

Study of the heterogeneous catalytic oxidation of furfural and glycerol from lignocellulosic waste

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Abstract— Biomass is the carbon-based resource with the potential to produce energy and the most notable for synthesizing valuable chemicals that are currently produced from fossil fuels. The transformation of lignocellulosic biomass, mainly waste from agrochemical industries, requires the search for environmentally friendly and sustainable catalytic routes that reduce environmental impact, considering the principles of green chemistry. This work proposes the microwave-assisted oxidation of substrates derived from biomass, such as glycerol and the furfural derivatives, 5-(hydroxymethyl)furfural (HMF) and 5-hydroxymethyl-2-furancarboxylic acid (HFCA), and, with the use of green oxidants such as *tert*-butyl hydroperoxide (TBHP), using a graphene-supported C-scorpionate gold(III) complex as catalyst. The gold C-scorpionate complex is synthesised avoiding the use of solvents thanks to mechanochemical procedure using a ball mill. Other C-scorpionate metal (Co, Ni or Cu) complexes are also synthesised by ball milling. Graphene is produced by a Portuguese company in collaboration. In this project, the effects of the main reaction parameters such as temperature and reaction time, the ratio of the reactants and mechanochemical parameters are investigated. Synthesis (*e.g.*, mechanochemistry and liquid phase), and characterization and quantification techniques (*e.g.*, FTIR, XPS, NMR, SEM/EDS and elementary analysis) are used. The experimental work and dissertation were developed in 6 months.

Keywords: Sustainable catalytic chemistry; microwave-assisted oxidation; mechanochemical synthesis; metal C-scorpionate catalysts; glycerol; furfural.

I. INTRODUCTION

Global warming is presented nowadays as one of the humanity's major concerns with the depletion of fossil fuel resources, the continuous generation of greenhouse gas (GHG) emissions and the dramatic increase of the world population (near 8 billion people) [1]. A big part of these GHG emissions is related to the huge amount of waste generated. Only in Europe in 2018, the total waste generated by all economic activities and households amounted to 2 317 million tons. [2]. The use of greener fuels is identified as one of the most promising solutions, leading to a competitive, energy efficient, and low carbon future. A new sustainable alternative to traditional petrochemical feedstock processes can be attained by using organic wastes as feedstock for producing fuel, that is critically important, particularly to the transport sector but also in chemical industry where a major part of commodity chemicals come from fossil fuel resources [3]. Biomass appears

as one of the most promising resources to produce biofuel and fine chemicals.

Following the idea on promote and improving biofuels production and using biomass to produce valuable products, this dissertation cases of study are the oxidation of glycerol and the furfural derivatives 5-(hydroxymethyl)furfural (HMF) and 5-hydroxymethyl-2-furancarboxylic acid (HFCA), using greener techniques that also allows to use less or no solvents. Glycerol, that is an important by-product of biodiesel production, is produced in significant amounts by transesterification of triglycerides with methanol and can be used as feedstock to produce high-added-value products [4]. On the other hand, the furfural derivatives, produced by glucose or fructose dehydration, can be a key reagent to produce many important products as polymers, pharmaceuticals, solvents, and fuels [5]. Herein, we have performed the microwave-assisted oxidation of glycerol and of the furfural derivatives 5-(hydroxymethyl)furfural (HMF) and 5-hydroxymethyl-2-furancarboxylic acid (HFCA) with *tert*-butyl hydroperoxide (TBHP). All reactions were catalysed by a C-scorpionate gold(III) complex in homogeneous conditions and supported on graphene, to compare the performance in both conditions.

All the procedures made in this thesis aimed at to be aligned with the principles of the green chemistry: prioritizing the prevention of waste rather than cleaning up and treating waste after it has been created (1); reducing the waste at the molecular level by maximizing the number of atoms from all reagents that will be incorporated into the final product (2) (excess reagents were not used); designing chemical reactions and synthetic routes to be as safe as possible, minimizing the toxicity and choosing safest solvents available (or no solvents in our case in mechanochemistry or MW-assisted reactions) (3-5). Thanks to the use of microwave-assisted reaction, less energy-intensive chemical route was used (6). Commercial glycerol and furfural derivatives were used as model raw materials, but they can come from lignocellulosic feedstock and can be reused (7,10); no temporary derivatives were used (8) and the study of the catalysed oxidations was the main goal of this study (9). Finally, again thanks to microwave-assisted reaction monitoring the chemical reaction is possible and it is possible to have a safe control of the reaction performance (11,12).

As a representative new technique of green chemistry, mechanochemistry was known by IUPAC like one of the top 10

world-changing chemistry innovations [6]. This enabling technology is characterized by mechanical grinding of reactants and induces chemical reactivity by mechanical force (*e.g.*, by compression, shear, or friction). In general, mechanochemical procedures provide advantages like preventing the utilization of excessive solvent, enabling short reaction time, high efficiency, unique reactivity, and unlocks an alternative route toward numerous compounds not achievable by alternative synthetic techniques [7].

Microwave technologies have been showed up to be efficient to get better reaction yields and product selectivity comparing to conventional methods during the last years [8]. There are many advantages of microwave assisted reactions [9]. Among them, fast heating rates, uniform temperature and easy reaction control can be highlighted. These are the reasons why microwave technologies were used first to immobilize the C-scorpionate gold(III) complex on graphene and also to perform the different microwave-assisted oxidations of glycerol and furfural derivatives.

C-scorpionate complexes (Figure 1) are known as one of the few mononuclear types of metal compounds that can catalyze the oxidation of hydrocarbons like xylene [10], secondary alcohols [11], ketones [12] and alkenes [13]. They can be used as homogeneous or heterogeneous catalysts and in the last years their application has experienced interesting advances [14] due to C-scorpionate ligands and their stability toward hydrolysis [13].



Figure 1: a) C-scorpionate tris(pyrazol-1-yl)methane binding to a metal centre; b) illustration of how a scorpion resembles the C-scorpionate [15]

The introduction of microwave-assisted synthesis for the production of tris(pyrazol-1-yl)methanes played an important role on the development of this promising class of ligands [16], for which, in the last decades have attracted considerable interest with their application in bio-inorganic, organic and catalytic chemistry. [10, 13, 14] With carbon scorpionates, several complexes are reported, including zinc [17], vanadium [18], iron [19], rhenium [20], copper [21], molybdenum [22], silver [23], ruthenium [24], among others, including gold.

Four different metal C-scorpionate complexes are chosen for this work. $[\text{CuCl}_2(\text{Tpm})]$ (**1**) was recently reported as a promising green catalyst in the oxidation of styrene to benzaldehyde [25] with hydrogen peroxide (H_2O_2) in an ultra-fast way, achieving 70% of yield after 5 min of reaction at 80 °C (TOF, $1.4 \cdot 10^4 \text{ h}^{-1}$).

The $[\text{NiCl}(\text{Tpm})]\text{Cl}$ complex (**2**) was reported [26] as promising low-cost metal catalyst to replace the palladium ones towards the development of sustainable Heck C-C coupling synthesis. Among the several requirements for a suitable catalyst, its recyclability with possibility to be used in consecutive cycles is often crucial for an economically feasible process.

Some cobalt complexes bearing scorpionate ligands were reported [27] along with their effects on DNA, but, to the best of our knowledge, no cobalt C-scorpionate $\text{HC}(\text{pz})_3$ has been reported in the literature. Thus, in this work is the first time that the synthesis of $[\text{CoCl}_2(\text{H}_2\text{O})(\text{Tpm})]$ (**3**) is going to be tried.

Organometallic gold complexes have experienced great success as catalysts for several reactions such hydrogenation, low temperature CO oxidation and selective oxidations like oxidation of alcohols, aldehydes, and epoxidations, among others [28]

The design of environmental and economically better catalytic processes for selective oxidations additionally addresses catalysts stability and their reuse, aiming at to overcome issues presented by the current homogeneous systems. The chance of mixing the benefits of homogeneous and heterogeneous catalysts by the immobilization of metal complexes on solid supports such as graphene is thus of great importance [13].

A general strategy to convert a homogeneous process into a heterogeneous one is to support the soluble C-scorpionate metal catalyst onto a solid matrix [29]. To this purpose, many sorts of materials can be used, being the zeolitic and carbon materials obtained by different approaches most recently proposed in the literature [30]. It has been reported [30] that recovering the catalyst from the reaction mixture (cyclohexane oxidation with hydrogen peroxide) by an easy filtration and reusing it without loss of activity for five consecutive cycles (it was at the sixth cycle when the activity dropped to 94%) while maintaining the high selectivity of the reaction it's possible. Thus, in this work, the support of complex $[\text{AuCl}_2(\text{Tpm})]\text{Cl}$ (**4**) on graphene is performed.

It is reported [4] that an effective utilization of glycerol and its efficient conversion into various value-added products will have a positive effect on biodiesel production economics, increasing the production and utilization of this alternative fuel resource.

The production of bio-based products from glycerol has become a priority in the chemical market, especially in the plastic, solvents, lubricants and surfactants industries and it is forecasted to increase its demand in the following years [31]. It also offers a great alternative in reducing fossil feedstocks dependence, decreasing the CO_2 emissions in this sector, boosting cleaner, more efficient, modern, and better oriented industries finding satisfied the increasing demand on eco-friendly, safer, and healthier products.

Among all reaction pathways of glycerol, its oxidation will be addressed by our research.

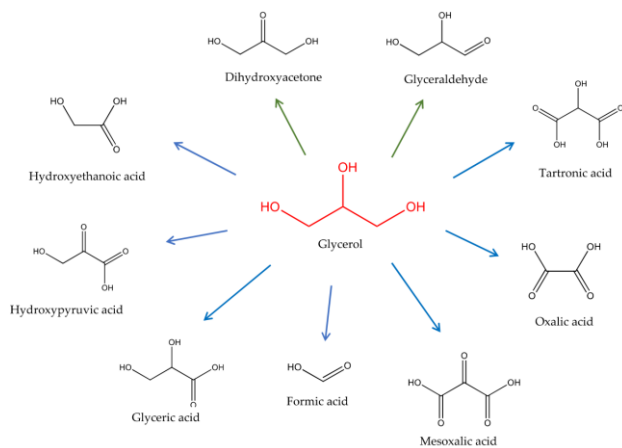


Figure 2: Products from glycerol oxidation [31, 32].

Polymeric materials such as polyethylene terephthalate, polyamides, and polyurethanes have played vital roles in the modern economy. Several industries have started considering using bio-based chemicals to produce bioplastics. In a recent attempt, bioplastics have been successfully produced from bio-based ethylene glycol and 2,5-Furandicarboxylic acid (FDCA) [33]. As mentioned, one of the objectives of this work is focused on the conversion of HMF to produce FDCA, catalyzed by a gold C-scorpionate complex supported on graphene. Depending on the system applied, the conversion of HMF to FDCA can proceed through the preferred aldehyde group oxidation to 5-hydroxymethyl-2-furan carboxylic acid (HFCA) (Figure 3, route A), or the alcoholic group oxidation to 2,5-furan carboxaldehyde (Figure 3, route B). These process intermediates are then oxidized to 5-Formyl-2-furancarboxylic acid (FFCA), which is in turn transformed into FDCA as the final product

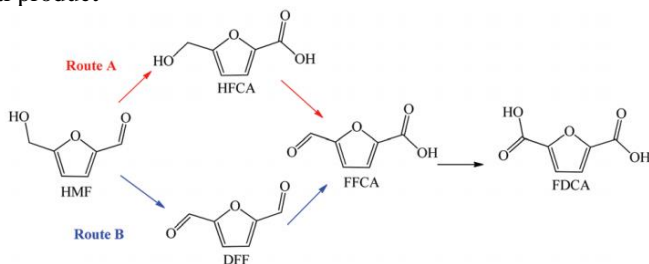


Figure 3: Reaction pathway of HMF oxidation to produce FDCA [33]

II. EXPERIMENTAL PROCEDURE

A. Synthesis of the C-scorpionate metal complexes

C-scorpionate complexes of nickel(II), cobalt(II), copper(II) and gold(III) were synthesized by a green method. We have chosen the mechanochemical synthesis using a ball mill (solid state conditions), instead of the traditional method reported in literature [25, 34, 35], to prepare the complexes **1** – **4**: [CuCl₂(Tpm)] (**1**), [NiCl(Tpm)]Cl (**2**), [CoCl₂(H₂O)(Tpm)] (**3**), and [AuCl₂(Tpm)]Cl (**4**).

All complexes were obtained by the reaction of hydrotris(pyrazol-1-yl)methane (HCpz₃, pz = pyrazol-1-yl; Tpm) and the appropriate metal chloride.

Different reaction conditions have been performed such as mixing time, number of spheres and stirring speed for non-precious metals such as copper(II), nickel(II), and cobalt(II) before producing the C-scorpionate gold(III) complex that is the one that have been used for the microwave-assisted oxidations. For every complex, 7 different reaction conditions were tested:

1. 5 min, 3 spheres, 250 rpm
2. 10 min, 3 spheres, 250 rpm
3. 15 min, 3 spheres, 100 rpm
4. 15 min, 3 spheres, 500 rpm
5. 15 min, 1 sphere, 250 rpm
6. 15 min, 5 spheres, 250 rpm
7. 15 min of manual grinding.

The C-scorpionate complexes **1-4** were prepared using the following reagents: commercial metal salt, used as received [copper(II) chloride dihydrate, 99+%, (ACROS OrganicsTM) for complex **1**; nickel(II) chloride hexahydrate, 98% (Sigma Aldrich) for complex **2**; cobalt(II) chloride hexahydrate (Sigma Aldrich) for complex **3**; and gold(III) chloride hydrate 99.995% trace metal basis (Sigma Aldrich), for complex **4** and hydrotris(pyrazol-1-yl)methane (Tpm) that synthesized in our laboratory according to methodologies described in the literature [35]. The amount of reagents was the appropriate to work under equimolar conditions (0.2 mmol). Both reagents were added together into the grinding jar of the Retsch[®] Planetary Ball Mill PM100 [36] under the above conditions 1-7.

All samples were characterized to confirm that expected structures were obtained by:

- MIR (4000–400 cm⁻¹) and FAR-IR (400–100 cm⁻¹) were recorded on a Vertex 70 (Bruker).
- Elementary analysis (IST analysis laboratory).
- SEM/EDS (MicroLab- Electron Microscopy Laboratory of IST).
- XPS performed by Dr Ana Ferrara from IBB.

B. Immobilization of [AuCl₂(Tpm)]Cl on graphene

Different ways on supporting the gold complexes into graphene were tested: Wet impregnation (WI), microwave (MW) and by Liquid Assisted Grinding (LAG). The purpose of trying different techniques was compare the results as LAG will use 1-2 mL of solvent, MW, 10-15 mL and traditional WI 20 mL. If results are similar LAG method could avoid the excessive use of solvents. On the other hand, two different types of graphene were used to compare, again its performance on support and catalysis

For all three different ways of supporting, two samples were made:

- 2% wt of complex **4** made by BM supported on graphene and
- 10% wt of complex **4** made by reported method in literature [34] on ultra-pure graphene.

1) *Wet impregnation (WI)*

Graphene and catalyst are both put together with 20 mL of solvent (distilled water) under continuous stirring for 24h, then the observed liquid and solid phases are separated after another 24h and dried in vacuum oven at 50 °C overnight.

2) *Microwave(MW)*

Microwave support was made with Monowave 400 Anton Paar® [37] microwave reactor. Microwave assisted reaction conditions were: 30 min, 40°C, 650 rpm with magnetic stirrer, 25 W and 30 mL borosilicate vial. After microwave assisted reaction, solid and liquid phases were separated after 24h and then dried in vacuum oven at 50°C overnight for later, get the solid phase.

3) *Liquid Assisted Grinding (LAG)*

To perform LAG, the Emax High Energy Ball Mill of Retsch® [38] was used. The parameters and conditions for the Emax machine for perform the LAG were: 3 spheres, 15 mins and 800 rpm. After LAG, the grinding jar was dried overnight by vacuum oven at 50°C, and the solid phase was recollected.

To confirm the surface of the supported catalyst and the intake of gold supported on the different samples of graphene and ultra-pure graphene, SEM/EDS characterization was performed by MicroLab-Electron Microscopy Laboratory of IST.

C. *Microwave-assisted oxidation reactions*

1) *Glycerol microwave-assisted oxidation*

For glycerol microwave-assisted oxidations, the general conditions were: 5 mmol glycerol, 10 mmol TBHP 70%, 650 rpm, 25 W, and 2h reaction. Temperature was changed between 50 and 80°C, both homogeneous and heterogeneous conditions were tested, and different amounts of catalyst (5-10 mg) were performed to compare the influence of those parameters.

First, the needed amount of catalyst is introduced in the vial, following the glycerol (Sigma Aldrich) [39] used as received, and the stirring bar. When the equipment is properly programmed for starting the reaction, TBHP (Sigma Aldrich) [40] used as received, is introduced slowly, as is the oxidating agent. The vial is closed with the cap and introduced inside the microwave equipment. After microwave reaction stops, the final solution is collected inside a little glass flask and kept refrigerated in fridge (3-5°C).

2) *HMF microwave-assisted oxidation*

For HMF microwave-assisted oxidation general conditions were 5 mmol HMF, 10 mmol TBHP 70%, 650 rpm, 25 W, 2 h reaction, 50 °C and 5 mg of catalyst. First oxidation sample was

performed with no catalyst to compare differences with several graphene supported complex **4** catalysts.

First, the needed amount of catalyst is introduced in the vial, following the HMF obtained from TCI Chemicals [41], used as received and the stirring bar. When the equipment is properly programmed for starting the reaction, TBHP is introduced slowly, as is the oxidating agent. The vial is closed with the cap and introduced inside the microwave equipment. After microwave reaction stops, the final solution is collected inside a little glass flask under nitrogen atmosphere and kept refrigerated and protected from light in fridge (3-5 °C).

3) *HFCA microwave-assisted oxidation*

For HFCA microwave-assisted oxidation general conditions were: 0,5 mmol HFCA, 1 mmol TBHP 70%, 650 rpm, 25 W, 2h reaction. Temperature was changed between 50 and 80°C, both homogeneous and heterogeneous conditions were tested, and different amounts of catalyst (5-10 mg) were performed to compare the influence of those parameters.

The needed amount of catalyst is introduced in the vial, following the HFCA obtained from TCI Chemicals [42], used as received, 1 mL of acetonitrile and the stirring bar. When the equipment is properly programmed for starting the reaction, TBHP is introduced slowly. The vial is closed with the cap and introduced inside the microwave equipment. After microwave reaction stops, the final solution is collected inside a little glass flask under nitrogen atmosphere and kept refrigerated and protected from light in fridge (3-5°C).

¹H NMR characterization was performed for glycerol and furfural derivatives on Bruker Advance 400 MHz at room temperature and using deuterated acetone as solvent. This characterization method was used to identify the compounds obtained in each oxidation test.

III. RESULTS AND DISCUSSION

A. *C-scorpionate complexes synthesis and characterization*

The four metal C-scorpionate metal complexes synthesized were: [CuCl₂(Tpm)] (**1**), [NiCl(Tpm)]Cl (**2**), [CoCl₂(H₂O)(Tpm)] (**3**), and [AuCl₂(Tpm)] (**4**). Their structures are depicted in figure 4.

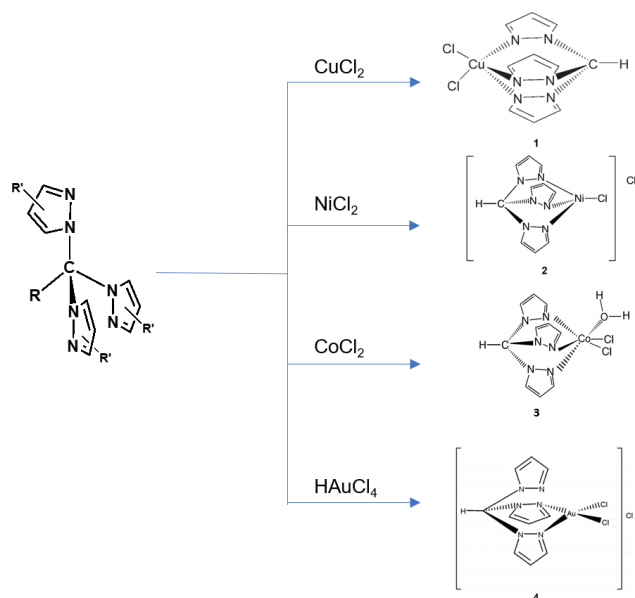


Figure 4: Synthesis of Complexes **1** – **4** from hydrotris(pyrazol-1-yl)methane and the appropriate metal chlorides.

For the different complexes **1-4**, elementary analysis was performed. Additionally MIR (4000–400 cm^{-1}) and FAR-IR (400–100 cm^{-1}) were recorded on a Vertex 70 (Bruker) instrument in KBr pellets for IR and CsI for the FAR analysis. Two representative samples of each complex were selected to perform the characterization.

1) $[\text{CuCl}_2(\text{Tpm})]$ complex **1**

For PGCuBM4L sample (15 min, 3 spheres, 500 rpm): IR (cm^{-1}): 3436.62 br [v(O-H)], 3152.59 sh, 3119.77 m [v(C-H)], 1653.67 br[v(O-H)], 1519.58 m, 609.52 s [v (Cu-Cl)]. FAR (CsI pellet) (cm^{-1}): 375.50 s, 267.94 s [v(Cu-Cl)].

For PGCuBM6L sample (15 min, 5 spheres, 250 rpm): IR (cm^{-1}): 3447.25 br [v(O-H)], 3125.30 sh, 2967.35 m [v(C-H)], 1642.94 br[v(O-H)], 1519.95 m, 609.78 s [v (Cu-Cl)]. FAR (CsI pellet) (cm^{-1}): 375.29 s, 267.57 s [v(Cu-Cl)].

Elementary analysis found (calculated): C: 32.61 (34.44); H: 2.76 (2.89); N: 22.36 (24.10)

It can be highlighted that the best conditions to prepare the C-scorpionate copper(II) complex $[\text{CuCl}_2(\text{Tpm})]$ (**1**) were: time of reaction 15 min, using 5 spheres and 250 rpm, since PGCuBM6 was the sample that get the best yield (82.6%). It was followed by PGCuBM4 (15 min, 3 spheres, 500 rpm and yield of 82.3%). As expected, the worst yield was obtained for PGCuM7 (mortar sample).

Comparing with the method reported in literature [25] where the yield of 83% of complex **1** was obtained, mechanochemistry method showed great performance and quick obtention of the same complex with practically same yield.

2) $[\text{NiCl}(\text{Tpm})]\text{Cl}$ complex **2**

For PGNiBM4 sample (15 min, 3 spheres, 500 rpm):

IR (cm^{-1}): 3191.01 sh, 3075.42 m [v(C-H)], 1632.63 br, 1521.72 m [v(O-H)], 605.08 s [v (Ni-Cl)]. FAR (CsI pellet) (cm^{-1}): 227.73 s [v(Ni-Cl)]

For PGNiBM6' sample (15 min, 5 spheres, 250 rpm):

IR (cm^{-1}): 3366.52 sh, 3136.84 sh, 2973.87 m [v(C-H)], 1632.20 br, 1520.47 m [v(O-H)], 660.40 s, 504.65 s [v (Ni-Cl)]. FAR (CsI pellet) (cm^{-1}): 227.73 s [v(Ni-Cl)].

Elementary analysis found (calculated): C: 30.22 (34.93); H: 3.8 (2.93); N: 20.92 (24.44)

Best conditions to prepare the C-scorpionate nickel(II) complex $[\text{NiCl}(\text{Tpm})]\text{Cl}$ (**2**) were: reaction time 15 min, using 3 spheres and 500 rpm (yield of 55.9%), which led to almost the same value as the obtained with 15 min. reaction time, 5 spheres and 250 rpm (54.6%). Again, as expected, the worst yield was obtained for PGNiM7 (mortar sample).

Worst yield result was obtained compared with the 86% of yield reported on literature [26], the reason was probably the fact that the Nickel chloride was hexahydrate and was difficult to remove the product from reactor and spheres of the ball mill machine.

3) $[\text{CoCl}_3(\text{Tpm})]$ complex **3**

For PGCoBM4 sample (15 min, 3 spheres, 500 rpm):

IR (cm^{-1}): 3401,00 br[v(C-H)], 1635,69 br, 1519,23 m [v(O-H)], 607,25 s [v (Co-Cl)] FAR (CsI pellet) (cm^{-1}): 379,456 s, 312,60 s [v(Co-Cl)].

For PGCoBM6 sample (15 min, 5 spheres, 250 rpm):

IR (cm^{-1}): 3072,92 br, 2975,79 m [v(C-H)], 1635,71 br, 1517,84 m [v(O-H)], 607,02 s [v (Co-Cl)]. FAR (CsI pellet) (cm^{-1}): 379,89 s, 311,57 s [v(Co-Cl)].

Elementary analysis found (calculated): C: 28.26 (33.17); H: 3.41 (3.34); N: 19.58 (23.21)

PGCoBM4 was the sample that get the best yield (69.5%, being time of reaction 15 min, using 3 spheres and 500 rpm) followed by, PGCoBM2' (66.9%, 10 min, 3 spheres, 250 rpm washed with diethyl ether) and PGCoBM2 (65.3%, 10 min, 3 spheres and 250 rpm). The worst yield was obtained for PGCoM7 (mortar sample).

As mentioned before, there is no literature to compare the synthesis yield for complex **3**, but another Co C-scorpionate complexes were reported [27] with yields under 60%, being the obtained yields for ball milling method higher than these ones.

4) $[\text{AuCl}_2(\text{Tpm})]\text{Cl}$ complex **4**

For BMAu3L sample (15 min, 3 spheres, 500 rpm):

IR (cm^{-1}): 3466.53 br, 3123.24 sh, 2812.80 m [v(C-H)], 1635.64 br [v(O-H)], FAR (CsI pellet) (cm^{-1}): 357.67 s [v(Au-

Cl)] asymmetric, 300.13 s [v(Au-Cl)] symmetric for complex **4** made by mechanochemistry.

For the complex **4** prepared by the reported method in literature [34]:

IR (cm⁻¹): 3441.28 br, 3121.77 sh, 2963.60 m [v(C-H)], 1612.34 br, 1522.62 m [v(O-H)], 421.37 s [v(Au-Cl)] FAR (CsI pellet) (cm⁻¹): 359.30 s, 201.94 s [v(Au-Cl)] asymmetric, 295.85 s [v(Au-Cl)] symmetric.

Elementary analysis found (calculated): C: 18.46 (23.21); H: 2.00 (1.95); N: 12.36 (16.24)

It can be highlighted that the best conditions to prepare the C-scorpionate gold(III) complex [AuCl₂(Tpm)]Cl (**4**) are: reaction time of 15 min, 3 spheres and 500 rpm, since PGAuBM4 was the sample that get the best yield (59.9%). It was followed by PGAuBM6 (yield of 52.1%, 15 min, 5 spheres, 250 rpm). As expected, the worst yield was obtained for PGAuM7 (mortar sample).

The synthesis yield reported [34] for the traditional method was of 72%, being better than the ones obtained for ball milling samples. This could be, again, due to the difficulties removing the product from the spheres and jar, being the gold chloride hydrated.

XPS analysis was performed for the gold(III) complex **4** used for performing the catalytic studies. As presented in Table 1, the XPS global quantification shows accordance with the reported structure **4** and with the oxidation state of the gold (Au³⁺). The analysis was kindly performed by Dr. Ana Ferraria, from IBB.

Table 1: XPS global quantification of gold(III) C-scorpionate complex [AuCl₂(Tpm)]Cl (**4**)

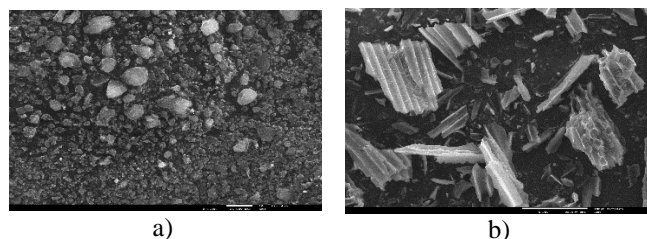
[AuCl ₂ (Tpm)]Cl	
At. Conc. (%)	
Au	5.00
Cl	11.9
C	59.3
O	7.0
N	16.8

B. Graphene supported gold(III) C-scorpionate complex [AuCl₂(Tpm)]Cl (**4**) characterization

SEM and EDS were performed for observe the morphology of the surface of the supported complex, and its elements at the surface for the support made by different techniques. Both SEM and EDS were performed by MicroLab-Electron Microscopy Laboratory of IST.

1) WI graphene supported gold(III) C-scorpionate complex [AuCl₂(Tpm)]Cl (**4**)

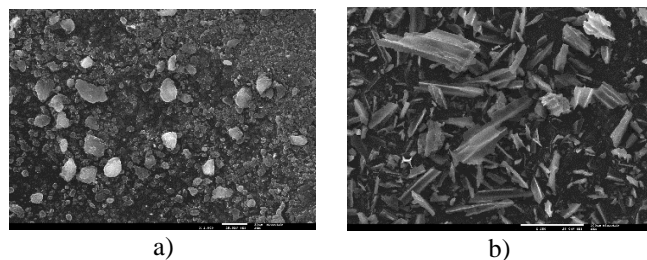
Table 2: SEM of the gold complex made by the wet impregnation method with carbon supports. a) is graphene and b) is ultra-pure graphene.



The structure of the supports is not affected, although the intake of gold seems to be better at the surface, for the graphene sample.

2) MW graphene supported gold(III) C-scorpionate complex [AuCl₂(Tpm)]Cl (**4**)

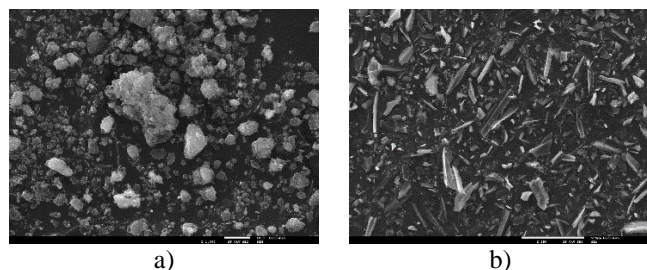
Table 3: SEM of the gold complex made by the microwave method with carbon supports. a) is graphene and b) is ultra-pure graphene.



This method worked much better to produce the supported catalysts, without losing the structure of the supports.

1) LAG graphene supported gold(III) C-scorpionate complex [AuCl₂(Tpm)]Cl (**4**)

Table 4: SEM of the gold complex made by LAG method with carbon supports. a) is graphene and b) is ultra-pure graphene



This technique crushes the support and the gold complex in smaller size particles, in the case of the sample with graphene, the intake of gold seems to be better but there is also a contamination with iron and chromium. This contamination is probably due to the spheres and the reactor that are from stainless steel and most likely the spheres were becoming

D. HMF microwave-assisted oxidation characterization

The reaction that occurs for HMF MW-assisted oxidation is presented in Figure 10.

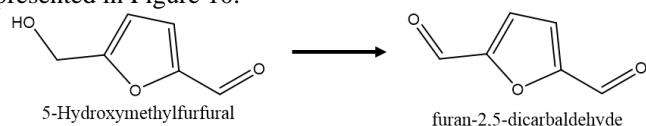


Figure 10: 5-Hydroxymethylfurfural oxidation to furan-2,5-dicarbaldehyde

As with glycerol oxidation samples, the different conversion of the targeted products for both furfural derivatives, were obtained as detailed in referenced literature [43] after ^1H NMR spectrum analysis.

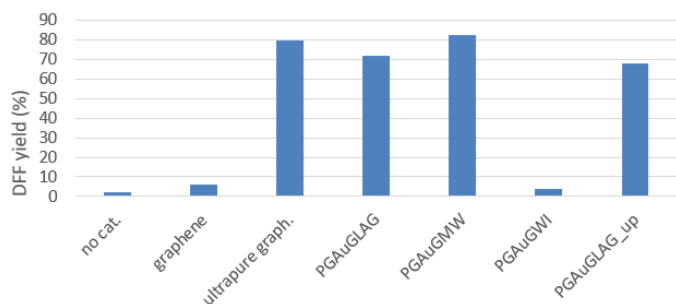


Figure 11: Different DFF yields on HMF oxidation- influence of catalyst

As it can be observed in Figure 11, best DFF yield was for PGff5 sample (83.2%) being MW the method used for supporting complex 4 made by mechanochemistry on graphene. Comparing with literature [33], better yields were obtained for FDCA, with higher temperature and reaction time, but is important to highlight that the selectivity to DFF was high as no other possible products were observed in the ^1H NMR spectra.

Different conditions and more samples were thought to be performed, but due to limited time and problems with the supply of the reagent, this could not be done.

Recycling of PGff5 was performed, leading to a DFF yield of 10.4% as it can be observed in Figure 12. Characterization of the recovered catalyst is thus, of great importance, to observe if the intake the gold was lost, or the structure of the supported catalyst poisoned.

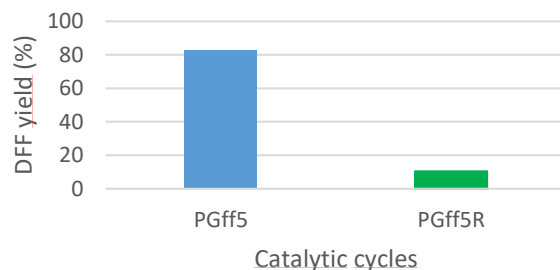


Figure 12: DFF yield for original vs. recovered catalyst.

E. HFCA microwave-assisted oxidation characterization

The reaction that occurs for HFCA MW-assisted oxidation is presented in Figure 13

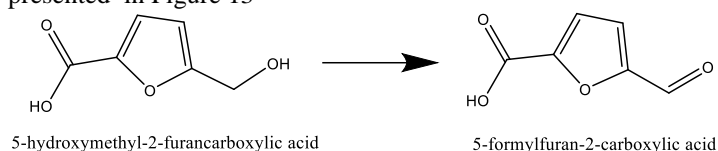


Figure 13: 5-hydroxymethyl-2-furancarboxylic acid oxidation to 5-formylfuran-2-carboxylic acid

Heterogenized catalysts showed an improvement in catalytic behaviour as all homogeneous experiences lead to a FFCA yield of 0%. On the other hand, switching the temperature from 50°C to 80°C, in the case of PGAuGLAG_up improves the FFCA yield from 12 to 29.1% (PGff9 and PGff16). Different yields obtained for this oxidation reaction are presented in Figure 14

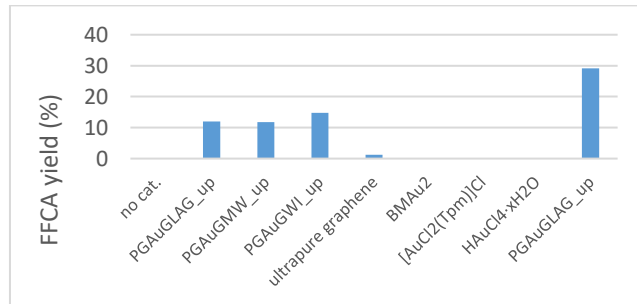


Figure 14: Yields obtained for all samples of HFCA oxidation

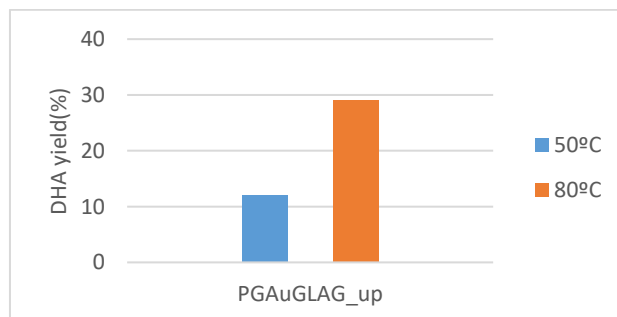


Figure 15: Influence of temperature on HMF oxidation

In this particular case, with 80°C the DHA yield obtained is more than 2 times higher than with 50°C. As observed in Figure 14, in this case, with 80 °C the FFCA yield obtained is more than 2 times higher than with 50 °C, showing better performance at higher temperatures. More samples should be performed and compared at same conditions but different temperatures in order to get better analysis of temperature influence.

Again, the recover of the best sample was mad, and the same reaction performed, showing this time no conversion an no products. As with HMF oxidation, characterization of the recovered catalyst is thus, of great importance, to observe if the intake the gold was lost, or the structure of the supported catalyst poisoned.

Aiming to summarize the 3 different oxidation results : For glycerol microwave-assisted oxidation, DHA yield results showed that the best reaction conditions were: 50 °C and 10 mg of supported complex **4** on ultra-pure graphene by LAG method, yielding 85.7% DHA yield. These conditions are followed by: 50 °C and 10 mg of supported complex **4** on ultra-pure graphene by MW method. As expected, the worst DHA yield was obtained for 80 °C and 5 mg of HAuCl₄·H₂O.

For the HMF microwave-assisted oxidation, DFF yield results showed that the best reaction conditions were: 50 °C and 5 mg of supported complex **4** on graphene by MW method, yielding 82.68% of DFF.

HFCA microwave-assisted oxidation showed that the best reaction conditions were: 80 °C and 10 mg of 10 mg of supported complex **4** on ultra-pure graphene by LAG yielding 29.1 % of FFCA. Many of the samples obtained 0% of FFCA yield, being all performed in homogeneous conditions.

Best results and conditions are presented in Table 5:

Table 5: Best results an conditions obtained for the oxidation reactions.

Oxidation	Catalyst	Conditions	Yield(%)
Glycerol	PGAuGLAG_up	50°C 10 mg cat.	85.7
HMF	PGAuGMW	50°C 5mg cat.	82.68
HFCA	PGAuGLAG_up	80°C 10 mg cat.	29.1

Reaction conditions: 650 rpm, 2 h, and 25 W

IV. CONCLUSIONS AND FUTURE WORK

The main objectives of this work were the synthesis of a gold(III) complex using a C-scorpionate as ligand by a sustainable technique, the ball milling mechanochemistry, its heterogenization in graphene and its use in industrial oxidation reactions as a heterogeneous catalyst. The evaluation of its

activity was performed for the glycerol and furfural derivatives oxidation.

The synthetic results show that the complexation of Tpm with the gold(III) precursor is quickly and possible to achieve without solvent, when using ball milling. Its structure obtained was confirmed by several techniques and showed that the gold metallic centre is coordinated with two pyrazolyl rings and that the spectroscopic characteristics are in agreement with the referenced in the literature.

Different methods for support complex **4** were performed, trying to avoid the use of solvents if a possible scale-up of the process is made, appearing as an alternative to traditional WI methods. MW and LAG support methods showed better intake of gold when characterized and better oxidation results.

The glycerol and furfural derivatives oxidation was successful, using homogeneous and heterogeneous catalysis and the best results were obtained for the later.

In the case of glycerol oxidation, appropriated values of DHA yield were obtained, comparing with literature, highlight the selectivity for DHA of complex **4**, as no other possible products were observed in the different 1H NMR spectra.

Furfural derivatives oxidation showed better results for HMF than for HFCA, being probably due the fact that HMF is more reactive due to the absence of an acid group in its structure.

As an area still little explored, the use of gold(III) complexes can be a focus of investigation as they have an excellent selectivity to reactions. Some possible suggestions are described below:

- Further analysis of the glycerol and furfural products to ensure a better insight into the reaction path of both catalyts, thus improving conditions.
- Investigation of reaction mechanisms for all oxidations studied.
- Testing of different compounds that are essential to produce commodities.

It is also important to highlight that if available time and circumstances were better, more samples of supported complex **4** on graphene would have been made, and the use of the complexes **1**, **2**, and **3** for perform the oxidations tried, as all three complexes are promising low-cost catalysts for the future. A better and more thorough characterization and recovery of catalysts would have been done, as is of great importance for the study of the heterogeneous catalysis.

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