

A New Application of Nano-Graphene Oxide (NGO) as a Heterogeneous Catalyst in Oxidation of Alcohols Types

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Abstract

We describe an efficient method for oxidation of alcohols to related aldehydes and ketones by hydrogen peroxide as oxidizing agent, under reflux conditions. Nano-graphene oxide (NGO) as a heterogeneous catalyst was used and had their activity compared with other various catalysts. This catalyst was found to be an excellent catalyst for oxidation of alcohols. The effects of various parameters, including catalyst type, nature of the substituent in the alcohols and temperature, on the yield of the carboxylic acids were studied. Nano-graphene oxide was synthesized by the oxidation of graphite powders. The structural nature of the nano-graphene oxide was characterized by a variety of techniques including XRD, TEM, FT-IR and UV/Vis. The functional groups on its basal planes and edges of nano-graphene oxide play important role in catalytic activity. This nanocatalyst was found to be highly efficient in this reaction and products were obtained in good to excellent yields. The recovered nano-catalyst was successfully reused for several runs without significant loss in its catalytic activity. The structure, morphology and properties were characterized using X-ray diffraction (XRD) and Transmission Electron Microscope (TEM).

Keywords

Nano-Graphene Oxide, Oxidation, Aldehyde, Ketone, Catalyst

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1. Introduction

Graphene, one of the important research and application topics in recent years, has attracted the attention of many scientists, which found to have many important applications. Graphene is produced by reduction process of graphene oxide, which contains reactive oxygen function groups such as carboxylic, epoxides and alcohols with a carbon to oxygen ratio to be approximately three to one [1, 2]. Graphene oxide is different from graphite oxide by the fact that, it can be exfoliated into monolayers. Different techniques have been used to transfer graphite oxide to graphene oxide including thermal, mechanical and different chemical methods [3-8].

The chemical reactions targeted graphene oxide for different applications such as sensors [1, 2, 10], batteries [1], capacitors [12], conducting [13, 15] and biological applications [15-17]. On the other hand, finding new applications for graphene and graphene oxide is still under investigation. Graphene, the amazing two-dimensional carbon nanomaterial, has attracted extensive interest in recent years and emerged as the most intensively studied material [18]. In 2004, Geim and Nosovlov at Manchester University successfully isolated single layer graphene by the mechanical cleavage of graphite crystal [19]. This “thinnest” known material exhibits extraordinary electronic, chemical, mechanical, thermal and optical properties which bestowed

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graphene as a miracle material of the 21st Century. From applicative perspectives, graphene holds a great promise with the potential to be used as energy-storage materials, in nanoelectronics, in catalysis, biomedical, in polymer composites and many more [20-22]. Structurally, graphene is a one-atom-thick planar sheet of sp^2 bonded carbon atoms (Figure 1) that are densely packed in a honeycomb crystal lattice. The high versatility of properties and numerous projected applications have triggered the development of graphene synthesis using various methodologies and substrates. Several production techniques for mass production of graphene encompassing bottomup and top-down methods ranging from the mechanical exfoliation of high quality graphite to the direct growth on carbides or suitable metal substrates and from the chemical routes using graphene oxide have been developed [22] (Figure 1).

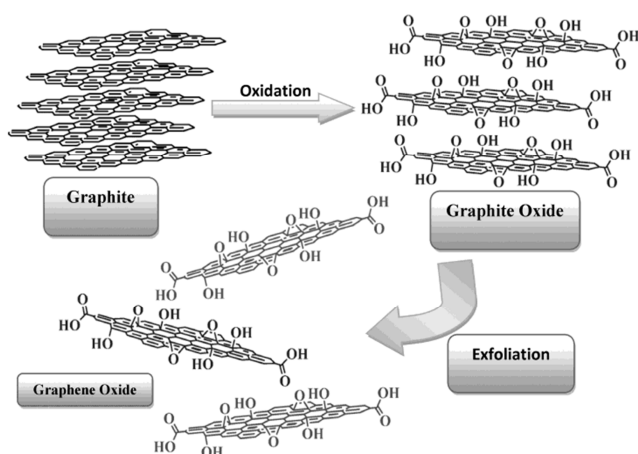


Figure 1. Prepare method of graphene oxide (GO).

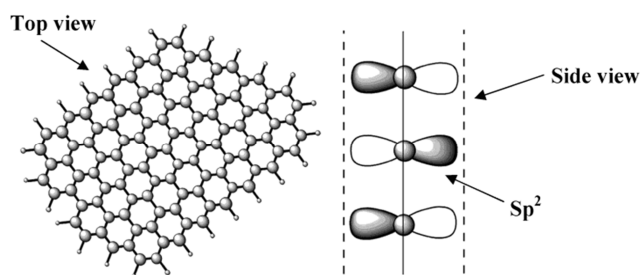


Figure 2. Structure of single layer graphene oxide.

Amongst, graphene derivatives i.e graphene oxide (GO) and reduced graphene oxide (RGO) obtained from chemical oxidation process contains substantial oxygenated functional groups that even after sufficient reduction, cannot be completely removed [23]. The resulting graphene oxide contains abundant oxygen functional groups on both the basal planes and edges (Figure 2) [24]. Similar to carbon nanotubes, these functional groups can offer a platform for various chemical reactions [25]. Hence, graphene offers a wide range of possibilities to synthesize graphene-based

functional materials with potential in numerous applications including catalysis. Recently, owing its surface decorated myriad oxygenated functions and conductivity with very high surface area, use of graphene materials either as metal-free catalysts or as supports for immobilizing active species for facilitating synthetic transformations is emerging as an area of great potential [26,27].

The first is to dope heterogeneous atoms onto the basal plane (form covalent bond directly with C atoms of graphene), mainly tuning the electronic structure and introducing defect sites; the second is to establish covalent bond between the functional group native to GO and the guest functional group. Various kinds of functional groups have been chemically anchored onto graphene, giving rise to a diversity of graphene based nanocomposites that were widely investigated in various applications. In this part, we will provide a comprehensive picture for this subject in term of how the covalent bonds are formed. One of the urgent issues for chemical industries in the twenty-first century is the search for 'clean' or 'green' technologies [28]. Two-phase catalysis represents one of the most important alternatives for the design, development, and implementation of green chemistry [29].

The oxidation of alcohols into aldehydes and ketones is a fundamental reaction in organic synthesis, and numerous oxidizing agents are available to influence this key reaction [30]. However, these reagents are usually toxic and their use induces hazardous problems [31]. In recent years, a two-dimensional single-layered nano-graphene oxide (NGO) has attracted a tremendous amount of attention because of its remarkable properties such as low cost, ease of synthesis, high stability to ambient conditions and novel layered structures [32-34]. NGO exhibits a hydrophilic nature owing to the wide range of oxygen carrying functional groups on its basal planes and edges [35-36]. These functional groups allow NGO to be noncovalently functionalized by DNA [37-39], carbon nanotubes [40] organic molecules [41], and by p -stacking interactions, hydrogen bonding interaction or Vander Waals forces. NGO is readily functionalized with various surfactants, polymeric materials, and nanoparticles in order to provide enormous potential for applications in materials science and engineering [42-43]. Recently, NGO catalyzed reactions such as oxidation of sulfides and thiols, oxidation of benzylic position, and benzyl alcohol, ring opening of epoxides, aza-Michael addition reaction, synthesis of aldehydes or ketones, Friedel-Crafts and addition of indoles to α,β -unsaturated ketones [44-50]. Oxidation of alcohols to related carboxylic acids is important and has been studied by many researchers. Ishii and coworkers reported oxidation of aldehydes to carboxylic acids catalyzed by transition metal-substituted heteropolyacids [46].

2. Experimental

2.1. Materials and Apparatus

Graphite powder was obtained from Aldrich Company. All chemicals were purchased from Merck Company and used without purification. Hydrogen peroxide was obtained from Merck Company and was standardized by well-known methods (Hydrogen Peroxide Product Information Manual, Analytical Procedure). The resulting NGO was characterized by FT-IR, UV/Vis, TEM and XRD patterns. The infrared spectra (IR) were recorded on a Perkin-Elmer FT-1710 spectrophotometer. ^1H and ^{13}C NMR (Bruker at 400 and 100 MHz using TMS as internal standard) spectra were recorded in CDCl_3 . UV-Vis spectra were recorded on Perkin-Elmer Lambda 35 spectrophotometer. Powder XRD were recorded on a Bruker Discover 8 X-ray diffractometer. The catalytic reaction products were analyzed by gas chromatography on an Varian 3400 CX chromatograph with FID detector, equipped with a polydimethylsiloxane column 30 m, 0.25 mm id and film thickness of 0.2 μm , working between 50 and 200 $^\circ\text{C}$ with a heating rate of 10 $^\circ\text{C min}^{-1}$. The products were isolated by distillation (water was the sole by-product observed) or extracted with organic solvents. The conversion (based on the starting alcohol) and selectivity into carbonyl compound were determined by gas chromatography. The isolated products were characterized by GC-MS, IR, with FID detector and GLC analysis was performed on a Pu 4500 gas chromatograph with FID detector.

2.2. Preparation of Nano-Graphene Oxide (NGO)

Graphene Oxide (GO) was synthesized by the modified Hummer's method [51].

In generally, to a reaction flask were added graphite powder (3 g), NaNO_3 (1.5 g) and concentrated H_2SO_4 (70 mL), and then cooled on an ice bath. An amount of 9 g of KMnO_4 was slowly added over 1 h and stirring for 2 h in an ice-water bath, and the temperature was kept below 20 $^\circ\text{C}$. The mixture was then stirred at 35 ($\pm 3^\circ\text{C}$) for 30 min. The flask was then cooled to room temperature and deionized water (150 mL) was slowly added to the mixture, and the temperature was increased to 98 $^\circ\text{C}$. The resultant mixture (yellowish suspension) was further stirred for 2-3 h at 98 $^\circ\text{C}$. After 15 min, the mixture was further treated with 400 mL of deionized water and 30 mL of 5% H_2O_2 solution to remove residual permanganate ions. Then, the solution filtered and washed successively with 10% HCl aqueous solution completely until sulfate could not be detected with BaCl_2 . The resultant solid was recovered and washed with deionized water and ethanol and then dried in air at 40 $^\circ\text{C}$. The brown powder of NGO (4.2 g) was characterized by XRD, TEM,

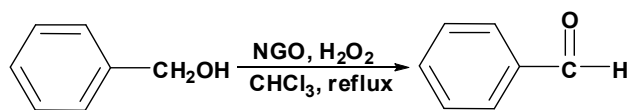
FT-IR and UV/Vis. Aqueous colloids of single layer graphene oxide nanosheets were produced by exfoliation of graphite oxide dispersed in deionized water with ultrasonication [52].

2.3. General Procedure for Oxidation Alcohols

All reaction mixtures were refluxed in a round-bottom flask equipped with magnetic stirrer, reflux condenser, and thermometer. In all cases, a mixture of alcohol (5 mL), NGO catalyst (10 mg) and solvent (Choloroform 10 mL) were placed and 30% hydrogen peroxide (0.08 mol) was added. The mixture was stirred under reflux conditions for 6 h. The progress of the reaction was monitored by thin layer chromatography. After completion, the product was extracted with ethyl acetate (3×15 mL). The reaction mixture was stirred and refluxed for 8 h under reflux conditions. To the final mixture, a 5% aqueous solution of NaHCO_3 was added and the mixture was filtered. The organic layer was dried and concentrated under reduced pressure to obtain the crude product. The product was recrystallized from ethanol to afford pure product and characterized by ^1H and ^{13}C NMR, IR and Mass spectroscopy analysis. All of the physical and spectroscopic data were compared with those reported in the literature.

3. Result and Discussion

We used nano-graphene oxide (NGO) catalyst for these reactions (Scheme 1, Table 1). The catalytic activity of other various catalysts such as $\text{Co}_2(\text{CO})_8$, ZnO , $\text{Bi}(\text{OTf})_3$, $\text{Yb}(\text{OTf})_3$, $\text{Zn}(\text{HSO}_4)_2$, $\text{Fe}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$, CuO , KMnO_4 and I_2 was less than NGO. The effects of various parameters such as solvent type, temperature, catalyst type, and time of reaction were studied.



Scheme 1. Oxidation of alcohols in presence of H_2O_2 (30%), nano-graphene oxide (NGO) catalyst under reflux conditions.

The yields of the oxidation of alcohols into aldehydes and ketones with NGO catalyst are given in Table 1.

3.1. Effect of the Catalyst Type

Initially, we compared the catalytic performance of I_2 , $\text{Yb}(\text{OTf})_3$, $\text{Bi}(\text{OTf})_3$, ZnO , $\text{Fe}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$, $\text{Zn}(\text{HSO}_4)_2$, KMnO_4 , CuO , $\text{Co}_2(\text{CO})_8$ and nano-graphene oxide (NGO) catalyst, in the oxidation of alcohols. The results are shown in Table 2, eq. (1).

The yield of product decreases in the following order:

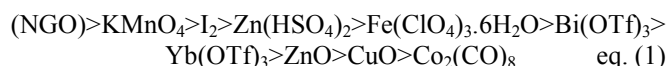


Table 1. Oxidation of alcohols using nano-graphene oxide (NGO) catalyst in presence 30% hydrogen peroxide as oxidant agent and chloroform as solvent in reflux conditions.

Entry	Alcohol	Time (h)	^a Yield (%)
1	<chem>C2H5OH</chem>	6	97
2	<chem>CCCCCO</chem>	6	85
3	<chem>CCCCO</chem>	6	87
4	<chem>CCCCCO</chem>	6.5	82
5	<chem>C1CCCCC1O</chem>	7	89
6	<chem>c1ccc(CO)cc1</chem>	7	90
7	<chem>COc1ccc(CO)cc1</chem>	7.5	86
8	<chem>Nc1ccc(CO)cc1</chem>	8	85
9	<chem>Oc1ccc(O)cc1</chem>	8	89
10	<chem>COc1ccc(CO)cc1</chem>	9	88
11	<chem>Brc1ccc(CO)cc1</chem>	8	80
12	<chem>Clc1ccc(CO)cc1</chem>	8.5	84
13	<chem>O=[N+]([O-])c1ccc(CO)cc1</chem>	9	85
14	<chem>COc1ccc(O)cc1</chem>	9	86.5
15	<chem>COc1ccc(O)cc1</chem>	7	86
16	<chem>Cc1ccc(CO)cc1</chem>	8.5	74
17	<chem>c1ccc(C=CCO)cc1</chem>	6	88
18	<chem>c1ccc(CCCO)cc1</chem>	8	76

^aIsolated yield.

As could be seen, nano-graphene oxide (NGO) catalyst is more effective than the other catalysts, and in the presence of this catalyst the highest yields of products are obtained. The results (Table 2) show that nano-graphene oxide (NGO) catalyst is better with respect to yield and to reaction. In all cases, the nano-graphene oxide catalyst shows higher activity compared with other catalysts, $\text{Co}_2(\text{CO})_8$, ZnO , $\text{Bi}(\text{OTf})_3$, $\text{Yb}(\text{OTf})_3$, $\text{Zn}(\text{HSO}_4)_2$, $\text{Co}_2(\text{CO})_8$, CuO , KMnO_4 and I_2 (Table

2). Nano-graphene oxide (NGO) catalyst shows a higher selectivity, and this catalyst is an efficient solid acid catalyst for oxidation of alcohols.

Table 2. The effectiveness of various catalysts in oxidation of ethanol (Table 1, entry 1) in CHCl_3 as solvent.

Entry	Catalyst	Time (h)	^a Yield (%)
1	NGO	6	97
2	ZnO	8	61
3	$\text{Yb}(\text{OTf})_3$	10	68
4	$\text{Bi}(\text{OTf})_3$	12	70
5	I_2	8	79
6	$\text{Co}_2(\text{CO})_8$	11	56
7	KMnO_4	9	88
8	$\text{Zn}(\text{HSO}_4)_2$	9	76
9	$\text{Fe}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$	9	74
10	CuO	10	59

^aIsolated yield.

During the oxidation process, hydroxyl, carbonyl, epoxy, and proxy groups were bonded to the edges of basal planes of the graphite structure. Figure. 1 shows the model described by Lerf-Klinowski [53], graphene oxide (GO) with the omission of minor groups (carboxyl, carbonyl, ester, etc.) on the periphery of the carbon plane of the graphitic platelets of NGO. The high magnification TEM image of NGO (Fig. 5) shows large sheets to be situated on the top of the grid and have the tendency to scroll and wrinkle, illustrating the flake-like shapes of graphene [54], also, The efficiency of NGO was compared with several catalysts [55-61].

Table 3. The effectiveness of various solvents in oxidation of ethanol (Table 1, entry 1) using nano-graphene oxide (NGO) catalyst under reflux conditions.

Entry	Solvent	Time (h)	^a Yield (%)
1	CHCl_3	6	97
2	CCl_4	6	78
3	CH_2Cl_2	6	76
4	DMF	6	67
5	Pyridine	6	69
6	DMSO	6	65
7	THF	6	77
8	Free	6	45

^aIsolated yield.

3.2. Effect of the Solvent Type

Chloroform 1, 2-dichloromethan, carbon tetrachloride, acetonitrile, dimethylformamid, 2-dimethyl tetrahydrofuran and dimethylsulfoxide were examined as solvents. Among these solvents, chloroform gave good result. The effect of these solvents on the oxidation of alcohols is shown in Table 3 and it shows the results for the other solvents (after 6 h).

3.3. Effect of Temperature

We also observed that this oxidation depends on temperature. In all solvents in the presence of various catalysts, the yields of the products were examined at reflux temperature, and

lower temperatures. The results showed that the reaction temperature is an effective factor on the yield of oxidation under the optimized conditions. Thus, the highest yields of products were obtained at reflux temperature. The oxidation of alcohols at lower temperatures is relatively slow reactions and the lower yields of the reaction were obtained when the temperature was further decreased. This result was expected, since increasing the temperature is apparently favorable for the acceleration of the forward reaction. When the experiment was conducted at reflux temperature, a good and convenient amount of the corresponding product was generated (Table 4, entries 1, 3).

Table 4. The effectiveness of temperature in the oxidation of ethanol (Table 1, entry 1) in CHCl_3 as solvent.

Entry	Catalyst	Temp ($^{\circ}\text{C}$)	Time (h)	^a Yield (%)
1	NGO	Reflux	6	97
2	NGO	25	8	70
3	NGO	35	9	87
4	ZnO	Reflux	8	61
5	ZnO	25	9	42
6	ZnO	35	9	53
7	$\text{Yb}(\text{OTf})_3$	Reflux	10	68
8	$\text{Yb}(\text{OTf})_3$	25	11	
9	$\text{Yb}(\text{OTf})_3$	35	11	59
10	$\text{Bi}(\text{OTf})_3$	Reflux	12	70
11	$\text{Bi}(\text{OTf})_3$	25	13	50
12	$\text{Bi}(\text{OTf})_3$	35	14	65
13	HCl	Reflux	8	79
14	HCl	25	9	54
15	HCl	35	9	72
16	$\text{Co}_2(\text{CO})_8$	Reflux	11	56
17	$\text{Co}_2(\text{CO})_8$	25	12	39
18	$\text{Co}_2(\text{CO})_8$	35	12	51
19	HNO_3	Reflux	9	88
20	HNO_3	25	9	71
21	HNO_3	35	10	82

^aIsolated yield.

3.4. Characterization of Nano-Graphene Oxide (NGO)

FT-IR spectrums of NGO are shown in Figure 3. An intense and broad peak appeared at around 3447 cm^{-1} , assigned to the stretching mode of an O-H bond, reveals the abundance of hydroxyl groups in NGO. The strong band at 2365 cm^{-1} ,

1750 cm^{-1} and 1630 cm^{-1} revealed the presence of (O-C=O), (C=O) and (OH bending) functional groups in NGO and the bands at 1292 cm^{-1} and 1100 cm^{-1} are attributed to the presence of (C-OH) and (C-O) (epoxy) groups. The UV-Vis of graphene oxide presented: UV-Vis (λ_{max}) (H_2O) = 235 nm, (DMF) = 269 nm (Figure 4).

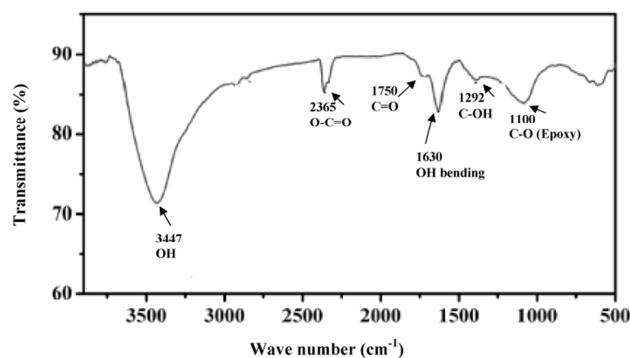


Figure 3. IR spectra of nano-graphene oxide (NGO), (The wet graphite oxide was dewatered by vacuum drying ($50\text{ }^{\circ}\text{C}$)).

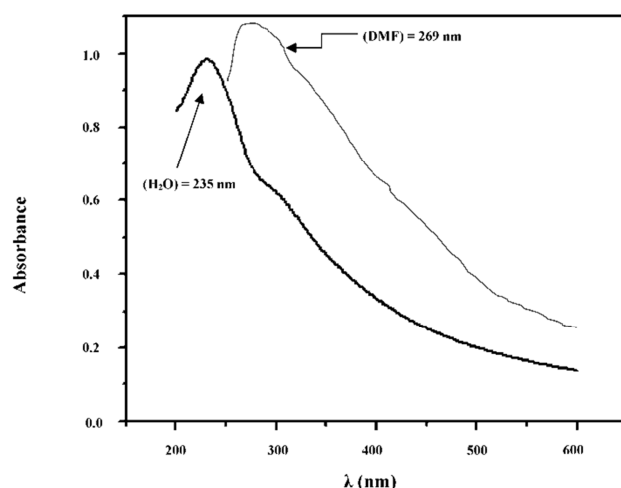


Figure 4. UV-Vis spectra of nano-graphene oxide (NGO), (UV-Vis (λ_{max}) (H_2O) = 230 nm, (DMF) = 269 nm).

To synthesize oxidized graphene, a modified Hammers method [55,56] using multiwalled carbon nanotubes (MCNTs) with a bulk density of 25 to 30 g/dm^3 , purified of catalyst impurities by treatment with a hydrofluoric acid solution, was employed. The outside diameter of nanotubes was approximately 10 to 30 nm, and the specific surface area was $126\text{ m}^2/\text{g}$ (determined by the BET method). Figure 5. shows the TEM images of prepared graphene, It was shown that a wrinkled paper like structure appeared in low magnification. Scanning Electron Microscope (SEM) image of nano-graphene oxide (NGO) was shown in Figure 6.

To identify the successful steps of the synthesis of nanocomposite, x-ray diffraction measurements have been done during different preparation steps. Figure 7. shows the XRD pattern corresponding to graphene oxide materials,

which comes as successful oxidation process of graphite. The characteristic peak at 2θ of $11.5\text{--}12^\circ$ indicates the effective oxidation of graphite and the formation of graphene oxide.

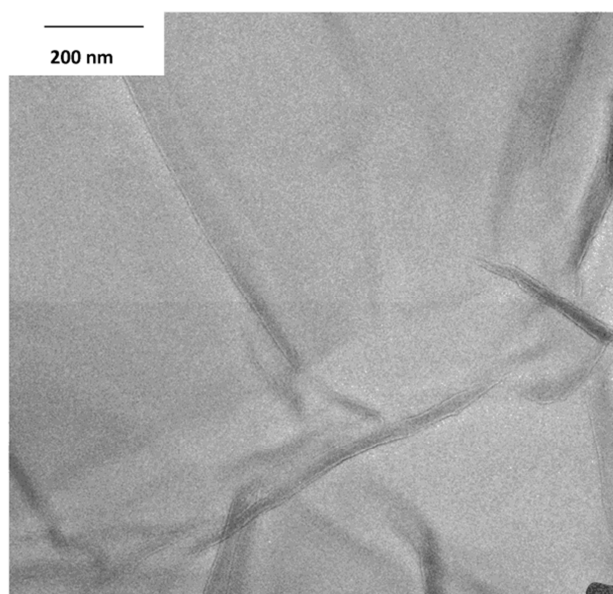


Figure 5. Transmission Electron Microscope (TEM) image of nano-graphene oxide (NGO).

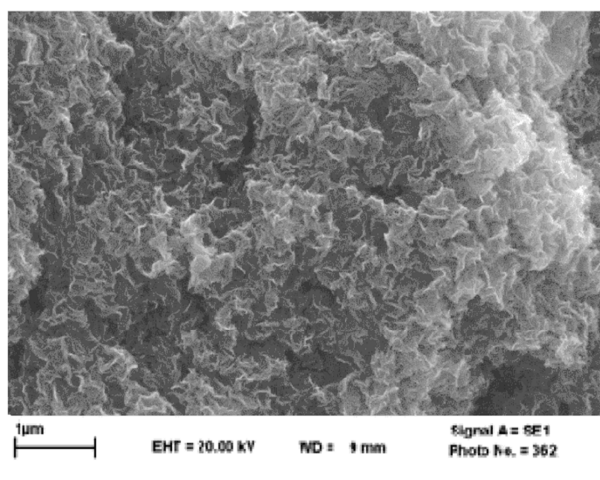


Figure 6. Scanning Electron Microscope (SEM) image of nano-graphene oxide (NGO).

Herein is reported a relatively simple and useful method for the oxidation of alcohols in good yield using nano-graphene oxide (NGO) catalyst in chloroform as solvent. In the results of various solvents, chloroform was good solvent and reflux temperature was suitable conditions for oxidation of alcohols. Nano-graphene oxide (NGO) is good catalyst and a safe and recoverable heterogeneous system for promoting this oxidation. The advantages of this catalytic system is mild reaction conditions, short reaction times, high product yields, easy preparation of the catalysts, non-toxicity of the catalysts, stable, simple and clean work-up of the desired products.

3.5. Catalyst Recovery

In our experiments, the reusability of nano-graphene oxide (NGO) catalyst were examined by repetitive use of the catalyst. The wet catalyst was recycled and no appreciable change in activity was noticed after four cycles (Table 5).

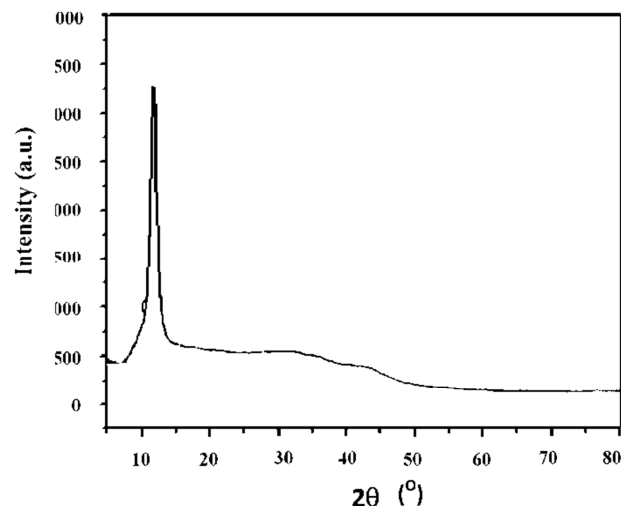


Figure 7. X-ray diffraction (XRD) spectra of nano-graphene oxide (NGO).

Table 5. Oxidation of ethanol (Table 1, entry 1) using recovered and recycled nano-graphene oxide (NGO) catalyst under reflux conditions for 6 h.

Run	^a Yield (%)
1	97
2	95
3	94
4	94

^aIsolated yield.

4. Conclusion

In summary, The advantages of the present procedure are simplicity of operation, recyclability of the catalyst, easy work up, mild reaction condition, and economic viability, work-up and good yields of products. We have described an efficient method for oxidation of alcohols catalyzed by NGO under chloroform solvent and reflux conditions. Also, NGO is easily synthesized, green, ecofriendly, environment friendly, cheap, air and moisture stable, heterogenic and could be easily recovered after the reaction and reused for additional runs. It is noteworthy to mention that the catalyst is recyclable and could be reused without significant loss of the catalytic activity. It could be recovered by filtration, washing with chloroform, and subjected to a second or even another reaction. Also, in this reaction H_2O_2 is oxidant agent, and its product is water in the oxidation reaction final. This oxidant agent is environmentally friendly. Generally, This is a green chemistry method for the oxidation of alcohols and its similar compounds.

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