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Highly carboxyl-decorated graphene oxide sheets as metal-free catalytic system for chemoselective oxidation of sulfides to sulfones

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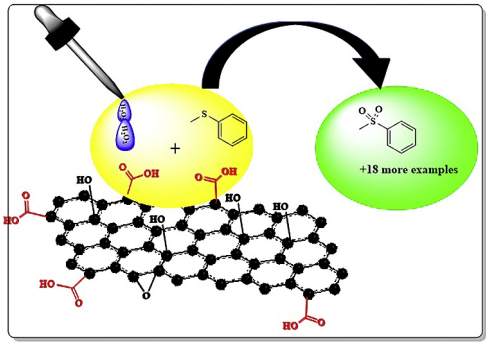
HIGHLIGHTS

- Acidic graphene oxide as metal-free catalyst in sulfides oxidation.
- Chemoselective of sulphides to sulfones over sulfoxides.
- Graphene oxide with amphiphilic structure as reusable catalyst.
- Pseudo-first order kinetics mechanism with modified graphene oxide.

GRAPHICAL ABSTRACT



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ABSTRACT

Highly-acidic graphene oxide in the presence of hydrogen peroxide was found to act as an efficient metal-free heterogeneous catalyst for oxidation of sulfides to sulfones under mild and neutral condition. Several factors such as catalyst amount, solvent, and reaction time pertaining to achieve the reactivity were also discussed. Sulfone formation increased with an increase in hydrogen peroxide concentration, temperature, and catalyst amounts. The uniqueness of this catalyst lies in its stability, cost-effective, ease in removal at the end of reaction, and chemoselective oxidation of alkyl and aryl sulfides to the corresponding sulfones. The catalyst is recyclable for at least four times only with the little reduction in oxidation of sulfides. Reaction kinetics was found to be pseudo-first order and the calculated activation energy was 32.11 kJ/mol.

1. Introduction

Sulfones and sulfoxides are useful synthetic reagents in organic chemistry [1,2] and medicinal chemistry [3]. Oxidation of sulfides to obtain sulfoxides [4] and sulfones [5] is a straightforward synthetic route and have attracted wide interests of organic chemists from a long time [6,7]. However, a large number of such oxidation reactions often require the use of toxic metal reagents or catalysts [8,9]. Among various oxidants employed to this transformation, hydrogen peroxide is an attractive and environmentally friendly oxidant due to its low cost, high availability and cleanliness. However, hydrogen peroxide alone is a relatively weak electrophile and a catalytic activation is required to access its full potential [10].

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Many papers concerning oxidation of sulfides have been published, including the oxidation using hydrogen peroxide and acids such as trifluoroacetic acid [11], formic acid [12], acetic acid [13–15], heteropolyacid [5,16], and so on. Use of these homogenous catalysts represents a considerable progress of the process, however, the catalyst is difficult to recover and reuse. Therefore, the replacement of current homogenous oxidation procedures with recoverable solid catalysts [17] is one of the major tasks for the production of sulfoxides and sulfones.

Graphene oxide (GO), is the product of chemical oxidation and exfoliation of graphite and has been known for more than a century [18]. Graphene oxide sheets have a hydrophobic basal plan and hydrophilic edges. GO's water dispersity and hydrophilicity has been mainly attributed to the ionisable edge −COOH groups [19,20]. Carboxyl groups might give carboxylic anhydrides or condense to lactone groups or form lactols (in close neighbourhood to hydroxyl groups or carboxyl group) [21]. Heterogeneous and solid oxidation catalysis are attainable by carboxyl-decorated at the edge of graphene oxide sheets.

Herein, to introduce enough carboxyl groups to oxidation reaction, graphite oxidized under serious oxidation method, concentrated sulfuric acid, followed by potassium permanganate, which was proved to be an efficient method to introduce carboxyl groups to graphene oxide sheets. Due to our interest in using heterogeneous catalysis [22,23] and organic synthesis [22,24–26], in the present work we have reported the results obtained with Acidic graphene oxide (AGO) as a recoverable heterogeneous catalyst under solvent free condition at room temperature, for selective oxidation of various types of sulfides to the corresponding sulfones using H_2O_2 solution (30 wt%).

2. Experimental

2.1. Materials

Graphite powder <20 μm, Potassium permanganate were purchased from Sigma Aldrich. Hydrochloridric acid, Ethanol, orthophosphoric acid, sulphoric acid, and TLC Silica gel 60 F_{254} were procured from Merck. All other reagent used in this study were analytical grade, and distilled or double distilled water was used in the preparation of all solutions.

2.2. Analysis instruments

AGO was characterized by X-ray photoelectron spectroscopy (XPS, ESCA 2000, VG Microtech) using Al Kα radiation (hv = 1486.6 eV). All binding energy values were corrected by calibrating C1s peak at 284.6 eV. The measurements of X-ray diffraction (XRD) were recorded on D/MAX-250,Rigaku, Tokyo, Japan, 40 kV with Cu Kα irradiation (λ = 1.541 Å). Fourier transform infrared (Bruker FTIR) spectra were recorded in KBr pellets in the range of 400–4000 cm^{-1}. Scanning electron microscopy (SEM) images of the product were taken using a JSM-6701F microscope (JEOL, Japan) equipped for (EDS). A small part of scaffold was placed on the SEM sample holder and sputter coated with platinum. An accelerating voltage of 10 kV was used. Transmission electron microscopy (TEM) were performed on JEOL JEM-1010n. The magnetic measurements were carried out in a vibrating sample magnetometer (VSM, BHV-55, Riken, Japan) at room temperature. UV–visible spectra were recorded by Perkin Elmer Lambda 25 spectrometer. UV lamp which emits UV light having the 254 nm wavelength was used to visualization of spot on the surface of TLC plates. Rotary Evaporator Laborata 4003 for gentle removal of solvents from samples by evaporation was applied.

2.3. Methods

2.3.1. Synthesis of acidic graphene oxide (AGO)

Graphene oxide was synthesized by oxidation of graphite using the method described in Ref. [27]. To a mixture of 6 g $KMnO_4$ and 1 g graphite, 120 mL of concentrated sulfuric acid and 15 mL orthophosphoric acid were poured. It was heated to 50 °C and stirred for 24 h. The resulting mixture was added to ice (150 mL) with 6 mL of H_2O_2 solution (30 wt%), which turned the color of the solution from dark brown to yellow. The solution was centrifuged and separated solid product was washed two times with water and HCl solution (30 wt%) and ethanol. Then the powder was dissolved in water and after 2 h sonication, the solution was centrifuged and the brown AGO solution was obtained.

2.3.2. General procedure for the preparation of sulfones

In a 100 mL round bottom flask, to a solution of AGO (25 mg), 0.3 mL H_2O_2 solution 30 wt% (3 mmol) and sulfide (various types of sulfides represented in Table 4) (1 mmol) were added at room temperature with continuous stirring for the desired time as indicated in Table 1. The progress of the reaction was monitored by TLC. After accomplishment of the reaction, 4 mL ethanol was added to the reaction mixture and stirred for 5 min. Then the catalyst and product was separated by centrifuging of the mixture. The solvent was removed by rotary evaporator to give the corresponding sulfones. The catalyst was washed by water/ethanol mixture (1:1) and dried in vacuum before every recycling experiment. All products were known and characterized by comparison of their spectroscopic and physical data with authentic samples synthesized by reported procedures.

2.3.3. Determination of the content of carboxylic acid groups of AGO

The content of carboxylic acid groups was determined by standardized Boehm titration [21,28]. For Boehm titration ~0.5 g of AGO was placed in 50 mL of the following 0.05 M solutions: NaOH and $NaHCO_3$. The amount of acidic sites of various types were calculated under the assumption that NaOH neutralizes carboxylic, phenolic and lactonic groups, and $NaHCO_3$ only carboxylic groups. The samples were agitated by shaking for 24 h and then filtered to remove the carbon, and 10 mL aliquots were taken by pipette from the samples. The aliquots were then acidified by the addition of 20 mL of 0.05 M HCl. The acidified solutions were then back-titrated with 0.05 M NaOH. The results of back titration gave 1.2 mmol/g for all acidic groups and 0.83 mmol/g for carboxylic groups on the surface of AGO sample.

3. Results and discussion

Fig. 1A depicts the characteristic absorption peaks for AGO at 3390 cm^{-1}, 1737, 1622, 1419, 1228 and 1049 cm^{-1}, which can attributed to stretching vibrations of the hydroxyl and carbonyl in

Table 1
Quantitative EDS analyses of the element proportion in AGO.

Element	Weight %
	GO
C K	47.18
O K	52.82
N K	–
S K	–
Fe L	–
Totals	100