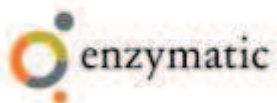
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Apoios



Programa Científico

19 (Quinta-feira)	
9:30	Registo
10:30	Sessão de Abertura
11:00	IL1. Biofuels And Bio-Based Products: How Oxygen From Bioresources Is Hunted Down By Transition Metal Sulfide Catalysts? <u>Antoine Daudin</u>
11:30	O1. Sulfur-Free Diesels Through Sustainable Oxidative Desulfurization With Porous MOF <u>Carlos M. Granadeiro</u> , Susana O. Ribeiro, Mohamed Karmaoui, Rita Valença, Jorge C. Ribeiro, Baltazar de Castro, Luís Cunha-Silva, Salete S. Balula
11:45	O2. Valorisation of Bio-Based Furfural Using Multifunctional Catalysts <u>Margarida M. Antunes</u> , Sérgio Lima, Patrícia Neves, Ana L. Magalhães, Enza Fazio, Fortunato Neri, Manuel T. Pereira, Andreia F. Silva, Carlos M. Silva, Sílvia M. Rocha, Martyn Pillinger, Atsushi Urakawa, Anabela A. Valente
12:00	O3. Influence of Ru Catalyst Support on the Direct Conversion of Cellulose to Sorbitol <u>Lucília S. Ribeiro</u> , José J.M. Órfão, M. Fernando R. Pereira
12:15	O4. From Hemicellulose to Furfural Through Solid Acid Catalysts <u>Andreia F. Peixoto</u> , Eva Correia, Cristina Freire
12:30	Almoço
14:00	PL1. Solid Catalysts Design From the Laboratory to the Industrial Application <u>Avelino Corma</u>
Prémio Luso-Espanhol de Química 2016	
15:00	O5. Insights Into the Synergies Between Zeolites in Hydrocracking Hybrid Catalysts <u>Pedro S. F. Mendes</u> , André F. C. Gregório, Antoine Daudin, Christophe Bouchy, João M. Silva, M. Filipa Ribeiro
15:15	O6. Highly Efficient Reduction of 4-Nitrophenol Mediated By Gold Nanoparticles Immobilized Onto L-Serine Functionalized Clay <u>Mariana Rocha</u> , Paula Costa, Carlos A. D. Sousa, Clara Pereira, José E. Rodríguez-Borges, Cristina Freire
15:30	O7. Orange II Dye Degradation By Photo-Assisted Wet Peroxidation Using Gold Based Catalysts <u>Ricardo M. Silva</u> , Carmen S.D. Rodrigues, Sónia A.C. Carabineiro, F.J. Maldonado-Hódar, Luís M. Madeira
15:45	Café & Posters
Patrocinado pela Paralab	
16:45	IL2. Hybrid Materials: At the Front End of Catalysis <u>Mariette M. Pereira</u> , Mário J.F. Calvete, César A. Henriques, Fábio M.S. Rodrigues
17:15	O8. Efficient Oxidative Desulfurization System Based On Oxomolybdenum@Ionic Liquids <u>Diana Julião</u> , Ana C. Gomes, Martyn Pillinger, Rita Valença, Jorge C. Ribeiro, Isabel S. Gonçalves, Salete S. Balula
17:30	O9. MW-Induced Oxidation of Alcohols Using M(II)-EDTA Functionalized Magnetic Nanoparticles <u>Nuno M. R. Martins</u> , Luísa M. D. R. S. Martins, Armando J. L. Pombeiro
18:00	Reunião da DCOMP
20:30	Jantar do Encontro

20 (Sexta-feira)	
9:00	PL2. "More Things In Heaven and Earth Than Are Dreamt Of": Silicates & Coordination Polymers João Rocha
9:45	O10. CO₂ Sorption Over Improved Hydrotalcites Joel M. Silva, R. Trujillano, M.A. Vicente, M.A. Soria, Luis M. Madeira
10:00	O11. Importance of Impregnation Methodology To Control Activated Carbons Pore Structure Ana S. Mestre, Fabian Hesse, Cristina Freire, Conchi O. Ania, Ana P. Carvalho
10:15	O12. Processing Of Functionalized Cellular Ceramic Monoliths Nuno M. Vitorino, Andrei V. Kovalevsky, Jorge R. Frade
10:30	Café
Patrocinado pela CUF	
11:00	IL3. Solar Fuel Production By Reducing CO₂: Prospects And Open Problems In The Design Of Photo-Electrocatalytic (PEC) Cells And Related Nanostructured Electrodes Claudio Ampelli, Chiara Genovese, Francesco Tavella, Siglinda Perathoner, Gabriele Centi
11:30	PRR. Breaking Bonds For Water Treatment: A Catalysis Journey Adrián M.T. Silva
Prémio Ramôa Ribeiro	
12:00	O13. Photocatalytic Reduction of CO₂ With Water Using Titania - Graphene Oxide Composites Luisa M. Pastrana-Martínez, Adrián M.T. Silva, José L. Figueiredo, Joaquim L. Faria
12:15	O14. Synthesis, Characterization and Catalytic Performances of SBA-15 Supported Catalysts For CO₂ Methanation M.C. Bacariza, S.S. Bebiano, I. Graça, J.M. Lopes, C. Henriques
12:30	Almoço
14:00	IL4. Challenging Catalysis With Cheap and Abundant Metals Beatriz Royo
14:30	O15. P-Nitrophenol Degradation By Heterogeneous Fenton Process Over AC-Based Catalysts C.S.D. Rodrigues, M.T. Pinho, O.S.G.P. Soares, V.N. Lima, M.F.R. Pereira, L.M. Madeira
14:45	O16. Ball-Milling Effect in the Catalytic Activity of Cryptomelane for VOC Oxidation Diogo F.M. Santos, Olívia S.G.P Soares, José L. Figueiredo, Manuel F.R. Pereira
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15:15	O18. Metal-Free Catalysts Derived From Lignin For Efficient Wet Peroxide Oxidation Maria Martin-Martínez, Maria Filomena F. Barreiro, Adrián M.T. Silva, José L. Figueiredo, Joaquim L. Faria, Helder T. Gomes
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Patrocinado pela Labor Spirit	
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16:45	O19. Green Esterification Reactions By Metal Phosphates and Phosphonates Graça Rocha, Teresa Santos, Liliana Costa, André Francisco
17:00	O20. Biodiesel Production Using Eggshell And Oyster Shell Derived Catalysts Rúbia Risso, Sara Meireles, Isabel Fonseca, Joaquim Vital
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Plenary Lectures Abstracts

SOLID CATALYSTS DESIGN FROM THE LABORATORY TO THE INDUSTRIAL APPLICATION

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The design of a successful solid catalyst relies on the synthesis of materials with controlled adsorption and reactivity, to maximize selectivity towards the desired product. Thus, solid catalysts with well defined single or multiple sites have to be generated. We will show that this is possible by preparing structured inorganic micro and mesoporous materials with controlled porosity and framework chemical compositions. Further possibilities can be envisaged by preparing structured hybrid organic-inorganic materials in where the active sites can be introduced in the organic, the inorganic or in both the organic and inorganic moieties. This will allow the preparation of multifunctional solid catalysts for performing multistep reactions in a cascade manner. Then, it will be presented that the preparation of multifunctional catalysts can go beyond the lab and to reach industrial application.

Finally, mono and bifunctional solid catalysts based on metal nanoclusters with a few atoms (3-10) and metal nanoparticles with controlled sizes and shapes within the range of 1 to 10 nm will be presented. With the metal nanoclusters entities it is possible to achieve turnover frequencies close to those obtained by enzymes under very mild reaction conditions. The challenge in this case is to stabilize those “molecular like” metal entities for long time. We have attempted to do that by generating the nanocluster within a polymeric matrix. In the case of catalysts based on metal nanoparticles, their activity and selectivity depend on size and shape of the crystallites, the interaction with the support and the introduction of a second metal to form a bimetallic catalyst.

We will show that it is possible by controlling catalysts preparation to convert traditionally non selective into selective metal catalyst.

“MORE THINGS IN HEAVEN AND EARTH THAN ARE DREAMT OF”: SILICATES & COORDINATION POLYMERS

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I shall highlight some of the work carried out in Aveiro, in the last few years, on nanoporous transition-metal and lanthanide (Ln) silicates and on Ln-bearing coordination polymers (or metal organic frameworks, MOFs). The main focus will be on the design of (nano) materials for sensing small molecules [1] and temperature [2-4] and for drug delivery [5], treating bone tissue disorders [6] and use as pharmaceuticals.

While nanoporous (zeolite-like) silicates are highly robust (thermal and chemical) systems, allowing applications in relatively harsh conditions, it is very challenging to synthesise the desired architectures and modify them post-synthesis. In contrast, MOFs operate in milder conditions and often lack robustness but they are much more amenable to ‘rational synthesis’ and post-synthetic modification. Thus, together, metal silicates and MOFs provide a wonderful playground for chemists and a toll box for engineering applications.

Acknowledgements

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Invited Lectures Abstracts

BIOFUELS AND BIO-BASED PRODUCTS: HOW OXYGEN FROM BIORESOURCES IS HUNTED DOWN BY TRANSITION METAL SULFIDE CATALYSTS?

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To limit the carbon footprint of fuels or chemical intermediates, the substitution of fossil resources by renewable ones is a promising routes (vegetable oils, animal fats, pyrolysis oils, lignin, etc...). One of the specific characteristics of these substances is their high oxygen content, which is often incompatible with the properties and specifications of the target products. It is therefore necessary to process these bioresources using a catalytic treatment to eliminate, either partially or totally, the oxygen heteroatom [1].

In this way, hydroprocessing technologies involving transition metal sulphide catalysts offer a real interested routes to achieve this goal. Indeed, nickel-promoted molybdenum sulphide (NiMoS) catalysts are very versatile and enable the purification and conversion of hydrocarbons of either fossil or biomass origin. Combining an experimental kinetic approach with quantum molecular modelling, we identified the reaction mechanisms involved in the deoxygenation of model molecules used on an active site scale [2]. The key role of the promoter (Ni) on deoxygenation and decarbonylation activity and selectivity has thus been demonstrated. It opened the way for further optimization of catalyst formulations and has been revealed of primary importance for vegetable oil hydrotreatment processes.

More recently, thanks to a multi-technical approach (based on two dimensional chromatographic analysis), further progress has been made in terms of our understanding of the mechanisms and steps involved in the conversion of complex oxygenated feeds, as lignin [3]. This research help us manage the reaction conditions in order to control conversion and selectivity into valuable products bio-based fuels and chemical products.

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HYBRID MATERIALS: AT THE FRONT END OF CATALYSIS

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The development of organic-inorganic hybrid materials with different structures and porous size is nowadays considered a frontier area for development of new selective and more sustainable catalytic processes. This transformation of homogenous catalysts and their properties onto heterogeneous ones is still in the beginning stage but it is expected that in the near future these successful combinations may open relevant new perspectives for industrial applications of homogeneous catalysts.[1]

In this communication we will present and discuss the Coimbra *Catalysis & Fine Chemistry* group (C&FC) experience to promote the immobilization of organic ligands, such as BINOL and porphyrins onto several inorganic supports (silica, mesoporous materials, carbon nanotubes and magnetic nanoparticles) and their application in many catalytic processes. The effect of inorganic support and/or metal leaching will be critically appraised. Finally, a more detailed description of the synthesis of hybrid magnetic nanoparticles-copper porphyrins and its useful application in oxidation of hydrocarbons using exclusively O₂ as oxidant will be presented and discussed, Figure 1.[2]

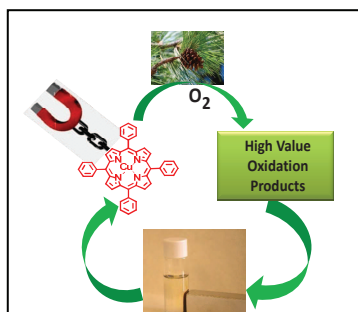


Figure 1. Hybrid magnetic nanoparticles-Cu(II)-porphyrins as reusable oxidation catalysts

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SOLAR FUEL PRODUCTION BY REDUCING CO₂: PROSPECTS AND OPEN PROBLEMS IN THE DESIGN OF PHOTO-ELECTROCATALYTIC (PEC) CELLS AND RELATED NANOSTRUCTURED ELECTRODES

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One of the most important challenges in human society is the development of new, renewable and sustainable, energy systems to deal with the urgent global growing energy needs, falling fossil fuel reserves and drastic rise in CO₂ levels in the atmosphere [1]. In this context, the photo-electrocatalytic (PEC) conversion of CO₂ into liquid fuels is an attractive route to close the CO₂ cycle and produce alternative chemical energy [2]. Many efforts have been devoted to develop advanced materials able not only to adsorb CO₂ but also to catalyse its reduction to liquid fuels [3]. Particularly, there is the need to synthesize suitable materials to be used as electrodes in solar PEC devices for a delocalized production of energy [4].

In this contribution, we report on the development of new nanodimensional catalytic materials for the process of CO₂ reduction, as well as the realization of lab-scale PEC set-ups designed on purpose to maximize photo-conversion and faradaic efficiencies. The experimental data were obtained by the synthesis, characterization and assembling of: i) TiO₂-based nanostructured materials (doped with metal nanoparticles to improve photo-response under visible light irradiation) as photo-anodes; ii) C-based composite materials (doped with metal nanoparticles to provide the active sites for CO₂ reduction) as electro-cathodes. Specifically, we investigated different reactor operating conditions (conventional slurry, liquid and gas phases) both in anode and cathode hemi-cells, and tested the as-prepared catalysts in water photo-electrolysis and/or ethanol photo-reforming processes, as well as in the CO₂ reduction process.

Results, in terms of solar fuel production (H₂ and liquid fuels), show the higher performances obtained working in gas phase, both in anode and cathode compartments, with respect to the more common studied slurry/liquid conditions, opening new routes in the sustainable production of energy and chemicals.

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CHALLENGING CATALYSIS WITH CHEAP AND ABUNDANT METALS

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A key scientific challenge of the 21st century in metal-mediated catalysis is the search for catalysts based on Earth-abundant metals. The limited availability of noble metals (Pd, Pt, Rh, Ir, Ru), their high price and significant toxicity make desirable to search for more economical and environmentally friendly alternatives [1]. In addition to these economical and environmental reasons, the investigation of first-row transition metals *eg.*, Mn, Fe, Co, Ni constitutes an exciting endeavour since new reactivity modes and reaction pathways can be disclosed. During the last few years, our research group has been involved in developing the coordination chemistry and catalytic applications of iron [2] and nickel [3] complexes containing N-heterocyclic carbenes (NHC), a useful class of ligands for catalysis.

In this contribution, results from our recent ventures into the preparative, structural and reactivity aspects of the organometallic chemistry of Fe- and Ni-NHC will be presented. This includes our latest results on the application of these organometallic complexes in catalytic reduction and oxidation processes, as well as in the catalytic dehydrogenative coupling of silanes with alcohols and aromatic thiols.

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TAILORING METAL-FREE CARBON CATALYSTS: FROM THE NANO TO THE MACRO SCALE

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In addition to their more traditional use as catalyst supports, carbon materials can find application as catalysts on their own, both in liquid and gas phase reactions [1]. The advantages of using carbon materials as metal-free catalysts are enormous, in particular when they replace rare and precious metal based catalysts in different catalytic reactions, as can be the case of advanced oxidation processes (AOP) for water treatment [2], oxidative dehydrogenation of alkanes to produce the corresponding olefins [3] and the cathodic oxygen reduction reaction (ORR) in fuel cells.

In the present work, recent advances on the design of carbon materials as metal-free catalysts are reviewed, starting from the active site on the carbon surface to the macrostructured catalysts to be applied in large scale operation.

At the nanoscale, the focus is in the preparation of carbon materials with an appropriate texture (pore network) to avoid mass transfer limitations, and with large amounts of the specific surface groups that are the active sites for the target reaction. The texture can be controlled by using carbon materials from different origins (from the traditional activated carbons to the more recent nanocarbons), while the surface chemistry can be tailored by appropriate physical and chemical treatments to selectively introduce different types of heteroatoms, like O, N, S and B [4].

In most studies, carbon catalysts are used in powder form, which is a problem for their practical application. A solution to overcome this drawback is to attach the carbon materials onto a macrostructure, such as honeycomb cordierite monoliths [5] and SiC foams. An example of this methodology applied to AOP will be presented.

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Prémio Ramôa Ribeiro

BREAKING BONDS FOR WATER TREATMENT: A CATALYSIS JOURNEY

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Priority substances and contaminants of emerging concern have been found in the aquatic environment, often up to $\mu\text{g L}^{-1}$ levels. Directive 2013/39/EU and Decision 2015/495 were launched to update the water framework policy in Europe, emphasizing the need to develop new water treatment technologies to deal with such problem [1-2]. This communication aims to present an overview of the author's experience in the synthesis, characterization and application of active and stable catalysts, including catalytic membranes, for different water treatment technologies [3-4]. Special emphasis will be placed on the use of carbon materials (activated carbons, carbon nanotubes, graphene derivatives, among others) and their respective functionalization [5-6]. Carbon materials with no added metals can be used as active catalysts in some of these processes, or combined with a semiconductor material in the particular case of photocatalysis [7-8]. Hybrid systems are also alternatives, and some of them have not yet been applied in full-scale plants [4].

Acknowledgements

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Oral Communications Abstracts

SULFUR-FREE DIESELS THROUGH SUSTAINABLE OXIDATIVE DESULFURIZATION WITH POROUS MOF

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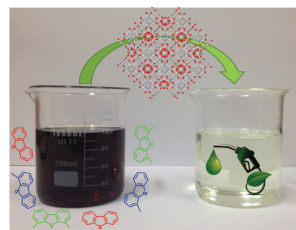
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The conventional technology for the desulfurization of fuel, hydrodesulfurization, presents some drawbacks including high cost and severe operational conditions necessary to produce sulfur-free fuels. The increasingly stringent regulations for fuels have motivated the development of cost-effective alternatives for the production of ultra-clean fuels. Oxidative desulfurization (ODS) is one of the most promising alternatives, allowing the efficient removal of the most refractory sulfur compounds under mild conditions while avoiding the use of costly hydrogen.[1] The UiO-type materials are a class of highly stable metal-organic frameworks (MOFs) based on $Zr_6O_4(OH)_4(CO_2)_{12}$ secondary building units. In particular, the porous Zr(IV) terephthalate UiO-66 has attracted the attention of the scientific community due to its high surface area and exceptional chemical, thermal and mechanical stability.[2]



In the present work, structural-engineered UiO-66(Zr) samples were prepared with different extents of linker deficiencies and degrees of crystallization. The samples were evaluated as heterogeneous catalysts in the ODS process of a multicomponent model diesel using sustainable conditions. The results obtained allowed to establish a correlation between the structure and the desulfurization performance of the MOFs. The most promising samples have been used in an ODS system for the desulfurization of untreated real diesel (provided by Galp Energia).

Acknowledgements

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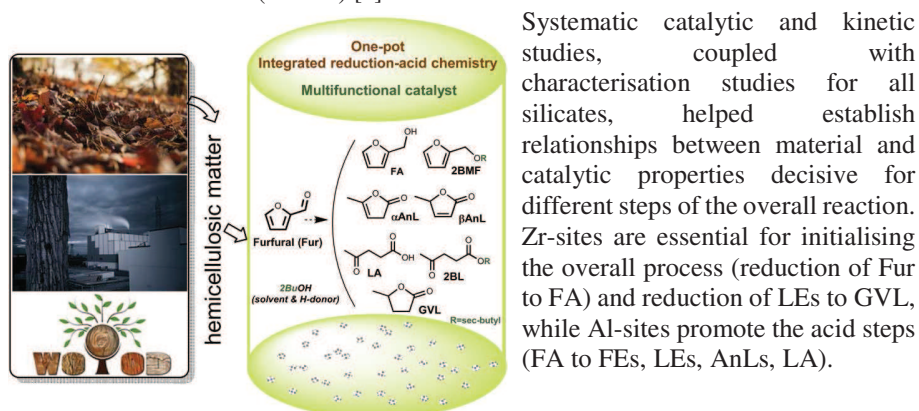
VALORISATION OF BIO-BASED FURFURAL USING MULTIFUNCTIONAL CATALYSTS

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Furfural (Fur) is one of the most important platform chemicals that can be produced from hemicellulose-rich biomass. The conversion of Fur to useful bio-products, namely, furfuryl alcohol (FA), alkyl furfuryl ethers (FEs), alkyl levulinate esters (LEs), levulinic acid (LA), angelica lactones (AnLs), and γ -valerolactone (GVL) involves reduction and acid reactions. In this work the integrated reduction-acid reaction system has been promoted using multifunctional catalysts comprising ordered porous silicates of the type TUD-1 and zeolite Beta possessing zirconium and aluminium sites [1]. Catalysts with different Si/Al and Si/Zr ratios were prepared, characterised and evaluated as eco-friendly and stable heterogeneous catalysts using 2-butanol as solvent and H-donor. Up to 76% total yield of bio-products was achieved at 85% Fur conversion (120 °C) [1].



Systematic catalytic and kinetic studies, coupled with characterisation studies for all silicates, helped establish relationships between material and catalytic properties decisive for different steps of the overall reaction. Zr-sites are essential for initialising the overall process (reduction of Fur to FA) and reduction of LEs to GVL, while Al-sites promote the acid steps (FA to FEs, LEs, AnLs, LA).

Acknowledgements

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INFLUENCE OF Ru CATALYST SUPPORT ON THE DIRECT CONVERSION OF CELLULOSE TO SORBITOL

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The hydrolytic hydrogenation of cellulose to sugar alcohols, especially sorbitol, over heterogeneous catalysis is one of the most efficient pathways for a sustainable society dependent on biomass. Sorbitol is a promising platform chemical, which can be used in pharmaceuticals, cosmetics and textiles, and also as raw material for the synthesis of many other fine chemicals [1]. The aim of this work is to develop an efficient catalyst for the one-pot selective conversion of cellulose to sorbitol by testing various carbon supported ruthenium catalysts under H₂ pressure.

Ruthenium catalysts supported on different materials were prepared by the incipient wetness impregnation method and characterized by N₂ adsorption at -196 °C, ICP, microscopy (TEM) and temperature programmed reduction (TPR). The materials were then tested in a stainless steel Parr reactor, where 300 mL of water, 750 mg of cellulose (previously ball-milled) and 300 mg of catalyst were introduced. After heating under N₂ to the desired temperature (205 °C), the reaction was initiated by switching to H₂ (50 bar). Samples were periodically taken for analysis by HPLC and total organic carbon (TOC). Carbon nanotubes (CNT), activated carbon (AC), graphite (GIT), graphene (GEN), carbon black (P80), carbon xerogel (XG), alumina (Al₂O₃) and zeolite (HY) were the different supports studied.

The different catalysts were tested in the direct conversion of cellulose to sorbitol and showed to be highly efficient, with conversions of cellulose higher than 75% after 5 h of reaction. The highest selectivities to sorbitol were reached when using CNT, AC or GIT as support (Figure 1). Ru/CNT showed to be the most selective catalyst to sorbitol, with selectivities over 60%. On the other hand, Ru/HY was the less selective catalyst, presenting a selectivity to sorbitol of only 16% after 5 h of reaction.

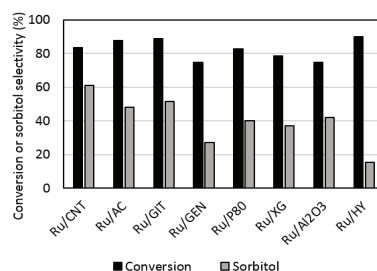


Figure 1. Effect of the support on cellulose conversion and selectivity to sorbitol.

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FROM HEMICELLULOSE TO FURFURAL THROUGH SOLID ACID CATALYSTS

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The development of economical and energy-efficient processes for the valorization of biomass to secure energy, fuel and chemical supplies for future needs is one of the challenges throughout the world. Therefore, catalytic processes that transform biomass into valuable products under competitive and sustainable condition have become an interesting option in recent years [1].

Hemicellulose is one of the main components of biomass and is mainly composed by xylose and arabinose. Furfural is identified as a versatile platform molecule and can be produced through conversion of carbohydrates using heterogeneous acid catalysis [2-4].

In collaboration with INNOVCAT we have been working on biomass valorization, through solid-acid-catalyzed conversion of hemicellulose (xylose) into furfural. Catalytic reactions were performed on a batch reactor using pure xylose with different solvents, temperature, pressure and reaction time and catalysts in order to reach the maximum conversion and selectivity for furfural. The reusability of the best catalytic system was also studied. To compare the catalytic performance obtained with INNOVCAT catalysts, the reactions were also carried out using commercial catalysts (ex: Lewatit GF 101). The results showed that 50 - 90 % conversion of xylose could be achieved depending on the catalytic experimental conditions. The conversion and selectivity was achieved by HPLC, gas chromatography and ¹H NMR analysis. Catalytic results with real feedstocks containing hemicellulose or xylose, from crop wastes, will be also presented.

Acknowledgements

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INSIGHTS INTO THE SYNERGIES BETWEEN ZEOLITES IN HYDROCRACKING HYBRID CATALYSTS

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The enhancement of bifunctional catalysts performance is playing a key role on the increasing demand of high-quality fuels [1]. Particularly, hybrid catalysts based on mixtures of FAU and BEA zeolites have been successfully used in hydrocracking processes since the last decade [2]. Nevertheless, the origin of the improved performances compared to the individual zeolite catalysts remains unclear. In this work, we evaluate hybrid Pt/zeolite catalysts based on mixtures of HUSY and HBEA in the hydrocracking of *n*-C₁₆.

Concerning individual catalysts, results depicted in Figure 1 show that Pt/HUSY catalyst has higher maximum isomer yield than Pt/HBEA, but the last one is more active (higher kinetic constant for C₁₆ consumption).

For hybrid catalysts, both impregnated and mechanical mixture catalysts present similar maximum isomer yield to that of Pt/HUSY catalyst which does not match with an average yield of the individual catalysts. This reveals an improved balance between metal and acid function than the expected for hybrid catalysts.

In summary, the origin of the synergies observed between zeolites combined in an hydrocracking bifunctional catalyst could be related to a better metal-acid balance. From the industrial point of view, the hybrid catalysts should be able to keep high isomer yield for improved activity.

Acknowledgements

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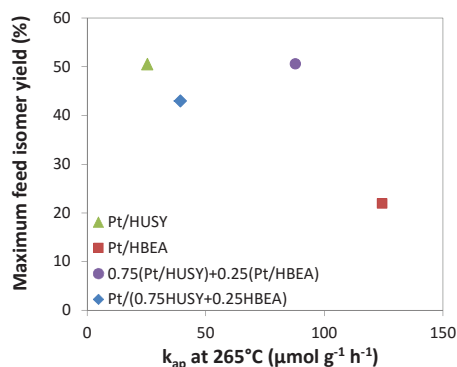


Figure 1. Maximum C₁₆ isomer yield plotted against the apparent kinetic constant for *n*-C₁₆ consumption at 255 °C for 0.4% Pt catalysts.

HIGHLY EFFICIENT REDUCTION OF 4-NITROPHENOL MEDIATED BY GOLD NANOPARTICLES IMMOBILIZED ONTO L-SERINE FUNCTIONALIZED CLAY

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Catalysis by gold nanoparticles (Au NPs) is a fast growing area within the field of metal-based nanocatalysis due to their unique physicochemical properties. One of the most important reactions catalyzed by Au NPs is the reduction of 4-nitrophenol (4-NP), which is one of the most common organic pollutants found in industrial and agricultural wastewaters [1]. The reduction of 4-NP leads to the formation of 4-aminophenol (4-AP), which is a valuable compound used as intermediate in the synthesis of numerous pharmaceutical and natural products [2]. Nevertheless, Au NPs show a tendency to form aggregates, which reduces their catalytic performance. Thus, their immobilization onto solid supports is a good alternative to overcome this disadvantage. Clays are of particular interest since they are cheap, environmentally-friendly and readily available. Nevertheless, the direct immobilization of the active metal species onto clays usually leads to significant leaching during the catalytic reaction [3]. Hence, the functionalization of the inorganic support *via* covalent attachment of organic ligands is the best solution. L-serine derivatives are particularly interesting linking agents since they are cheap and have several coordinating groups. In this work, we report the preparation, characterization and successful application of Au NPs immobilized into L-serine functionalized clay (K10) in the reduction of 4-NP. The catalyst led to nearly 100% 4-NP conversion in only 1 minute, presenting pseudo first-order rate constant normalized for Au loading of $K = 638 \text{ mmol}^{-1} \text{ s}^{-1}$. The catalyst showed outstanding stability upon 10 consecutive catalytic cycles leading to conversions up to 95%.

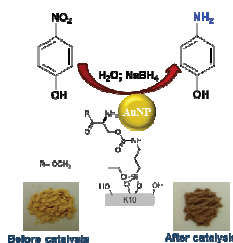


Figure 1. Scheme of 4-NP reduction

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ORANGE II DYE DEGRADATION BY PHOTO-ASSISTED WET PEROXIDATION USING GOLD BASED CATALYSTS

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The wet peroxide oxidation (WPO) can be combined with ultraviolet-visible (UV-Vis) radiation to enhance the formation of hydroxyl radicals, thus favoring the degradation of organics present in wastewaters [1]. Gold based catalysts have been employed in this advanced oxidation process due to their stability and efficiency [2].

The main goal of this study is to use different supports in order to determine the most suitable for Au deposition. The catalysts used (0.8% Au-Fe₂O₃; 1.6% Au-TiO₂; 1.2% Au-ZnO; 0.7% Au-Al₂O₃) were prepared by the deposition-precipitation method; a reference World Gold Council catalyst (4% Au-Fe₂O₃) was also used for comparison. For all catalysts, experiments were performed in a slurry batch photo-reactor to determine the effect of the oxidant and UV/Vis light per se, and to compare the adsorption and the oxidation reaction using the support (without gold) or the catalyst (with gold). For all catalysts, no gold leaching was found (< 0.04%), proving their stability. In order to compare catalysts with different gold loading, the turnover frequency (TOF) was calculated. The Au-Al₂O₃ material presented the highest TOF value (see Figure 1) with better performances (~100% for dye and 80% for TOC removal). The characterizations performed on the materials allowed to explain the differences in their catalytic performance.

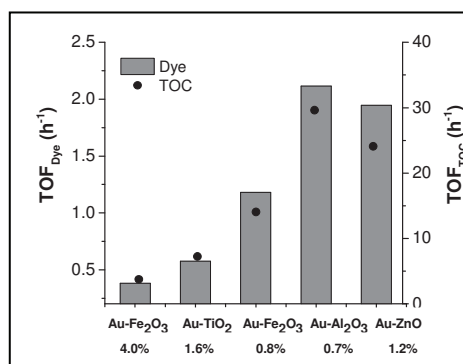


Figure 1. TOF for dye and TOC removals using different Au catalysts.

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EFFICIENT OXIDATIVE DESULFURIZATION SYSTEM BASED ON OXOMOLYBDENUM@IONIC LIQUIDS

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Transportation fuels contain different types of sulfur compounds, namely thiols, thioethers, disulfides, and especially aromatic sulfur compounds such as dibenzothiophenes and their derivatives, which require severe conditions (high temperature, pressure, high hydrogen consumption) to be removed efficiently through the conventional hydrodesulfurization (HDS) process.[1,2] Therefore, to produce ultra-low sulfur fuels and at the same time avoid the disadvantages of HDS, new approaches have been developed. One of the most promising methods is oxidative desulfurization (ODS), which combines sulfur oxidation with removal of oxidized products by liquid-liquid extraction or adsorption processes. In the liquid-liquid extraction process, ionic liquids (ILs) have proven to be environmentally benign substitutes of flammable and volatile organic solvents.[1]

Transition metal-oxo species with active Mo(VI) centers have been employed as active catalysts for the oxidation of sulfur compounds but only a few reports of their application in ODS systems are present in the literature.[3,4]

In the present work, the complex MoO₂Cl₂(di-tBu-bipy) was applied as a homogeneous catalyst for the oxidative desulfurization of a model oil and an untreated diesel using ILs as extraction solvents and H₂O₂ as oxidant. The complex proved to be an effective catalyst and the ODS system could be recycled for desulfurization of various diesel samples without losing efficiency.

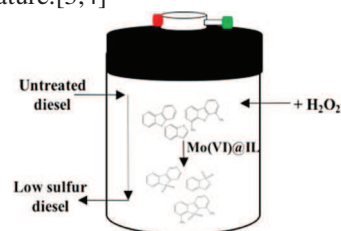


Figure 1- Representation of ODS system.

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MW-INDUCED OXIDATION OF ALCOHOLS USING M(II)-EDTA FUNCTIONALIZED MAGNETIC NANOPARTICLES

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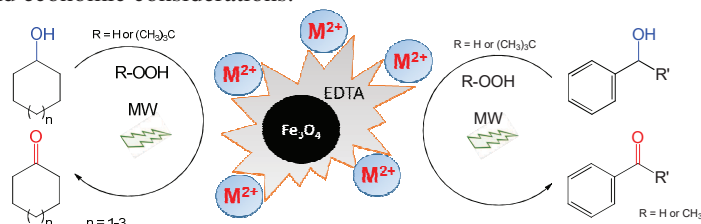
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A series of late-first-row-transition-metal combined with EDTA (ethylenediamine tetraacetic acid), as metal-based *N,O*-chelating ligands, at the surface of ferrite magnetic nanoparticles (NPs) was prepared by a co-precipitation method [1,2]. Those EDTA functionalized magnetite NPs with general formula Fe₃O₄@EDTA-M²⁺ (M= Mn²⁺, Fe²⁺, Co²⁺, Ni²⁺, Cu²⁺ or Zn²⁺) were characterized by FTIR spectroscopy, powder XRD, SEM, EDS, VSM and TGA.

The application of the magnetic NPs towards the microwave-assisted oxidation of various alcohol substrates in solvent-free medium (Scheme 1) was evaluated. Also the influence of reaction parameters such as temperature, time, type of oxidant, presence of organic radicals and chemoselectivity was screened.

This study has demonstrated that these NPs can act as efficient catalysts for the conversion of alcohols to the corresponding ketones or aldehydes with high selectivity and yields up to 34 %. Moreover, they have the advantage of being magnetically recoverable catalysts that can be reused in following consecutive runs.

Herewith, we report a simple, efficient and mild catalytic oxidation of alcohols protocol that overcomes some issues of homogeneous systems and also in conventional heterogeneous conditions, which is quite attractive in terms of green chemistry and economic considerations.



Scheme 1. Solvent-free microwave-assisted catalytic oxidation of alcohols using reusable Fe₃O₄@EDTA-M²⁺ (M= Mn²⁺, Fe²⁺, Co²⁺, Ni²⁺, Cu²⁺ or Zn²⁺).

Acknowledgements

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CO₂ SORPTION OVER IMPROVED HYDROTALCITES

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The removal of CO₂ from the reaction medium to shift the equilibrium in reversible reactions is being widely considered since it would allow the use of lower process temperatures (e.g. 300-400 °C for sorption enhanced of either glycerol steam reforming or water gas shift). At such temperatures, hydrotalcites are the best option for CO₂ capture. Hydrotalcites are anionic clays with a layered double-hydroxide structure derived from brucite and general formula $[M^{II}_xM^{III}_{(1-x)}(OH)_2][A^{n-}]_{x/n} \cdot mH_2O$, where M^{II} and M^{III} are di- and trivalent metal cations inside the brucite-like layers and Aⁿ⁻ is a charge compensating anion [1,2].

In this work, several hydrotalcites were prepared via co-precipitation followed by impregnation with potassium. The base material is an Mg-Al hydrotalcite with CO₃²⁻ as the charge compensating anion (HTC). The other materials consist of HTC submitted to microwave irradiation (HTC-MW), HTC and HTC-MW impregnated with approximately 20 wt.% K₂CO₃ (K-HTC and K-HTC-MW, respectively) and HTC partially substituted with Ga, impregnated with the same amount of K₂CO₃ and with or without microwave treatment (K-HTCGa-MW and K-HTCGa, respectively). The CO₂ sorption isotherms of these materials were obtained under dry conditions. The results obtained so far are very promising, with outstanding capacities, especially for K-HTC-Ga where a sorption equilibrium value of 2.11 mol/kg at 2.99 bar of CO₂ was obtained (Figure 1). Properties of these materials will be related with their detailed physico-chemical characterization data by several techniques (nitrogen adsorption, XRD, FTIR, SEM and TG/DTG).

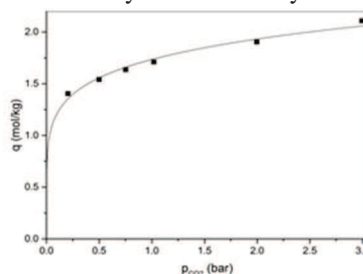


Figure 1. CO₂ sorption equilibrium isotherm at 573 K for K-HTCGa-MW.

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IMPORTANCE OF IMPREGNATION METHODOLOGY TO CONTROL ACTIVATED CARBONS PORE STRUCTURE

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The use of activated carbons in new applications involving the immobilization or adsorption of bulky molecules, or processes requesting fast transport of species within the pore network, can only be envisaged if the materials have a high percentage of large mesopores. However the synthesis of mesoporous carbons remains a challenge for the scientific community since the commonly used procedures result in micropore or micro+small mesopore networks [1].

Herein we report a new synthetic route for the preparation of micro+mesoporous activated carbons. The materials were prepared from sisal waste by a two-step procedure involving the carbonization of the saccharic units extracted from the biomass with H₂SO₄ and further activation with K₂CO₃ at 800 °C for 1 h. The control of the impregnation methodology revealed to be of paramount importance for the mesoporosity development.

The materials prepared by solution impregnation (Fig. 1) attained apparent surface areas near 1500 m²/g, with up to 50 % of mesopores (2 < φ < 20 nm), and have acidic surface chemistry (pH_{PZC}=3.8). Preliminary results of iopamidol adsorption – a bulky medicine – illustrate the higher removal efficiency of the micro+mesoporous sample over the essentially microporous carbon obtained by physical impregnation.

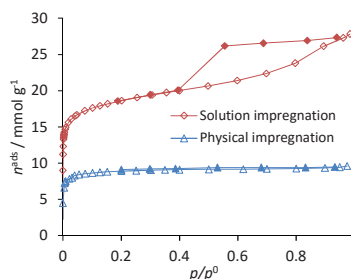


Figure 1. N₂ isotherms at -196 °C.

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PROCESSING OF FUNCTIONALIZED CELLULAR CERAMIC MONOLITHS

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A variety of methods is proposed to process highly porous ceramics with adjusted microstructural features, and to design their properties targeting potential catalytic and separation applications for sustainable energy and chemical technologies [1, 2]. In this context, an innovative method to process well consolidated porous cellular ceramic monoliths was developed in our group, based on emulsification of a ceramic suspension in liquid organic media (e.g.: melted paraffin), which allows tunable microstructural features by adjusting the emulsification conditions. A wide set of important ceramic materials was already processed, and the method robustness was successfully proved for several important pure oxides including Al_2O_3 Fig.1 and Fe_2O_3 [3], traditional clays as kaolin and red clays [4] and some spinels, MgAl_2O_4 [5], NiAl_2O_4 , obtained by reactive sintering of their oxides or carbonates. A feasible approach to upscale the production of monolithic cellular bodies retaining the key microstructural features by extrusion was demonstrated for selected ceramics.

Furthermore, an additional step is required to achieve appropriate functionality of the monoliths. Thus, a set of procedures based on hydrothermal synthesis were developed to obtain cellular monoliths functionalized with boehmite ($\text{AlO}(\text{OH})$), gamma-alumina ($\gamma\text{-Al}_2\text{O}_3$) [6], Ni/ NiO particles, $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ and even zeolites as sodalite, cancrinite and fajaussite. In case of NiAl_2O_4 spinel, functionalization was performed by high temperature reduction, promoting the Ni segregation from the NiAl_2O_4 matrix and resulting in cellular ceramics, with pore surfaces modified with Ni nanoinclusions.

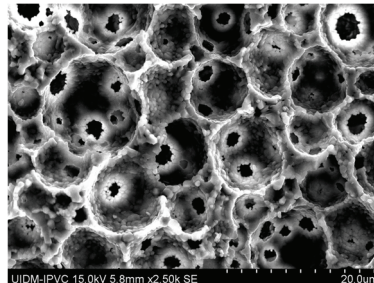


Fig. 1 – SEM microstructure of Al_2O_3 cellular monolith

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PHOTOCATALYTIC REDUCTION OF CO₂ WITH WATER USING TITANIA - GRAPHENE OXIDE COMPOSITES

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Realizing a sustainable, resource-efficient and low-carbon economy is one of the key fundamental challenges of the 21st century [1]. The conversion of CO₂ and water into fuels using solar energy presents a potential solution to reduce the consumption of limited fossil fuels, contributing to carbon footprint reduction, while providing a sustainable source of fuels [2].

In this work, composites prepared from graphene oxide (GO) and titanium dioxide (TiO₂) were applied in the photocatalytic water reduction of CO₂ into methanol and ethanol. The composite (hereafter referred as GOT) was synthesized by the liquid phase deposition method at room temperature, as described elsewhere [3]. The photocatalytic runs were carried out in a cylindrical glass immersion photo-reactor with a Heraeus TQ 150 medium-pressure mercury vapor lamp located axially in the reactor and held in a quartz immersion tube. In a typical run, the photoreactor was loaded with 250 mL of a solution and catalyst load of 1 g L⁻¹. The effect of initial pH and different precursors of copper as co-catalyst were assessed and their influence on the photocatalytic reaction inferred. It was found that the GOT composite exhibited superior photocatalytic activity for ethanol production at pH 11.0 and for methanol production at pH 4.0 (Figure 1). The presence of copper significantly increases the photocatalytic activity towards both methanol and ethanol formation, especially in the case of the catalysts prepared with copper nitrate as precursor.

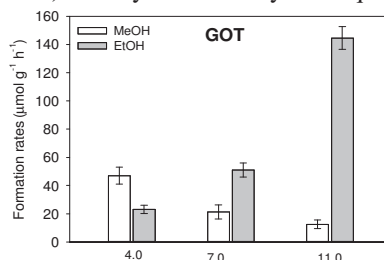


Figure 1. Methanol and ethanol formation rate at different initial pH

Acknowledgements

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SYNTHESIS, CHARACTERIZATION AND CATALYTIC PERFORMANCES OF SBA-15 SUPPORTED CATALYSTS FOR CO₂ METHANATION

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CO₂ methanation is a promising route for CO₂ emissions mitigation and has been focus of several studies on the last years [1]. In terms of catalysts, the most studied metals have been noble metals or others such as Ni, the last representing a good alternative due to its initial high catalytic activity and low cost when comparing with noble metals. Concerning the supports, various oxides such as TiO₂, SiO₂, Al₂O₃ or CeO₂-ZrO₂ have been investigated [2]. In addition, some micro and mesoporous materials such as zeolites, SBA-15 or MCM-41 have been recently referred as suitable supports for this reaction [1]. SBA-15 is a type of ordered mesoporous silica with large and uniform pores presenting interesting textural properties as well as thermal, mechanical and chemical stability.

In this work, CO₂ methanation reaction was studied on Ni and Ni-Ce based SBA-15 catalysts. Two SBA-15 materials were synthesized by different techniques. Samples were impregnated with Ni and Ni-Ce and were characterized by X-Ray Powder diffraction, N₂ adsorption, hydrogen temperature programmed reduction, diffuse reflectance UV-Vis spectroscopy and transmission electron microscopy. Catalytic tests were carried out in a fixed-bed reactor at atmospheric pressure. Before the reaction, catalysts were pre-reduced in-situ at 470°C. Reactants were introduced into the reactor at a molar ratio of H₂:CO₂:N₂=36:9:10 being the reaction performed at temperatures from 250 to 450°C and using a constant mass of catalyst.

The impregnation of the different metals did not affect SBA-15 structure (whatever the SBA-15 synthesis method). NiO and CeO₂ were observed as the main Ni and Ce species on the samples. Ni particles were mainly located on the outer surface of the materials and most of them were reduced during the pre-treatment. The catalytic performances obtained were comparable to the reported for a HNaUSY (2.8) zeolite and considerably better than the reported for other mesoporous materials in the literature [1].

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p-NITROPHENOL DEGRADATION BY HETEROGENEOUS FENTON PROCESS OVER AC-BASED CATALYSTS

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p-Nitrophenol (PNP) is widely used in the manufacture of drugs, explosives, dyes, fungicides and is a typical pollutant present in industrial wastewaters. It is very toxic ($LD_{50} = 250$ mg/kg [1]) and high levels of PNP have been found in water courses; for example a concentration of 60 g/L has been reported in drinking water [1]. Thus, there is a need to remove PNP from wastewater before discharge, to minimize the impact on the environment and human health.

In this study, the PNP degradation was evaluated by the heterogeneous Fenton process using iron (2.0 wt.%) based catalyst, supported on activated carbon (AC) prepared by incipient wetness impregnation method. Prior the impregnation the AC was modified by chemical and thermal treatments, in order to obtain supports with different surface properties, namely different amount of oxygen surface groups and also N-containing groups. The supports were characterized by N_2 adsorption at -196 °C, elemental analysis and by TPD. The catalysts were also characterized by TPR.

For all samples the contribution of the adsorption phenomena was evaluated as it co-exists with catalysis during Fenton-oxidation runs. Then, the AC-based catalysts were tested in a slurry batch reactor in the presence of the oxidant (H_2O_2). For the catalyst with the best performance (Fe-ACM, support doped with melamine as nitrogen precursor), the effect of the reaction pH, temperature, catalyst dose and hydrogen peroxide concentration was evaluated for process optimization.

It was found that the catalyst is stable, there is no iron leaching ($< 0.07\%$) and the removals of PNP and TOC and the effectiveness of oxidant use ($X_{TOC}:X_{H_2O_2}$) are constant during five consecutive cycles – see Figure 1.

Acknowledgements

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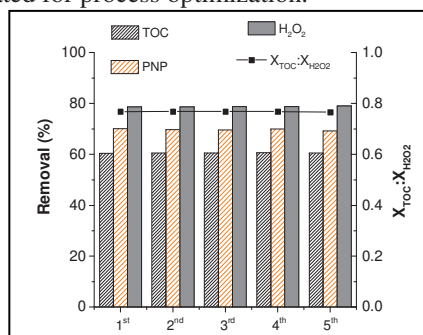


Figure 1. PNP and TOC removals, H_2O_2 consumption and $X_{TOC}:X_{H_2O_2}$ in consecutive reaction cycles ([PNP] = 500 mg/L; pH=3.0, T=30 °C, $[H_2O_2] = 1$ g/L and [catalyst] = 0.25 g/L).

BALL-MILLING EFFECT IN THE CATALYTIC ACTIVITY OF CRYPTOMELANE FOR VOC OXIDATION

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The emission of volatile organic compounds (VOCs) entails several environmental and human health problems [1]. Catalytic oxidation is one of the most efficient and economically viable technologies for VOC removal [2]. Noble metals, such as platinum and palladium, are the most used catalysts for this application due to their high efficiencies for the oxidation of several VOCs; however, their application is limited due to high costs and sensitivity to poisoning. Transition metal oxides have been studied as a low-cost alternative to noble metals. Cryptomelane-type manganese oxides have already shown high activity for the oxidation of several VOCs such as ethyl acetate [3]. In this work, cryptomelane-type manganese oxides were prepared by a novel solvent free method with ball milling. After the calcination step, the obtained samples were mechanically treated in the ball-mill at different intensities. The catalysts were characterized and tested in the oxidation of ethyl acetate, ethanol and toluene. The cryptomelane-type manganese oxide milled at low vibration presented a high catalytic activity for the oxidation of ethyl acetate and ethanol achieving 90 % conversion into CO₂ at 200 °C; however, a temperature of 270 °C was necessary to achieve the same conversion with toluene. For all VOCs tested, it was observed that the catalytic activity decreases when the severity of the mechanical treatment after the calcination step increases, most likely due to the reduction of the surface area and total pore volume. A platinum-based catalyst (1%-Pt-Al₂O₃) was also tested for comparison purposes. The activity of the Pt-based catalyst is much lower for the oxidation of ethyl acetate, and much higher for the oxidation of toluene, compared to the cryptomelane catalysts. The different reaction mechanisms established for the two types of catalysts (Langmuir-Hinshelwood for noble metals and Mars and Van Krevelen for metal oxides) can explain their catalytic performances.

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MICROPOROUS TITANOSILICATES FOR THERAPEUTIC NITRIC OXIDE RELEASE

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Nitric oxide (NO) is involved in several important physiological processes, like vasodilatation, prevention of platelet aggregation and thrombus formation, neurotransmission, and wound repair. NO delivery to the human body is becoming an attractive therapeutic alternative for a large number of pathologies. Traditional molecular donors are inadequate due to their wide non-selective distribution in the body ensuing unwanted side effects and may form carcinogenic compounds.

We started to explore the possibility of NO storage, for later therapeutic release, in microporous titanosilicates of the ETS family. The unsaturated Ti⁴⁺ framework centres in the ETS-4 can serve as NO binding sites to obtain a high NO storage capacity and slow NO delivery [1]. The presence of Co²⁺ and Cu²⁺ extra framework cations on ETS-4 increase significantly the storage and delivery capacity [2]. In this work, the results of the storage and release of NO by ETS-10 and samples where the silicon was substituted by aluminium (ETAS-10) or gallium (ETGS-10) [3] are presented and analysed in the context of previous works. ETAS-10 and ETGS-10 exhibit an increase in the storage capacity of 95% and 55%, respectively, attaining the highest values observed for titanosilicates, while maintaining an exceptionally low cytotoxicity (Figure 1).

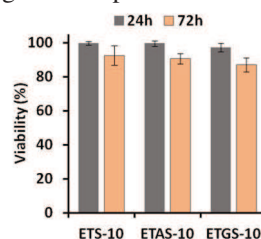


Figure 1. Cell viability after 24 and 72h contact with solutions of 0.45 mg cm⁻³.

Acknowledgements

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METAL-FREE CATALYSTS DERIVED FROM LIGNIN FOR EFFICIENT WET PEROXIDE OXIDATION

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In this work, a wheat and hemp lignin (Sarkanda, Granit S.A.) has been used as raw material for the development of metal-free activated carbons. These materials were tested in the catalytic wet peroxide oxidation (CWPO) of 4-nitrophenol (4-NP; 5 g L⁻¹) during 24 h experiments conducted at relatively mild operating conditions ($p = 1$ atm, $t = 50$ °C, pH = 3, catalyst load = 2.5 g L⁻¹ and $[H_2O_2]_0 = 17.8$ g L⁻¹).

First, the lignin was carbonized under N₂ atmosphere followed by the activation of the obtained non-porous carbon (LG) under air atmosphere at different temperatures (150 to 350 °C), leading to the generation of significant porosity. All materials present high concentration of basic groups at their surface, pointing them as appropriate for CWPO processes [1], even though the ratio basicity/acidity decreases when increasing the activation temperature. The materials activated at higher temperatures (300 and 350 °C) promoted an efficient H₂O₂ decomposition into HO• radicals, removing *ca.* 70 % of 4-NP (Figure 1). The H₂O₂ yields of homolysis ($\eta_{H_2O_2}$) observed in the elimination of the pollutant were close to 100 % in both cases. On the contrary, the materials prepared at the lower activation temperatures (150 and 200 °C) promoted a faster but inefficient H₂O₂ decomposition, conducting to a 4-NP removal lower than 25 % after 24 h. This low efficiency is mainly attributed to the formation of non-reactive species due to the recombination of the HO• radicals, and to the poor adsorption capacity of these materials, which do not favour the approximation of 4-NP to the active sites where HO• radicals are generated.

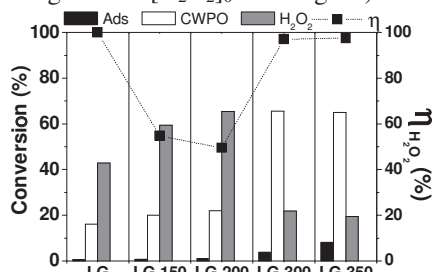


Figure 1. Removal of 4-NP by adsorption and CWPO; H₂O₂ decomposition and efficiency.

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GREEN ESTERIFICATION REACTIONS BY METAL PHOSPHATES AND PHOSPHONATES

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Green esterification reactions are of great importance to the industry worldwide.

The main product obtained by esterification of long chain fatty acids is biodiesel whose use has several environmental benefits. Esters obtained from small chain acids and alcohols are very important industrially. Several reactions, including oxidations, dehydrations and hydrogenations have been successfully catalysed by metal phosphates and phosphonates¹ due to their strong acidic nature^{2,3}. In our laboratory, in order to perform a comparative study with other catalysts, the esterification reactions of palmitic acid with methanol and of acetic and benzoic acid with several alcohols, were performed using α - and γ -zirconium phosphate (α - and γ -ZrP), zirconium phenylphosphonate (ZrPhP), zirconium carboxyethylphosphonate (ZrCEP), zirconium phosphate molybdate (ZrMoP), zirconium phosphate tungstate (ZrWP) and zirconium molybdate phenylphosphonate (ZrMoPhP). The reaction conditions of the different acetates and benzoate were optimized with **ZrMoPhP** by varying the amount of catalyst and solvent and the molar ratio of the alcohols relatively to the acids (**Table below**).

<i>Catalysts</i>	<i>Butyl Acetate</i>	<i>Pentyl Acetate</i>	<i>Ethyl Acetate</i>	<i>Butyl Benzoate</i>	<i>Methyl Palmitate</i>
Blank	45.0 %	37.0 %	40.2 %	14.8 %	20.0 %
ZrMoPhP	78.0 %	68.5 %	75.5 %	38.0 %	—
ZrMoPhP	80.5 %	86.0 %	86.0 %	60.0 %	—
γ -ZrP	—	—	—	—	45.0 %
γ -ZrP	—	—	—	—	86.0 %

The reaction conditions of the methyl palmitate were optimized with **γ -ZrP** following the former strategy (**Table above**). The optimization studies were very valuable because all the esters synthesized experienced an increase of their yield. The method followed for the variation of the different parameters will be discussed during the presentation with detail.

Acknowledgements

The authors would like to thank the Chemistry Department of the University of Aveiro for support.

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BIODIESEL PRODUCTION USING EGGSHELL AND OYSTER SHELL DERIVED CATALYSTS

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Heterogeneous basic catalysts have been widely studied as alternative to reduce the cost and the environmental pollution of biodiesel production. Test results have indicated the good catalytic performance of calcium oxide (CaO), a material easily obtained, for example, from industrial wastes [1, 2].

In this study, CaO was obtained by calcination of CaCO₃ of powdered eggshell and oyster shell under 900°C for 4h. Ultrasound irradiation and hydration-dehydration cycles were tested with these biocatalysts to improve the transesterification activity of CaO.

Eggshell samples were sonicated to reduce the particle size. The treatment was carried out for 1, 3, 5 and 7 hours before calcination.

Since these calcium oxide materials obtained from natural sources have little porosity [3], the calcined powdered oyster shells were subjected to a hydration technique to develop porosity. Six cycles of hydration-dehydration were performed. In the hydration step, the CaO remains in suspension in water for 4 hours and the solid is filtered and dried at 120°C overnight. In the dehydration step, the solid product is calcined at 600°C for 3 hours.

The biocatalysts were characterized by X-ray diffraction, N₂ adsorption and laser light scattering. The transesterification reaction of soybean oil with methanol, carried out in batch reactor is used as catalytic test. The activity of the catalyst samples was evaluated as the maximum reaction rate.

The preliminary results showed the increase in catalytic activity of CaO with the ultrasonic irradiation technique. The highest activity was obtained from the treatment with 5 hours of ultrasonic irradiation. This rate was 3 times higher than the rate obtained with untreated CaO. The catalysts derived from oyster shell showed even a higher catalytic activity.

Results are indicating that ultrasonic irradiation and hydration-dehydration cycles are promising techniques for activity improvement of CaO obtained from biologic sources.

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Poster Communications Abstracts

SYNTHETIC COBALT CLAYS FOR THE STORAGE AND SLOW RELEASE OF THERAPEUTIC NITRIC OXIDE

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Nitric oxide (NO) is one of the smallest endogenous molecules with particularly interesting roles in biological systems, despite its toxicological potential. [1] Solid carriers have potential biomedical interest in the delivery of exogenous NO for anti-bacterial, anti-thrombic and wound healing applications. [2, 3]

In this work, a smectite clay was successfully synthesized with incorporated cobalt ions in its structure, with the main goal of studying its potential in the field of storage and release of nitric oxide for therapeutic applications. Materials were characterized by X-ray diffraction (Philips PW 1730 diffractometer, nitrogen adsorption at -196 °C (Micrometrics, ASAP 2010), DLS (Zetasizer Nano ZS, Malvern Instruments) and chemical analysis of cobalt contents were obtained by Atomic Absorption Spectroscopy of digested samples using a Unicam 929 (ATI UNICAM) spectrophotometer.

The nitrogen adsorption-desorption isotherms show a high specific surface area, as recorded in Table 1, which is the result of a finely divided structure. In this table there are also the values of basal spacing (d_{001}).

The kinetic data for the nitric oxide storage and release was obtained in gas and liquid phases, as recorded in Table 1. The released amounts of NO in the liquid phase were within the biological range and slow release kinetics with a near direct relationship between the released fraction and time was observed. Toxicological assays with HeLa cells indicated that the materials have low cytotoxicity.

Table 1 – Textural parameters.

	$d_{(001)}$ (Å)	A_{BET} (m ² g ⁻¹)	[NO] _G (mg _{NO} /g _{solid})	[NO] _L (μg _{NO} /g _{solid})
MMT	12.6	20	2.1	8
CoAS-A	14.2	218	8.0	16
CoAS-B	11.9	41	8.5	47
CoOS	13.0	246	6.9	33

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CATALYSIS IN PHOSPHITE ADDITION TO UNSATURATED HYDROXAMATES: EN ROUTE TO ANTIMALARIALS

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Malaria is an important parasitic disease [1]. According to the World Health Organization, around 200 million cases were reported worldwide in 2013, including nearly 600 000 deaths [2]. The eradication of this disease is one of the UN's Millennium Development Goals. There are no vaccines available and chemical drugs are used both for prevention and control. Since the *Plasmodia* protozoa responsible for the disease develop resistance to existing drugs, the development of novel medicines or analogues of existing ones are active areas of research.

Fosmidomycin is an antimalarial antibiotic currently undergoing phase II trials. Known analogues of this phosphonohydroxamate have structural changes in the phosphonic group, the hydroxamate and the carbon spacer [3]. Fosmidomycin inhibits the enzyme 1-deoxy-D-xylulose-5-phosphate reductoisomerase, essential for isoprenoid biosynthesis in eubacteria and plasmodia, but not in humans. We envisioned that by constraining the mobility of the carbon spacer, enclosing both the phosphonic and hydroxamate groups into a ring, it would be possible to have a "better fit" to the enzyme and analogues with increased potency (Fig. 1). To obtain phosphonyl-substituted cyclic hydroxamates, a phospho-Michael addition reaction was developed. Due to the poor reactivity of the required unsaturated hydroxamates towards nucleophilic addition, catalysis was needed. Tetramethylguanidine was effective and products were obtained in good to high yields. Elaboration into prodrugs, provided one of the most potent analogues of fosmidomycin known today (IC₅₀ 27.4 nM against *P. falciparum* Dd2 resistant strain) with no significant cytotoxicity, i.e. a promising new lead for further research.

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INTERNALIZATION OF ZEOLITES AS CARRIERS FOR CELLULAR DELIVERY

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Scientists have been exploring new strategies in anticancer therapies using novel nanomaterials [1, 2]. Zeolites are solid inorganic crystalline nanomaterials with silicon, aluminum, and oxygen in 3D-dimensional structure and well-defined pore networks [3]. Their structure allows the preparation of drug delivery systems (DDS), improving the biodistribution of chemotherapy drugs by protecting them from degradation, delivering them directly to the tumour site and/or preventing them from affecting healthy tissues.

In the present work, we focused on the interaction of zeolites with breast cancer cells and epithelial mammary cells in order to evaluate the toxicity and cellular uptake of zeolites and to understand the mechanism underlying the endocytosis of zeolites. Thus, first we investigated the cytotoxicity of zeolites on normal and tumor cells and then we studied the interactions of zeolites with cells by using fluorescence microscopy, confocal laser scanning microscopy (CLSM) and scanning electron microscopy (SEM).

The results showed that the zeolites alone are non-toxic for both type of cells. The interaction studies showed that the cellular uptake is higher and faster in tumor cells than in normal cells and that the nanoparticles are mainly localized in the cytoplasm. These results support the potential of zeolites as carriers for cellular delivery.

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OZONATION OF SALICYLIC ACID OVER MONO AND BIMETALLIC ZSM5 CATALYSTS

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A large number of the administered pharmaceuticals is discharged in its active form or in form of metabolites, being hence present as contaminants into surface waters. The increasing presence of these pharmaceutical compounds in effluents can give rise to serious consequences, such as high risks to public health and to the environment. One of these emerging contaminants is salicylic acid (SA), a beta hydroxy acid chemically classified as monohydroxybenzoic acid, which is commonly used to treat comedonal or non-inflamed acne; SA is also the major metabolite and active component of aspirin (acetylsalicylic acid). Monitoring and elimination of the organic pollutants in waste water are of high importance. Catalysis employing structured materials is one of the methodologies proposed to reach this objective. In particular, catalytic ozonation has emerged as a powerful technology for the removal of such organic pollutants in water and waste water. In the present work, the ozonation of SA was found to be successfully catalyzed by mono and bimetallic catalysts based on ZSM5 zeolite.

ZSM5 with copper and palladium catalysts were prepared by the ion exchange method according to a previously published procedure [1] and were characterized by several techniques (N₂ adsorption, FTIR, XRD, SEM, TPR and adsorption microcalorimetry). The experimental conditions for the catalytic tests are reported in previous works [2]. The presence of metals (Cu or Pd) in the zeolite structure significantly improves the degradation of SA when compared to ozonation alone. After 3 h of reaction, the bimetallic catalysts lead to the highest mineralization degrees, with CuPd-ZSM5 presenting the best catalytic performance.

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ETS-10 SUPPORTED FERROCENIUM IONS: APPLICATION IN ISOMERISATION OF α -PINENE OXIDE

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Ferrocenium ions, $[\text{Fc}]^+$, have been immobilised in the microporous titanosilicate ETS-10 by ion exchange of Na^+/K^+ ions under hydrothermal conditions, giving a deep blue solid denoted as $\text{ETS-10}/[\text{Fc}]^+$. The obtained solid was characterised by elemental and thermogravimetric analysis, UV-Vis and FT-IR spectroscopies, powder X-ray diffraction and scanning electron microscopy [1].

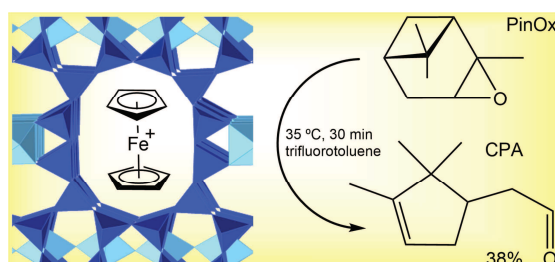


Figure 1. Structure of ETS-10 (polymorph B) and supported ferrocenium, $[\text{Fc}]^+$, which promotes the isomerisation of PinOx to CPA.

The hybrid inorganic-organometallic material $\text{ETS-10}/[\text{Fc}]^+$ was tested as a catalyst for the isomerisation of α -pinene oxide (PinOx), under mild conditions. The influence of the initial $\text{Fe}:\text{PinOx}$ molar ratio, the reaction temperature and type of solvent (trifluorotoluene, hexane, toluene, CH_3CN) were studied. Campholenic aldehyde (CPA) was always the main product, formed with 38% yield at 100% conversion (30 min reaction at 35 °C). $\text{ETS-10}/[\text{Fc}]^+$ was fairly stable towards metal leaching [1].

Acknowledgements

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[FeCl₂(HCpz₃)] HETEROGENIZED AT HIERARCHICAL FAU FOR ECO-FRIENDLY ALKANE OXIDATIONS

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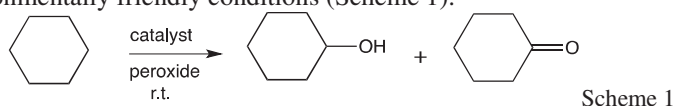
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The purpose of this work is i) the preparation of hierarchical materials based on FAU zeolite to work as supports for the immobilization of a C-scorpionate iron(II) complex, the [FeCl₂(HCpz₃)] (pz = pyrazolyl) [1], and ii) their use as heterogeneous catalysts for the oxidation alkanes, namely of cyclohexane to cyclohexanol and cyclohexanone under environmentally friendly conditions (Scheme 1).



Hierarchical FAU supports were prepared according to the procedure from [2] using NaOH or TPAOH in the presence of hexadecyltrimethylammonium bromide under autogenous pressure. Table 1 shows the main properties of the supports.

Table 1. Crystallinity (C_{XRD}) from X-ray patterns and textural parameters calculated from N₂ adsorption isotherms: microporous (V_{micro}) and mesoporous (V_{meso}) volumes.

Sample	C _{XRD} (%)	V _{micro} ^a (cm ³ g ⁻¹)	V _{meso} ^b (cm ³ g ⁻¹)
FAU	100	0.29	0.08
FAU/NaOH	94	0.26	0.15
FAU/TPAOH	92	0.23	0.18

^aEstimated from α_s method; ^bV_{meso}=V_{total}-V_{micro}, where V_{total} is volume adsorbed at p/p^o=0.95

The heterogeneous catalysts were prepared using two immobilization procedures: the wet impregnation and the incipient wetness impregnation.

The catalytic tests have shown that these heterogeneous systems exhibit a similar catalytic activity to that found for the C-scorpionate complex in homogeneous media [1] with the advantage of easy separation and re-use.

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LIGHT HYDROCARBONS PRODUCTION OVER BIMETALLIC Ca-F BLOCK ELEMENT NANOPARTICLES

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The oxidative coupling of methane (OCM) to light hydrocarbons using oxide catalysts has been investigated for many research groups in the last decades. Recently, the nitrous oxide has been shown to be an excellent oxidant for performing some difficult oxidation processes [1, 2], but for production of C₂ hydrocarbons have never been referred in literature. The use of a number of calcium oxide-based catalysts [3-4] for the OCM has been reported in the literature.

The purpose of this work was to study the catalytic behavior of bimetallic Ca-f block element for the C₂ hydrocarbons production (ethylene and ethane) using nitrous oxide as oxidant agent. The results demonstrated that nanoparticles of calcium-rare earth oxides (Fig. 1A) were active and selective for production of C₂ at 750 °C. At isoconversion of methane (around 27±2 %) the selectivity to C₂ hydrocarbons is very different (e.g. 56% for Ca-Gd and 30% for Ca-Ce oxides) (Fig. 1B). These results suggest that catalytic behavior is dependent of the actinide/lanthanide properties.

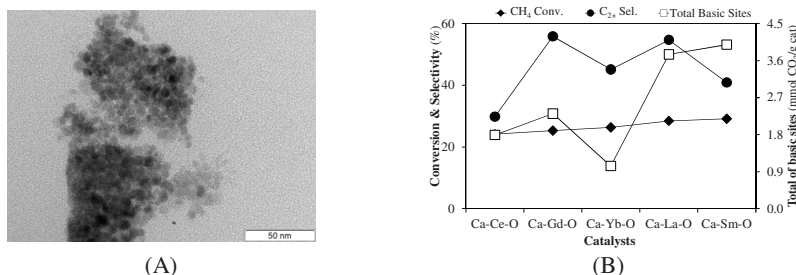


Figure 1. (A) TEM image of bimetallic Ca-Yb nanoparticles; (B) Influence of basicity on the catalytic performance of bimetallic Ca-Ln nanocatalysts.

Acknowledgements

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INFLUENCE OF THE NANOSTRUTURE OF BIMETALLIC *f* BLOCK ELEMENTS OXIDES IN OXIDATION OF METHANE

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Electrospinning is a technique that has been originally developed to produce ultra-fine polymer fibers [1-3]. Herein, we describe the use electrospinning for the preparation of bimetallic oxides nanofibers/nanoparticles containing *f*-block elements, who's expected high surface areas can bring benefits to their catalytic properties, namely, for the valorization of primary pollutants (e.g. CH₄, CO₂ or N₂O). So far, electrospinning was successfully applied to the preparation of bimetallic nanoparticles of 4NiO.LaNiO₃, Co₃O₄.SmCoO₃ and Fe₃O₄.DyFeO₃, with a particle size <30 nm in all cases. All nanostructured bimetallic oxides were characterized by XRD and SEM-EDS. Other parameters such as calcination temperature and the reducibility of these oxides were also studied. Figure 1 shows the he XRD patterns of NiO and LaNiO₃ (a), SEM image of 4NiO.LaNiO₃ nanoparticles (b) SEM image of 4NiO.LaNiO₃ nanofibers (c).

The influence of the nanostructure in the catalytic activity will be discussed.

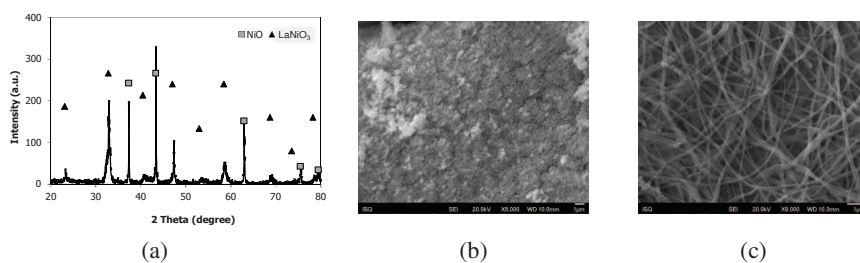


Figure 1. Bimetallic oxide La-Ni characterization (a) XRD pattern, (b) SEM image of La-Ni nanoparticles, (c) SEM image of La-Ni nanofibers.

Acknowledgements

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CATALYTIC REDUCTION OF HEXACYANOFERRATE(III) BY GOLD NANOPARTICLES PRODUCED IN TEA

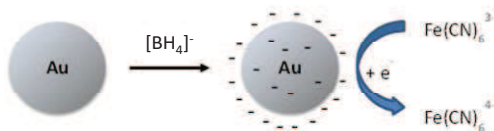
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A rapid and room temperature eco-friendly reaction for the synthesis of gold nanoparticles (AuNPs) in aqueous solution of $[\text{HAuCl}_4]$, using tea extract as a reducing and capping agent, was performed. The resulting NPs were characterized with transmission electron microscopy (TEM), SEM, UV-Visible (UV-Vis), energy dispersive X-ray spectroscopy (EDX), and X-ray diffraction (XRD). TEM experiments showed that AuNPs presented a spherical shape and size ranging within 10-30 nm. The obtained AuNPs were successfully tested as efficient catalysts in the reduction of hexacyanoferrate(III) in aqueous solution under mild conditions.



The effects of a variety of factors (*e.g.*, reaction time, type and amount of reducing agent, and shape, size or amount of AuNPs) were studied towards the optimization of the processes. Kinetic studies for the reduction reactions using these AuNPs fitted well to a pseudo first-order reaction kinetics model.

Acknowledgements

This work has been supported by the Fundação para a Ciência e a Tecnologia (FCT), Portugal, its project UID/QUI/00100/2013 and fellowship SFRH/BPD/90883/2012 to A.P.C.R.

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GC-MS AS A VALIABLE TOOL FOR THE IDENTIFICATION OF PRODUCTS FROM HYDROFORMILATION OF NATURAL PRODUCTS

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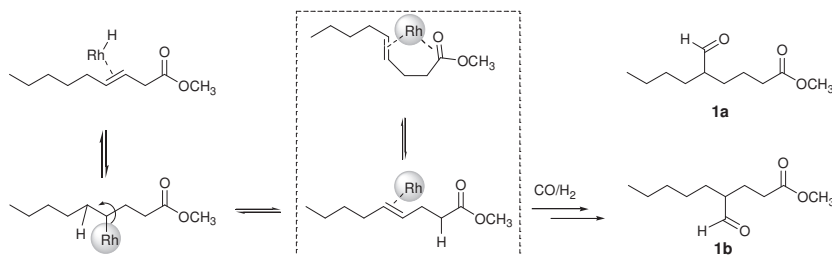
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Mass spectrometry is a sensitive technique used to detect and identify molecules based on m/z values and fragmentation patterns, which coupled with gas chromatography allows the separation and characterization of volatile compounds in complex samples, particularly relevant for natural products [1].

In this communication, we present the preparation of value-added products *via* hydroformylation of methyl non-3-enoate as model substrate and natural products such as methyl oleate, terpenes and steroids, using rhodium/monophosphite catalysts either under conventional heating or microwave irradiation using a CEM® Discover system equipped with syngas addition kit.

The development of an analytical method for the identification of the resulting aldehydes revealed to be a crucial tool for the full understanding of the reaction mechanism and for determination of conversion chemo- and regioselectivity.



Scheme 1. Proposed pathway for Rh/phosphite-catalysed hydroformylation of methyl non-3-enoate.

For example, the formation of both aldehydes 1a and 1b suggested by observation of two ¹³C NMR signals at $\delta = 202.2$ ppm and 203.6 ppm was corroborated by the mass fragmentation, which proved to be essential to clarify the unexpected regioselectivity [2], Scheme 1.

Acknowledgements

The authors thank Fundação para a Ciência e a Tecnologia (FCT) for the financial support to Coimbra Chemistry Centre (PEst-OE/QUI/UI0313/2014) and to the UC-NMR facility.

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PERFORMANCE STUDY OF Au-TiO₂ CATALYSTS IN THE LOW-TEMPERATURE WATER GAS SHIFT REACTION

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The water-gas shift (WGS) is an industrially relevant reaction with application in several important processes (e.g. ammonia manufacture, methanol production, Fischer-Tropsch synthesis or hydrogen production). However, active and stable WGS catalysts for low temperature processes (aiming for instance their use in hydrogen-fed fuel cell applications) are still a challenge.

Different Au/TiO₂ catalysts were synthesized by three methods: Double Impregnation Method (DIM), Deposition-Precipitation (DP) and Liquid Phase Reductive Deposition (LPRD). For each synthesized method three different gold loadings were obtained, up to ca. 2.5 wt. %, identified as 1, 2 or 3 for low, intermediate or high amounts, respectively. The catalysts were tested for the low temperature WGS reaction. The prepared materials were characterized by High-Resolution Transmission Electron Microscopy (HR-TEM), X-Ray Diffraction (XRD), X-Ray Photoelectron Spectroscopy (XPS), Temperature Programmed Reduction (TPR) and Absorption Atomic Spectroscopy (AAS). The performance of the synthesized catalysts was compared between them and with a commercial material – Au/TiO₂-WGC (supplied by the World Gold Council). Based on the CO conversions (X_{CO} ; cf. Figure 1) and turnover frequencies (TOFs) obtained in the WGS reaction, the Au/TiO₂ DP-3 material was selected as the best synthesized catalyst, with a $X_{CO} \approx 85\%$ at 300 °C (X_{CO} of the WGC sample was $\approx 52\%$ at 300 °C). The Au/TiO₂ DP-3 material has small gold nanoparticles before and after use, which can account for the improved catalytic activity, well known to be related with gold nanoparticle size. However, stability was found to be better for the WGC sample.

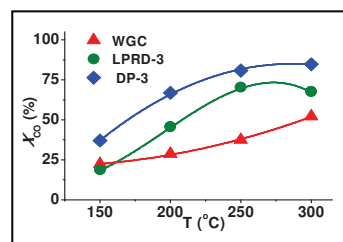


Figure 1. Best catalysts performances (Feed Composition: 4.76%-CO, 10.06%-CO₂, 28.46%-H₂, 35.38%-H₂O and 21.34%-N₂).

Acknowledgements

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BROMATE REDUCTION UNDER HYDROGEN USING METAL CATALYSTS ON DIFFERENT SUPPORTS

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Heterogeneous catalysis has already been demonstrated to be an efficient method for the bromate removal from water by hydrogen reduction to more desirable species [1]. The use of different supports for active metallic phases has shown to potentially modify activity in similar catalytic reactions [2]. In addition, the utilization of monolithic catalytic reactors in water treatment has demonstrated to present advantages in continuous operations [3]. In this work we aim to evaluate the catalytic reduction of bromate by using different supports for the catalytic metallic phase, and their application in continuous operation as structured catalysts.

Three different supports for the metal catalysts (Pd, Pt, Rh, and Ru) were previously selected through screening [1] were selected for the bromate reduction under hydrogen: activated carbon (AC), multiwalled carbon nanotubes (MWCNT) and titanium dioxide (TiO₂). In all cases, the metal catalysts supported on MWCNT and TiO₂ showed a widely better performance when compared with those supported on activated carbon (increase of TOF in the order of 10³-10⁴). TiO₂ support was observed to be the best performing catalysts (Figure 1) due to the interactions between metal and support. Pd catalyst supported on MWCNT and TiO₂ covered monolithic supports showed bromate conversions up to 87% and 85%, respectively.

Acknowledgements

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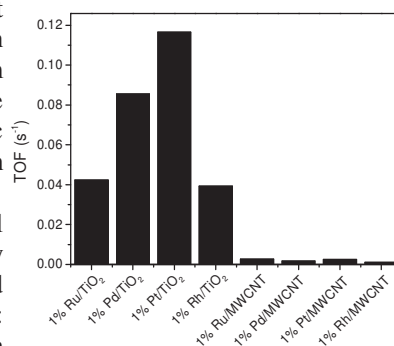


Figure 1. Turnover frequencies after 1 min of reaction using catalysts supported on TiO₂ and MWCNT.

HETEROGENEOUS ACID CATALYSTS FOR CONDENSATION OF FURFURAL AND 2-METHYLFURAN

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Filling the gap between energy demand and petroleum availability is the key word for recent researches, preferably from green sources and using cost competitiveness concepts.[1] Biomass-derived fuel hydrocarbons have been prepared by catalytic conversion of sugar-derived compounds. Furfural, levulinic acid or 5-hydroxymethyl furfural and their derivatives are used as oxygenated additives in fuels and added-value chemicals. [2]

In this work we report on the activity and selectivity of heterogeneous acid catalysts in the condensation of furanic derivatives, which can serve as viable platforms for the production of diesel, starting from biomass-derived reactants.

SiO₂, MWCNTs and SWCNTs were functionalized with 2-(4-chlorosulfonylphenyl)ethyltrimethoxysilane (CSPTMS) and with GPTMS (Glycidoxypropyltrimethoxysilane). The functionalized materials were applied as heterogeneous acid catalysts in the selective condensation of furfural and 2-methylfuran into 5,5'-bis(2-methylfuranyl)furan-2-ylmethane (BMFFM). The condensation reaction proceeded at room temperature and 65 °C. Conversion of almost 100% of furfural into the condensation product was obtained in only 15 min. Conversion and selectivity were obtained by ¹H NMR and gas chromatography. The recovery and reusability were also evaluated and a good reusability was obtained, with no losses of activity, up to the 7th catalytic cycle.

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POLYOXOMETALATES @ SBA-15 TO CATALYZE OXIDATIVE DESULFURIZATION OF MODEL DIESEL

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Crude oil remains the major energy source from fossil fuels, which has high sulfur content because of its high levels of organic polyaromatic sulfur compounds such as dibenzothiophene derivatives (DBTs). The desulfurization of such crude oil is of extremely importance due to the impact of SO₂ release during combustion of fuels, in the environment and human health. Hydrodesulfurization is the conventional method implemented in the refining industry to deal with this problem. However, this is an expensive process, which requires severe reaction conditions such as high pressure and temperature as well as high hydrogen consumption. As so, alternatives to this process have been proposed, one of which is the oxidative desulfurization (ODS). This process exhibits mainly high efficiency on the removal of aromatic sulfur compounds operating under mild reaction condition of pressure and temperature and without hydrogen consumption.

Polyoxometalates are metal oxygen clusters that possessing high efficient catalytic properties in oxidative desulfurization processes. [1,2] Over the last years, mesoporous silica materials with uniform mesoporous channel structure and high specific surface areas, thermal stability, lightweight, and extending framework composition have been employed as supports to form novel robust heterogeneous catalyst. Among the various mesoporous materials, SBA-15 stands out for its higher hydrothermal stability and its large pore sizes. [3]

In this work, heterogeneous catalysts based in amine functionalized SBA-15 and Keggin-type POMs were prepared and investigated in oxidative desulfurization processes using a model diesel containing various refractory sulfur compounds (1-benzothiophene, dibenzothiophene, 4-methyldibenzothiophene and 4,6-dimethyldibenzothiophene), using H₂O₂ as oxidant. Total desulfurization was achieved under mild reaction conditions and the recyclability and the robustness of the catalysts were investigated.

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BENZAFIBRATE REMOVAL BY COUPLYNG OZONATION AND PHOTOCATALYSIS: A KINETIC STUDY

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Benzafibrate (BZF) is a lipid regulator for the treatment of hyperlipidaemia and it is included in the list of the most used pharmaceuticals in the world [1]. Due to large consumption and inefficient removal, BZF has been frequently detected in the aquatic environment [2, 3]. The present study is focused on the degradation of BZF by coupling ozonation and photocatalysis under different operational conditions. The kinetic results were evaluated in terms of BZF and total organic carbon (TOC) removals, toxicity, by-products and ions released.

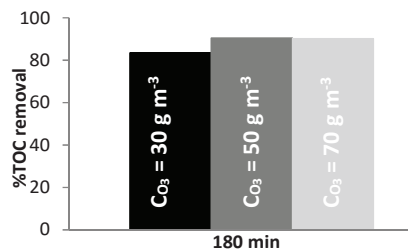


Figure 1. % of TOC removal during BZF degradation.

The half-life of the first-order reaction decays for BZF degradation by photocatalytic ozonation in the presence of P25 (commercial TiO₂) under different O₃ gas concentrations are presented in Table 1.

Table 1. Half-life of the first-order reaction decays on the photocatalytic ozonation of BZF under different O₃ dosages (C₀ = 20 mg L⁻¹, C_{cat} = 0.5 g m⁻³, pH_{natural} ≈ 4.4).

C ₀₃ (g m ⁻³)	t _{1/2} (min)
30	2.1
50	1.6
70	1.1

The experimental results revealed that BZF degradation rate increased with the O₃ concentration. O₃ by itself is an extremely powerful oxidant capable of reacting with a vast range of compounds, and it attacks selectively aromatic moieties and unsaturated bonds, such as those present in BZF. Therefore, an increase in O₃ dosage would result in an increase in dissolved O₃, which means a higher molar ratio of O₃ to BZF. On the other hand, the TOC removal was not practically affected by the O₃ dosage.

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[VO₂{HB(3,5-Me₂pz)₃}] SUPPORTED AT HIERARCHICAL MOR FOR ECO-FRIENDLY CYCLOHEXANE OXIDATION

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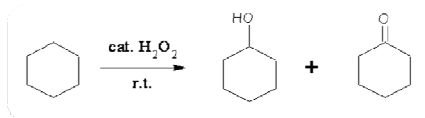
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In this work hierarchical MOR zeolite was used as support for the immobilization of B-scorpionate dioxido-V(V) complexes, *e.g.*, [VO₂{HB(3,5-Me₂pz)₃}] [1]. The immobilized complexes were tested as catalysts for the oxidation of cyclohexane, with hydrogen peroxide, to cyclohexanol and cyclohexanone under environmentally friendly conditions (see Scheme below).



Hierarchical MOR supports were prepared according to the procedure from [2] using NaOH or TPAOH in the presence of hexadecyltrimethylammonium bromide under autogenous pressure. Table 1 shows the main properties of the supports.

Table 1. Crystallinity (C_{XRD}) from X-ray patterns and textural parameters calculated from N₂ adsorption isotherms: microporous (V_{micro}) and mesoporous (V_{meso}) volumes.

Sample	C _{XRD} (%)	V _{micro} ^a (cm ³ g ⁻¹)	V _{meso} ^b (cm ³ g ⁻¹)
MOR	100	0.19	0.04
MOR/NaOH	90	0.16	0.11
MOR/TPAOH	88	0.14	0.09

^aEstimated from α_c method; ^bV_{meso}=V_{total}-V_{micro}, where V_{total} is volume adsorbed at p/p^o=0.95

The heterogeneous catalysts were prepared by the incipient wetness impregnation method. The catalytic tests have shown that the V(V) heterogeneous systems can be used as selective catalysts for the oxidation of cyclohexane to the mixture of cyclohexanol and cyclohexanone, under very mild conditions, allowing their easy separation and recycling.

Acknowledgements

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NANOCARBONS AS ADDITIVES FOR THE BAEYER-VILLIGER OXIDATION OF KETONES

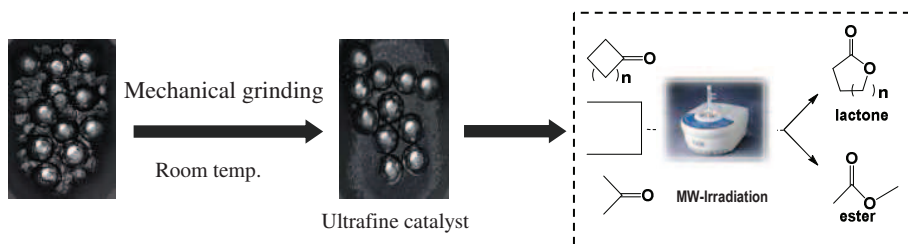
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Bimetallic composites (Re/V, Re/Cu and Re/Fe) were prepared by ball milling and characterized by scanning electron microscopy (SEM), field emission gun scanning electron microscopy (FEGSEM), energy-dispersive X-ray spectroscopy (EDX) and transmission electron microscopy (TEM). The catalytic properties of the prepared bimetallic composites were explored for the microwave-assisted Baeyer-Villiger oxidation of cyclohexanone with hydrogen peroxide. Addition of small amounts (0.1-5%) of nanocarbon materials, carbon nanotubes (CNTs) or graphene oxide (GO) leads to a significant improvement (up to *ca.* 35 times) in the catalytic performance of the prepared composites.



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SUPPORTED GOLD NANOPARTICLES AS REUSABLE CATALYSTS FOR ALKANE OXIDATION REACTIONS

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Four different types of oxides: Al₂O₃, Fe₂O₃, ZnO and TiO₂ were used as supports for gold nanoparticles. The metal was deposited on the oxide supports (1% wt.) by a deposition-precipitation method [1].

The oxides and the AuNPs@oxide catalysts were characterised by N₂ adsorption at -196 °C, XRD, TPR, SEM and XPS. EDS confirmed the nature of the components, namely the presence of gold. Images of oxides and gold loaded materials were obtained by TEM (Figure 1). Gold nanoparticles are seen as darker spots.

The catalytic activity of gold nanoparticles supported on Al₂O₃, Fe₂O₃, ZnO and TiO₂ exhibits pronounced activity towards the heterogeneous oxidation of inert alkanes, namely cyclohexane, in a H₂O₂ or *t*-BuOOH (TBHP)/HNO₃ (if used)/CH₃CN+H₂O system, at 60 °C. Control experiments in the absence of the Au NPs (yielding up to 0.2% of oxygenated products) confirm the crucial role of the nanoparticles to efficiently catalyse the oxidation of cyclohexane. Au@Al₂O₃ is the less active (1.3%), whereas for Au@TiO₂ and Au@ZnO the yield values (*ca.* 4%) are comparable with those of the current homogeneous Co catalyst industrial process. Au NPs supported on Fe₂O₃ led to the best results (13.5%). The presence of an acidic medium (*e.g.*, nitric acid), as well as the use of TBHP, show an inhibitory effect of the catalytic activity of the Au@Fe₂O₃ system. Another advantage of these systems is their easy separation from the reaction products and their recyclability.

Acknowledgements

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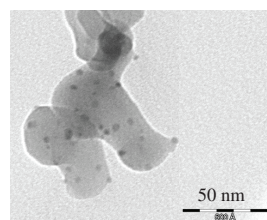


Figure 1. TEM image of Au@Fe₂O₃.

SUSTAINABLE CARBON MATERIALS AS SUPPORT FOR OXIDATION CATALYSTS

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Despite the greater number of studies focused on the immobilization of catalytically active metal complexes onto solid matrices this remains a hot research topic since the use of immobilized catalysts allows an ease separation of the reaction medium enabling successive reuses.

Inorganic materials, such as, silicas, clays or zeolites, and carbon materials, like carbon fibers, are among the most explored solids as catalyst support matrices. On the contrary, the use of activated carbons or other carbon materials prepared by less conventional methodologies is much more restricted. In this context the goal of this work is to test the potential of carbon materials obtained by acid hydrolysis of biomass followed by polycondensation [1], as catalyst supports.

A sisal derived carbon material was derivatized with a Mo complex – $[\text{MoI}_2(\text{CO})_3(\text{MeCN})_2]$ which binds to the surface of the carbon material with displacement of the labile acetonitrile ligands.

Materials were characterized by spectroscopic methods (FTIR, DRX), as well as SEM, TEM, thermogravimetry analysis, and N_2 adsorption at $-196\text{ }^\circ\text{C}$.

Selective olefin epoxidation is a very important process as epoxides are relevant building blocks across many areas. The synthesized materials have been tested in oxidation catalysis of enantioselective epoxidation of olefins (*cis*-cyclooctene, styrene and R-limonene) with tertiary butyl hydroperoxide at $55\text{ }^\circ\text{C}$ in dichloromethane during 24 h. Results (conversions, yields and enantiomeric excesses) were analyzed by gas chromatography-mass spectrometry (GC/MS). Kinetic profiles reproduced in Fig. 1 exemplify the results obtained, showing that the carbon material does not hold any intrinsic catalytic activity towards epoxidation of *cis*-cyclooctene but, conversely, Mo-derivatized material showed high catalytic activity towards the epoxidation of this olefin.

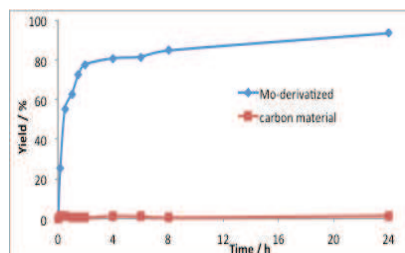


Figure 1. Kinetic profile for *cis*-cyclooctene epoxidation catalyzed by carbon material and Mo-derivatized catalyst.

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SUPPORTED COPPER(II) COMPLEXES OF ARYLHYDRAZONE OF 1H-INDENE-1,3(2H)-DIONE AS CATALYST FOR ALCOHOL OXIDATION

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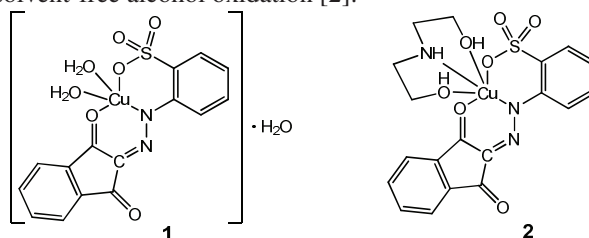
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1H-indene-1,3(2H)-dione or its derivatives are one of the most versatile families of reagents in organic chemistry [1]. Cu^{II} complexes (Scheme 1) have been synthesized and supported in MWCNT (microwalled carbon nanotubes) and Al₂O₃, by wet impregnation method. They have been characterized by SEM, TEM and XRD and applied to the solvent-free alcohol oxidation [2].



Scheme 1 - Schematic representations of Cu(II) complexes (1 and 2).

Results show that the activity of the catalyst is enhanced, and that for the same reactional time, higher yield is achieved when compared with the homogeneous process. Several reactional parameters will be presented and discussed.

Acknowledgements

Funding from FCT (Fundação para a Ciência e a Tecnologia, Portugal) (UID/QUI/00100/2013, PTDC/REQ-ERQ/1648/2014 and G.A.O.T. and A.P.C.R. are thankful to the CATSUS doctoral and post-doctoral programs of FCT for their PhD and post-doc fellowship, respectively.

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METAL-ORGANIC FRAMEWORKS PREPARED IN IONIC LIQUIDS: CATALYTIC PERFORMANCE

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Over the last decade ionothermal syntheses has been the subject of wide attention by taking advantage of ionic liquids' (ILs) numerous distinguishing features: high ionic conductivity, non-flammability and negligible vapour pressure, among many other.[1] ILs have been applied as reaction media, structural templates or charge-compensating groups, thus contributing greatly to the formation of new materials with unique structural properties.[2] Metal-Organic Frameworks (MOFs) consist of metal centres connected by organic molecules, known as ligands or linkers, usually obtained by conventional hydro/solvothermal methods, and this type of porous materials possess remarkably interesting applications in gas storage, catalysis and electronic chemistry, among others [3].

In the present work, two cobalt MOF materials (Figure 1) have been synthesized by means of 1,4-benzenedicarboxylic acid (H₂BDC) reacting with a Co(NO₃)₂·6H₂O salt in two different 1-alkyl-3-methylimidazolium bromides, acting as ionic medium instead of the traditional hydro-solvothermal one. Both MOFs structures were determined by single-crystal X-ray diffraction as layered metal-organic frameworks with the chemical formula [RMI]₂[Co₃(BDC)₃Br₂], (R = ethyl and propyl; MI = imidazolium) and further characterization was ensued by Powder X-ray diffraction, FT-IR and TGA techniques.

Posteriorly, the materials were tested as heterogeneous catalysts under sustainable environments for styrene oxidation.

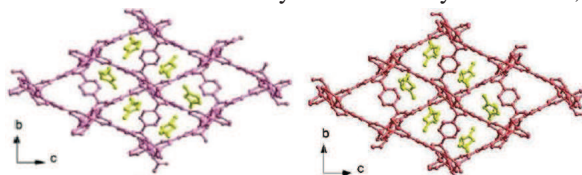


Figure 1. Structural representation of the Co-MOFs obtained by ionothermal synthesis

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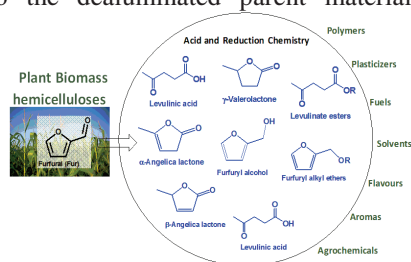
ONE-POT CONVERSION OF FURFURAL IN THE PRESENCE OF A Sn,Al-CONTAINING ZEOLITE BETA CATALYST

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The one-pot conversion of furfural (Fur) to useful bio-products, namely furfuryl alkyl ethers, levulinate esters, levulinic acid, angelica lactones and γ -valerolactone, was investigated using a heterogeneous inorganic catalyst, in 2-butanol, at 120 °C (Scheme 1) [1]. Different catalytic materials which consisted of modified versions of zeolite beta containing Al and Sn sites, were prepared from commercially available nanocrystalline zeolite beta via post-synthesis partial dealumination followed by solid-state ion-exchange. The material with Si/(Al + Sn) = 553 (Sn/Al = 27.6) was the best performing catalyst, with 83% total yield of bio-products at 86% Fur conversion, and steady catalytic performance in six consecutive batch runs. The superior catalytic performance was attributed to homogeneous Sn dispersion and enhanced incorporation of (tetrahedral) Sn-sites into the dealuminated parent material. Systematic catalytic studies using the prepared catalysts with different intermediates as substrates, together with the molecular level and microstructural characterisation of the materials, helped understand the effects of different material properties on the specific reaction pathways in the overall system. These studies led to mechanistic insights into the reaction network of Fur to the bio-products in alcohol media.



Scheme 1. Conversion of Fur in alcohol media to give useful bio-products via acid/reduction chemical routes.

Acknowledgements

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INFLUENCE OF THE POROUS SUPPORT ON POLY-OXOMETALATE-BASED DESULFURIZATION CATALYSTS

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Sulfur is the most abundant element in petroleum after carbon and hydrogen. The removal of sulfur from oil is one of the central requirements in most refineries and the price of crude oil is influenced by its sulfur content. The strict sulfur directives together with the high cost of the hydrodesulfurization process currently used is motivating the development of alternative or complementary desulfurization technologies. Much more research needs to be performed by the scientific community on novel desulfurization technologies, in particular the development of stable and selective catalytic systems capable of efficiently desulfurizing fuels, with a high capacity to be reused. In the last decade, polyoxometalates (POMs) have been shown to be efficient catalysts for the activation of oxidants in desulfurization processes. Successful results using POMs and hydrogen peroxide to desulfurize model oils and liquid fuels were reported.[1] Our research work has focused on the development of more efficient and sustainable oxidative desulfurization systems using POM catalysts. Various porous materials have been used and the performances of the heterogeneous desulfurization systems have been compared with the corresponding homogeneous POM catalysts.[2-3]

The present communication aims to identify and to compare the efficiency of different porous heterogeneous POM-based catalysts (mainly using MOFs and silica support materials) for the oxidative desulfurization of model and untreated diesels (provided by Galp Energia).

Acknowledgements

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CATALYTIC ESTERIFICATION USING HYDROTHERMALLY SYNTHESISED CARBON SPHERES

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Carbon spheres have drawing the attention of the scientific community due to their high electrical conductivity and excellent chemical stability, that can also be allied to a developed porosity. As a consequence, the potentialities of these materials as supercapacitors, catalyst supports and adsorbents have being explored.

One possible strategy to synthesize these type of materials is through hydrothermal treatments. The most commonly used carbon precursors to prepare hydrochars are renewable biomasses, *e.g.*, glucose, xylose, maltose, sucrose, amylopectin or starch.[1]

The carbon spheres tested in this study were obtained by a one-step procedure using sucrose or glucose aqueous solutions in the presence of acrylic acid. The solids have acidic surfaces due to the presence of carboxylic acids and alcohols, as demonstrated by the Bohems titration results, and pH_{pzc} values of *ca.* 2.0. These surface characteristics allowed us to consider their use as catalysts for esterification reactions which in industry (*e.g.* production of biodiesel and food industry) are usually catalysed by strong acids as H_2SO_4 . [2] The results obtained so far point out the potentialities of these materials as alternatives to strong inorganic acids, being a step forward to turn esterification a more green process.

Acknowledgements

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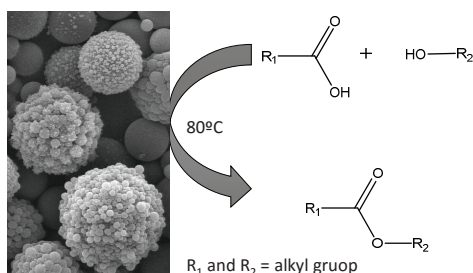


Figure 2. Esterification catalysed by synthetic carbon spheres.

SYNTHESIS AND CHARACTERIZATION OF MAGNETICALLY RECOVERABLE PORPHYRINS CATALYSTS

César A. Henriques^{a,*}, Auguste Fernandes^b, Liane M. Rossi^c, M. Filipa Ribeiro^b, Mário J. F. Calvete^a, Mariette M. Pereira^a

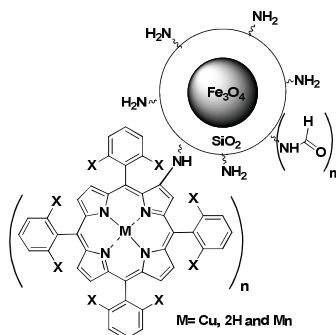
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Magnetic nanoparticles (MNP) possess superparamagnetic behavior under certain particle size, as they agglomerate upon application of an external magnetic field and immediately redispersed after magnet field removal.¹ This feature, combined with straightforward modulation ability bestows them unsurpassable applicabilities, particularly in catalysis and imaging. Additionally, metalloporphyrins are excellent biomimetic catalysts in a vast array of transformations, especially in oxidations, nevertheless presenting some limitations regarding reusability and degradation issues.² Thus, the symbiotic effect of anchoring metalloporphyrins onto MNPs may offer an advantageous process to promote non-laborious, inexpensive and often highly scalable oxidation reactions, possessing high magnetic recyclability, which might be particularly valuable both for academia and industry.³



In this work, an efficient synthetic method for magnetically recoverable hybrid metalloporphyrins nanomaterials and characterization by TG-DSC, IR and N₂ sorption are reported.

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[VCl₃{η³-HC(pz)₃}]@CNT AS CATALYST FOR THE MICROWAVE-ASSISTED OXIDATION OF XYLENES

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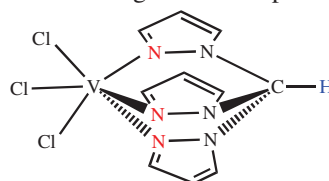
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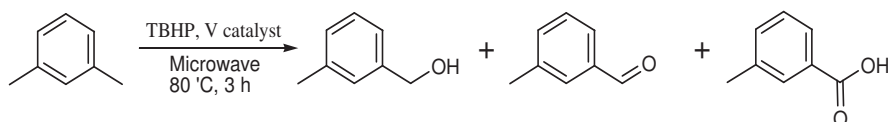
Oxidation is a widely used synthetic route for a large range of chemicals. Important oxidation substrates are alkyl aromatics, such as xylenes [1]. However, the oxidation of xylenes with peroxides, as well as under heterogeneous conditions, is scarce. This prompted us to consider the application of a catalyst able to oxidize alkanes in homogeneous conditions [2] to the heterogeneous oxidation of different xylenes. This was carried out through heterogenisation of a homogeneous complex on a heterogeneous carbon support.

The C-scorpionate trichloro-vanadium (III) complex [VCl₃{η³-HC(pz)₃}] (pz = pyrazolyl) [1], shown in Scheme 1, was supported on multi-walled carbon nanotubes (CNT) and characterized by SEM, TEM, BET and XPS.



Scheme 1 – Vanadium complex [1].

The heterogenized complex was used as catalyst for the MW-assisted solvent-free oxidation of xylenes with *tert*-butyl hydroperoxide (TBHP), under mild conditions (see Scheme 2 for *m*-xylene, where the main products are *m*-methylbenzylalcohol, *m*-methylbenzaldehyde and *m*-methylbenzoic acid). The effects of different reaction parameters are discussed.



Scheme 2 – Oxidation of xylene under solvent free conditions.

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Au NPS @ CARBON MATERIALS AS CATALYSTS FOR MW-ASSISTED SOLVENT FREE OXIDATION OF ALCOHOLS

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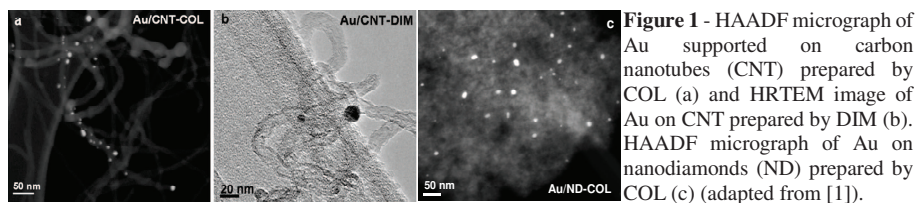
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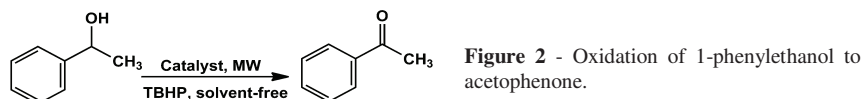
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Gold catalysts are currently a “hot topic” of research, as they show application in many reactions of industrial and environmental importance.

Au (1 wt.%) was loaded on different types of carbon materials, such as activated carbon, silicon carbide, graphite, polymer based carbon xerogels, multi-walled carbon nanotubes, nanodiamonds and microdiamonds using colloidal immobilisation (COL) and double impregnation (DIM) methods [1]. Materials were characterised by N₂ adsorption at -196 °C, TPD, XRD, XPS, AAS, HAADF and HRTEM (Fig. 1).



The Au/carbon materials were used as catalysts for the oxidation of 1-phenylethanol to acetophenone (as a model reaction, see Fig. 2) with aqueous *tert*-butyl hydroperoxide (TBHP), under several reaction conditions. The differences in the catalytic activity of the hybrid materials are discussed.



Acknowledgements: FCT for projects UID/QUI/00100/2013, PTDC/QEQ-ERQ/1648/2014 and PTDC/QEQ-QIN/3967/2014. The LA LSRE-LCM acknowledges. The LA LSRE-LCM was co-financed by FCT and FEDER through COMPETE 2020 (Project UID/EQU/50020/2013 - POCI-01-0145-FEDER-006984). SACC acknowledges Investigador FCT program (IF/01381/2013/ CP1160/CT0007). YY is a MS in Nanochemistry and Nanomaterials from Univ. of Madeira.

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NANOFLUIDS AS CATALYSTS FOR MICROWAVE ASSISTED SONOGASHIRA C-C COUPLING

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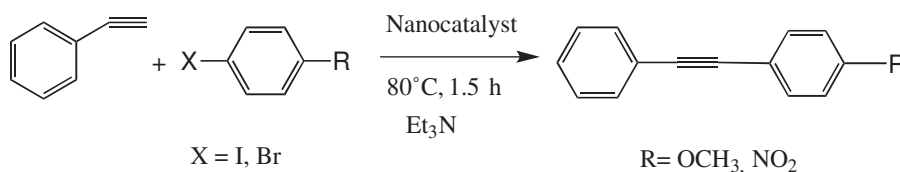
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Sonogashira coupling is a widely-applied transition metal catalysed carbon-carbon bond forming reaction.[1] However, the Sonogashira coupling performed under unconventional (more sustainable) conditions, namely in the presence of a nanofluid, where the base fluid is an ionic liquid (IL), is still understudied. [2]

Here we present the coupling between phenylacetylene and an aryl halide to afford 1,2-diphenylethyne, using Pd/C and Cu/C as nanocatalyst in various ILs (Scheme 1).



Scheme 1

With IL based nanofluids (nanocatalyst + IL), Sonogashira coupling reaction presents higher conversions and an easier separation and recycling of the catalyst.

Characterization by TEM (Fig. 1), EDS and SEM of the used nanofluids are reported and the results compared as a function of the nanofluid composition.

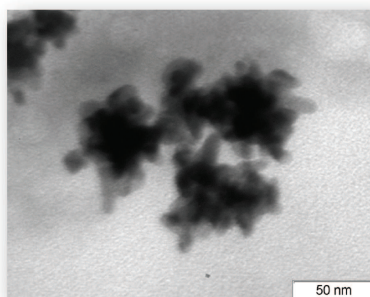


Figure 1

Acknowledgements

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SUPPORTED AND NON-SUPPORTED CHIRAL IONIC LIQUIDS FOR ASYMMETRIC CATALYSIS

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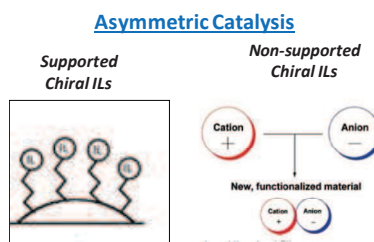
In recent years, the search of efficient homogeneous and heterogeneous catalytic processes became a relevant research topic in academic and industrial fields. Several publications reported the advantages to use supported catalysts in order to recycle the catalytic media during several reaction cycles without loss of efficiency [1,2]. The possibility to combine the peculiar properties of chiral ionic liquids as organocatalysts for asymmetric catalytic reaction seems an attractive field [3,4].

Herein, we describe recent studies of the use of supported and non-supported chiral ionic liquids for catalytic approaches:

a) Homogeneous catalysis using non-supported chiral ILs: applications of chiral ILs based on L-proline and cholic acid derivatives as chiral anions for asymmetric aldol, Michael reactions and epoxidation reactions. For some cases, it was possible to obtain the desired pure chiral products in good yields and enantiomeric excesses

comparable with the conventional systems. Additionally, for the best homogeneous catalytic processes, the recycling and re-using of the chiral reaction media (ILs or green solvents and chiral catalyst) have been evaluated.

b) Heterogeneous catalysis using supported chiral ILs: the adequate incorporation of chiral ILs already tested as efficient organocatalysts into silica mesoporous supports. All supported chiral ILs have been completely characterized by NMR, FTIR, elemental analysis and microscopic techniques. The most promissory supported chiral ILs will be tested for asymmetric catalytic processes.



Acknowledgements: We thank the Fundação para a Ciência e Tecnologia for financial support (PEst-C/EQB/LA0006/2011 project) and Solchemar Company.

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SBA-15 AS SUPPORT AND FILLER FOR THE SYNTHESIS OF POLYETHYLENE NANOCOMPOSITES

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Ultra-high molecular weight polyethylene exhibits unique properties useful for a wide scope of applications. Despite these remarkable properties, the widespread application is limited by the difficulties encountered in conventional melt processing due the high degree of entanglement of the polymer chains.

Mesoporous silicas present unique features for the synthesis of nanometer scaled polyethylene through space-confined polymerization [1-3]. The porous system of SBA-15, with well-defined channels at the nanometric scale, is well suited for the immobilization of several organometallic complexes and may act both as catalyst support and filler in the preparation of nanocomposites.

The aim of this work is the synthesis of polyethylene based by *in situ* polymerization. For this purpose a metallocene (bis-(*n*-butylcyclopentadienyl)-dichloro-hafnium) and a post-metallocene catalyst (the bis [N-(3-*tert*-butylsalicylidene)-2,3,4,5,6-pentafluoroanilinato] titanium (IV) dichloride) were immobilized by different methods on mesoporous silica SBA-15. The effect of the distinct immobilization methodologies on the polymerization activity is investigated. In addition, the thermal properties and the mechanical behavior of the materials has been assessed. The performance of these materials is discussed in terms of morphology and crystalline structure assessed by SEM, DSC and XRD.

Acknowledgements

Support for this work was provided by FCT (UID/QUI/00100/2013 and SFRH/BD/72761/2010), CYTED Rede Temática 311RT0417 and PAULIF (Project TC 07/13) are acknowledged.

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SYNTHESIS OF SAPO-11 MATERIALS USING MICROWAVE OR ELECTRICAL HEATING: A COMPARATIVE STUDY

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Hierarchical porous materials with micro and mesopores possess large external surface area [1] and are relevant for catalysts where reactions preferentially occur at the surface of the crystals, i.e. pore mouths. Microwave (MW) heating assisted-synthesis is one of the methods that allow producing such nanosized materials [2]. In this work, we studied the influence of the experimental MW parameters (ramp time, crystallization time and temperature) along with the use of different Si sources and organic additives on the physicochemical properties of SAPO materials, and compared those materials with their corresponding conventional materials, obtained by using electric heating. All the materials were further tested catalytically, using hydroisomerization of long chain *n*-alkanes reaction.

All the samples synthesized are pure AEL phase and highly crystalline. SAPO-11 samples, prepared with the aid of MW radiation, systematically present higher yield while crystallization time is dramatically shortened, from hours (conventional heating method) to minutes (MW method). Furthermore, MW radiation allows to obtain materials with smaller particles sizes (see Fig. 1), also evidenced by larger surface areas and pores volumes obtained for those MW samples. ²⁹Si NMR results suggest that Si source depolymerisation and Si incorporation within AIPO framework are strongly influenced by the heating method used. Finally, MW SAPO-11 materials combined with Pt-Alumina support demonstrate promising catalytic behaviour in *n*-decane hydroisomerization.

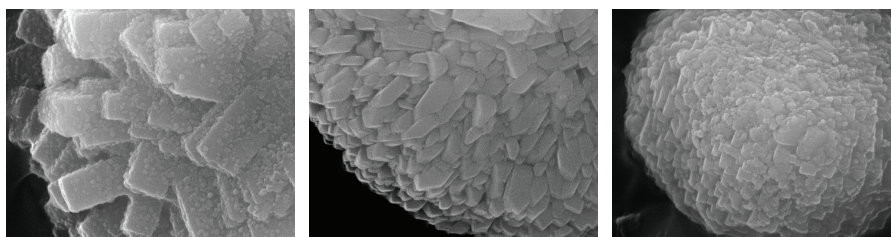


Figure 3. SEM images of SAPO-11 materials synthesized by conventional (left) and MW methods (middle, Si source AS-40; right, Si source A380).

Acknowledgements

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DYNAMIC MODELLING OF ACETYLENE HYDROGENATION IN INDUSTRIAL CONTEXT

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In this work a dynamic model was developed to describe a reaction system for the hydrogenation of acetylene in an ethylene stream by selective hydrogenation over Pd/Al₂O₃. In order to improve the ethylene selectivity, i.e. to decrease the ethane formation from both acetylene and ethylene, CO is controlled in the process. The system consists of three adiabatic fixed-bed reactors, in series, with cooling between them.

The kinetics equations used and an approximation a pseudo-homogeneous model of an adiabatic reactor were applied to simulate the conversion and the temperature profiles outlet of the reactor in industrial hydrogenation unit^{[1],[2]}.

In the below figure is represented the temperature profile at the outlet of the first reactor. In this figure is shown more than 12h of the operation of the reactor. After 33000s it was performed three disturbances: reduction of the flow, reduction of the concentration of CO and inlet temperature in the first reactor decrease. The kinetic model used to simulate the acetylene hydrogenation reactor was:

$$r_{C_2H_2} = \frac{k_1 K_{C_2H_2} K_{H_2} P_{C_2H_2} P_{H_2}}{(1 + K_{C_2H_2} P_{C_2H_2} + K_{CO} P_{CO})(1 + K_{H_2} P_{H_2})} \quad r_{C_2H_6} = \frac{k_2 K_{C_2H_4} K_{H_2} P_{C_2H_4} P_{H_2}}{(1 + K_{C_2H_2} P_{C_2H_2} + K_{C_2H_4} P_{C_2H_4} + K_{CO} P_{CO})^3}$$

Analyzing the kinetics that was used in this graph it can be seen that there is a correlation between them.

Acknowledgements

The authors gratefully acknowledge financial support from Fundação para a Ciência e a Tecnologia and Repsol (under Grant No. PDE/BD/ 52612/2014).

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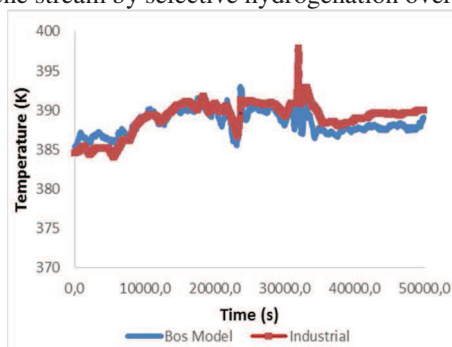


Figure 1. Comparison between the industrial data and the model developed using the Bos [2] kinetic rate equations.

MECHANISTIC AND KINETIC MODELLING STUDIES OF FURFURAL CONVERSION TO BIO-PRODUCTS

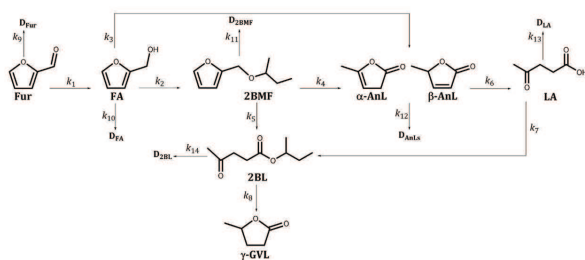
Ana L. Magalhães^{a*}, Margarida M. Antunes^a, Sérgio Lima^b, Patrícia Neves^a, Enza Fazio^c, Auguste Fernandes^d, Fortunato Neri^c, Carlos M. Silva^a, Silvia M. Rocha^e, Maria F. Ribeiro^d, Martyn Pillinger^a, Atsushi Urakawa^b, Anabela A. Valente^a

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Biomass can partly replace non-renewable fossil resources in the production of energy and chemicals in order to diversify their sources, enhance energy security and decrease the global warming. Furfural (Fur) is a renewable platform chemical and industrially produced from hemicelluloses which is one of the main components of lignocellulosic, non-edible biomass. Fur in alcohol medium, e.g. 2-butanol, can be converted to the bio-products furfuryl alcohol (FA), furfuryl alkyl ethers (2BMF), levulinic acid (LA), levulinic acid (LA), angelica lactone isomers (AnL) and γ -valerolactone (GVL), useful in different sectors of the chemical industry. The conversion of Fur to the bio-products involves complex multistep catalytic routes consisting of acid and reduction reactions.

In this work, one-pot conversion of Fur to bio-products was investigated using different types of ordered porous (Zr, Al)-containing silicates as multifunctional catalysts, possessing different acid and textural properties [1]. Based on the overall Fur reaction mechanism represented in the scheme, a pseudo-homogeneous kinetic model was developed assuming perfectly stirred batch reactors, and first-order



elementary reactions, which fitted reasonably well the experimental data for all catalysts tested. Comparisons of the calculated rate constants of each step for different catalysts led to insightful mechanistic considerations.

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METHANE PRODUCTION FROM CO₂ OVER Ni-HYDROTALCITE DERIVED CATALYSTS

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Growing environmental concern regarding the increasing levels of CO₂ has resulted in the renewed interest for CO₂ methanation reaction. In this way, CO₂ methanation is the more favourable alternative in terms of thermodynamics [1]. Furthermore, methane is easier to handle and store and can be used as feedstock for producing various industrially important chemicals. Although CO₂ methanation is advantageous when compared to other options, a good catalyst is still needed to overcome the kinetic barrier of the reaction and activate the stable CO₂ molecules increasing at the same time the selectivity to the desired product [1]. Due to the high efficiency and lower cost, Ni supported catalysts have been widely investigated for methanation reaction. Hydrotalcite, because of its thermal stability, is widely studied as a favourable support for exothermic reactions [2]. In addition, due to its basic properties, it was referred as advantageous for CO₂ activation [2].

This work involves the study of CO₂ methanation over Ni-Hydrotalcite derived catalysts. The effects of Ni content and Al/(Mg+Ni) ratio were evaluated. Catalysts were prepared by co-precipitation method and characterized by X-Ray diffraction, N₂ adsorption, diffuse reflectance spectroscopy UV-Vis, temperature programmed reduction with H₂ and temperature programmed desorption with H₂ and CO₂. Catalytic tests were carried out at temperatures from 200 to 450°C, at atmospheric pressure. Catalysts were reduced ex-situ at 800°C under H₂ flow. During catalytic tests, reactants flow was constituted by 300 ml/min of H₂, CO₂ and Ar (H₂/CO₂=4). The amount of catalyst was kept constant for all tests (GHSV = 15 000 h⁻¹).

Increasing amounts of Ni lead to a shift on the reduction profiles obtained by H₂-TPR to lower temperatures. In terms of catalytic performances, an enhancement of CO₂ conversion was observed with the increasing amount of Ni being CH₄ selectivity not significantly affected. Concerning the Al/(Mg+Ni) ratio effect, it was observed that for samples with identical Ni contents, lower ratios lead to higher CO₂ conversions and CH₄ selectivity.

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Authors would like to thank to Fundação para a Ciência e Tecnologia through CQE (Project UID/QUI/00100/2013) and KIC InnoEnergy for its Master scholarship.

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NEW SUSTAINABLE APPROACHES FOR TANDEM DOUBLE-CARBONYLATION-CYCLIZATION REACTIONS

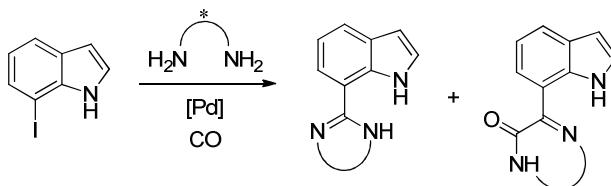
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The development of sustainable catalytic processes is one important challenge in organic synthetic chemistry. Carbonylation reactions, particularly aminocarbonylation reactions using diamines as nucleophiles have received great attention because enables amide bond formation with high atom economy [1, 2].

The development of tandem processes, such as carbonylation-cyclization processes, is of great importance since they allow the synthesis in one step of a variety of products, for example N-heterocycles, with evident advantages, in terms of efficiency, selectivity, atom and energy economy [3]. Among several compounds, the functionalization of the indole nucleus has been a topic of interest for many years. Moreover, indole derivatives containing either pyrimidine or piperazine units exhibit powerful biological activities [4, 5].



Herein, we present our recent achievements on the application of Pd-catalyzed tandem double-carbonylation-cyclization reactions of 7-iodoindole using diamines as nucleophiles as a versatile synthetic tool for the synthesis of novel indole-pyrazinones and indole-pyrimidines with potential biological activity.

Acknowledgements

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SELECTIVE PORPHYRIN-BASED CATALYSTS FOR CO₂ /EPOXIDE COPOLYMERIZATION VS. CYCLOADDITION

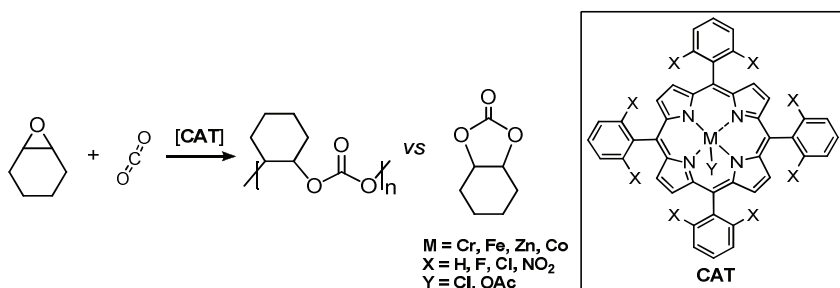
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The development of active and selective catalysts to promote transformations of carbon dioxide (CO₂) and epoxides into useful organic compounds, such as cyclic carbonates and/or polycarbonates is still a great challenge due to economic and environmental benefits arising from the utilization of renewable sources and the growing concern on the greenhouse effect [1,2]. Moreover, such products may find numerous applications in both fine and bulk chemistry [2]. Among the most efficient catalytic systems so far studied, metalloporphyrins are particularly promising, not only due to the straightforward modulation of their aromatic heterocycle but also because different metal complexes can be easily prepared, which allows fine-tuning their Lewis acidity, thereby increasing their catalytic activity and selectivity [3].



Scheme 1. Carboxylation of cyclohexene oxide with porphyrin-based catalysts.

Herein we present our recent results on the synthesis of a set of different *meso*-tetra-arylporphyrin metal complexes and their evaluation in coupling reactions of epoxides with CO₂ (Scheme 1). The effects of metal, axial counterion, electron withdrawing substituents in the *meso*-phenyl ring and reaction conditions on catalytic activity and selectivity for the formation of cyclic carbonates *versus* polycarbonates will be presented and discussed.

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A NEW CALIXARENE-COBALT(II) COMPLEX AS CATALYST FOR MW-ASSISTED OXIDATION OF ALCOHOLS

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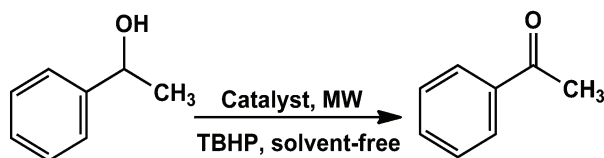
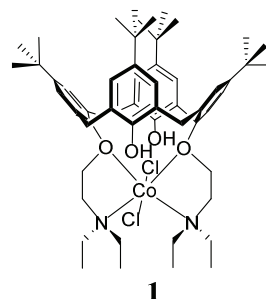
The search for efficient, selective, eco-friendly and economic catalytic oxidation processes toward a sustainable ketone production remains a challenge.[1] One approach to meet the above requirements is the design of new improved catalysts for the oxidation of secondary alcohols.

The use of calixarene-metal compounds as catalysts for oxidation reactions is scarce, which prompted us to synthesize new compounds and investigate their catalytic activity.

A new calixarene-cobalt(II) complex, the dichloro-25,27-bis-(2-diethylaminoethoxy)-26,28-*p*-*tert*-butylcalix[4]arene)-cobalt (II) (**1**), was prepared and characterized by the usual spectroscopic and electrochemical techniques.

Complex **1** was tested as catalyst for the microwave-assisted oxidation of 1-phenylethanol to acetophenone (as a model reaction, see Scheme below) with aqueous *tert*-butyl hydroperoxide (TBHP) and under mild conditions.

Almost quantitative yields of acetophenone were achieved after 45 min of MW irradiation, by optimizing reaction conditions.



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HYDROSOLUBLE METAL COMPLEXES FOR HOMOGENEOUS CATALYSIS

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As part of our interest on water soluble transition metal complexes with applications in catalysis,[1] we have obtained novel Cu(II) or Ni(II) species by reacting the water soluble compounds of the types (Figure 1) arylhydrazones of β -diketones (AHBD) — viz., 3-(2-sulfonic phenylhydrazo) pentane-2,4-dione and of 3-(2-sulfonic phenylhydrazo) acetoacetamide —, as well as the 3,7-diacetyl-1,3,7-triaza-5-phosphabicyclo[3.3.1]nonane (DAPTA) and the tris-(pyrazolyl)-methanesulfonate (Tpms), [2,3] with the salts of those metals.

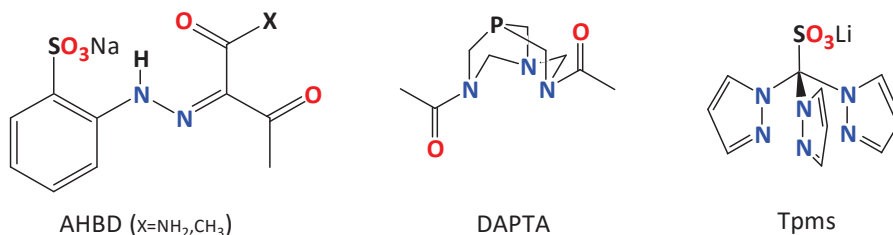


Figure 1

The obtained compounds were fully characterized and applied as catalysts, under mild conditions, for aldehyde cyanosilylation (with trimethylsilyl cyanide) to produce the corresponding cyanohydrin trimethylsilyl ethers in high yields.

Acknowledgements

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MOLYBDENUM(II) COMPLEXES AS CATALYSTS IN REDUCTION REACTIONS

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Different molybdenum complexes from the family $[\text{MoX}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{L})]$ were synthesised by reaction of the precursor $[\text{MoBr}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{CH}_3\text{CN})_2]$ with different bidentate ligands (L) derived from 1,10-phenanthroline, as well as by substitution of the Br halide ligand with acetonitrile, pyridine or triflate. All new compounds prepared were characterized by FTIR, ^1H and ^{13}C NMR, as well as elemental analysis.

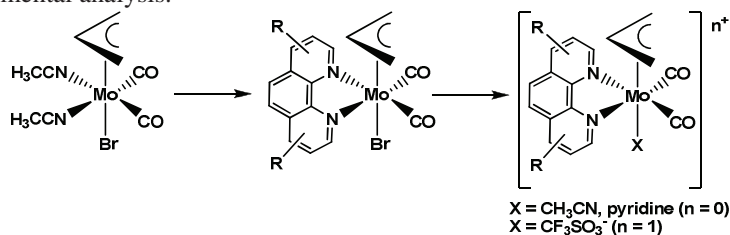


Figure 1. Complexes $[\text{MoX}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{L})]$.

All the molybdenum(II) complexes were tested as catalysts in the reduction of two sulfoxides, methylphenyl sulfoxide and diphenyl sulfoxide. The reaction conditions were optimized by studying different reduction agents (triphenylphosphine and phenylsilane), co-catalysts (NaBF_4 , KBF_4 , AgPF_6), temperatures (room temperature, 55 °C, 80 °C and 100 °C) and solvents (dichloromethane, chloroform, acetonitrile, tetrahydrofuran and toluene). All these studies helped to understand the influence of the different ligands on the complexes catalytic activity for reduction reactions. The best result was achieved with the precursor complex which presented 100% conversion after 3h.

Acknowledgements

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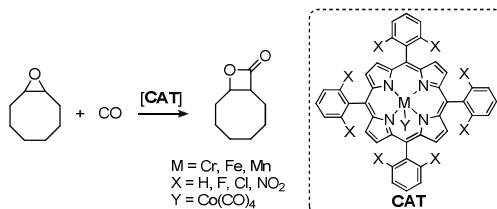
SOLVENTLESS CARBONYLATION OF EPOXIDES CATALYSED BY METALLOPORPHYRINS

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Oxetane-2-ones (β -lactones) are attractive intermediates in organic chemistry, since they are often present as structural units of biologically active compounds, with a wide range of applications in biopolymer synthesis and in medicinal chemistry.[1] Regarding their synthetic preparation, the catalytic carbonylation of epoxides emerged as a versatile strategy due to extensive availability of the substrates, low price of CO and high atom economy of the process.[2] Among the studied systems, bimetallic catalysts of type [Lewis acid][Co(CO)₄] were shown to be the most efficient ones.[1-3] In particular, those that provide metalloporphyrins as Lewis acids are highly advantageous, since the aromatic macrocycle can be easily modulated by introduction of peripheral substituents and/or by complexation with different metals, which offer the possibility of increasing catalytic activity and fine-tuning the reaction's selectivity.



Scheme 1. Carbonylation of cyclooctene oxide with porphyrin-based catalysts.

In this communication, we present our recent achievements on the carbonylation of epoxides promoted by *meso*-aryl-metalloporphyrin-based catalysts (**Scheme 1**). So far, promising results were obtained with *in situ* generated [Cr(III)-porphyrin/Co(CO)₄] catalysts in the absence of solvent, which achieved high activity and a remarkable selectivity for β -lactones. The effects of reaction's conditions and porphyrin structure (metal and *meso*-phenyl substituents) on catalytic activity and selectivity are discussed.

Acknowledgements

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OXIDATION OF ALCOHOLS IN WATER WITH IRON CATALYSTS BEARING N-HETEROCYCLIC CARBENES

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The field of iron N-heterocyclic carbene (NHC) chemistry has attracted increasing interest during the last decade.¹ The low price, high abundance, and non-toxicity of iron, along with the great popularity of NHCs in catalysis have motivated the growing interest in this area of research. Iron complexes supported by chelating bis(NHC) ligands that are not part of a multidentate framework have been described in the literature. However, their application in catalysis is rather unexplored.²

We became interested in exploring the reactivity of complexes containing the Fe-bis(NHC) fragment in combination with 2,2-bipyridine (bipy) and 1,10-phenanthroline (phen) ligands. Metal complexes containing polypyridine ligands have displayed interesting results in catalysis, in particular in oxidation reactions.³ In this work, we describe the synthesis and characterisation of

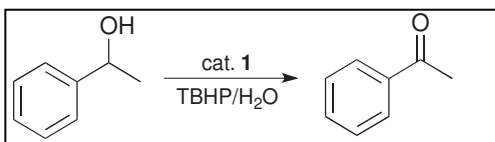


Figure 4 Oxidation of alcohols in water with TBHP using the iron catalyst $Fe(\text{bis-NHC})(\text{bipy})\text{I}_2$.

iron(II) complexes bearing bis(NHC) and 2,2-bipyridine and 1,10-phenanthroline ligands, and their application in catalysis. We found that $Fe(\text{bis-NHC})(\text{bipy})\text{I}_2$ (**1**) is an effective catalyst for the oxidation of 1-phenylethanol in water with *tert*-butyl hydroperoxide (TBHP), Figure 1. The stability of complex **1** in different solvents, and the scope of the catalytic reaction will be discussed.

Acknowledgements

We thank FCT for financial support through project PTDC/QEQ-QIN/0565/2012, and grant fellowship PD/BD/105994/2014 (M.P), and B. R. thanks for IF/00346/2013, and project UID/QUI/00100/2013.

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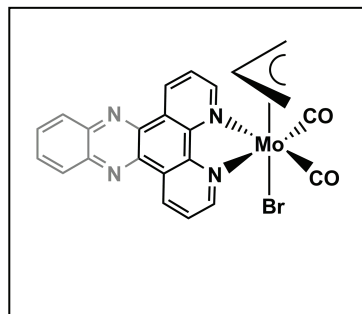
MOLYBDENUM(II) COMPLEXES FOR CO₂ REDUCTION

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Carbon dioxide is the main greenhouse gas resulting from everyday human activities.[1] The increasing concentration of CO₂ in the atmosphere affects Earth's energy balance. Changes in the greenhouse effect, in the energy reaching Earth's surface and alterations in its atmosphere and surface reflectivity are some of the known consequences. For these reasons it is urgent to find efficient pathways for carbon utilisation and recycling to form products with significant commercial value. Recent reports of reaction of pressurised CO₂ with epoxides to form polycarbonates[2] or cyclic carbonates[3] have attracted both academic and industrial interest. Conversion to CO has been widely studied using well-defined transition metal catalysts that are able to couple both electron and proton transfer reactions.[4] Among these, group 6 carbonyl complexes, namely Mo(II) derivatives, showed activity towards electroreduction of CO₂. In this work, the activity of Mo(II) complexes [Mo(η^3 -allyl)(CO)₂(L)Br] (L = 1,10-phenanthroline and dipyridophenazine) in the conversion of CO₂ was explored (Figure 1, black and grey, respectively). Cyclic voltammetry and bulk electrolysis experiments were performed to evaluate the CO₂ electroreductive performance of these complexes and identify the reduction products. The gaseous products were analysed by gas chromatography.



Acknowledgements

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MICROWAVE ASSISTED HYDROGEN TRANSFER REDUCTION OF KETONES WITH Fe-NHC BIFUNCTIONAL CATALYSTS

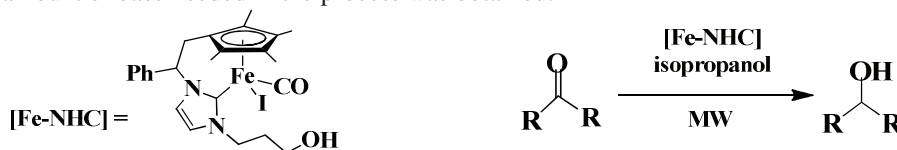
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The selective reduction of carbonyl functionalities is an important and useful reaction in organic synthesis. Catalytic transfer hydrogenation process is an attractive alternative to direct hydrogenation procedure for the reduction of ketones to alcohols, since offers selective reduction avoiding the use of eventually hazardous H₂ gas, and using hydrogen donors readily available and easy to handle [1]. Usually, hydrogen transfer processes are catalysed by noble metals such as Pd, Pt, Ir, Ru, and Rh. However, these metals have limited availability, are very expensive and toxic. The use of iron, an earth-abundant, cheap and non-toxic metal, as catalyst for the reduction of organic functionalities is highly desirable. Our group has been involved during the last few years in the development of well-defined iron metal complexes for reduction reactions [2]. Herein, we describe the synthesis of a new family of iron complexes with N-heterocyclic carbenes (NHCs) bearing an OH functionality, Scheme 1, and their application in the catalytic transfer hydrogenation of ketones using microwave heating. Under these conditions, an interesting improvement on reaction time and amount of base needed in the process was obtained.



Scheme 1: Fe-NHC catalysts in hydrogen transfer of ketones

Acknowledgements

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CARBON NITRIDE-BASED PHOTOCATALYSTS FOR GREEN CHEMICAL SYNTHESIS

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Increasingly stringent environmental limitations for chemical synthesis processes are driving researchers to find alternative routes based on leach-proof heterogeneous catalysts, capable of producing high yields of the desired product while acting in environmentally benign solvents. In this scenario new perspectives are open for the development of medium to large-scale photocatalytic processes for the synthesis of a number of organics, widely used in pharmaceutical, food and cosmetic industries [1]. The advantages of photocatalytic organic synthesis are huge, namely: i) no need of using dangerous heavy metal catalysts; ii) avoid strong chemical oxidant/reducing agents; iii) higher selectivity to the desired product; iv) production of substances that are unstable at high temperatures; v) possibility of using sunlight as energy source; vi) reactions following either oxidative or reductive routes.

Graphitic carbon nitride ($g\text{-C}_3\text{N}_4$), has attracted much attention in recent years because of its similarity to graphene and its properties as semiconductor (Fig. 1) [2]. Compared to TiO_2 , the benchmark photocatalyst, $g\text{-C}_3\text{N}_4$ presents a smaller bandgap of 2.7 eV, corresponding to a blue light absorption up to 450 nm (contrasting to the 380 nm absorption edge of TiO_2).

In the present work, $g\text{-C}_3\text{N}_4$ nanosheets obtained by thermal, chemical and mechanical techniques were tested for the photocatalytic oxidation of benzyl alcohol into benzaldehyde. The photocatalytic results were correlated with the characterization of the synthesized materials, namely with the surface area, the band gap, and the thickness of the $g\text{-C}_3\text{N}_4$ sheets.

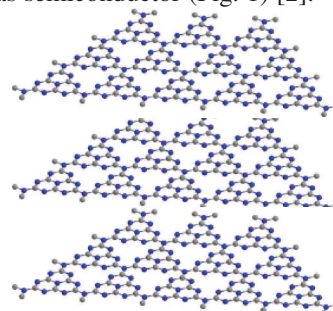


Figure 1. Layered structure of $g\text{-C}_3\text{N}_4$.

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REVERSE SELECTIVITY OF ZEOLITES AND MOFS IN THE ETHANE/ETHYLENE SEPARATION BY ADSORPTION

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Ethylene is a key building block for plastics and has a major importance in petrochemical industry. The separation of ethylene from ethane is made by distillation which implies that more than 75% of the ethylene costs are due to the high energy consumption that is needed to separate it from ethane [1]. Advances in the ethane/ethylene separation will be related with the discovery of adsorbents that present preferential adsorption of ethane over ethylene. Metal-organic frameworks (MOFs) are crystalline materials consisting of metal ions, or ion clusters, and organic ligands. Gas chromatography is most informative for materials screening for the ethane/ethylene separation since it needs only few mg of sample, and gives selectivity results at various temperatures [2]. This is illustrated by the methodology presented in this work where materials from two types of families (zeolites and MOFs) were used to show the reversed selectivity that can be found towards the ethane/ethylene separation.

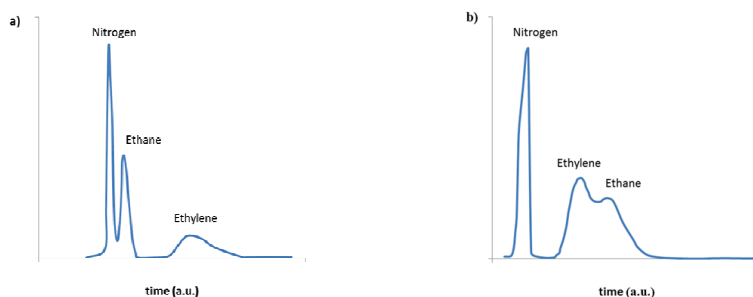


Figure 1. TCD signal obtained at the end of (a) HZSM-20 and (b) IRMOF-8 filled columns in flow separation of ethane/ethylene mixtures

Acknowledgements

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METAL-ORGANIC FRAMEWORKS FOR CLEAN ENERGY APPLICATIONS

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Metal-Organic Frameworks (MOFs) have been recently used with success in photovoltaic devices and other clean energy applications, due to their semi-conductor behavior. This are promising results for the use of MOFs as light-harvesters and semi-conductors in solar and electroluminescence cells. Moreover, MOFs allow the introduction of light harvesting dyes with high electron-accepting behavior in their structure to leverage the performance.

In this communication we will report two cases where MOFs have been applied as active material in electroluminescence devices.

In the first case, we report the entrapment of perylene dianhydride molecules into MOF5 pores with strong interaction between host and guest, and with a remarkable electroluminescence response. Optical microscopy, SEM, PXRD and fluorescence spectra clearly show the stabilization of isolated PDA molecules inside the MOF5 pore structure, after careful host activation. Laser flash photolysis reveals a strong interaction between perylene dianhydride molecules and MOF5 through changes in the charge separation state characteristic of MOF5. A electroluminescence cell was prepared using PDA@MOF5 as active material.[1]

In the second case we report the preparation of a MOF containing an anthracene moiety. The reaction of 9,10-di(4-pyridyl)anthracene and biphenyl-4,4'-dicarboxylic acid and zinc nitrate under solvothermal conditions yields a microcrystalline powder. The obtained DPyA-MOF was characterised by single crystal X-ray diffraction, and its photophysical and electrochemical properties were studied.[2]

Acknowledgements

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NITROGEN-DOPED CARBON NANOTUBES AS CATALYSTS FOR THE OXYGEN REDUCTION REACTION

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Platinum-based materials are so far the most efficient catalysts for the oxygen reduction reaction (ORR) at the cathode of Fuel Cells; however, their high cost, limited supply (high Pt-loadings are prohibitive for widespread applications) and weak durability limit their large scale commercialization. In the particular case of the direct methanol fuel cell, where the crossover of methanol from anode to cathode through the polymer electrolyte membrane may occur, the performance of platinum electrocatalysts is also impaired, since Pt catalyses the oxidation of methanol together with the ORR, generating a mixed cathodic potential, and simultaneously reducing the operation efficiency of the fuel cell.

The versatility of carbon nanomaterials combined with their low cost, availability and adequate properties, such as high surface area, good mechanical, chemical and thermal properties, makes them promising catalysts for the ORR. In particular, doping of carbon nanomaterials has become a key strategy to enhance their functionality.

In this work, N-doped carbon nanotubes (N-CNT) prepared by an easy and scalable method based on ball milling [1] were used as electrocatalysts towards ORR. Although the enhancement of ORR performance by N-doped carbon nanotube based electrocatalysts has been reported in a large number of studies, the impact of nitrogen atom type and content is still a subject of intense debate. Consequently, in this work we endeavor to contribute to unveil the role of the different N-type heteroatoms introduced into the CNT structure through an eco-sustainable protocol using two N-precursors, melamine and urea, towards ORR under alkaline conditions.

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N-DOPED ORDERED MESOPOROUS CARBONS FOR OXYGEN REDUCTION REACTION

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Oxygen Reduction Reaction (ORR) is of main importance for novel energy converting devices, specifically for fuel cells. Up to now, platinum-based materials are the best electrocatalysts for ORR, showing low overpotential and a preference for direct mechanism. However, Pt scarcity and high costs limit the widespread use of fuel cell technology. Nitrogen doped porous carbons are alternative materials exhibiting high electrocatalytic activity for ORR. Porous carbons provide a large surface area to accommodate the required amount of active sites. However, the diffusion of oxygen in purely microporous carbons will be slow. Ordered mesoporous carbons (OMC) present an adjustable and interconnected regular porous network which enhances the diffusion of molecules from the surface to the bulk of the material. The combination of the enhanced diffusion provided by nanostructured mesoporous materials, together with the catalytic activity of the nitrogen functional groups is expected to provide high-performance for ORR.

In the present work, ordered mesoporous carbons containing nitrogen groups as active sites were prepared through slight modification of the “soft-templating” method [1] using melamine, resorcinol and formaldehyde as precursors. Further chemical activation with KOH was performed to some selected samples to increase the micropore volume. Both the surface chemistry and the texture of the ordered mesoporous carbons were adjusted by varying the amount of melamine in the reaction medium or the activation parameters.

The influence of all these variables on ORR was evaluated, and some conclusions were extracted. Samples with lower nitrogen doping (0.38 wt. %) presented higher catalytic activity than those with higher amounts (1.31 wt. %). On the other hand, the activated materials presented less negative potentials of ORR regardless of the surface chemistry.

Acknowledgements

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DEVELOPMENT OF MAGNETIC CARBON XEROGELS FOR CATALYTIC WET PEROXIDE OXIDATION

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Hybrid magnetic carbon composites have been recently proposed as the next step in the evolution of catalysts for catalytic wet peroxide oxidation (CWPO), with several synergistic effects arising from the combination of the high catalytic activity of metal species with the proven catalytic properties of carbon-based materials in CWPO [1]. Bearing this in mind, this work sought the development of novel magnetic carbon xerogels, composed by interconnected carbon microspheres with iron (Fe) and/or cobalt (Co) microparticles embedded in their structure. As inferred from the extensive characterization performed, materials with distinctive properties were obtained upon inclusion of different metal precursors during the sol-gel polymerization of resorcinol and formaldehyde, followed by thermal annealing. A carbon xerogel without added metals (CX) was also prepared for comparison purposes. The performance of the carbon xerogel materials in CWPO was evaluated using highly concentrated 4-nitrophenol solutions (4-NP, 5 g L⁻¹). As observed in Figure 1, an important synergistic effect between phases arises when Co and Fe are simultaneously included in the carbon xerogel denoted as CX/CoFe, when its performance in CWPO is compared to that of the monometallic CX/Co and CX/Fe, as well as with the bare CX. The improved performance of CX/CoFe was ascribed to the enhanced accessibility of Fe species promoted by the simultaneous inclusion of Co.

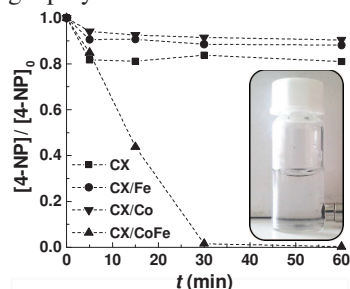


Figure 1. 4-NP removal from concentrated aqueous solutions (5 g L⁻¹) obtained in CWPO runs performed with the carbon xerogel materials in the presence of stoichiometric amounts of H₂O₂. Inset: magnetic separation of CX/CoFe.

Acknowledgements

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N-DOPED CARBON NANOTUBES FOR THE CATALYTIC WET AIR OXIDATION OF ORGANIC COMPOUNDS

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Catalytic wet air oxidation (CWAO) is a promising technology to treat highly polluted industrial waste-waters by oxidation [1]. Carbon nanotubes (CNTs) can be used as catalysts for this process, with the advantage of reducing, or even eliminating, diffusion limitations [2]. The presence of nitrogen groups on the surface of CNTs has been shown to significantly increase their performance as metal-free catalysts. Several methods have been developed in order to incorporate N onto the carbon surface.

In this work, CNTs were modified by different methods to incorporate nitrogen surface groups into the CNTs sp² network. Melamine, urea and ammonia were used as N-precursors. With melamine and urea, an easy to handle, solvent-free post-doping method developed in our group [3] was applied, involving a mechanical treatment under ball-milling followed by a thermal treatment under inert atmosphere (N₂). Three different CNT/N-precursor ratios were explored in each precursor. In the case of ammonia, ball milled CNTs were thermally treated under gaseous ammonia at 600 °C using pure NH₃ and NH₃ diluted with N₂ (50%). The obtained samples were tested as catalysts for the oxidation of oxalic acid (T=140 °C) and phenol (T=160 °C) by CWAO (total pressure of 40 bar, P_{O₂}=7 bar). The catalytic results are discussed in terms of the CNT textural properties and surface chemistry, investigated by different characterization techniques (N₂ adsorption isotherms, XPS, TPD, TGA and elemental analysis), focusing on the influence of N-precursor, N-content and nature of N-surface groups.

Acknowledgements

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SYNTHESIZED MESOPOROUS CARBON FOR ADSORPTION/DESORPTION OF ANTIOXIDANT COMPOUNDS

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Wastewater from cork industry has a high concentration of phenolic derivative compounds [1] which are considered biorecalcitrant and the main cause of its pollution load. On the other hand, the potential of these phenolic compounds as antioxidants is well-known and its recovery seems to be an alternative to reduce its presence in the environment and to valorise these wastewaters.

The aim of this work was the synthesis of a carbon which could be able to adsorb four phenolic derivative compounds (gallic acid, protocatechuic acid, vanillic acid and syringic acid) on both single and multi-component synthetic solutions. The adsorbent was characterized regarding its textural and chemical properties (Table 1).

Table 1. Textural and chemical characterization of synthesized carbon

Textural analysis				Chemical analysis				pH _{PZC}
S _{BET} (m ² g ⁻¹)	V _p (cm ³ g ⁻¹)	V _{micro} (cm ³ g ⁻¹)	V _{meso} (cm ³ g ⁻¹)	N (%)	C (%)	H (%)	O (%)	
798	0.97	0.20	0.77	0.08	90.71	0.37	8.84	9.24

The N₂ adsorption-desorption isotherms of the carbon belong to type IV. The activated carbon possesses a large internal surface area and its mesoporous nature sample is confirmed by the high mesopore volume, which accounts for more than 70% of the overall pore volume.

Concerning the adsorption-desorption results, negative effects were observed in the multi-component mixture probably due to competition for the active centres of the adsorbent surface. Vanillic acid was the compound with the higher adsorption (80%) and interestingly it is then possible to desorb a relatively high amount (43%) of it from the adsorbent, which may represent a possibility for its selective recovery

Acknowledgements

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POTATO PEEL WASTE BASED ACTIVATED CARBON FOR THE ADSORPTION OF TETRACYCLINE AND CAFFEINE

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Pharmaceutical compounds such as the antibiotic tetracycline (TTC) and the stimulant caffeine (CAF) are considered emerging contaminants of aquatic media. These compounds are able to be readily removed by adsorption processes that can be supported by low-cost and easily available precursors, such as biomass wastes, to synthesize activated carbon adsorbents. In the present work, activated carbon from potato peel waste (CPPW) was obtained by chemical activation with K_2CO_3 and applied to the removal of TTC and CAF in liquid-phase. CPPW sample presented an apparent surface area of $866 \text{ m}^2 \text{ g}^{-1}$ and a well-developed microporous structure with a large amount of ultramicropores (width $< 0.7 \text{ nm}$). Kinetic data of TTC and CAF adsorption (Figure 1) were best fitted by the pseudo-second order kinetic model. CPPW adsorbent presented a higher uptake (q_e) and a much higher kinetic constant (k_2) for CAF compound (Table 1), in line with the critical dimension of these two compounds.

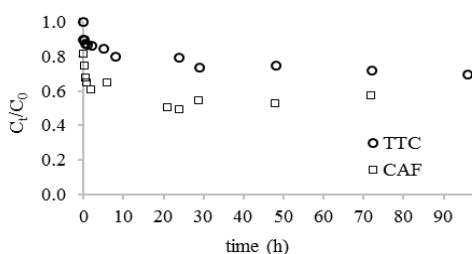


Table 1. Kinetic parameters obtained with pseudo-second order model for CPPW carbon.

	q_e (mg g^{-1})	k_2 ($\text{g mg}^{-1} \text{ h}^{-1}$)
TTC	71.7	0.005
CAF	78.4	0.04

Figure 1. Kinetic curves of TTC and CAF adsorption.

The adsorption isotherms obtained for TTC and CAF were best fitted by the Freundlich and Langmuir models, respectively. CPPW carbon presented a higher adsorption capacity and affinity for caffeine molecule.

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CO-PYROLYSIS OF ELECTRICAL CABLE PLASTIC WASTE WITH HYDROCARBON N-C₅₀

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With the prospect of co-pyrolysis of plastic waste with crude oil fractions in a refinery [1], n-C₅₀ hydrocarbon was inserted in different proportions in the catalytic pyrolysis of the plastic waste of electrical cables (WEC), the catalyst used for pyrolysis and co-pyrolysis was HZSM-5 with a Si/Al ratio of 15. A typical test starts by equilibrating the sample at 40°C for 10 min; the sample is then heated from 40°C up to 700°C at 10°C/min. Figures 1, 2 and 3 show the results of the thermogravimetric analysis for pyrolysis, catalytic pyrolysis and co-pyrolysis of (WEC). Table 1 shows the results for the temperatures of degradation of samples.

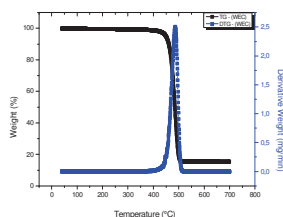


Figure 1: TG and DTG curves of pyrolysis (WEC).

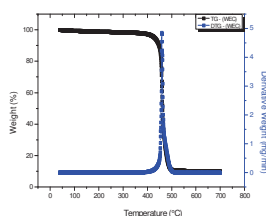


Figure 2: TG and DTG curves of catalytic pyrolysis (WEC).

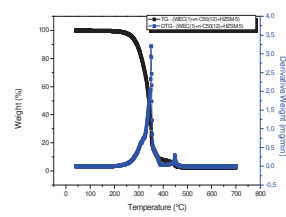


Figure 3: TG and DTG curves of catalytic co-pyrolysis (WEC).

Table 1. Comparison of the Degradation Temperatures for the samples studied.

Sample	Degradation Temperature (°C)
WEC	487
WEC+HZSM-5	461
WEC(1)+n-C ₅₀ (12)+HZSM-5	350/448

The WEC degradation temperature is consistent with high-density polyethylene (HDPE) [2], which leads to the conclusion that the WEC sample is formed mostly by this polymer. In the catalytic degradation of WEC using HZSM-5, the degradation temperature is only reduced by a small amount and the inclusion of an hydrocarbon improves the performance of the catalyst studied.

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TUNNING THE SIZE OF MESOPOROUS SILICA NANOPARTICLES BELOW 100 nm

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Mesoporous silica nanoparticles (MSNs) have received considerable attention for biomedical applications due to their excellent biocompatibility, high surface areas, large pore volumes, high loading capacity, uniform and tunable pore sizes, and versatile surface functionalization. The most common processes to synthesize MSNs use ammonium bases and co-solvents or hydroxide base in aqueous media, leading to diameters that are usually higher than 100 nm [1]. However, for applications in sensing and/or delivery, particle diameters below a few tens of nm are desirable. In the literature, only a few cases describe particles below 100 nm diameter, by changing the silica source or the temperature [1].

Here, we describe the preparation of MSNs with controlled diameters below 100 nm, under mild synthesis conditions [2]. The synthesis is performed using a sol-gel method, in an aqueous medium, with TEOS as silica source, an ionic surfactant, without ammonium bases or co-solvents, at constant temperature. We are capable of controlling the diameter of MSNs from 20 to 80 nm, with low size dispersity (Figure 1), as also the dimension and shape of their pores by varying the pH or the ionic strength of the reactional mixture. Additionally, during the synthesis we can covalently incorporate a fluorescent hydrophobic dye in the silica network. This way, it is possible to synthesize fluorescent MSNs, with sizes below 100 nm, controlling the pore diameter and morphology, for applications in bioimaging and drug delivery.

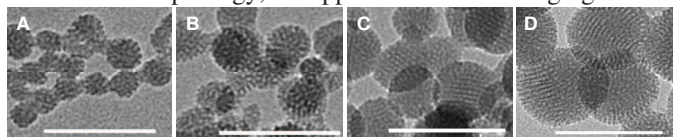


Figure 1. TEM images (scale bar 100 nm) of MSNs (average diameters: A – 25 nm; B – 38 nm; C – 55 nm; D – 70 nm).

Acknowledgements

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SOLUTION NMR METHODS FOR FUNCTIONALIZED SILICA NANOPARTICLES

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Nanoscale materials offer excellent opportunities for bio-imaging and therapeutic applications [1]. Particularly, silica-based nanoparticles are a promising class of materials due to their well-defined and tunable structures and versatile functionalization chemistry [2]. Furthermore, nano-sized silica materials have excellent biocompatibility and degradability that arise from the ability of silica to decompose into relatively harmless by-products. In many cases where silica nanoparticles are involved, further surface functionalization of these materials is usually used to improve their chemical and physical properties. An accurate quantification of active functional groups on a nanoparticle surface is important to know the number of molecules that can be linked to the surface. Although solid-state NMR methods can be used to characterize the functionalization of nanomaterials, they present important drawbacks, such as needing large amounts of sample generally in dried powder form, and long analysis times. Solution NMR methods have recently been applied to colloidal nanomaterials [3].

Here we present a fast and simple method for quantification of surface ligands and for tracking chemical modifications on silica nanoparticles based in solution NMR spectroscopy.

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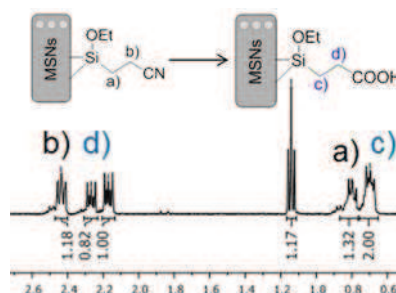


Figure 1. Chemical conversion determined by solution NMR on mesoporous silica nanoparticles (MSNs).

LIQUID-PHASE EXFOLIATION OF GRAPHITE INTO GRAPHENE FLAKES

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Scalable methods for graphene preparation have been developed since it was first isolated using Scotch tape [1]. Chemical vapour deposition and epitaxial growth yield graphene of high quality with small number of defects, making these processes promising for electronic applications. However, these processes do not scale well for applications requiring high quantity of graphene. Significantly larger amounts of graphene can be produced by physical and chemical exfoliation of graphite.[2] Exfoliation methods using inexpensive graphite are cost-effective and versatile, as they can be combined with other chemical treatments, e.g. chemical functionalization, to produce a variety of graphene and graphene-based materials.

In this work, liquid-phase exfoliation of graphite to produce graphene flakes (GF) was used. Graphite was dispersed in *N,N*-dimethylformamide and *N*-methylpyrrolidone, followed by sonication and centrifugation. The exfoliation was monitored by UV-Vis. The parent graphite and resulting GF were characterized by FTIR and Raman spectroscopy, TEM and XRD. The results confirmed the presence of few layers graphene. Fig. 1 shows the TEM image of isolated graphene flakes as representative example.

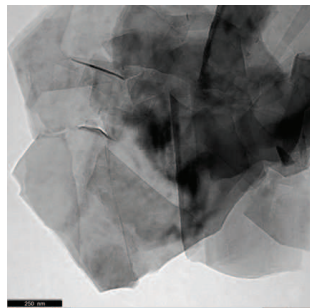


Figure 1. TEM image of isolated graphene flakes.

Acknowledgements

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Pd-CATALYSED AMINOCARBONYLATION REACTION FOR PHTHALOCYANINES FUNCTIONALIZATION

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With the increasing number of applications of phthalocyanines and derivatives in the field of biomedicine, particularly in medical imaging techniques [1], research has been focused on the modeling of these macrocycles structures in order to increase their biocompatibility. Hence, the amide linkage (peptide bond) is one of the most natural conjugations available, present in many biological synthons, such as peptides, proteins or amino acids. Nevertheless, when compared with other functionalities, amide substituted phthalocyanines are quite rare [2].

In this study we present a new strategy for direct modulation of phthalonitriles through palladium catalysed amino-carbonylation reactions. Particularly, we have synthesised for the first time a phthalonitrile-DO₃A conjugate (DO₃A = amino functionalised 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetic carboxylic acid ester), a versatile and easily accessible chelator, with great potential for the development of highly targeted contrast agents for optical imaging, namely magnetic resonance imaging (MRI) or positron emission tomography (PET). Additionally, we have also prepared the corresponding zinc phthalocyanine conjugates, as promising probes to be further exploited as suitable sensitizers in a variety of *in vivo* imaging techniques.

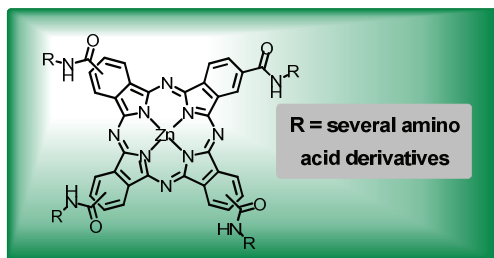


Figure 5. Amide substituted phthalocyanines.

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