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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.

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].

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

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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 $NaNO_3$, H_2SO_4 and $KMnO_4$. Reduced GO (rGO) was also kindly provided by NanoInnova. rGO has a surface area of around 100 $m^2\ g^{-1}$ 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 θ/θ system, using CuKa-radiation, and X'Celerator detector. Samples were scanned between 5 and 100° (2θ) using a step size of 0.0167° (2θ) and a count time of 100 s.

Thermogravimetric analysis was performed with a TGA Q-500 (TA Instruments) at 1 °C/min (temperature range 20–900 °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^{-1} range as well as in the 1800–600 cm^{-1} 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 multimode 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 × 0.32 mm × 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^{-1}), C═C from aromatics (1615 cm^{-1}), C–O (carboxylic acid groups, 1317 cm^{-1}; epoxy and alkoxy 1221, 1028 cm^{-1}, 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

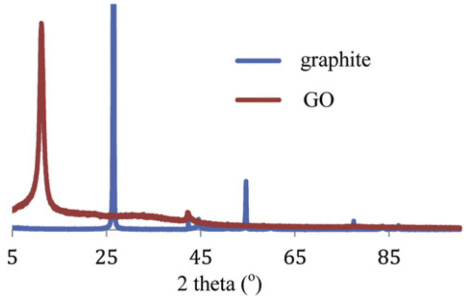

Fig. 1. XRD patterns of the GO prepared and the graphite used as precursor.