Herme, GB.; Krüger, M.; Reinsch, H.; Alvaro Rodríguez, MM.; Stock, N.; García Gómez, H. (2015). Transient absorption spectroscopy and photochemical reactivity of CAU-8. Journal of Materials Chemistry C. 3(15):3607-3613. doi:10.1039/C4TC02518K.

Graphenes as metal-free catalysts for the oxidative depolymerization of lignin models

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Abstract: Graphene oxide promotes the oxidative degradation of α–guaiacylglycerol-β-guaiacyl ether, a lignin model compound, in different solvents including acetonitrile, toluene and water mainly to guaiacol, 2-methoxyquinone, vanillic acid and coniferyl aldehyde. Reduced graphene oxide and B-doped graphene exhibit similar activity as graphene oxide. Control experiments indicate that metal impurities should play a marginal role in the observed catalytic activity.

Introduction

Among the reaction network for biomass transformation into chemicals, one of the most important processes is lignin depolymerization and its conversion into valuable aromatic compounds[1]. One possibility for this transformation consists in the oxidative depolymerization (OD) of lignin using oxygen to assist the rupture of the ether bonds.[2, 3] Although organic peroxides have been used for lignin OD,[4] oxygen is the preferable oxidizing chemical from the point of view of sustainability and affordability.[5]

Typical homogeneous catalysts reported for lignin OD are transition metals ions, such as vanadium,[6, 7] rhenium[8] and cobalt .[9] In this context, one current line of research in catalysis is the evaluation of metal-free catalysts and OD of lignin can offer an opportunity to develop this type of catalytic process.[3-5] Graphene oxide (GO) and other doped graphenes (G) have been reported to act as metal-free catalysts for the aerobic oxidation of benzylic hydrocarbons,[10] benzylic alcohols[11] and cycloalkanes.[12] Therefore, it would be interest to check if carbocatalysts based on G can also promote OD of lignin.

In a recent precedent, it has been found that N-containing G [(N)G] is able to catalyze the oxidation of simple lignin models using *tert*-butyl hydroperoxide (TBPH) as terminal oxidant.[4] Continuing with this line of research it would be of interest to determine if G-based carbocatalysts can also promote the cleavage of ether bonds in lignin models using molecular oxygen as the only oxidation reagent. For the present study α-guaiacylglycerol-β-guaiacyl ether (**1**), (see structure in Scheme 1) was selected as lignin model to evaluate the potential of some Gs as catalysts for lignin OD by cleavage of the guaiacyl ether bond.

Results and Discussion

Table 1 summarizes the carbocatalysts used in the present study, their preparation procedure and relevant analytical data. In the present study we have evaluated the catalytic activity of different graphenic materials including GO obtained from graphite by Hummers oxidation and exfoliation. The composition for this GO is 17 % C, 3 % H, 1 % S and 49 % O_2. XPS indicates that 13 % of this carbon is C=C, 40 % C-O, C=O 44 % and 2 % corresponding to O-C=O.[13, 14] Besides GO, we have also included in our study a reduced GO (rGO)[15] prepared by hydrothermal reduction of GO in water at 200 ºC. XPS of rGO shows 74 % C=C, 14 % C-O and 12 % C=O. The series of G catalysts tested also includes a [(N)G] sample prepared by pyrolysis of chitosan at 900 ºC under inert atmosphere and subsequent exfoliation. XPS analysis show about 50% of pyridinium like nitrogen, 48 % of pyridine like nitrogen, and a small amount of N-oxide, while the elemental analysis shows that the amount of N is 6.65%.[14, 16, 17] Finally, B-doped G [(B)G] obtained by pyrolysis of borate ester of alginate was also tested. I n (B)G, the concentration of boron is 13 %. XPS indicates that about 70 % is graphitic boron and the rest is similar to boric acid.[14] Raman spectroscopy shows for all Gs the expected 2D, G and D bands. The intensity of the G versus D peak ranges from 1.3 to 1.6. Most of these G catalysts were active to promote OD of **1**, leading to compounds **2-10** as the main reaction products as indicated in Scheme 1. The catalytic activity of these G samples for lignin OD is summarized in Table 2 (the corresponding yields are indicated in Table S1 in supporting information). For the sake of comparison, the activity of commercial graphite was also included in the study.

Table 1. Carbocatalysts used in the present study including their origin and analytical data.

	Graphite	GO	rGO	(B)G	(N)G
Origin	Comercial	Hummmers oxidation and exfoliation	Hydrothermal reduction of GO	Pyrolysis of borate doped alginate	Pyrolysis of chitosan
Dopant content (wt%)	--	O: 45	O: 18	B: 1	N: 5

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Preliminary studies were carried out using acetonitrile as solvent and moderate O_2 pressure (5 bars) in order to compare the catalytic activity of the materials under study. The results are presented in Table 2.

Table 2. Results of the catalytic activity of Gs used inn the present study for the OD of **1.**[a,b,c]

Catalyst	Conversion (%)	Product Selectivity (%)						
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Graphite	32	3	1	6	1	3	4	59
GO	100	0	6	2	5	7	15	87
rGO	65	0	0	1	2	5	9	37
(B)G	44	0	6	0	1	4	9	17
(N)G	1	0	0	0	0	88	0	90

[a] Reaction conditions: **1** (0.01 mmol), O_2 pressure (5 bars), catalysts (1.5 mg) time 24 h, temperature 140 ºC acetonitrile (1.5 mL). [b] Conversion and selectivity determined by HPLC using nitrobenzene as internal standard. [c] Traces of compounds **9** and **10 were also detected.**

In all cases the products observed were the same with some remarkable differences in conversion and selectivity depending on the catalyst. As it can be seen in Figure 1, compound **1** can split in two fragments. The major product for fragment B is guaiacol (**8**). Guaiacol can also derive from deep oxidation of fragment A. However, in the case of the fragment A, other possible products are coniferyl aldehyde (4), vanillin acid (**5**), vanillin (**6**) and 2-methoxyquinone (**7**). Selectivity is defined as moles of product divided per moles of converted 1 in percentage. Since guaiacol (**8**) can derive from both moieties of the molecules a selectivity up to 200 % could be possible although the occurrence of a significant degree of oxidative degradation should decrease selectivity.

As can be seen in Table 2, [(N)G] was highly inefficient for the OD of compound **1** that in the presence of this catalyst was converted in a low extent. On the other extreme, GO was the catalyst that exhibits the highest activity (see Figure 1 for the corresponding time-conversion plot). rGO and (B)G show an intermediate behavior between GO and [(N)G], achieving moderate conversion values of **1** under the same conditions. For the sake of comparison, Table 2 also includes the catalytic activity of graphite powder since its structure is related to that of G and is the precursor material for the preparation of GO. Notably, graphite was able to promote OD of compound **1** in a significant extent. Figure 2 shows the time-conversion plot of model compound **1** using GO as catalyst.

Due to the possible interference of adsorption increasing the apparent conversion of substrate **1** and decreasing product selectivity when large amounts of graphene materials are used as catalysts, a series of adsorption tests were carried out for the most important reaction products observed for OD of **1** (see Table SI2 in the supporting information). In these isothermal adsorption tests, 0.01 mmol of each product was added to the catalyst suspension and aliquots were taken periodically to follow the adsorption. No significant adsorption was observed for substrate 1 or any reaction product under conditions analogous to that of the reaction.

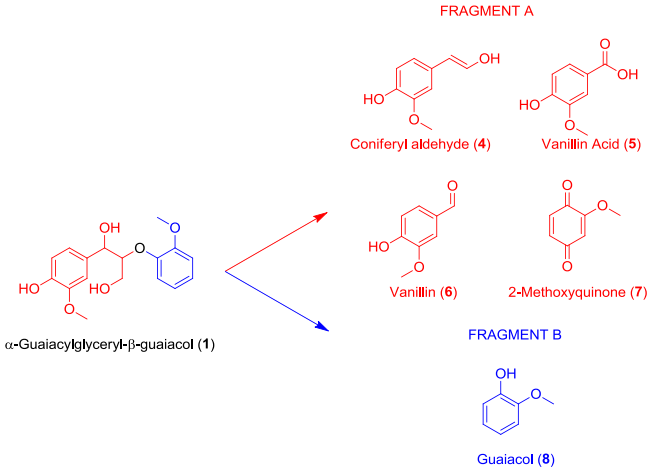
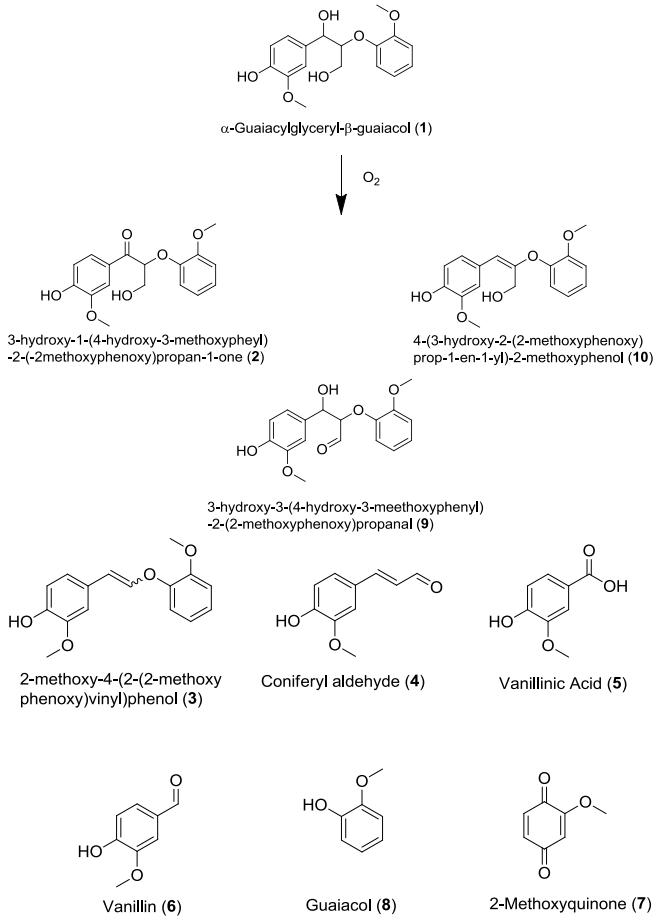


Figure 1. Possible fragmentation products derived from compound **1**.

According to Table 2, GO is a suitable OD catalyst for compound 1 where in an attempt to moderate the oxidative activity of GO in the process, a screening of different solvents was made. Besides acetonitrile, the oxidative degradation of compound **1** was also carried out in a series of solvents including toluene, ethyl acetate, ethanol and water. The results obtained are shown in Table 3 (the corresponding product yields are indicated in Table SI3 in the supporting information).

As can be seen in Table 3, the catalytic activity of GO is notably influenced by the nature of the solvent, ethyl acetate being the one exhibiting the highest selectivity towards guaiacol, vanillic acid and vanillin. On the other extreme, ethanol and toluene were found not suitable solvents for the oxidation due to the poor selectivity towards products **2**-**10**, indicating a large extent of mineralization. When similar experiments were carried out in water, it was noticed that the catalytic activity of GO and other G catalysts was very high, but the selectivity toward the corresponding products **2-10** was again significantly lower than when using acetonitrile as solvent. Figure 2 shows a comparison of the time-conversion plots for OD of **1** in acetonitrile and water.

Figure 3 presents the variation of the selectivity for compound **8** derived from fragment B, while the selectivity for the products derived from fragment A is presented in Figure 4.



Scheme 1. Structure of lignin model **1** and the different pproducts characterized in its OD.

catalyst (1.5 mg), time 24 h, temperature 140 ºC, solvent (1.5 mL). Legend: water (■), acetonitrile (○).

Eventually, at sufficiently long reaction time negligible amounts of organic compounds remained in the aqueous phase due to the complete mineralization of **1** and the corresponding products derived therefrom.[16]

Table 3. Product selectivity at complete conversion or the OD of model compound **1** in different solvents.[a,b,c]

Selectivity (%)	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Acetonitrile	0	6	2	5	7	15	87
Water	0	1	0	5	3	16	1
Toluene	0	0	1	8	1	12	64
Ethanol	6	0	2	5	4	10	54
Ethyl acetate	0	3	2	9	7	2	94

[a] Reaction conditions: **1** (0.01 mmol), O_2 pressure (5 bars), GO (1.5 mg), time 24 h, temperature 140 ºC. [b] Conversion and selectivity determined by HPLC using nitrobenzene as internal standard. [c] Traces of compounds **9** and **10** were also detected**.**

Particularly remarkable is the decrease in the percentage of guaiacol from above 87 % to less than 40 % at long reaction times without being accompanied by the increase in the selectivity of any product (see Figure 3).

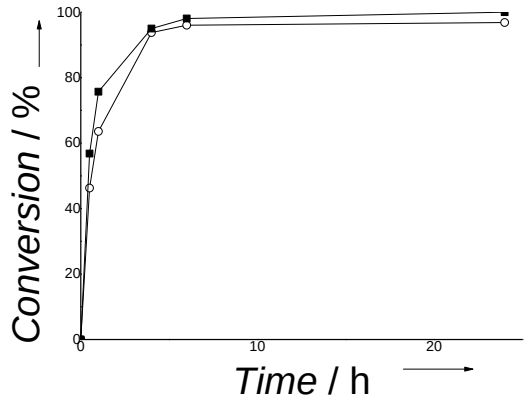


Figure 2. Time-conversion plot for the OD of model compound **1** using GO as catalyst in two solvents. Reaction conditions: 1 (0.01 mmol), O_2 (5 bars),

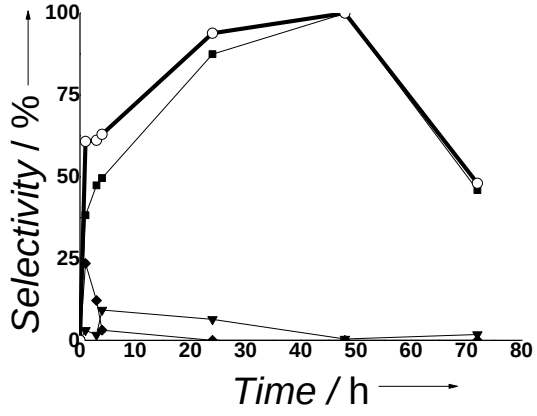


Figure 3. Time-selectivity plot for the oxidative degradation of 1 using GO as catalyst in acetonitrile. Reaction conditions: 1 (0.01 mmol), O_2 pressure (5

bars), catalyst (1.5 mg), temperature 140 ºC, acetonitrile (1.5 mL). Legend: Compound **2** (■), **3** (♦), **8** (▼) and total fragment B selectivity (○) (maximum 100%).

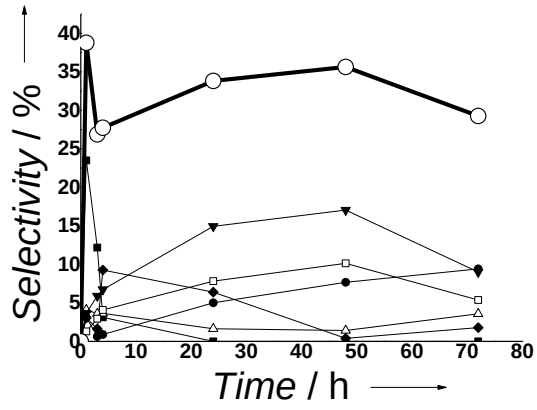


Figure 4. Time-selectivity plot for the oxidative degradation of **1** using GO as catalyst in acetonitrile. Reaction conditions: 1 (0.01 mmol), O_2 pressure (5 bars), catalyst (1.5 mg), temperature 140 ºC, acetonitrile (1.5 mL). Legend: Compound **2** (■), **3** (♦), **4** (Δ),**5** (●), **6** (□), **7** (▼) and total selectivity for products derived from fragment A (○) (maximum 100%).

The influence of the oxygen pressure on the OD of model compound **1** catalyzed by GO was studied by performing a series of reactions under the same conditions varying the oxygen pressure from 5 to 1 bars, as well as under inert atmosphere (see Table 4 and Table SI4 for the corresponding product yields). It was found that full conversion was achieved at 24 h reaction time for 2.5 bars oxygen pressure, but also for 1 bar a high conversion was achieved. The best conditions in terms of higher product selectivity was 2.5 bars in which guaiacol (**8**) in 96 % and coniferyl aldehyde (**4**) in 20 % were the mayor products, accompanied by vanillin (**6**) as well as vanillic acid (**5**).

A control experiment carried out under Ar deserves some comment with regard to the oxidation mechanism and the role of oxygenated functional groups present on GO. In contrast with the presumed lack of conversion under inert atmosphere, substrate **1** undergoes under Ar almost complete conversion giving a reaction mixture in which guaicol (**8**) was the predominant product, but in which propiophenone (**2**) and aldehyde (**4**) having lateral chain connected to the aromatic rings were also present in a notable percentage. Also a study where the catalyst load were modified were carried out under oxygen and argon atmosphere (5 bars). This result indicates that the some oxygenated functional of GO should promote OD of **1**, while GO should be reduced to rGO. The tendency of GO to undergo reduction is a well-established fact and this should be the driving force for the process.[5, 18-20] In this regard, there are precedents in the literature in which it has been proposed that the active oxidation sites are the oxygenated functional groups of GO (epoxides or quinones) and the role of molecular oxygen as terminal oxidizing reagent is to reoxidize the depleted oxygen sites on the GO sheet.[18, 19] Following the literature, Boukhvalow and co-workers carried out a study for the oxidation of benzyl alcohol to benzaldehyde using GO. They proposed that the reaction carried out via the transfer of hydrogen atoms from the organic molecule to the GO surface, and then a subsequent ring opening of the epoxide groups present on GO and final dehydration. In this cases a partially reduced GO can be reoxidized by molecular oxygen, regenerating the active sites after the reaction.

Table 4.Conversion of 1 and product selectivity in the OD of lignin model **1** catalysed by GO at different oxygen pressures.[a,b,c]

	(bars)	Conversion (%)	Product Selectivty (%)						
		1	2	3	4	5	6	7	8
O_2 pressure	5	100	0	6	2	5	7	15	87
	2	100	4	0	20	2	6	5	96
	1	91	0	0	14	1	9	3	85
Ar pressure	1	98	11	0	15	1	8	0	91

[a] Reacion conditions: **1** (0.01 mmol), CO (1.5 mg), time 24 h, temperature 140 ºC, acetonitrile (1.5 mL). [b] Conversion and selectivity were determined by HPLC using nitrobenzene as internal standard. [c] Traces of compounds **9** and **10** were also detected

To learn about the nature of the possible active sites of GO catalyzing the reaction, a study testing various organic compounds that can mimic some moieties in GO was carried out (see Table SI5 in supporting information). The results suggest that acid groups can promote the OD of **1.** As it can be seen in Table SI5 when the acidity of the organic compound increases the conversion of **1** also increased, although the product distribution was somewhat different that when the OD of **1** was promoted using a carbocatalysts. It is worth commenting that previous studies in the literature have shown that GO can act as acid catalyst,[21,22] for instance for the conversion of carbohydrates into hydroxymethylfurfural derivatives[23], due to the presence of residual hydrogensulfate groups. However, in the present study it should be mentioned that besides GO, other G types that have not been exposed to sulfuric acid also exhibit catalytic activity (see Table 2).

In order to clarify the role of acidity, titration of the GO sample used in the study by NaOH was made, measuring an acidity of 1.5 meq of H^+ per g of GO. Then, to rule out acidity as the sites responsible of the transformation of **1**, the reaction was carried out under the optimal conditions, but in the presence of

triethylamine as base (1.5 meq.×g^{-1}) to neutralize acidity of GO (see Table SI6 in supporting information). It was observed that in the presence of triethylamine, conversion of **1** was again 100 % as in the absence of base. However, changes in the product distribution were measured, guaiacol (**8**) accounting under these conditions only for 40% and products **2** and **3** in which the ether bond present in compound **1** is not broken were 12 %. Thus, these results indicate that while acidity is not necessary for the OD of **1**, acid sites influence the selectivity of the process.

A point of mayor concern when using GO and related G materials as metal-free catalysts is the potential role that metal impurities could play in the catalysis. Literature data show that GO can have around 100 ppm of Mn accompanied by other first row transition metals, such as Cu and Zn in much lesser quantities.[24] In our case, inductively coupled plasma atomic emission spectroscopy (ICP-AES) of GO was performed and detected the presence of Mn and Cu in 628 and 110 ppm, respectively. Other metals present in the sample are Zn and Al (<50 ppms). A large part of these metals are introduced in the GO sample during Hummers graphite oxidation using an excess of $KMnO_4$ as strong oxidant, but starting graphite also contains a detectable concentration of Fe.[25] A percentage of these metals remains, probably as cations associated to carboxylate groups, during purification of GO. Considering the general high catalytic activity of transition metals promoting aerobic oxidations, it could be that the presence of these metals, even at the trace level could be the real active site responsible for the OD of **1**. To address this possibility we performed a control in which the amount of Mn as $Mn(OAc)_2$ present on GO was dissolved in acetonitrile containing **1** and the resulting solution was tested with respect to its activity in the OD of compound **1**. It was observed that after 24 h, a conversion of **1** about 20 % was achieved. This conversion value of **1** is much lower and requires considerably longer time than that achieved by GO under the same conditions (see Figure 1). Therefore, it was concluded that although Mn has some activity for **1** oxidation and part of the catalytic activity of GO could be due to metal impurities, most of the activity of GO cannot be attributed to metals impurities, but to the intrinsic catalytic activity of GO.

The influence of the amount of GO used as catalyst was determined by performing experiments under oxygen and argon atmosphere in where the amount of GO employed was lower than in the experiments previously commented (see Tables SI6 and SI7 in supporting information). A substantial decrease in **1** conversion for these experiments having lesser GO amounts was observed, thus, reinforcing the conclusion that GO is acting as catalyst for OD of **1.** When the amount of catalyst is low, the conversion decreases. However, for sufficiently long times, total conversions can be obtained even with a 5 wt% of catalyst. The selectivity for the different products also changes and, as a general trend, lower catalysts amounts decreased the selectivity for the more oxidized products as vanillin acid (**6**).

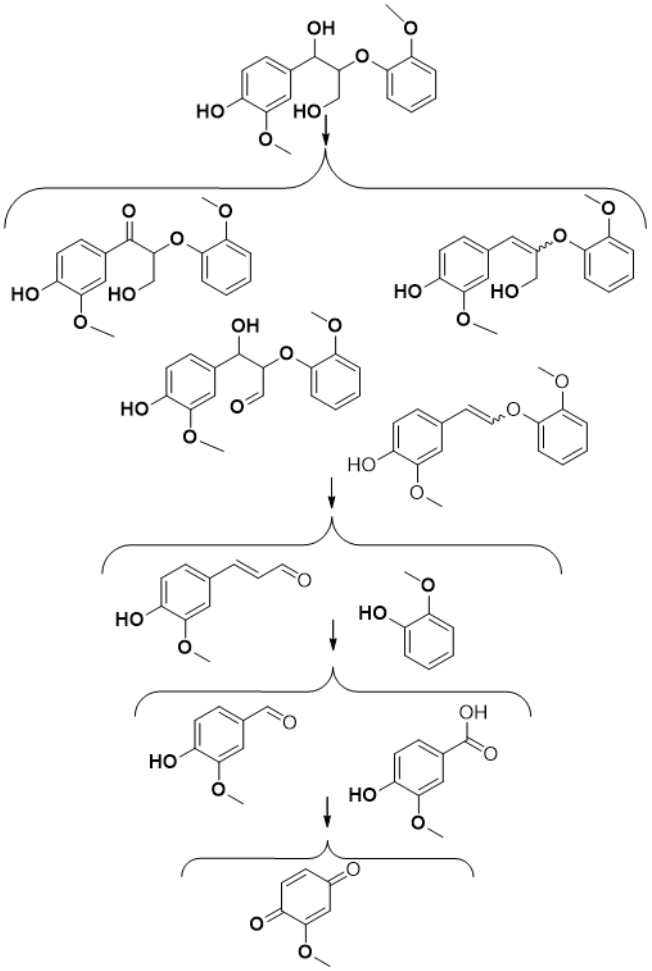
Temperature (ºC)	Conversion (%)	Product Selectivity (%)						
	1	**2**	3	**4**	**5**	**6**	**7**	**8**
140	100	0	6	2	5	7	15	87
120	99	0	11	4	4	5	15	76
100	56	42	4	5	1	3	6	34
80	40	89	4	0	0	1	2	6

[a] Reaction conditions: **1** (0.01 mmol), GO (1.5 mg), time 24 h, O_2 pressure (5 bars), acetonitrile (1.5 mL). [b] Conversion and selectivity were determined by HPLC using nitrobenzene as internal standard. [c] Traces of compounds **9** and **10** were also detected.

Table 5. Influence of the temperature in the conversion and the selectivity to the differents products in thee OD of **1** catalysed by GO.[a,b,c]

The influence of the temperature on the OD of **1** was studied in the range between 80-140 ºC. The results are presented in Table 5 and the corresponding yields are listed in Table SI8. As can be seen there, the conversion of **1** decreased as the reaction temperature decreased. The temperature also modifies the product selectivity. As expected, the general rule that lower conversions favors higher selectivity to the less oxidized products was observed. In particular, at the lowest temperature, a significant percentage of 89 % selectivity to propan-1-one (**2**) was observed. This compound was also observed in the final reaction mixture of the reaction carried out at 100 ºC, but it was absent for the experiments at 120 and 140 ºC.

Based on the product distribution at various reaction times and at different conditions, Scheme 2 summarizes a plausible pathway to explain the formation of the products observed.



Scheme 2. Possible pathways for the OD of **1**.

This proposal is in agreement with earlier precedents and with the mechanistic studies reported for analogous reactions catalyzed by transition metals like Re,[26] V,[7] Co,[27] and metal-free catalysts.[3, 28]

Conclusions

GO has been reported to be an efficient metal-free catalyst for the aerobic oxidation of alcohols,[29] benzylic hydrocarbons[10] and thiols.[19] Similarly in the present case, we have found that GO acts as metal-free catalyst for the oxidative degradation of the lignin model 1. Although other G materials such as rGO and B-doped G also exhibit catalytic activity for the process, it was found that the efficiency of GO is higher. Controls using a Mn salt in trace levels indicates that most of the catalytic activity of GO cannot be attributed to metal impurities. This intrinsic activity of GO is also supported by the fact that even under Ar atmosphere the OD of **1** can take place. Our report opens the way for the use of G-based catalyst in biomass transformation, showing that it is a possible to gain some control on the activity and product distribution by modification of the G sheet.

Experimental Section

Materials. α–Guaiacylglycerol-β-guaiacyl ether (**1**) was a commercial sample from Alfa Aesar. Graphite, coniferyl aldehyde, vanillic acid, vanillin, guaiacol, 2-methoxyquinone, N,O-bis(trimethylsilyl)trifluoroacetamide with 10 % of trimethylchlorosilane were commercial samples from Sigma-Aldrich. The other reagents were of analytical or HPLC grade.

Catalysts preparation and characterization. The graphenic materials employed in the present study namely GO,[14] rGO,[15] (B)G[14] and (N)G[14, 17] have been fully characterized previously and the properties of the samples used coincide with those reported in the literature. Briefly, GO was obtained from commercial graphite by Hummers oxidation and subsequent exfoliation. [14] rGO was obtained by thermal reduction of GO at 200 ºC.[15] (B)G and (N)G were obtained by pyrolysis of boric acid modified alginate and chitosan, respectively.[14, 17]

General reaction procedure. The required amount of G catalyst was suspended in the solvent by sonication using an ultrasound horn operating at 750 W power pulsed every 3 s for 90 min. An aliquot of 1.5 mL of the suspended G catalyst was introduced into a reinforced glass reactor that allows working under pressure up to 20 bars. Compound **1** (3.2 mg) and nitrobenzene (0.48 mg) as internal standard were charged in the reactor that was sealed and pressurized at the required pressure. The reactor was introduced into an oil bath preheated at the reaction temperature and the mixture magnetically stirred, this moment corresponding to the zero reaction time. At the required time, the reaction was quenched by immersing the system into a cold ice-water bath and the reaction mixture was immediately analysed by using an HPLC provided with a diode array UV detector.

ICP-AEs measurement. At the end of the reaction, the catalyst was filtered through a 0.2 μm Nylon filter and the reaction solvent removed under reduced pressure. Then, 30 mL of an HNO_3 (3 M) aqueous solution was put into contact with the evaporated residue and the system was heated at 80 ºC for 24 h. Finally, the presence of metal impurities in the aqueous phase was analysed by using an ICP-OES instrument. The detection limit is below 10 μg L^{-1}.

HPLC-UV measurements. Time conversion plots of compound **1** and its reaction products were determined by analysing aliquots, previously filtered through 0.2 μm Nylon filter and 20-fold dilution in H_2O/acetonitrile (1:1 in volume), by using a stationary reverse phase column Kromasil-C18 functionalized with cyano groups (5 μm 25x0.46 cm). The products were eluated using gradient conditions employing distilled H_2O and acetonitrile as solvents in the following proportions at constant flow (0.9 mL min^{-1}): 0-30 min 83 % H_2O, 30-31 min gradient from 83 to 60 % H_2O, 31-40 min 60 % H_2O, 40-41 min gradient from 60 to 83 % H_2O, 41-50 min 83 % H_2O. A photodiode array detector (200-400 nm operation range) was used to detect the eluted products.

Product characterization. Product identification and characterization was carried out by using different instruments including HPLC-UV (see above), high resolution HPLC-MS and GC-MS. Formation of compounds **1**, **4**, **6**, **7** and **8** was firmly confirmed by comparison with commerncially available compounds. Non-commercially available products **2**, **3**, **9** and **10** were quantified assuming that the absorbance at λ_{max} is the same as that of compound **1.** Identity of the products was also based on HPLC-

MS instrument that allows recording the high resolution MS of the peaks. The column of HPLC-Ms was a UPLC-C18 and the mobile phase and elution ramp were the same as that used for HPLC-UV. GC-MS was also employed to identify and characterize the reaction products after silylation. Derivatisation by silylation was performed by taking an aliquot at the required reaction time, filtering it through a 0.2 μm Nylon filter and using N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) with 10 % of trimethylchlorosilane (TCMS) as silylating reagent. After addition of silylating reagent, the samples were heated at 80 ºC for 24 h following previously reported procedures.[30] When H_2O or ethanol were used as reaction solvents, these solvents were previously evaporated under reduced pressure and, then, acetonitrile and BSTFA-TCMS added. Finally, the samples were injected in a GC-MS apparatus (Hewlett Packard HP6890 Chromatograph and mass detector Agilent 5973) using as stationary phase a HP-5MS (5% crosslinked phenylmethyl siloxane) capillary column (30 m x 250 μm x 0.25 μm) and helium as carrier gas (1.2 mL min^{-1}). The injection volume was 1 μL and the sample injected in splitless mode. Injection and detection temperatures were 250 and 280 ºC, respectively. The oven temperature programme starts at 60 ºC for 3 min, then the temperature increases at a rate of 10 ºC min^{-1} up to 280 ºC that is maintained for 10 min. For commercially available products, identification of GC peaks was based on comparison of the retention time in GC-MS.

Acknowledgements

Financial support by the Spanish Ministry of Economy and Competitiveness (Severo Ochoa and CTQ2012-32315) and Generalitat Valenciana (Prometeo 2012-013) is gratefully acknowledged. Partial financial support by the European Union (Novacam project) is also acknowledged. J. F. B. thanks to the Technical University of Valencia for a PhD scholarship.

Keywords: heterogeneous catalysis • carbocatalysis • lignin depolymerisation • graphene as catalyst

[1] J. Long, Q. Zhang, T. Wang, X. Zhang, Y. Xu, L. Ma, Bioresour. Technol. 2014, 154, 10-17; A. K. Deepa, P. L. Dhepe, ACS Catal. 2014, Ahead of Print; S. Nanayakkara, A. F. Patti, K. Saito, ACS Sustainable Chem. Eng. 2014, 2, 2159-2164.

[2] A. Azarpira, J. Ralph, F. Lu, BioEnergy Res. 2014, 7, 78-86; C. Crestini, M. Crucianelli, M. Orlandi, R. Saladino, Catal. Today 2010, 156, 8-22.

[3] A. Rahimi, A. Azarpira, H. Kim, J. Ralph, S. S. Stahl, J. Am. Chem. Soc. 2013, 135, 6415-6418.

[4] Y. Gao, J. Zhang, X. Chen, D. Ma, N. Yan, ChemPlusChem 2014, 79, 825-834.

[5] S. Navalon, A. Dhakshinamoorthy, M. Alvaro, H. Garcia, Chem. Rev. 2014, 114, 6179–6212.

[6] S. K. Hanson, R. Wu, L. A. P. Silks, American Chemical Society, 2011, pp. IEC-11; R. T. Baker, American Chemical Society, 2013, pp. IEC-40; S. Son, F. D. Toste, Angew. Chem. 2010, 122, 3879-3882.

[7] S. K. Hanson, R. T. Baker, J. C. Gordon, B. L. Scott, D. L. Thorn, Inorg. Chem. 2010, 49, 5611-5618.

[8] C. Crestini, M. C. Caponi, D. S. Argyropoulos, R. Saladino, Bioorg. Med. Chem. 2006, 14, 5292-5302.

[9] S. K. Badamali, R. Luque, J. H. Clark, S. W. Breeden, Catal. Commun. 2011, 12, 993-995; B. Biannic, J. J. Bozell, Org. Lett. 2013, 15, 2730-2733.

[10] S. E. Park, M. B. Ansari, E. Y. Jung, 2013, p. 17pp.

[11] J. Luo, F. Peng, H. Wang, H. Yu, Catal. Commun. 2013, 39, 44-49; M. Kakimoto, T. Hayakawa, Y. Kuang, K. Miyata, J. Ozaki, K. Iida, Y. Oshima, 2010, p. 18pp.

[12] D. J. Gale, J. F. K. Wilshire, Aust. J. Chem. 1974, 27, 1295-1308.

[13] W. S. Hummers, Jr., R. E. Offeman, J. Am. Chem. Soc. 1958, 80, 1339.

[14] A. Dhakshinamoorthy, A. Primo, P. Concepcion, M. Alvaro, H. Garcia, Chem. - Eur. J. 2013, 19, 7547-7554.

[15] M. Jin, H.-Y. Jeong, T.-H. Kim, K. P. So, Y. Cui, W. J. Yu, E. J. Ra, Y. H. Lee, J. Phys. D: Appl. Phys. 2010, 43, 275402; L.-Y. Meng, S.-J. Park, Adv. Mater. Res. 2010, 123-125, 787-790; C. D. Zangmeister, Chem.Mater. 2010, 22, 5625-5629.

[16] R. Ma, M. Guo, X. Zhang, ChemSusChem 2014, 7, 412-415.

[17] A. Primo, P. Atienzar, E. Sanchez, J. M. Delgado, H. García, Chem. Commun. 2012, 48, 9254-9256; A. Primo, E. Sanchez, J. M. Delgado, H. García, Carbon 2014, 68, 777-783.

[18] A. Primo, S. Navalón, A. M. Asiri, H. García, Chem. Eur. J. 2015, 21, 324-330; D. W. Boukhvalov, Dreyer, D.R., Bielawski, C.W., Son, Y.-W., ChemCatChem 2012, 4, 1844-1849.

[19] D. R. Dreyer, H.-P. Jia, A. D. Todd, J. Geng, C. W. Bielawski, Org. Biomol. Chem. 2011, 9, 7292-7295.

[20] A. Dhakshinamoorthy, M. Alvaro, P. Concepcion, V. Fornes, H. Garcia, Chemical Communications 2012, 48, 5443-5; A. Dhakshinamoorthy, M. Alvaro, M. Puche, V. Fornes, H. Garcia, Chemcatchem 2012, 4, 2026-30.

[21] A. Dhakshinamoorthy, M. Alvaro, M. Puche, V. Fornes, H. Garcia, Chemcatchem 2012, 4, 2026-30..

[22] H. Wang, T. Deng, Y. Wang, X. Cui, Y. Qi, X. Mu, X. Hou and Y. Zhu, Green Chemistry, 2013, 15, 2379-2383..

[23] A. Ambrosi, S. Y. Chee, B. Khezri, R. D. Webster, Z. Sofer, M. Pumera, Angew. Chem. Int. Ed. 2012, 51, 500-503.

[24] C. H. A. Wong, Z. Sofer, M. Kubesova, J. Kucera, S. Matejkova, M. Pumera, Proc. Natl. Acad. Sci. U. S. A. 2014, 111, 13774-13779.

[25] A. Ambrosi, S. Y. Chee, B. Khezri, R. D. Webster, Z. Sofer, M. Pumera, Angew. Chem. Int. Ed. 2012, 51, 500-503.

[26] C. Crestini, M. C. Caponi, D. S. Argyropoulos, R. Saladino, Biorg. Med. Chem. 2006, 14, 5292-5302.

[27] J. Zakeski, A. L. Jongerius, B. M. Weckhuysen, Green Chem. 2010.

[28] Y. Zhu, K. T. Yuanting, N. S. Hosmane, InTech, 2013, pp. 315-346; B. J. Cox, S. Jia, Z. C. Zhang, J. G. Ekerdt, Polym. Degrad. Stab. 2011, 96, 426-431.

[29] M. Mirza-Aghayan, E. Kashef-Azar, R. Boukherroub, Tetrahedron Lett. 2012, 53, 4962-4965.

[30] S. Navalon, M. Alvaro, H. García, J. Hazard. Mater. 2009, 164, 1089-1109.

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FULL PAPER

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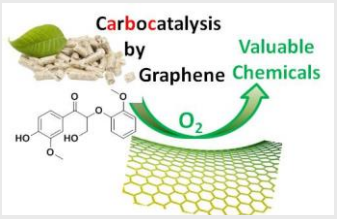

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