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Selective liquid phase oxidation of cyclohexene over magnetic Fe_3O_4/graphene oxide nanocomposite

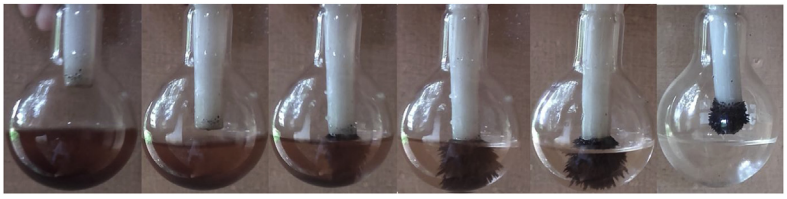
Sowmya Balasubramanyan [a], Sandhya Arayathody [a, b], Sankaran Sugunan [c], Binitha N. Narayanan [a, *]

[a] Department of Chemistry, Sree Neelakanta Government Sanskrit College Pattambi (Affiliated to University of Calicut), Palakkad 679306, Kerala, India
[b] Department of Chemistry, Little Flower College Guruvayoor (Affiliated to University of Calicut), Guruvayoor 680103, Kerala, India
[c] Department of Applied Chemistry, Cochin University of Science and Technology, Cochin 22, Kerala, India

HIGHLIGHTS

- Fe_3O_4-graphene oxide catalysts were used in cyclohexene oxidation reaction.
- Fe_3O_4/2 wt% GO lead to a conversion of 78% and diol selectivity of 87% using H_2O_2.
- Highest conversion of 92% has been obtained when TBHP is used as the oxidant.
- Reaction parameters were varied to attain the best suitable reaction condition.
- After the reaction, catalyst was effectively separated using a magnet and is reused.

GRAPHICAL ABSTRACT



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ABSTRACT

Magnetic graphene based nanocomposite catalysts were used for the first time in cyclohexene oxidation reaction. Fe_3O_4 was found to be the active phase of Fe in the catalysts as evident from the XRD analysis of the samples. Presence of graphene as graphene oxide in the nanocomposites is confirmed from FTIR spectral analysis. The distribution of more or less spherical particles of Fe_3O_4 over the graphene sheets was evident from the TEM photographs. The activity of bare Fe_3O_4 increased drastically upon graphene incorporation. Maximum conversion of 92% was attained using *tert*-butyl hydroperoxide as the oxidant over the best nanocomposite catalyst in which Fe_3O_4 was supported over 2 wt% graphene oxide. Using H_2O_2, double bond oxidation was the major reaction (78.27% conversion) and 1,2-cyclohexane diol was the major product (87.89% selectivity) under the selected reaction conditions of 0.05 g of catalyst with 5 mL of acetonitrile solvent at 70 °C in the 6 h reaction between 2 mmol of cyclohexene and 10 mmol of oxidant. Catalysts recovery from the reaction mixture was very easy by the use of a magnet that in turn facilitated the effective reusability of the Fe_3O_4 /graphene nanocomposite. The reused catalyst was characterized using TEM and FTIR spectral analyses and it is found that the partial loss in activity can be a resultant of the oxidation of graphenic C=C and the formation of epoxy linkage and −OH groups in the sheets, which hinders the efficient electron migration during catalysis.

* Corresponding author.
E-mail address: binithann@sngscollege.org (B.N. Narayanan).

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1. Introduction

Selective dihydroxylation of olefins that essentially occurs at mild oxidation conditions is an indispensable reaction in both industrial and academic point of view. Since 1,2-diols are useful building blocks in the designing of pharmaceuticals, many research groups put efforts to develop large number of efficient heterogeneous catalysts for epoxidation and subsequent hydrolysis reactions [1–4]. Specifically, cyclohexane diol, the precursor in the production of adipic acid, can be produced by the epoxidation of cyclohexene followed by hydrolysis. OsO_4, $KMnO_4$, peracids, etc. are the frequently used reagents for the selective dihydroxylation of cyclohexene. Being an ideal and non-toxic oxidizing agent, reactions with H_2O_2 has been well practiced [5,6]. Cyclohexene oxidation reaction over various heterogeneous catalysts also resulted in the formation of cyclohexene oxide, 2-cyclohexenol and 2-cyclohexenone using H_2O_2 as the oxidant [7–9].

Group VIII transition metals, metal oxides and metal complexes of Fe and Ru were proved to be active catalysts for the selective dihydroxylation [10–14]. Particularly, Fe, the cheap, non-toxic and most abundant metal has greater importance over the costly and toxic Ru and Os [15–17]. In recent years, the impact of magnetic Fe_3O_4 nanoparticle as heterogeneous catalyst has been effectively investigated due to its improved dispersability, reactivity and magnetic property [18–20]. Recently, *Dehkordia* et al. reported the effective use of a chiral carboxylic acid supported on Fe_3O_4 for asymmetric aerobic oxidation of cyclohexene [21]. The magnetic properties of this nanoparticles offered the facile reusability of heterogeneous catalyst. However, the metal oxide based nanoparticle catalysts have the drawbacks of sintering and agglomeration during preparation and reaction, which badly affect the catalyst activity and stability [22]. Thus the distribution of these oxides over different support materials is the effective way for maximizing the surface area as well as their catalytic activity [23]. Moreover immobilization over support materials will make the catalyst easier to handle and to separate from the reaction medium and also stabilizes or modifies the catalytic performance by influencing the chemoselectivity, regioselectivity and shape-selectivity of the reaction [24,25].

The two dimensional carbon sheet, graphene, possess high specific surface area, excellent electrical conductivity, chemical and thermal stability etc., facilitating its use in various applications [26–29]. Due to the incorporation of additional functionalities and superior productivity, graphene oxide (GO) and other chemically modified graphene based nanocomposites have been extensively studied in synthetically useful organic transformations [30,31]. GO contains various oxygen functionalities such as carboxyl, hydroxyl and epoxy groups originated during the harsh oxidising conditions in the synthetic process and the presence of these groups are very much beneficial to act as a platform to fix various metal and metal oxide nanoparticles on it to form graphene hybrid materials [32]. These hybrid materials have received enhanced attention due to the synergetic advantages of GO and metal components, which have potential applications in many technological fields, such as lithium ion battery, gas sensing, catalysis, photovoltaic devices, biosensors etc [33–35] There are a number of reports on the formation of composites of graphene and magnetic iron oxide nanoparticles and their applications in magnetic resonance imaging (MRI), magnetically targeted drug delivery, removal of contaminants from waste water etc.; but there are only limited studies about the catalytic transformations over magnetic iron oxide-graphene nanocomposites [36–39].

Herein, we report the use of magnetic iron oxide graphene nanocomposite, Fe_3O_4 supported over GO, in cyclohexene oxidation reaction for the first time. In this study, different catalysts were prepared by varying the amount of Fe_3O_4 over GO to attain the suitable percentage of Fe loading over the support to accomplish maximum catalytic performance. The active phase responsible for catalysis was investigated using different characterization techniques such as X-ray diffraction (XRD), Fourier transform infra-red (FTIR) spectroscopy, Scanning Electron microscopy (SEM), Field Emission Scanning Electron microscopy (FESEM), High-Resolution Transmission Electron microscopy (HRTEM) and Vibration Sample Magnetometer (VSM). After the reaction, the catalyst was easily separated from the reaction mixture with the help of a magnet.

2. Experimental section

2.1. Materials

Graphite flakes, cyclohexene and the standard products were purchased from Sigma Aldrich. H_2O_2 was purchased from MERCK. Ferric nitrate, ferrous sulphate and all other reagents used were procured from NICE Chemicals Pvt. Ltd. Cyclohexene was distilled before its use and all other reagents were of analytical grade and used as such without further purification.

2.2. Preparation of Fe_3O_4/GO nanocomposites

Graphite oxide synthesized *via* modified Hummer's method (Electronic Supplementary Material (ESM)) was exfoliated by ultrasound sonication in water to produce GO suspension [40]. Aqueous solutions of ferric and ferrous salts ($Fe(NO_3)_3.6H_2O$ and $FeSO_4$) were mixed in the molar ratio of 2:1 and were then added slowly to the GO suspension in water with stirring. Ammonia solution was added to precipitate Fe^{2+}/Fe^{3+} ions for the synthesis of magnetite (Fe_3O_4) nanoparticles. Further, the mixture was stirred for 6 h at 80 °C and kept it static for 12 h at room temperature. The resultant black colored precipitate was filtered, washed with water, dried at 70 °C and calcined at 200 °C for 3 h. For the catalytic reaction studies, different percentage of Fe_3O_4 incorporated GO composites were synthesized by varying the weight percentage of GO in the composites as 1%, 2%, 5% and 10%. The systems were designated as Fe_3O_4/nGO, where n indicates the weight percentage of GO used in the preparation of the catalysts.

2.3. Material characterization

The powder XRD patterns of catalysts were collected on a Bruker AXS D8 Advance X-ray diffractometer. FTIR spectral studies were conducted with traditional KBr pellet method on a Thermo Nicolet Avatar 370 spectrometer. Morphological indications of samples were obtained from a Jeol 6390LV scanning electron microscope and FESEM (Zeiss SUPRA55 scanning electron microscope at an operating voltage of 3 kV). The nature of graphene and Fe in the composite was identified by HRTEM which was carried out on a JEOL JEM-2100 transmission electron microscope. The room temperature magnetization curve of the samples, Fe_3O_4 and Fe_3O_4/2GO was measured using a Lake Shore 7410 vibrating sample magnetometer. Surface area of GO and its composites were measured using methylene blue adsorption from the aqueous suspension (ESM).

2.4. Catalytic activity studies

Cyclohexene oxidation was done over GO, Fe_3O_4 and Fe_3O_4/nGO systems, where the reaction was carried out mainly using H_2O_2 as the oxidant in acetonitrile solvent. All the reactions were kept at atmospheric pressure in a two necked RB equipped with water condenser with continuous stirring of the reaction mixture. In a