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Short communication

## Graphene oxide-catalysed oxidation reaction of unsaturated compounds under microwave irradiation



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## ABSTRACT

Graphene oxide (GO) was investigated as a catalyst in the oxidation of alkenes and alkynes in combination with microwave heating. Styrene and phenylacetylene were selected as model compounds for the study. Moderate catalyst loadings (25 wt.%) and short reaction times (1 h) were employed, demonstrating that the combination of GO and  $H_2O_2$  under microwave irradiation possessed an optimum oxidation capacity to oxidize double bonds to different alcohols and aldehydes.

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## 1. Introduction

During the last years, graphene and chemically modified graphenes (CMGs) have attracted much attention due to their outstanding physico-chemical properties [1–2]. Moreover, CMGs are expected to have a significant impact in different fields such as chemistry, physics, engineering and materials science [3–8]. Although in the early stages of research the synthesis of these materials was complex, the advances on this matter have already allowed access to high quality materials [3, 4,6,7].

The use of these materials in catalysis is gaining increasing interest [8,9,10], being a relatively new area with a huge potential but low developments. The application of graphene and CMGs in catalysis has been mainly focused on their use as supports for transition metal with catalytic activity [9,10,11]. However, the diminishing supplies of metals used in industrial processes as catalyst and the progress achieved in the use of metal-free carbons in synthetic chemistry drove a more direct application of CMGs as catalyst instead of their use as supports [9,10]. Graphene oxide (GO) accounts as most relevant CMG as it has been observed that functionalized carbons are comparatively more effective in catalysis as compared to unfunctionalized counterparts (e.g. graphene) [8,9,10,12,13].

\* Corresponding author. *E-mail address:* q62alsor@uco.es (R. Luque). GO is a readily available and inexpensive material that has been proven catalytically active for a number of organic transformations including oxidation of alcohols, alkenes and alkynes [10,12,13,14]. The main advantages of the use of GO as catalyst include simplicity and inexpensive nature, metal-free reactivity and easy recovery via simple filtration from the reaction media. However, the interesting results published to date have been obtained under extreme conditions, especially in terms of catalyst loading (400 wt.%) and reaction times (24 h +) [12, 13]. These conditions are an important drawback which needs to be overcome for a future application of GO as catalyst in the chemical industry. For this reason, recent research efforts have been focused on the improvement of the catalytic activity of GO to improve these extreme conditions of catalyst loading and reaction time.

Microwave heating is gaining interest due to its several advantages as compared to conventional heating [15–17]. Among these advantages it can be highlighted the rapid and homogeneous heating rates, selective heating, non-contact heating, quick start/stop and heating from within the material (i.e., energy conversion instead of heat transfer) [15,17,18]. In addition, its use in combination with carbon materials has given rise to a new generation of processes and materials that cannot be obtained under conventional heating [18,19,20] including catalytic applications [18,21]. The use of microwave heating has been reported to provide higher conversions and occasionally better selectivities in chemical reactions as compared to those obtained using conventional heating under otherwise similar reaction conditions. Moreover, it is possible to obtain higher reaction rates which can result in lower



reaction times [21–24]. Particularly, microwaves as non-conventional heating source had a significant impact in the field of organic chemistry in recent years. A countless number of studies have reported reduced reaction times and improved yields and selectivity obtained in chemical processes due to the previously mentioned rapid and homogeneous as well as selective heating achieved under microwave irradiation [22–24].

However, no studies can be found about the use of microwave heating to improve the performance of unmodified GO as catalyst in oxidation reactions of alkenes and alkynes.

For these reasons we envisaged the use of microwave heating in combination with GO as a novel possibility to achieve high conversions in oxidation reactions using lower catalyst loadings and milder operation conditions. In this work, we present a study of the catalytic activity of graphene oxide in different oxidation reactions of styrene and phenylacetylene under microwave heating, with the aim of reducing reaction times and catalyst loading as well as working under milder conditions to those previously reported.

## 2. Experimental

#### 2.1. Graphene oxide synthesis

A series of experiments under different conditions was performed in order to study the catalytic properties of graphene oxide (GO). GO was provided by NanoInnova Technologies (Madrid, Spain) and it was synthesized by using a modified Hummers' method [25]. Briefly, graphite powder (<150 µm Sigma-Aldrich) was chemically oxidized in a solution containing NaNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub> and KMnO<sub>4</sub>. Reduced GO (rGO) was also kindly provided by NanoInnova. rGO has a surface area of around 100 m<sup>2</sup> g<sup>-1</sup> and different structural features as compared to GO [26]. Full details, including characterisation of the materials, can be found at the website of the company http://www.nanoinnova.com/Product.

#### 2.2. Characterisation of GO

X-ray diffraction was performed using a Panalytical X'Pert PRO  $\theta/\theta$  system, using CuKa-radiation, and X'Celerator detector. Samples were scanned between 5 and 100° (2 $\theta$ ) using a step size of 0.0167° (2 $\theta$ ) and a count time of 100 s.

Thermogravimetric analysis was performed with a TGA Q-500 (TA Instruments) at 1  $^{\circ}$ C/min (temperature range 20–900  $^{\circ}$ C) under nitrogen atmosphere.

FT-IR spectra were collected on a "Jasco FT/IR-410", using KBr pressed pellet technique. Spectra were recorded in the 3600–500 cm<sup>-1</sup> range as well as in the 1800–600 cm<sup>-1</sup> range to identify the different functional groups in GO.

Photoelectron spectra (XPS) were recorded in a VG Escalab 200R spectrometer equipped with a hemispherical electron analyser and a Mg Ka ( $h\nu = 1254.6$  eV) X-ray source, powered at 120 W. Binding energies were calibrated relative to the C1s peak at 284.8 eV. High-resolution spectra envelopes were obtained by curve fitting synthetic peak components using the software "XPS peak". Symmetric Gaussian–Lorentzian curves were used to approximate the line shapes of the fitting components.

## 2.3. Catalytic experiments

Oxidation tests were performed under microwave heating in a pressure-controlled CEM-discover microwave reactor (www.cem. com). The reactor uses cylindrical vials of 10 mL. The reactor is a multi-mode microwave reactor which power varies in the range of 0–300 W with a frequency of 2450 MHz. An infrared sensor is used to monitor temperature during the experiment. Two different substrates were used: styrene (S) and phenylacetylene (PA).

In a typical experiment, in a sealed tube (10 mL) containing stirring bar acetonitrile (2 mL), the substrate (0.2 mL),  $H_2O_2$  (0.3 mL, 50% v/v

aqueous solution) and 50 mg of GO as catalyst were mixed. All the reactions were carried out at 150 °C during 1 h. The influence of the oxidant species was also studied, by carrying out an experiment with  $H_2O_2$  in a lower concentration than the reference test (using 0.2 mL, 35% v/v aqueous solution). Three additional blank experiments were performed, one in absence of catalyst and two of them in the absence of oxidant (one with GO as catalysts and the other one with rGO). Additionally, a conventionally heated experiment using identical quantities of reagents, namely 0.2 mL styrene, 2 mL acetonitrile, 0.3 mL  $H_2O_2$  (50% v/v aqueous solution) and 50 mg of GO was conducted at 85 °C (boiling acetonitrile/water solution) for 12–24 h.

After the microwave experiments, the reacting mixture was filtered and the filtrate was analysed by means of GC and GC/MS using an Agilent 6890 N fitted capillary column HP-5 (30 m  $\times$  0.32 mm  $\times$  0.25 µm) and a flame ionisation detector (FID). The recovered GO was then reused in subsequent tests (denoted as runs rS4-1 and rS4-2) under identical conditions to those of run S3 in order to check GO deactivation.

## 3. Results and discussion

Characterisation studies of GO were conducted in NanoInnova (http://www.nanoinnova.com/Product) using several techniques including XRD, TGA XPS and IR spectroscopy. Fig. 1 depicts XRD patterns of as-prepared GO with respect to graphite (used as starting material), evidencing a complete oxidation of graphite and the formation of the characteristic diffraction lines of GO [10-14]. The clear XRD pattern indicates a high purity of GO achieved after graphite powder treatment. The presence of the high purity GO was also confirmed by TGA and IR results (Fig. 2) in which a number of distinctive bands corresponding to C=O (carbonyl/carboxylic acid groups, 1714 cm<sup>-1</sup>), C=C from aromatics (1615 cm<sup>-1</sup>), C–O (carboxylic acid groups, 1317 cm<sup>-1</sup>; epoxy and alkoxy 1221, 1028 cm<sup>-1</sup>, respectively) could be clearly observed. The TGA trace shows three distinctive peaks, a first mass loss at ca. 100 °C (10.8%) due to the removal of water molecules from GO, followed by a peak at 300 °C corresponding to GO decarboxylation (32-35% mass loss). Further decomposition (20-22% mass loss) takes place up to 800-850 °C.

XPS measurements were also conducted to support IR data, clearly showing the presence of C–O and C=O groups (deconvoluted bands at 286.7 and 288.4 eV, respectively, for C1s as well as 532.2 and 531.9 eV for O1s) both clearly visualised in C1s and O1s spectra (Fig. 3).

Two model reactions were selected to investigate the activity and selectivity of characterised GO in oxidation reactions of unsaturated systems under microwave irradiation, starting from styrene and phenylacetylene, and employing  $H_2O_2$  as oxidant (Fig. 1).

Table 1 summarise the results achieved in the performed experiments. Blank runs (in absence of catalysts as well as in the absence of oxidant) were also performed, with a negligible conversion in the systems. However, a comparatively high conversion (>80%) can be achieved when the process is carried out in the presence of both GO as catalyst and  $H_2O_2$  as oxidant. This high conversion demonstrates that the combination of GO and  $H_2O_2$  has an optimum oxidative



Fig. 1. XRD patterns of the GO prepared and the graphite used as precursor.



Fig. 2. IR spectra (top images) and TGA trace of graphene oxide (GO, sample GO.Z.10-4 from NanoInnova).

capacity to oxidize double bonds under microwave irradiation. A comparative experiment under conventional heating provided low catalytic activities (<50%) and selectivities to benzaldehyde (ca. 25%) of the combination GO/H<sub>2</sub>O<sub>2</sub> even after 24 h reaction. Reactions run under microwave irradiation could provide high yields to products with improved selectivities (less number of byproducts generated) while decreasing reaction time (1 h vs 24 h) and catalyst loadings (25 wt.% vs 400 wt.%) as compared to previously reported results using conventional heating for the oxidation of alkenes [27,28]. The oxidative capacity of the catalytic system was observed to decrease when using diluted H<sub>2</sub>O<sub>2</sub> or when reduced GO was employed as catalyst instead of GO. Under these conditions, conversion decreased dramatically (<25%). This



Fig. 3. XPS C1s (A) and O1s (B) spectra of graphene oxide (GO, sample GO.Z.10-4 from NanoInnova).

decrease in conversion pointed out the combination of  $H_2O_2$  and GO as an efficient catalytic system in the oxidation of double bonds.

In terms of selectivity, benzaldehyde, styrene glycol and phenylethanol were observed as main products, with benzaldehyde and styrene glycol obtained as major products (phenylethanol was only observed in low quantities). Other products found were phenol and benzyl alcohol but together account for less than 10% of selectivity in all cases, except for the conventionally heated reaction (entry S7) for which larger quantities of these and other side products were obtained. Over-oxidation to benzoic acid was not observed under any investigated conditions as opposed to previous reports when high temperatures and more extreme conditions (longer reaction times and/or higher catalyst loadings) were utilised [12,13]. Apart from speeding up times of reaction, the use of microwave heating could provide a slight improvement in benzaldehyde selectivity (ca. 46-50 vs 20-25%) with respect to conventionally heated reactions. The effect of microwave irradiation in the proposed system is clearly a rapid ad homogeneous heating of the bulk solution (as well as the GO material) which leads to an effective reaction under the investigated conditions.

The ratio between benzaldehyde and styrene glycol was observed to be constant, regardless of the concentration of  $H_2O_2$ . The concentration of  $H_2O_2$  does not therefore seem to play a key role in the selectivity of the process. Comparatively, the use of GO or rGO influenced both conversion and selectivity in the process, since the ratio between benzaldehyde and styrene glycol was changed. This ratio (1.3:1, benzaldehyde:styrene glycol) observed for GO changed to 3:1 when rGO was used. These results pointed to an increase in benzaldehyde production as a consequence of the lower oxidative capacity of rGO. rGO also gave rise to values of conversion and selectivity very similar to those achieved with reused GO. These results pointed out that GO loses oxidative capacity upon reuse as well as activity.

However, characterisation studies of GO before and after reaction could not provide strongly supportive and conclusive insights for such activity decrease as shown in the comparative IR profiles of fresh and reused catalyst from Fig. 4. These characterisation experiments might

## Table 1

Conditions used and conversions and selectivities achieved in the GO-catalysed oxidation of styrene.

Run	Catalyst	Oxidant	Conversion	Selectivity			Others
					OH OH	CH OH OH	
S1	None	H <sub>2</sub> O <sub>2</sub>	-	-	-	-	-
S2	GO	_	-	-	-	-	-
S3	rGO	_	-	-	-	-	-
S4 <sup>a</sup>	GO	$H_2O_2$	$83 \pm 4$	$46 \pm 3$	$8 \pm 1$	$36 \pm 3$	$10 \pm 2$
S5	GO	$H_2O_2$ diluted	22	42	6	46	7
S6	rGO	$H_2O_2$	23	71	4	23	2
S7 <sup>b</sup>	GO	H <sub>2</sub> O <sub>2</sub>	38	24	8	28	40
rS4-1	Spent GO <sup>c</sup>	$H_2O_2$	24	63	6	26	5
rS4-2	Spent GO <sup>d</sup>	$H_2O_2$	17	71	4	21	3

<sup>a</sup> Run S4 was repeated 3 times to determine the experimental error.

<sup>b</sup> Reaction run under conventional heating (85 °C, 24 h reaction).

<sup>c</sup> The catalyst used in this run was GO recovered from run S4.

<sup>d</sup> The catalyst used in this run was GO recovered from run rS4-1.

point to a reduced intensity in C–O and C=O bands in the reused materials, which may be the main reason of the observed GO deactivation, but the contribution of surface C=O and C–O groups as measured by XPS (results not shown) did not significantly change after the oxidation reaction.

A proposed mechanism for the selective oxidation process can be shown in Fig. 1.

The oxygenated groups present on the surface of GO activate the formation of radicals •OH that are then able to oxidize the double bound of the alkene species. Three different reaction paths may give rise to the main reaction products. The interaction of OOH<sup>-</sup> radicals with surface groups of GO may give rise to a superoxide which interacts with the double bond of styrene to form the proposed transition state shown in Fig. 1. Finally, an electronic rearrangement takes place to produce benzaldehyde. Other possibility is a nucleophilic addition to give rise to phenylethanol. In the case of the styrene glycol, it is necessary to have an intermediate state in which the alkene is epoxidized. The epoxide is then opened to styrene glycol due to a nucleophilic addition. This second reaction of the mechanism also needs the presence of active sites from GO [29]. For this reason, the selectivity to this compounds decreases when rGO or reused GO were employed as catalysts since the oxidative capacity of these materials is not enough to catalyse the two consecutive reactions. This mechanism may also explain the decrease in conversion observed in runs rS4-1 and rS4-2. Upon catalyst reusing, less C–O and C=O groups seemed to be present in GO (although only qualitatively as shown in IR results, Fig. 4) to interact with the reactants and give rise to the products, thus a decrease in conversion is observed.

Table 2 shows the results achieved in experiments performed to study the oxidation capacity of the GO in alkynes using phenylacetylene (PA) as model compound. In the case of PA, a very low conversion was obtained (<15%) even when both GO and  $H_2O_2$  were employed. This means that this combination has not enough oxidative capacity to quantitatively oxidize triple bonds under the investigated reaction conditions and the selected catalysts loading and short times of reaction even under microwave irradiation. Longer reaction times and/or catalyst loadings are needed to oxidize triple bonds in order to achieve similar results to those reported under conventional heating.

#### 4. Conclusions

Graphene oxide can be a very efficient and selective catalyst for the oxidation of unsaturated compounds under microwave irradiation, particularly alkenes. Quantitative conversion of styrene could be achieved



Fig. 4. IR spectra of fresh GO (top images) and double reused GO (entry rS4-2, bottom images) in the microwave-assisted oxidation of styrene.

Ta	ble	2

Conditions used and conversions and selectivities achieved in the GO-catalysed oxidation of phenylacetylene.

Run	Catalyst	Oxidant	Conversion	Selectivity			Others
				С Ц Н	OH	OH	
P1	None	$H_2O_2$	-	-	-	-	-
P2	GO	None	-	-	-	-	-
Р3	GO	$H_2O_2$	15	59	41	-	-
P4	GO	H <sub>2</sub> O <sub>2</sub> diluted	5	38	62	-	-
P5	rGO	$H_2O_2$	<5	83	17	-	-

under the investigated conditions, producing a mixture of benzaldehyde, styrene glycol and phenylethanol (and other minor compounds). The selectivity of products was found to be highly dependent on the reaction conditions. Regardless of the conditions employed, benzaldehyde and styrene glycol were obtained as major products, but their ratio varied in the range of 1–3.

In the case of alkynes, conversions of phenylacetylene remained below 15%. This points out that, contrary to the case of alkenes, GO cannot oxidize alkynes using low catalyst loadings and short reaction times even under microwave irradiation.

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