



Short communication

Sulphur-doped graphene as metal-free carbocatalysts for the solventless aerobic oxidation of styrenes



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ABSTRACT

Pyrolysis of λ -carrageenan at 1000 °C and subsequent exfoliation lead to a S-doped graphene [(S)G]. Increasing pyrolysis temperature to 1200 °C or the use of other carrageenans with lower sulphate content results in the failure of S doping. XPS confirms the presence of S atom (4.5%) with environments alike sulphide and sulphoxide. (S)G promotes the aerobic oxidation of styrenes to their corresponding benzaldehydes accompanied by lesser amounts of styrene oxide. In contrast, under the same experimental conditions reduced graphene oxide exhibits a negligible activity. (S)G was reused with almost coincident catalytic performance.

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1. Introduction

For the sake of sustainability, availability and affordability, there is a considerable interest in developing metal-free catalysts [1–8]. Graphene (G) and related materials hold a considerable promise as metal-free catalysts [9–15], due to the combination of the unique features of single-layer sp^2 carbons with the possibility to design active sites on it [16–19]. Doping of G with heteroatoms has been found to be a general way to introduce catalytic activity for a range of reactions [16], including aerobic oxidation of benzylic hydrocarbons and of electron rich alkenes [20]. Recently, we have reported that N- and B-doped Gs can promote the aerobic oxidation of styrene to a mixture of benzaldehyde and styrene oxide [20]. Continuing in this line of research it would be of interest to determine if doped Gs having other heteroatoms also exhibit activity as catalysts of aerobic oxidation of hydrocarbons.

Specifically in the present work we report a convenient procedure for the preparation of S-doped G [(S)G] and it will be shown that this doped G can promote the aerobic oxidation of styrene (Table 1). In an earlier precedent we have disclosed that pyrolysis of chitosan in the absence of oxygen and subsequent exfoliation of the resulting graphitic carbon residue renders N-doped G [(N)G] [21]. The advantages of this process are that chitosan, a polysaccharide of glucosamine, acts as single source of C and N in the process and N-doping occurs simultaneously

with the formation of the G sheet. During the pyrolysis, a fraction of the N atoms of the chitosan amino groups become incorporated into the G layer in three different types of N dopant and in a percentage that decreases as the pyrolysis temperature increases in the range from 900 to 1200 °C.

A logical extension of the preparation of (N)G will be to test if other natural polysaccharides containing heteroatoms can similarly act as precursors of doped G. Carrageenans are linear, high-molecular weight polysaccharide of galactose having sulphate groups. Therefore, they are obvious candidates to become precursors of (S)G that subsequently could be tested as oxidation catalyst. The convenient preparation of (S)G shown below constitutes another example of the methodology that uses pyrolysis of natural biopolymers for the preparation of Gs.

2. Experimental section

2.1. Preparation of (S)G

There are three main types of carrageenans commercially available, but it was found that λ -carrageenan with the highest S content is the only one that according to XPS renders after pyrolysis G materials doped with S. λ -Carrageenan (Sigma Aldrich ref. 22049) was pyrolyzed in argon atmosphere heating at 200 °C for 2 h and then heating at 10 °C/min up to 1000 °C for 6 h. The resulting graphitic powder was sonicated at 700 W for 1 h in water to obtain dispersed (S)G suspensions. This method of preparing doped Gs from pyrolysis of natural polysaccharides was reported previously by our group to obtain N- and B-doped Gs [21].

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Table 1
Aerobic oxidation of styrene and its derivatives using (S)G catalyst.^a

Run no.	Catalyst	T (°C)	Substrate	Time (h)	Conv. (%) ^b	Sel. (%) ^b	
						BA	SO
1	–	100	Styrene	7	4	44	18
2	(S)G	100	Styrene	1	0.8	100	–
3				2	3	82	18
4				3	4.8	74	20
5				4	5.5	72	19
6				7	13	70	20
7 ^c	(S)G	100	Styrene	7	12	71	18
8 ^d	(S)G	100	Styrene	7	12	67	19
9	rGO	100	Styrene	7	–	–	–
10	(S)G	80	Styrene	7	–	–	–
11 ^e	(S)G	100	Styrene	7	<1	98	–
12	(S)G	100	α -Methylstyrene	1	3	87 ^f	10
13				5	9	85	13
14				7	13	76	20
15	(S)G	100	4-chlorostyrene	7	6	12	81 ^g
16	(S)G	100	4-methoxystyrene	7	23	–	–

^a Reaction conditions: substrate (1 mL), catalyst (10 mg), oxygen atmosphere, 100 °C.

^b Determined by GC.

^c First reuse.

^d Second reuse.

^e Reaction performed under inert atmosphere.

^f The product is acetophenone.

^g The selectivity corresponds to the mixture of the epoxide and carbonyl compounds.

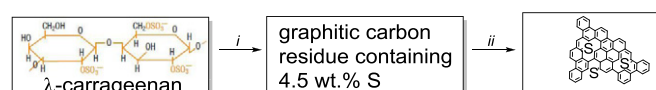
Two different temperatures were tested (1000 and 1200 °C) and only the G sample pyrolyzed at 1000 °C was doped. It is a general observation that the percentage of dopant heteroatoms in doped G prepared by pyrolysis decreases as the pyrolysis temperature increases [21].

2.2. Characterization techniques

FT-Raman spectra were recorded at ambient temperature with 514 nm laser excitation at 2 mW power by using a Renishaw In Via Raman spectrophotometer equipped with a CCD detector. TEM images were recorded in a Philips CM300 FEG system with an operating voltage of 100 kV. XP spectra were recorded on a SPECS spectrometer equipped with a Phoibos 150 9MCD detector using a non-monochromatic X-ray source (Al and Mg) operating at 200 W. The samples were evacuated in the pre-chamber of the spectrometer at 1×10^{-9} mbar. The samples have been activated in situ in nitrogen flow at 450 °C for 3 h followed by evacuation at 10^{-8} mbar. Deconvolution and fitting of the experimental peaks were carried out after nonlinear Shirley-type background subtraction and peak correction by the transmission function of the spectrometer. Combustion elemental analyses were measured using a Perkin-Elmer CHNOS analyser. The detection limit of the technique was 10 ppm.

2.3. Experimental procedure for aerobic oxidation

A 3 mL microreactor was charged with the catalyst (10 mg), followed by the addition of substrate (1 mL). The resulting slurry was sonicated for 30 min (700 W, horn sonicator). The reaction was carried out under magnetic stirring by heating the suspension at 100 °C in most of the experiments or the indicated temperature using a preheated thermostated oil bath. This reaction mixture was maintained with oxygen atmosphere. The course of the reaction was periodically monitored by analysing the sample with GC. An aliquot of 1 μ L of the reaction mixture was taken at different time intervals with a syringe, diluted with 0.1 mL of acetonitrile and filtered throughout a 0.2 μ m Nylon filter prior to GC injection and analysed immediately without delay to minimise possible on-going room temperature oxidations. The mass balances of the reaction mixture accounted for more than 96% of the initial substrate, as estimated by GC using nitrobenzene as the external standard. The yields of the product were determined by using nitrobenzene as the external standard



Scheme 1. Preparation procedure of (S)G using λ -carrageenan as precursor that is pyrolysed at 1000 °C (i) and exfoliated by sonication (ii).

considering the response factor unity. The reaction products were further confirmed by GC–MS and co-injecting with authentic samples.

3. Results and discussion

Scheme 1 summarizes the pyrolytic procedure followed in the preparation of (S)G. Combustion chemical analysis of the three commercial K, I and λ carrageenan samples differing in the number of sulphate groups per disaccharide unit, one, two or three, respectively, shows that only the residue from λ -carrageenan having the maximum sulphate content pyrolysed at 1000 °C contains S. The elemental analysis of (S)G was 80.8% C and 4.5% S. The presence of some residual percentage of N (0.2%) and H (0.3%) was also detected. When λ -carrageenan was pyrolysed at 1200 °C, no S was detected. Pyrolysis under inert atmosphere leading to G is strongly reducing conditions [22]. In earlier precedent using the phosphate ester of alginate, it has been observed the formation of elemental phosphorous that partly sublimes as the red allotrope in the pyrolysis process and partly becomes incorporated in the G sheet [23]. Also, alginate borate ester as precursor of (B)G should require a chemical reduction step of B atoms in the process of G doping [20]. Similarly, it is proposed here that the sulphate groups present in natural carrageenan would be reduced to elemental sulphur that partly would become incorporated during the formation of carbon residue on the G sheets and partly will sublime. In earlier precedents it was found that an excess of the precursor containing the heteroatom is necessary to produce G doping. For this reason, under our conditions, other carrageenans have been found to lead to carbon residues in which no sulphur is detected by combustion chemical analysis.

FT-Raman spectroscopy is a suitable characterization technique for graphitic materials. The Raman spectrum recorded for (S)G (Fig. 1) showed three expected peaks that correspond to the 2D band (2890 cm^{-1}), the G and D bands at 1592 and 1355 cm^{-1} , respectively.

The presence of S atoms and the fact that they are incorporated into G sheets was ascertained by XPS measurements. Deconvolution of the C1s peak (Fig. 2) leads to two components at binding energies of 284.5 eV and 285.7 eV that correspond to graphitic carbon atoms and C atoms bonded to S. The S2p peak was deconvoluted into two components at binding energies of 164.1 eV and 168.2 eV (Fig. 2), that according to the literature [24] can be attributed to S atoms bonded to C and S atoms bonded to C and O, respectively.

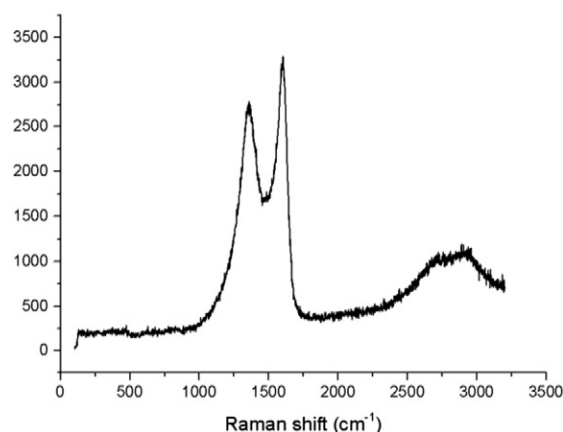


Fig. 1. The Raman spectrum of (S)G.

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