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Engineering active sites in reduced graphene oxide for aerobic benzylamine oxidation

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ABSTRACT

The influence of the graphene oxide (GO) reduction method on the activity of the resulting reduced graphene oxide (rGO) for the aerobic oxidation of benzylamine is reported. Starting from GO obtained by the Hummers method, a series of rGO samples obtained either by chemical (hydroquinone, hydrazine or ascorbic acid) or by thermal reduction were prepared. Analytical and spectroscopic techniques provided evidences showing that chemical reducing agents reduce GO introducing different functional groups that influence the catalytic activity of the resulting rGO for the activation of molecular oxygen in benzylamine oxidation. The highest activity was found for the rGO-HQ1 sample prepared using hydroquinone (HQ) as reducing agent in the aerobic oxidation of benzylamine at 80 °C after 24 h. It is proposed that hydroquinone introduces hydroquinone/*p*-benzoquinone-like moieties on the graphene sheet that act as active sites in the oxidation reaction. This proposal is supported by the activity of hydroquinone and/or *p*-benzoquinone as organocatalysts and by selective masking of oxygen-functional groups present in the most active rGO sample. The most active rGO sample exhibited good reusability and stability in five consecutive uses. Selective quenching experiments revealed that hydroperoxyl radicals are the primary reactive oxygen species generated in the system.

KEYWORDS: Carbocatalysis; Reduced graphene oxide; Graphene active sites; Aerobic oxidation; Benzylamine.

1. INTRODUCTION

Most of the industrial chemical transformations are catalyzed by homogeneous or heterogeneous transition metals.¹⁻⁵ For the sake of sustainability, it is important to develop efficient and renewable metal-free catalysts that minimize the environmental negative impacts of the chemical processes.⁶⁻⁹ Among the various studies in this area, it was shown that active carbons derived from biomass can catalyze reactions that are typically promoted by transition metals such as oxidative dehydrogenations¹⁰ and advanced oxidation processes for the degradation of organic pollutants.¹¹

Since the discovery of graphene (G) in 2004¹² and due to the availability of this type of materials, the area of catalysis based on carbon materials (carbocatalysis) has grown considerably.^{6-8, 13 14, 15} Among the main advantages offered by the use of Gs as carbocatalysts, the most important merits are their availability from graphite or biomass wastes,^{16, 17} their high theoretical surface area ($2650 \text{ m}^2 \text{ g}^{-1}$),¹⁸ the bidimensional configuration that facilitates diffusionless mass transfer, as well as the possibility to engineer active sites on Gs by chemical and/or thermal treatments.⁷ In this context, Bielawski and co-workers have reported a seminal work on the use of graphene oxide obtained by the Hummers method as carbocatalyst for the aerobic oxidation of alcohols.¹⁹ In recent years, carbocatalysis has expanded beyond GO showing the activity of 2D materials to perform several organic transformations including oxidations, reductions and couplings among others.^{8, 20-22}

One of the most widely used G materials employed as carbocatalysts is reduced graphene oxide (rGO).^{7, 8, 23} rGO is prepared from GO by chemical or thermal reduction.²³⁻²⁷ Chemical reduction can be performed using a large variety of inorganic compounds such as N_2H_4 or NaBH_4 , or organic compounds such as ascorbic acid, hydroquinone, amino acids and even

natural extracts as green reducing agents, among others.²³ The reduction of GO to rGO occurs through a complex mechanism and several reports have been attempted to gain insights into the structure of rGO as a function of the chemical reducing agent employed in its preparation by deep material characterization.^{25, 28} One of the most salient conclusions is that organic compounds as reducing agents for GO not only reconstitute sp^2 carbon domains, but also may introduce some specific functionalization on the graphene sheet depending on the nature of the reagent.²⁸ Therefore, it can be expected that the catalytic properties of rGO could somewhat change in a certain extent depending on the chemical agent used to produce rGO from GO.²⁸ In this context, there are already few examples in the literature about the influence of the reduction method employed for the preparation of rGO and its performance as electrocatalysts.²⁹ However, as far as we know there is not report exploiting on the opportunities that specific reducing agents could offer to optimize the performance of rGO as catalyst by introducing the appropriate functionalization that could further act as active center for a selected reaction. In this way, the use of different reducing agents for the preparation of rGO offers the possibilities to engineer active sites on the resulting GO structure making this sample as more efficient carbocatalyst.

To illustrate the potential of this approach, the present study focuses on some catalytic reactions that have been previously proposed to be promoted by quinone/hydroquinone-like sites on rGO. As reported by us and others,^{7, 30, 31} hydroquinone/quinone-like functional groups on Gs act as catalytic sites of oxidation reactions with H_2O_2 and O_2 as well as reduction reactions with hydrazine.

Considering these precedents, the present work reports that reduction of GO with hydroquinone (rGO-HQ1) affords a rGO sample that exhibits a superior catalytic activity for

molecular oxygen activation to promote the oxidation of benzylamine to its corresponding imine than other rGO samples prepared by alternative reducing agents such as hydrazine or ascorbic acid or by thermal reduction. The use of the graphite or GO as carbocatalysts resulted in lesser activity compared to rGO obtained by reduction of GO with hydroquinone. Spectroscopic and analytical techniques provide evidences in supporting that hydroquinone gives rise to the covalent anchoring hydroquinone/quinone-like units to the rGO sheet. Those hydroquinone-like units enhance the catalytic activity of rGO-HQ1 for molecular O₂ activation. The results of the catalytic activity of rGO-HQ1 after selective masking of different oxygen-functional groups are also in good accordance with the role of hydroquinone/*p*-benzoquinone-like moieties as active sites for the aerobic oxidation. Therefore, the results provided below show that the reduction procedure for the preparation of rGO can serve to engineer the material to optimize its performance as catalyst for a particular reaction.

2. EXPERIMENTAL SECTION

2.1 Materials

All the reactant and reagents employed in this work were of analytical or HPLC grade and were supplied by Sigma-Aldrich.

2.2 Catalyst preparation

The preparation and full characterization of GO and thermal rGO employed in this work have been previously reported by some of us.^{30, 31} Briefly, GO was obtained by Hummer's oxidation of commercial graphite powder using KMnO₄, H₂O₂ and H₂SO₄ followed by subsequent exfoliation of the resulting graphite oxide by ultrasonication. Then, GO was thermally reduced at 200 °C for 4 h to obtain the solid labelled as rGO-T. In addition, GO has

been chemically reduced by using hydroquinone,³² hydrazine³³ or ascorbic acid³⁴ as previously reported.^{23-25, 28} Briefly, the chemical reducing agent (32 mmol) was added to a GO aqueous solution (200 mL, mg/mL) and the resulting suspension was heated at 100 °C for 24 h. Then, the mixture was cooled down to room temperature. The resulting solids were recovered by filtration and thoroughly washed with Milli-Q water. The obtained samples were labelled as rGO-HQ1, rGO-HZ and rGO-ASC. An analogous rGO-HQ sample was also prepared by using lower amount of hydroquinone (1.6 mmol) and labeled as rGO-HQ2.

In addition to these samples, rGO-HQ1 was further modified by pyrolysis at higher temperature. In particular, rGO-HQ1 (200 mg) was placed in a ceramic crucible and introduced in a tubular oven under argon flow and the system was heated at 300 or 700 °C for 2 h. The resulting samples were labelled as rGO-HQ300 and rGO-HQ700.

rGO-HQ1 catalyst derivatization. Selective derivatization of some oxygen functional groups present in the rGO-HQ1 sample was carried out using previously reported methods.^{30, 31, 35} In one of these cases, carbonyl groups were transformed into hydrazone derivatives. Briefly, rGO-HQ1 (100 mg) was suspended in CH₃Cl (10 mL) followed by sonication for 20 min. Then, phenylhydrazine (200 μL) and HCl (10 μL) were added and allowed to react at 20 °C for 72 h under stirring under inert Ar atmosphere. The resulting solid was washed several times with CHCl₃, dried under vacuum at 60 °C. This sample was labelled as rGO-HQ-CO meaning that the CO groups have been masked. In other case, hydroxyl groups present in the rGO-HQ1 sample were transformed into esters by using benzoyl chloride. For this purpose, rGO-HQ1 (100 mg) was suspended in CHCl₃ (5 mL) followed by sonication for 20 min and, then, benzoyl chloride (420 μL) and trimethylamine (500 μL) were added. The system was allowed to react at 60 °C under continuous stirring in inert Ar atmosphere for 24 h. The resulting material was washed

several times with CHCl_3 , dried under vacuum and the sample labelled as rGO-HQ-OH, since part OH groups have been esterified. In a third case, carboxylic groups present in the rGO-HQ1 sample were esterified using 2-bromoacetophenone. This reaction was carried out by reacting a suspension of rGO-HQ1 (100 mg) in CHCl_3 (5 mL) with 2-bromoacetophenone (200 mg) at 20 °C under Ar atmosphere for 24 h. The resulting solid was washed with CHCl_3 , dried under vacuum at 60 °C. This sample was labelled as rGO-HQ-COOH.

2.3 Catalyst characterization

Combustion elemental analyses were carried out using a Perkin Elmer CHNOS analyzer. FTIR spectra were collected with a Bruker Tensor 27 FT-ATR spectrophotometer. Thermogravimetric analyses (TGA) were performed on a TGA/SDTA851e Mettler Toledo station. Raman spectra were recorded at room temperature with 514 nm laser excitation focused through a Leica microscope on a Renishaw InVia Raman spectrophotometer equipped with a CCD detector. X-ray photoelectron spectroscopy (XPS) analyses were carried out on a SPECS spectrometer with an MCD-9 detector using a monochromatic Al ($K\alpha= 1486.6$ eV) X-ray source. Temperature-programmed desorption (TPD) coupled to a mass-spectrometer (TPD-MS) analysis was carried out using a Micromeritics II 2920 apparatus connected to a quadrupolar mass-spectrometer. In particular, the solid sample (100 mg) was heated from room temperature to 900 °C at 10 °C min^{-1} . Solid state ^{13}C -NMR spectroscopy was recorded in a Bruker AV 400 instrument.

2.4 Catalytic activity

Oxidation of benzylamine was carried out in a round bottom flask (25 mL) by dispersing the corresponding solid catalyst (20 mg) in benzylamine (1 mL). This heterogeneous slurry was purged with oxygen from a balloon. This flask was placed in an oil bath maintained at 80 °C with

continuous stirring. Aliquots were periodically taken from the reaction mixture and analyzed by gas chromatography using nitrobenzene as internal standard. The products were characterized by gas chromatography coupled with mass spectroscopy. The conversion of benzylamine and product selectivity was determined by integration of the peak areas in gas chromatography. Identical procedures were employed in the radical scavenging experiments with DMSO, *p*-benzoquinone or NaN₃ employing the amounts indicated in Table 2. This procedure was also followed to determine the conversion of rGO-HQ catalysts with masked functionality.

A hot filtration experiment was performed starting the reaction as described above. Then, rGO-HQ1 was removed from the reaction mixture by filtration using a Teflon filter at 60 min reaction time and the resulting reaction solution in the absence of catalyst was allowed to continue the reaction for 24 h. Aliquots from the homogeneous solution were periodically taken, and the reaction kinetics in the absence of catalyst was compared with that in the presence of catalyst.

Reuse experiments of rGO-HQ1 catalyst were also carried out using the same procedure as discussed above but employing previously used sample as catalyst. After the reaction, the solid catalyst was removed from the reaction mixture by filtration, washed with acetonitrile and dried at 90 °C for 2 h. The dry used sample was employed as catalyst for the next cycle adding fresh benzylamine and oxygen under the typical conditions.

The aerobic oxidation of benzylamine was also evaluated under similar reaction conditions commented above, but using organic molecules such as hydroquinone or *p*-benzoquinone or manganese (II) acetate salt as homogeneous catalysts.

3. RESULTS AND DISCUSSION

3.1 Catalyst preparation and characterization

Commercial graphite has been employed as precursor for the preparation of the various rGO materials studied in the present work. GO was obtained by the Hummers method followed by ultrasonication.^{30, 31} As commented before, the aim of this work is to determine the influence of the procedure in the reduction of GO to rGO on its catalytic activity for oxidation reactions using molecular O₂. Specifically, it was of interest to explore the possibility to obtain rGO enriched with hydroquinone/quinone-like moieties that could act as active sites enhancing the catalytic activity of the resulting rGO sample.²⁸ The main hypothesis of the present study is that hydroquinone can promote not only the reduction of GO to rGO according to previous reports,³² but it also could become covalently attached to rGO introducing some additional hydroquinone/quinone-like functional groups that should contribute to the catalyst activity of the resulting rGO sample. Combustion elemental analysis confirms the graphite oxidation (Table 1, entry 1) to GO (Table 1, entry 2). GO reduction by hydroquinone to render the rGO-HQ1 sample (Table 1, entry 3) was supported by the simultaneous increase and decrease of carbon and oxygen content, respectively, compared to GO. Decreasing the amount of hydroquinone employed as reducing agent decreases the degree of rGO reduction (Table 1, entry 4). Subsequently, the rGO-HQ1 sample was submitted to a thermal pyrolysis at 300 (Table 1, entry 5) and 700 °C (Table 1, entry 6) to afford two additional samples. The objective of these treatments is to further remove additional oxygen functional groups present in the rGO-HQ1 sample and, then, evaluate the catalytic activity in the aerobic oxidation reactions of these two reduced rGO-HQ samples. In accordance to previous reports, the higher the pyrolysis temperature applied to rGO-HQ sample, the higher the carbon content measured by combustion analysis of the pyrolyzed material due to the removal of some oxygen functional groups present in the parent rGO-HQ1 sample. Further, comparison of the weight percentage of C and O of

these materials listed in Table 1 between elemental and XPS analyses indicated that these values are in close agreement with each other.

Table 1. Summary of the catalysts employed in the present work.					
Entry	Catalyst	Preparation method	Elemental analysis		
			C (wt%)	H (wt%)	O (wt%)
1	G	Commercial graphite	> 99.9	< 0.1	-
2	GO	Graphite oxidation by Hummers method	50.0 (46) ^b	2.3	47.7 (54) ^b
3	rGO-HQ1	GO chemical reduction using HQ (32 mmol) at 100 °C in water for 24 h	80.9 (79.5) ^b	1.0	18.1 (20.5) ^b
4	rGO HQ2	GO chemical reduction using HQ (1.6 mmol) at 100 °C in water for 24 h	69.6 (65.2) ^b	2.2	28.2 (24.8) ^b
5	rGO-HQ300	rGO-HQ1 pyrolysis at 300 °C for 2 h	83.0 (75.6) ^b	1.1	15.9 (24.4) ^b
6	rGO-HQ700	rGO-HQ1 pyrolysis at 700 °C for 2 h	92.9 (86.6) ^b	1.1	6.0 (13.4) ^b
7	rGO-ASC	GO chemical reduction using ascorbic acid (32 mmol) at 100 °C in water for 24 h	78.7 (75.2) ^b	1.4	19.9 (24.8) ^b
8	rGO-HZ ^a	GO chemical reduction using hydrazine hydrate (32 mmol) at 100 °C in water for 24 h	81.4 (82) ^b	0.9	14.8 (15.8) ^b
9	rGO-T	GO thermal reduction at 200 °C	81.1 (74.2) ^b	0.95	17.95 (25.8) ^b
^a 2.9 wt% of nitrogen has been found in this sample.					
^b Values in parentheses indicate C/O wt% from XPS analysis.					

In order to further validate our hypothesis about the influence of the reducing agent employed in the preparation of rGO on the resulting catalytic activity, two other analogous rGO materials were also prepared by using hydrazine³³ or ascorbic acid³⁴ as reducing agents. The obtained rGO samples exhibit a carbon and oxygen contents around 80 and 17 wt% that are similar values to those of rGO-HQ1 sample (Table 1, entries 7 and 8). In agreement with previous reports, the use of hydrazine as GO reducing agent results in the incorporation of nitrogen atoms (~2.9 wt%) in its composition.³³ For the sake of comparison, a rGO sample prepared by GO thermal reduction at 200 °C, labelled as rGO-T, containing similar carbon and oxygen content as those rGO samples obtained by reduction chemical reduction was also employed in the study (Table 1, entry 9).

The reduction of GO to afford the rGO samples was also confirmed by FT-IR spectroscopy (Figure S1). As expected, all the rGO samples prepared in this work exhibit a significant decrease or almost complete disappearance of the characteristic FT-IR peaks of GO. Thus, FT-IR spectra of rGO-HQ1 and rGO-HQ2 samples are characterized by the presence of absorption bands at about 1640 and 1100 cm^{-1} that can be attributed to the presence of C=C and C-O groups, respectively. The FT-IR spectra of both rGO-ASC and rGO-HZ exhibit similar, but weaker, bands than rGO-HQ1, rGO-HQ2 samples appearing at 1640 and 1100 cm^{-1} . The slightly higher intensity of the C=C and C-O bands in the case of the rGO-HQ1, rGO-HQ2 samples compared to rGO-ASC or rGO-HZ is compatible with a possible rGO functionalization with hydroquinone-like units. The thermal treatment of the rGO-HQ1 sample at 300 and 700 °C resulted in a slight decrease of the intensity of the 1640 and 1100 cm^{-1} bands, due probably to the partial decomposition of the hydroquinone-like groups in the parent rGO-HQ1 material. In fact,

the TGA profile of rGO-HQ700 confirms the higher stability of this material respect to the more functionalized rGO-HQ1 sample (Figure S2).

Raman spectroscopy of rGO samples prepared in this work shows the presence of the 2D, G and D bands characteristic of defective graphene materials (Figure S3). It should be commented that the highest I_D/I_G ratio, indicating larger density of defects, is observed for the rGO-HQ1 compared to rGO-HQ2 and rGO-HQ300, rGO-HQ700 samples. It seems that pyrolysis of rGO-HQ1 at 300 or 700 °C results in lower I_D/I_G ratios, a fact that is compatible with the additional removal of oxygen-functional groups present in the parent rGO-HQ1 sample and concomitant reconstitution of the graphene sheet.

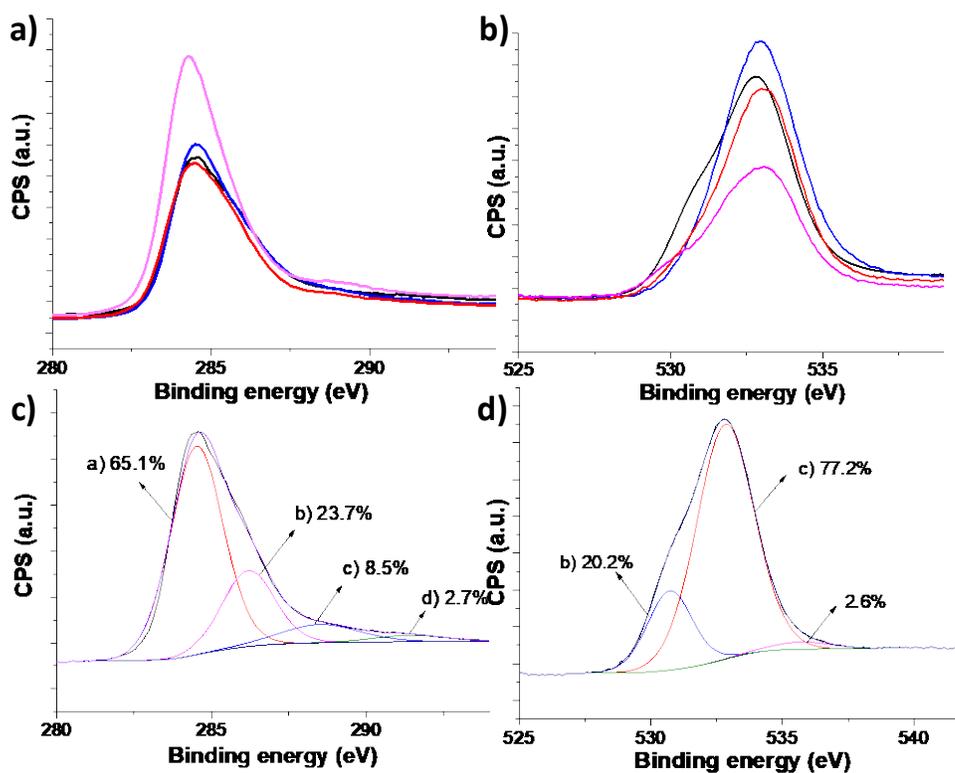


Figure 1. XPS C1s (a) and O1s (b) peaks of rGO-HQ1 (black line), rGO-HQ2 (blue line), rGO-300 (red line) and rGO-700 (pink line). Deconvoluted XPS C1s (c) and O1s (d) of rGO-HQ1 sample. Legend: a) C sp², b) alcohol/ether, c) carbonyl, d) carboxyl.

XPS was employed to further characterize the rGO samples prepared in this work (Figure 1 and Figures S4-S5). In general, the rGO samples prepared either by chemical or thermal treatments exhibit significantly higher population of sp² carbons in the graphene network compared with the pristine GO pattern.³¹ These sp² carbons are accompanied with oxygen functional groups including ethers, alcohols, ketones and carboxylic derivatives and with nitrogen functional groups in the case of the rGO-HZ sample (Table 1, entry 8). Figure 1 shows a comparison of the XPS C1s and O1s peaks for the rGO samples prepared using hydroquinone as reducing agent under study. rGO-HQ1 and rGO-HQ2 exhibit similar C1s spectra, while high-resolution O1s peak of the former sample clearly shows the presence of a shoulder appearing at about 532 eV characteristic of ether oxygen atoms (C-O-C). The higher amount of ether groups for the sample prepared with the highest amount of hydroquinone (rGO-HQ1) is indicative of a higher density of phenolic ethers presumably formed on the reaction of the epoxy groups present in the GO sheet with the hydroquinone used as reducing agent. XPS analysis of the two rGO-HQ samples pyrolyzed either at 300 or 700 °C resulted in a considerable decrease of the intensity of both the O1s peak and the shoulder at 532 eV (Figure S4).

TPD and TPD-MS analysis of the rGO-HQ1 sample revealed the presence of a broad band corresponding to CO₂ and/or CO evolution between 200 and 900 °C (Figure S6). At temperatures below 350 °C prevails the evolution of CO₂ gas that can be attributed to the decomposition of carboxylic acids and lactones still present in a residual amount in rGO. Further heating results in the simultaneous evolution of CO₂ and CO, frequently assigned to the presence

of anhydrides in the carbonaceous sample. Then, the broad CO band at temperatures above 650 °C can be ascribed to the presence of phenols, ethers and carbonyl/quinone groups. Solid state cross-polarization ^{13}C -NMR spectrum of the rGO-HQ1 sample (Figure S7a) also confirms the presence sp^2 carbons, together with hydroquinone-like functional groups and lesser intense signals attributed to ketones and carboxylic derivatives. Some weak broad bands in the region between 0 and 80 ppm were also observed and attributed to sp^3 carbon that may be bonded to oxygen functional groups such as alcohols or ether, among other possibilities. For comparison solid state cross-polarization ^{13}C -NMR spectrum of rGO-T sample was recorded, exhibiting weak signals and a negligible presence of hydroquinone-like functional groups (Figure S7b).

Based on the above characterization data of the rGO samples under study as well as on the knowledge of the fundamental steps involved in the reduction of GO to rGO using chemical or thermal treatments,^{23-25, 28} it is possible to propose different structures for the rGO samples under study. Figure 2 illustrates possible differences in the chemical structure of the various rGO samples depending on the chemical or thermal reduction method used in their preparation.

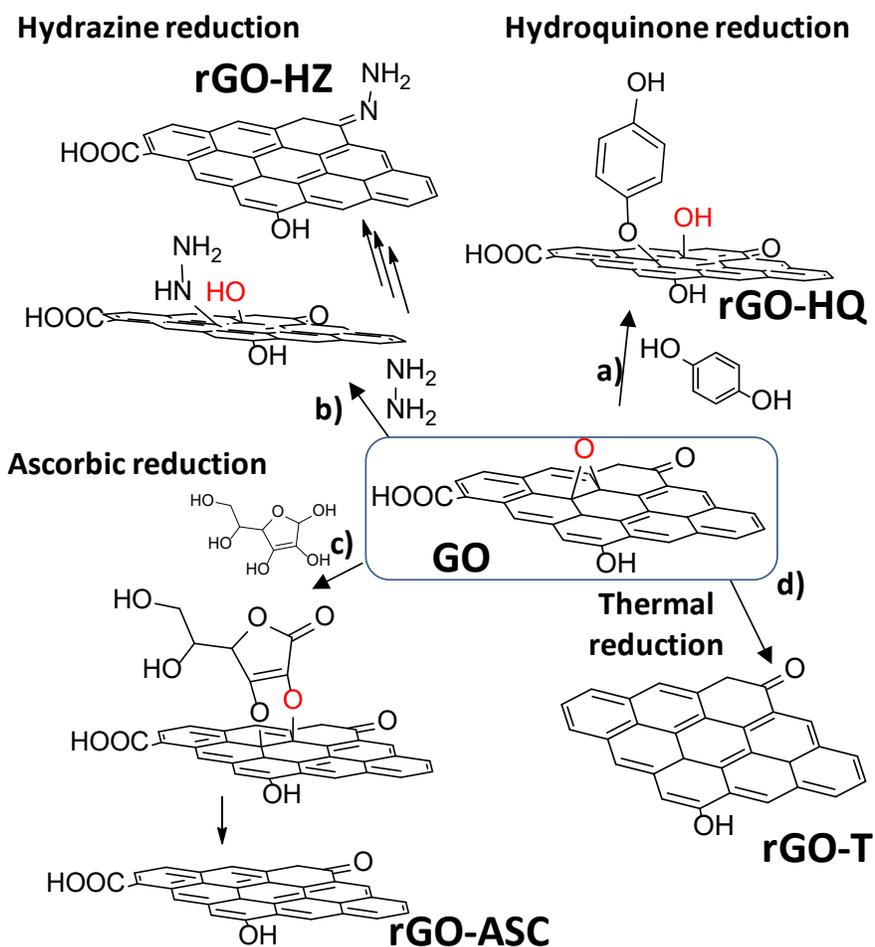


Figure 2. Procedures used to obtain the rGO samples under study and plausible functional groups present on their structure: a) hydroquinone; b) hydrazine; c) ascorbic acid as reducing agents, or d) by thermal reduction.

3.2 Catalytic activity

As commented in the introduction, the main objective of this work is to determine the influence of the GO reduction method on the catalytic activity of the resulting rGO samples in the aerobic oxidation of benzylamine. Aerobic oxidation of benzylamine to its corresponding benzylidene imine has been proposed in previous studies as a benchmark reaction to assess the

catalytic activity of graphenic materials (Figure 3).³⁶ Analogous works have also reported the presence of N-benzylbenzamide during benzylamine oxidation.^{37, 38}

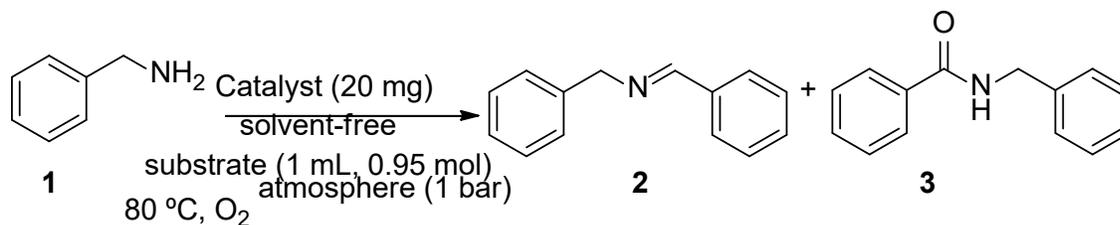


Figure 3. Aerobic oxidation of benzylamine using graphene-based carbocatalysts.

Table 2 summarizes the results of aerobic benzylamine oxidation under solvent-free conditions at 80 °C using the series of rGO materials as catalysts. It should be noted that this reaction has been frequently reported using noble³⁹ or transition metal-based catalysts at reaction temperatures higher than 120 °C.⁴⁰ A blank control experiment in the absence of catalyst revealed that the reaction practically does not take place under the present reaction conditions (Table 2, entry 1). In agreement with previous reports, GO can be employed as carbocatalyst for this aerobic oxidation (Table 2, entry 2) exhibiting an activity higher than the parent graphite. Interestingly, the catalytic activity of the rGO samples prepared in this work differs in a large extent depending on the reduction method (Table 1, entries 3-7). The catalytic activity of the most active sample namely rGO-HQ1 was double than that observed for GO, while still maintaining excellent selectivity to the target imine (Table 1, entry 3). The use of rGO-HQ2 material with lower degree of functionalization with hydroquinone-like functional groups on the graphene sheet resulted in lower catalytic activity than rGO-HQ1, but still higher than GO (Table 1, entry 4). In fact, the time-conversion plots for benzylamine oxidation using rGO-HQ1 or rGO-HQ2 as carbocatalysts reveal that the former catalyst exhibits higher reaction rate (Figure 4a). In

contrast, the catalytic activity of rGO-ASC was lower than that of GO. Even more, the use of rGO-HZ or rGO-T as carbocatalysts resulted in lower catalytic activity than that of commercial graphite. These results clearly illustrate the importance the GO reduction procedure on its catalytic activity and the possibility to introduce suitable functional groups on rGO during the reduction process. It is proposed that hydroquinone-like moieties present on rGO sheet are responsible for the high activity of rGO-HQ carbocatalysts. In fact, the catalytic activity of the most active sample rGO-HQ1 is considerably decreased or almost suppressed if the sample is submitted on purpose to pyrolysis at 300 or 700 °C (Table 1, entries 8-9) to decompose the hydroquinone-like active sites.

Table 2. Optimization of the reaction conditions for the aerobic oxidation of benzylamine to imine using various catalysts. ^a				
S. No	Catalyst	Conversion 1 (%) ^b	Selectivity (%) ^b	
			2	3
1	-	< 1	-	-
2	GO	50	97	3
3	rGO-HQ1	90	98	2
4	rGO-HQ2	68	99	1
5	rGO-ASC	38	95	5
6	rGO-HZ	8	97	3
7	rGO-T	13	100	-
8	rGO-HQ-300	61	99	1
9	rGO-HQ-700	4	100	-
10	HQ ^c	24	94	6
11	<i>p</i> -benzoquinone ^c	60	85	15
12	HQ + <i>p</i> -benzoquinone ^d	63	84	16
13	rGO-HQ ^e	39	100	-
14	rGO-HQ ^f	78	98	2

15	rGO-HQ ^g	62	100	
^a Reaction conditions: Benzylamine (1 mL), catalyst (20 mg), oxygen purged, 80 °C, 24 h. ^b Determined by GC. Compound 3 refers to N-benzylbenzamide. ^c With 20 mg of hydroquinone or <i>p</i> -benzoquinone as organocatalyst. ^d With 10 mg of hydroquinone and 10 mg of <i>p</i> -benzoquinone ^e With DMSO (0.150 mL) ^f With Benzoquinone (0.195 g) ^g with 150 mg of NaN ₃				

In order to get some evidences about the role of hydroquinone/quinone-like moieties on rGO-HQ1 as active centers in the catalysis, hydroquinone, *p*-benzoquinone and their mixture were employed as organocatalysts (Table 1, entries 10-12). It has been observed that *p*-benzoquinone is more active than hydroquinone when employed as individual organocatalyst. Interestingly, the combination of hydroquinone (10 mg) and *p*-benzoquinone (10 mg) as organocatalysts resulted in somewhat enhanced catalytic activity respect to the use of the individual compounds in double amount (20 mg). These catalytic results point to the importance of the presence of hydroquinone and/or quinone moieties in the rGO sheet to activate molecular O₂ and, then, promote the benzylamine oxidation.

The heterogeneity of the most active rGO-HQ1 carbocatalyst was confirmed by performing a hot filtration test. Figure 4 shows that if the catalyst is removed once the reaction has been initiated and conversion has reached about 15% (Figure 4a) and, then, the supernatant allowed to continue reacting under the same conditions, but in the absence of rGO-HQ1, the reaction does not takes place. This experiment confirms the heterogeneity of the reaction.

When using rGO as carbocatalyst one point of concern is the possible role of Mn(II) as active site.²⁸ It should be reminded that GO prepared by the Hummers method contains, even after careful purification, residual manganese content of around 100 ppm. The possible role of trace amounts of manganese present in rGO-HQ1 as active site was ruled out by performing a control experiment using manganese(II) acetate as catalyst. A low catalytic activity of Mn(II) compared to that of rGO-HQ1 was measured, even when using 3 mg of Mn(II) that would represent a concentration of 100 ppm in the solid carbocatalyst (Figure 4b). This low activity of Mn(II) under the present reaction conditions also agrees with the fact that the activity of GO, that is the starting material for rGO-HQ1 preparation and has a maximum of 100 ppm of Mn(II), is much lower than that of rGO-HQ with less than 50 ppm of Mn(II) (Table 2, entries 2-3).

The catalytic activity of rGO-HQ1 is almost maintained for five consecutive reuses under the optimized reaction conditions (Figure 4b), indicating the stability of rGO-HQ1. The excellent reusability of the rGO-HQ1 catalyst is in accordance with the covalent anchoring of hydroquinone-like moieties on the rGO that would act as active sites of the reaction (Figure 2). If HQ were merely adsorbed on the surface of rGO, the activity of the rGO-HQ1 catalyst upon reuse should have gradually decreased. Characterization of the five-times used rGO-HQ1 catalyst by XPS revealed that the catalyst surface has become partially oxidized and, this fact would be responsible for the small decrease of catalytic activity (Figure 4c,d).

In addition to these reuse experiments, a productivity test using a larger excess of benzylamine (2 mL; 18.3 mmol) for the same amount of rGO-HQ1 catalyst (20 mg) under solvent-free conditions at 80 °C resulted in a full conversion at 48 h with excellent selectivity (>98 %) to the corresponding imine. Considering an estimated amount of hydroquinone/*p*-benzoquinone in the rGO-HQ1 catalyst of about 8 wt% based on TGA and XPS analysis, a

turnover number (TON) of about 640 is estimated. Taking into account that rGO-HQ1 is a low cost carbocatalyst, the achieved TON value of 640 is competitive with those reported using noble metals such as Au/TiO₂ (TON~100 working at 5 bar O₂ and 100 °C using toluene as solvent)³⁹ or other catalyst containing base metals such as chromium in the MIL-101(Cr)-NO₂ solid (TON in the range from 500 to 6000 working at 1 bar O₂ at 120 °C)⁴⁰, among others.

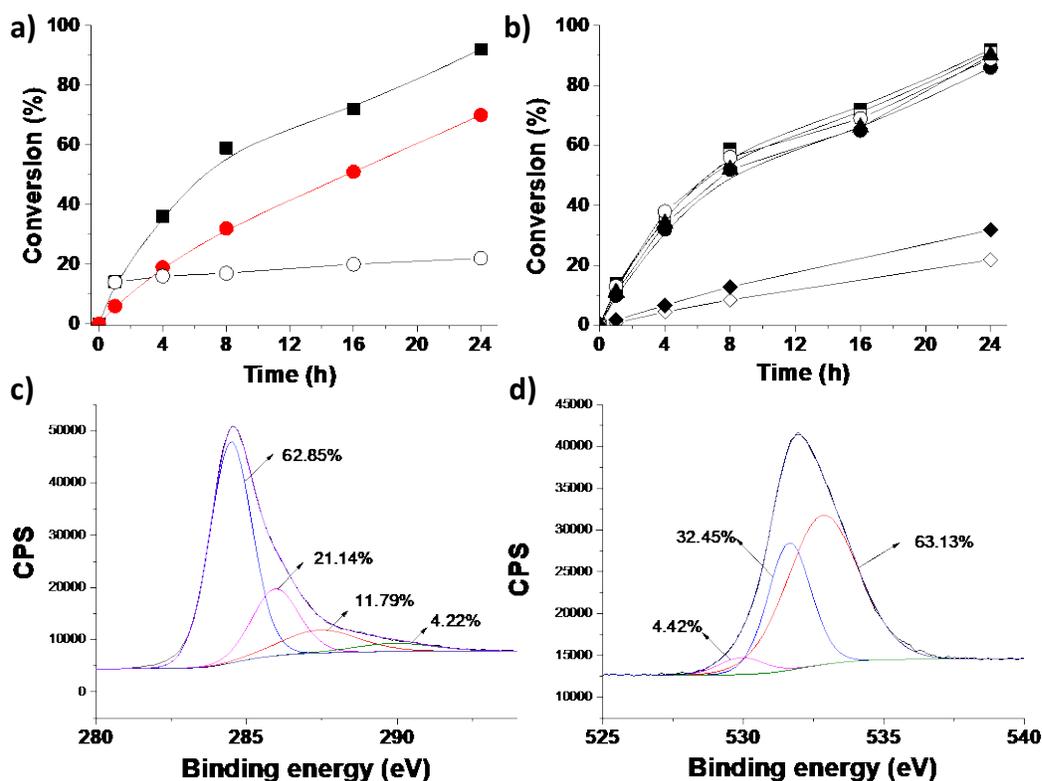
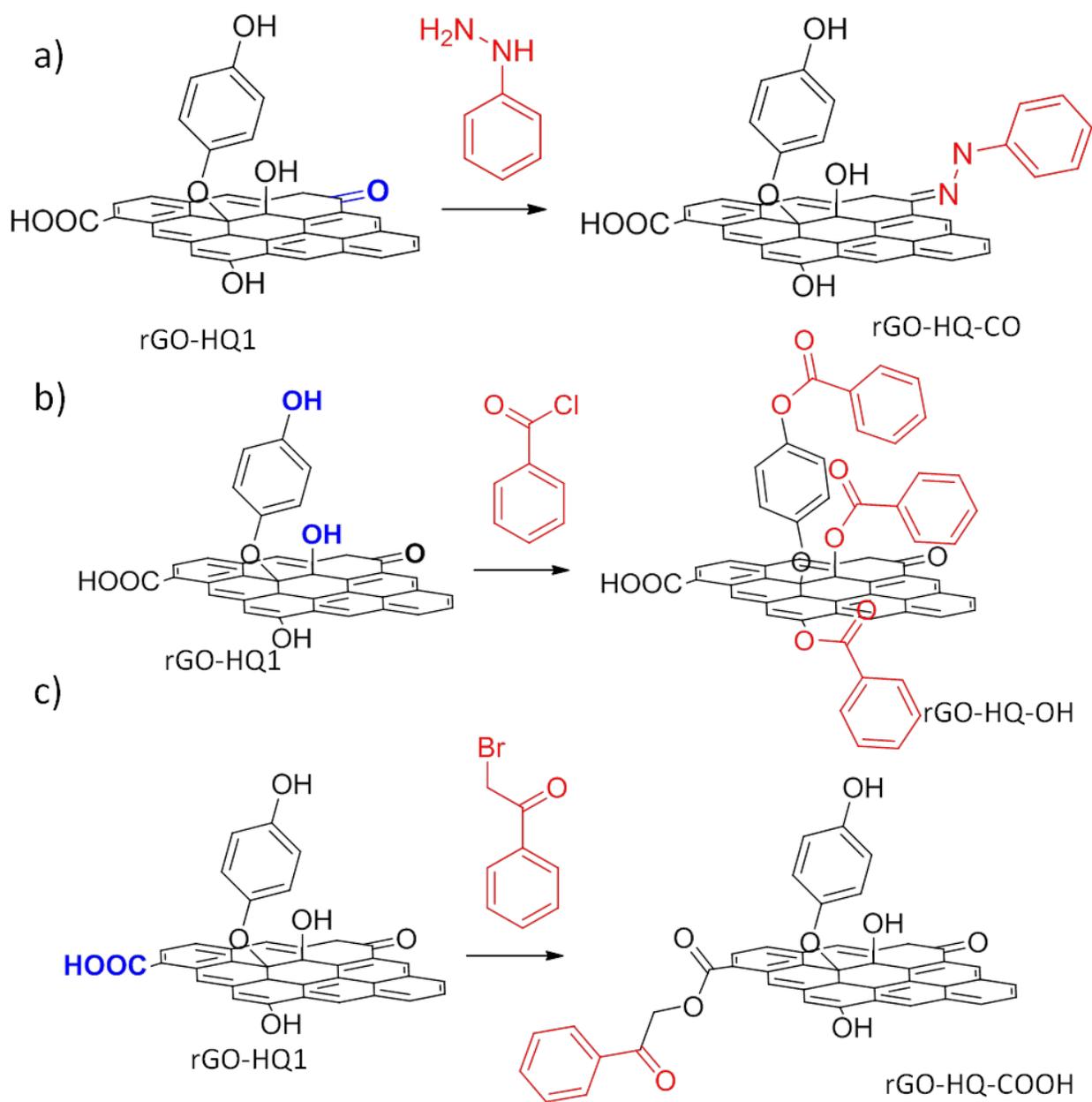


Figure 4. a) Time conversion-plot for the aerobic oxidation of benzylamine using rGO-HQ1 (■), rGO-HQ2 (●, red) and after hot filtration test using rGO-HQ1 (○); b) Reusability of rGO-HQ1 (1st ■, 2nd □, 3th ○, 4th ▲, 5th ●) and catalytic activity of manganese(II) acetate (0.6 ◇ or 2 ◇ mg of Mn(II) equivalent to 30 or 100 ppm of Mn(II) in the solid catalyst); c,d) XPS C1s and O1s peaks of the five-times used rGO-HQ1 carbocatalyst. Reaction conditions: Benzylamine (1 mL), catalyst (20 mg), oxygen purged, 80 °C.

3.3 Active sites and reaction mechanism

In order to get additional insights about the nature of the oxygen-functional groups responsible for the observed catalytic activity, the most active rGO-HQ1 sample was modified to obtain a series of rGO-HQ1 catalysts in which certain oxygenated groups have been selectively masked. Scheme 1 summarizes the reactions and reagents used for the selective oxygenated group masking. Characterization data of these samples by elemental analysis (Table S1) and XPS (Figures S8-S10) are presented in the SI.



Scheme 1. Selective masking of oxygenated functional groups in rGO-HQ1 by derivatization of carbonyl, hydroxyl and carboxylic acid groups.

Following precedents in the literature, phenylhydrazine has been employed as selective protecting group for carbonyl groups present on the rGO-HQ1 sample converting them to their corresponding phenylhydrazones (rGO-HQ-CO).³⁵ Elemental analysis of the rGO-HQ-CO

sample revealed 10.2 wt% of nitrogen content compared to the absence of N in rGO-HQ1 (Table S1). Respect to the rGO-HQ1 solid, XPS C1s and O1s peaks of rGO-HQ-CO shows the increase of sp² carbons at 284.4 eV accompanied by the diminution of the component at about 287 eV associated to carbonyl groups and a decrease of the O1s intensity signal (Figure S8). In another derivative, hydroxyl groups in rGO-HQ1 were masked as benzoate esters (rGO-HQ-OH) resulting in a decrease of the component at 287.00 eV associated to C-OH C1s and O1s (532 eV), while the new ester bond formed overlaps with the already existing functional groups present in the rGO-HQ1 (Figure S9). Analogously, esterification of carboxylic acids present on rGO-HQ1 (rGO-HQ-COOH) was achieved by reaction with 2-bromoacetophenone and the success of the masking reaction confirmed by observing by XPS an increase of the sp² C1s signal together with a shift to higher binding energies of the O1s signal respect to the parent rGO-HQ1 (Figure S10).

Figure 5 shows the benzylamine conversion to their corresponding imine by the series of rGO-HQ materials with selective functional group protection. As it can be seen, the masking of carbonyl or hydroxyl groups in rGO-HQ1 sample has a strong influence on the observed catalytic activity. In contrast, rGO-HQ-COOH sample showed no influence over the initial reaction rate and the final conversion. These data are in accordance with the assignment of hydroquinone- and/or p-benzoquinone-like moieties present in rGO-HQ1 as active centers for this catalytic reaction.

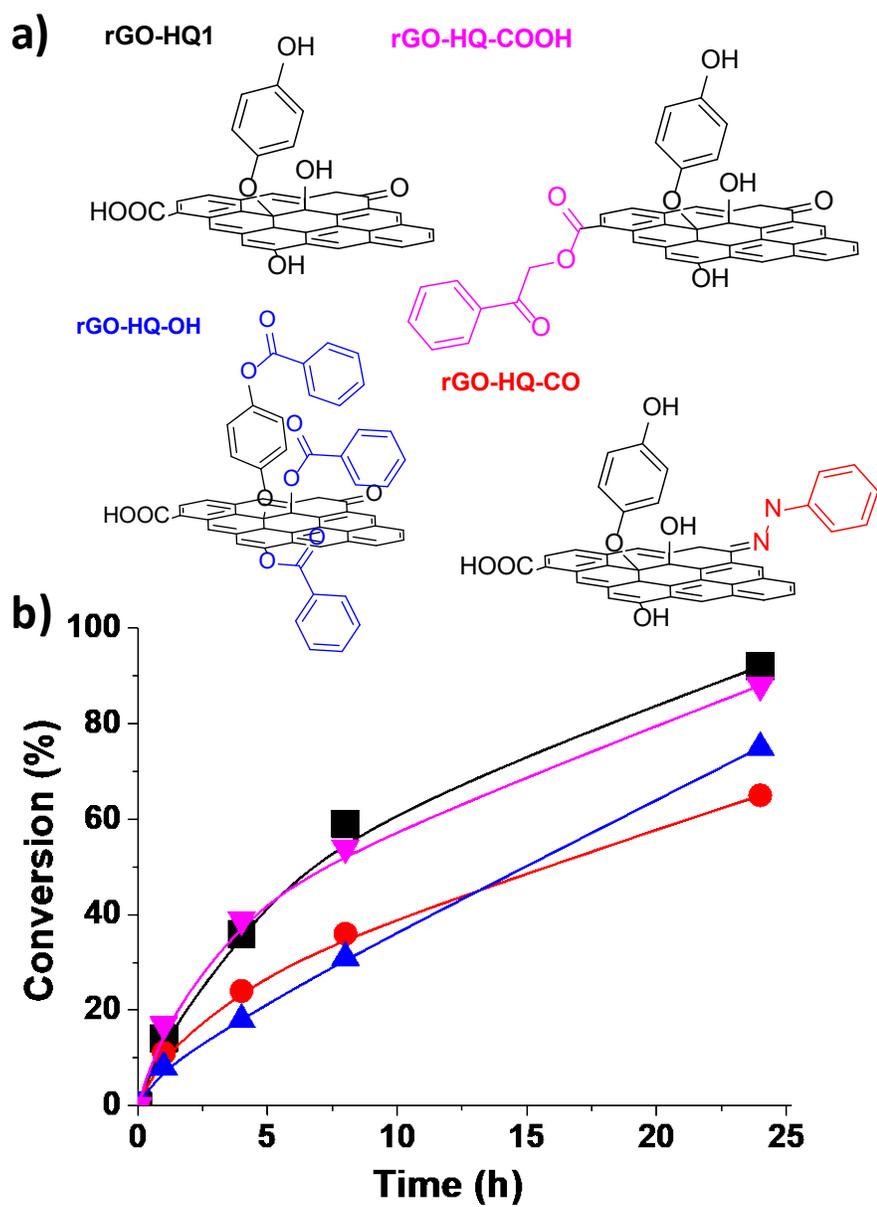


Figure 5. a) Selective masking of oxygen-functional groups present in the rGO-HQ1 sample including carboxylic groups (rGO-HQ-COOH), carbonyls (rGO-HQ-CO) or alcohols (rGO-HQ-OH). b) Time-conversion plots for the aerobic oxidation of benzylamine using rGO-HQ1 (■), rGO-HQ-COOH (▼, pink), rGO-HQ-CO (●, red) or rGO-HQ-OH (▲, blue) as carbocatalysts. Reaction conditions: Benzylamine (1 mL), catalyst (20 mg), oxygen purged, 80 °C.

To get some evidence about the nature of the reactive oxygen species (ROS) formed by activation of molecular O₂ with the rGO-HQ1 carbocatalyst, selective quenching experiments were performed. Previously, a blank control reveals that benzylamine does not react in the presence of rGO-HQ1 when O₂ is absent. In the presence of O₂ and rGO-HQ1 the presence of dimethylsulfoxide (DSMO) as selective OH· radical scavenger⁴⁰ partially inhibits the reaction, indicating that these radicals are generated in the reaction system (Table 2, entry 13). The presence of NaN₃ in the reaction medium considerably decreases the catalytic activity, indicating that ¹O₂ is also generated in the reaction system and participates in benzylamine oxidation (Table 2, entry 15). It is known that ¹O₂ can be formed from hydroperoxyl radicals, H₂O₂ and other peroxides whose ground state configuration is a singlet. It is difficult to address the possible implication of hydroperoxyl radicals (·OOH) or superoxide (O₂^{·-}) since *p*-benzoquinone is the typical quencher for these ROS and quinone-like moieties are likely the active sites in the present rGO-HQ1 system.

All together, the available data allow to propose a plausible reaction mechanism involving hydroquinone/quinone redox pairs on rGO-HQ1 that would be able to promote the formation of hydroperoxyl and hydroxyl radicals as well as the formation of ¹O₂. These ROS would be responsible for benzylamine oxidation. Figure 6 summarizes the proposed reaction mechanism.

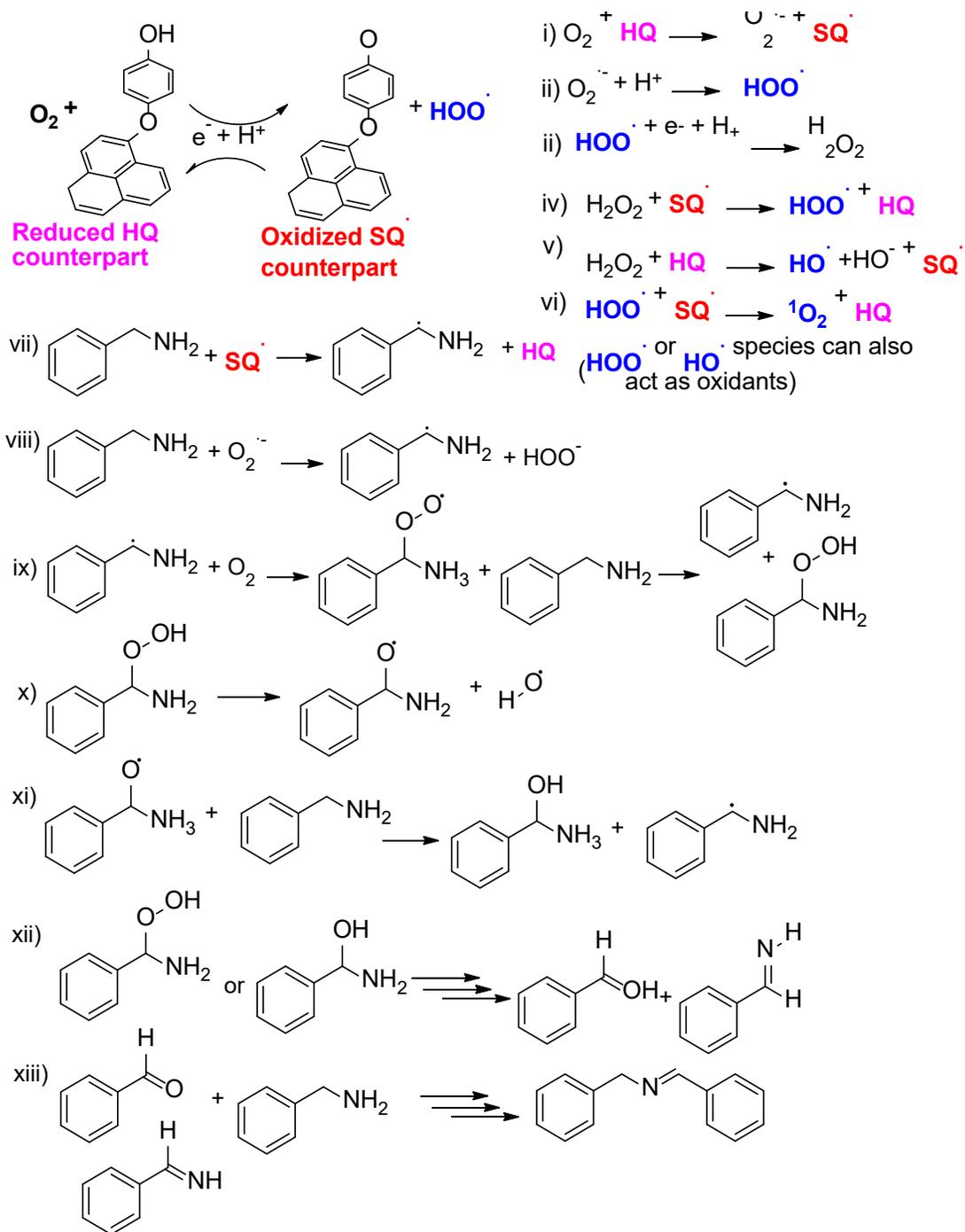


Figure 6. Plausible reaction mechanism involving activation of molecular O_2 by hydroquinone-like moieties present in the rGO-HQ1 sample with formation of ROS that generate benzylic radicals resulting in the final N-benzylidene benzylamine.

4. CONCLUSIONS

In the present work, it has been shown that the activity of rGO samples as carbocatalysts for the solvent-free aerobic oxidation of benzylamine to its corresponding imine strongly depends on the GO reduction procedure. Spectroscopic and analytical characterization data of a series of rGO samples revealed that chemical reducing agents such as hydroquinone, hydrazine or ascorbic acid cause a certain degree of functionalization of rGO. The reduction of GO by hydroquinone resulted in a rGO-HQ1 sample having covalently functionalized hydroquinone/quinone-like moieties and due to the presence of these units rGO-HQ1 exhibits the highest catalytic activity. The rGO-HQ1 sample was reused up to five times with slight decrease of activity (<10 %), this decay in activity being attributable to the partial rGO oxidation as revealed by XPS analysis. The heterogeneity of the process was assessed by hot filtration test, observing that the reaction stops if rGO-HQ1 is removed from the reaction medium. The use of hydroquinone and/or p-benzoquinone as organocatalysts and comparison of the catalytic activity of a series of analogous samples upon selective masking of oxygen functional groups present in rGO-HQ1 indicated that hydroquinone/quinone-like subunits are most likely the active sites for activation of molecular O₂. The use of selective radical quenchers such as DMSO or NaN₃ allowed to conclude that hydroperoxyl and hydroxyl radicals as well as ¹O₂ are the oxygen radicals formed during the reaction.

In general, this work opens new avenues for the development of highly active rGO carbocatalysts by selection of the adequate reducing agents that could introduce active sites on rGO to promote specific reactions at the same time that reconstitutes sp² domains on the defective graphene sheet.

ASSOCIATED CONTENT

The following files are available free of charge. Characterization of the materials employed in the present work by FT-IR, TGA, Raman, XPS, ¹³C-NMR, TPD-MS and elemental analysis.

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Notes

The authors declare no competing financial interest.

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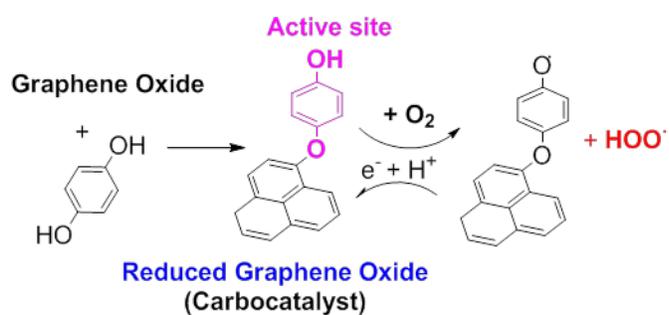
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Synopsis: A metal-free catalyst was developed for the aerobic oxidation through engineering of active sites on reduced graphene oxide by selecting hydroquinone as reducing agent.