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Mn (III) salen complex supported on graphene oxide nanosheets as a highly selective and recoverable catalyst for the oxidation of sulfides

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Abstract

In this study, Mn (III) salen complex was synthesized and immobilized onto the graphene oxide, which is modified by 3-chloropropyltrimethoxy silane. Heterogeneous catalyst was characterized by X-ray diffraction, transmission electron microscopy, thermogravimetric analysis, fourier transform infrared spectra, nitrogen adsorption−desorption isotherm and atomic absorption spectroscopy. The catalytic activity of heterogeneous Mn (III) salen complex and comparison with its homogeneous analogue was studied for green oxidation of sulfide derivatives using aqueous 30% H_2O_2 as an oxidant in water media. The results showed that heterogeneous catalyst was highly efficient in this reaction and corresponding products were obtained in good to excellent yields. The advantages of this catalyst include short reaction times, no side reactions, easy and simple work up, mild reaction conditions and excellent selectivity. The heterogeneous nanocatalyst was reused for several runs without significant loss in activity and selectivity.

Keywords: Mn (III) salen complex; sulfides; oxidation; graphene oxide.

Introduction

The partial oxidation of sulfide to the corresponding sulfoxide is a useful and fundamental organic reaction, because sulfoxides are important building blocks for the synthesis of valuable intermediates for the synthesis of various useful compounds, including antique, antibacterial, antifungal, and antihypertensive agents [1]. From economic and environmental viewpoints, developing novel, efficient and inexpensive catalytic system for the oxidation of sulfides under mild conditions is still an important goal in chemistry. Metal Schiff-base complexes both in homogeneous and heterogeneous form have been extensively studied as a powerful and extremely versatile synthetic tool to afford selectively oxidized products [2–7]. These types of complexes have been used as catalysts in reactions such as the oxidation of alcohols [8-10], olefins [11], enantioselective trimethylsilyl cyanation of carbonyl compounds [12], enantioselective epoxidation of olefins [13], asymmetric hetero-Diels–Alder reactions [14], enantioselective ring opening of meso-aziridines [15] and enantioselective cyclopropanation of olefins [16]. Due to easy preparation and handling, low cost and high activity, the use of heterogeneous Mn

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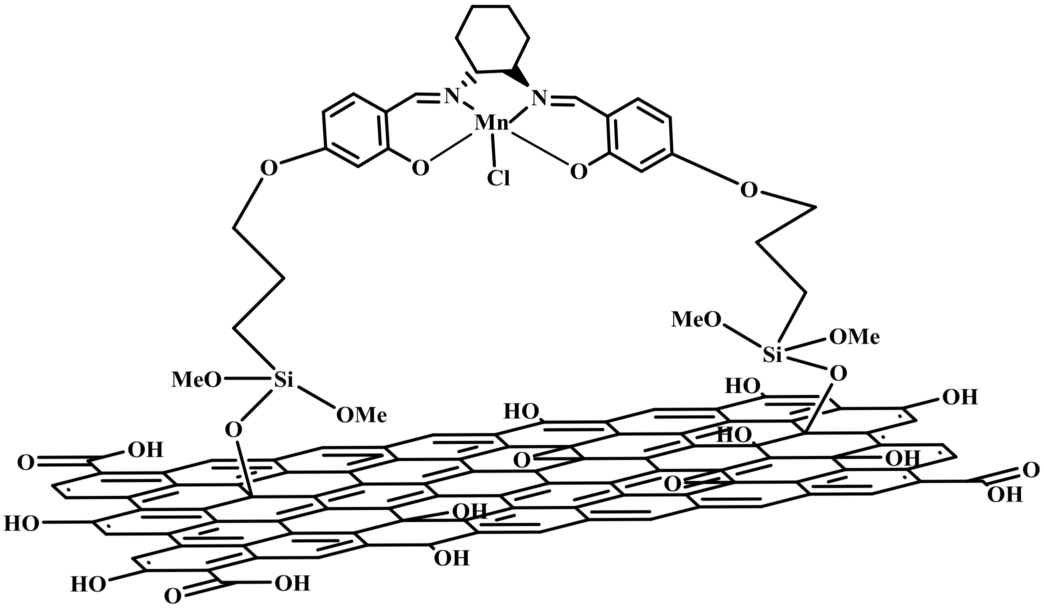
(III) salen complexes as oxidative catalysts is very attractive [17]. Recently, immobilization of Mn (III) salen complexes onto insoluble solid supports such as mesoporous materials, polymer, zeolites, clays, organic polymer-inorganic hybrid materials, SBA-15, MCM-41 and activated silica [18-27] has attracted great attention due to the some of the advantages such as easy separation from the reaction mixture and simple recycling of heterogeneous catalysts in the reaction system [28-31].

Graphene oxide nanosheets (GONs) with unique nanostructure (monolayer) and hydrophilic nature are a superior candidate for immobilization of Mn (III) salen complex. The functional groups (hydroxyl, carbonyl, epoxy and proxy groups) of GONs allow to be readily functionalized with various polymeric materials, surfactants and nanoparticles in order to provide enormous potential for applications in materials science and engineering. In addition, immobilization of transition metal nanoparticles on GONs nanosheets produced efficient catalysts [32-36]. Now, in continuation of our interest in exploring the catalytic properties of our synthesized Mn (III) salen complex, immobilized onto the modified graphene oxide (MnGONs) and the detail of synthesis and characterization of catalyst has been reported in our earlier publication [37], we described a very mild, efficient and selective oxidation of sulfide to sulfoxide with H_2O_2 using reusable heterogeneous Mn (III) salen complex in aqueous media (Scheme 1).



Scheme 1. The structure of heterogeneous MnGONs catalyst

Experimental and methods

Materials

Dichloromethane (DCM), ethyl acetate (EtOAc), toluene, ethanol (EtOH), CH_3CN, $CHCl_3$, THF, t-BuOOH, H_2O_2 (30%), methyl phenyl sulfide, 2-chlorothioanisole, 4-methoxythioanisole, 4-nitrothioanisole, 4-methylthioanisole, 4-bromothioanisole, di-phenyl sulfide, di-buthylsulfide were purchased from Merck Company and used without purification. Graphite powder was obtained from Aldrich Company. The

FT-IR spectra were carried out using Bruker Vector-22 FTIR spectrometer (AVATR-370) in a KBr pellet. The XRD measurements were carried out on a Bruker D8-advanceX-ray diffractometer with Cu Ka radiation (k ¼ 1.5406 °A). The TEM measurements were obtained using Philips CM10 instrument. The surface area was carried out by N_2 adsorption using Quanta chrome (Chem. Bet-3000). TGA analysis was performed by heating the samples in an Argon flow at a rate of 100 mL min^{-1} using a Perkin-Elmer Diamond TG/DTA thermal analyzer with a heating rate of 10 ^{0}C min^{-1}. The Mn content of the catalysts was determined by Shimadzu AA-6300 Atomic absorption spectroscopy (AAS).

The Conversion, selectivity and yields of products were determined by Shimadzu GC-17A gas chromatograph (GC) equipped with a flame ionization detector with a capillary column (CBP-1, 30 m × 0.25 mm × 0.25 mm), using helium as a carrier gas.

Synthesis of heterogeneous Mn@GONs

Mn@GONs was synthesized according to the literature procedure [37]. Briefly, GONs was synthesized from graphite powder. To synthesized modified GONs, 1 g of GONs was dispersed in 70 mL of dry toluene for 20 min. 3 mL of 3-chloropropyltrimethoxysilane (diluted in 20 mL dry toluene) were added dropwise to the mixture and the resulting mixture was heated to reflux with continuously stirring for 24 h under nitrogen atmosphere. The mixture was then cooled; the black powdery sample (CPGONs) was filtered, washed with toluene and EtOH and dried at 70 ^{0}C under vacuum oven for 6 h. The synthesized Mn (III) complex was chemically immobilized to the modified GONs. Initially, 2 g of GONs was dispersed in 140 mL dry toluene for 20 min followed by the addition of 0.6 g of homogeneous Mn (III) complex. The resulting mixture was refluxed for 24 h under inert atmosphere. Then, the heterogeneous catalyst was washed with dry toluene, EtOH and extracted repeatedly on a Soxhlet extractor with methanol and dichloromethane until the washing becomes colorless. The solid was dried at 70 ^{0}C under vacuum for 6 h. The Mn@GONs was characterized by TEM, XRD, UV-Vis, AAS, FT-IR, TGA and nitrogen adsorption at room temperature [37].

General procedure for the oxidation of sulfides to sulfoxides

An appropriate amount of MnGONs as catalyst (0.015 g, 0.005 mmol based on Mn element) was dispersed for 30 min in water (3 mL). Then, methyl phenyl sulfide (1.0 mmol, 0.11 mL), toluene (40 µL, as the internal standard) and hydrogen peroxide (2.0 mmol 30%, 0.2 mL) were added to the mixture. The reaction mixture was stirred for 45 min at room temperature (Scheme 1). The progress of the reaction was monitored by TLC. After completion of the reaction, the heterogeneous catalyst was separated by centrifuging. The product was extracted with ethyl acetate, dried over anhydrous Na_2SO_4(1 g) and the conversion, selectivity and yield of the products were determined by GC analysis using toluene as internal standard. The heterogeneous catalyst was washed with EtOH, dried and used for the next runs.

Spectral data for selected products

Methyl phenyl sulfoxide (Table 4, Entry 1)

IR (neat) 3055, 2994, 2910, 1722, 1655, 1583, 1478, 1442, 1417, 1295, 1090, 1073, 1044, 957, 751, 691 cm^{-1}; ^{1}H NMR ($CDCl_3$, 250 MHz) d 2.78 (s, 3H), 7.52-7.51 (m, 3H), 7.69 ppm (dm, J= 8.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) d 43.2, 123.8, 129.5, 131.5, 145.9.

_p_-Methoxyphenyl methyl sulfoxide (Table 4, Entry 3)

IR (KBr) 2962, 2873, 1647, 1464, 1412, 1384, 1019 cm^{-1}; ^{1}H NMR ($CDCl_3$, 250 MHz) d 2.73 (s, 3H), 3.81 (s, 3H), 7.1 (d, J= 8.8 Hz, 2H), 7.50 (d, J= 8.7, 2H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) d 44.2, 55.3, 115.0, 125.7, 136.1, 162.1.

Methyl _p_-methylphenylsulfoxide (Table 4, Entry 4)

IR (KBr) 2991, 2920, 1655, 1592, 1452, 1418, 1293, 1092, 1039, 956, 816 cm^{-1}; ^{1}H NMR ($CDCl_3$, 250 MHz) d 2.40 (s, 3H), 2.74 (s, 3H), 7.30 (d, J= 8.4 Hz, 2H), 7.58 (d, J= 8.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 62.9 MHz) d 21.5, 44.1, 124.0, 127.0, 141.0, 142.4.

Results and discussion

Characterization of the heterogeneous catalyst

The heterogeneous Mn (III) complex and the intermediate steps were synthesized and characterized by XRD, FT-IR, TEM, TGA, AAS and nitrogen adsorption at room temperature.

The FT-IR spectrum of GONs (Figure1a) shows a stretching band at 3446 cm^{-1}, related to the O–H band, and reveals the appearance of hydroxyl groups in GONs. The bands at 1716, 1619, 1224 and 1059 cm^{-1}assigned the presence of C=O, C=C, C–OH and C–O (epoxy) functional groups in GONs. Grafting the 3-chloropropyltrimethylsilane to the GONs shows an obvious decrease in intensities of peaks such as 3446, 1728 and 1395 cm^{-1} which are related to the OH, C=O stretching vibration and O–H deformation peak, respectively (Figure 1b). Also, the bands at 2880 and 2920 cm^{-1} are corresponding to the aliphatic C-H bonds. A strong band at 1614 cm^{-1} of the ligand salen is assigned to stretching vibration of C=N group (Figure 1e). This band shifts to the lower position (30 cm^{-1}) in homogeneous Mn (III) salen complex demonstrating the coordination of Mn through C=N functional groups (Figure 1d). Finally, the new stretching vibration bands at 2930, 2880, 1580 and 1190 cm^{-1}prove the immobilization of homogeneous Mn (III) salen complex on the CPGONs (Figure 1c).

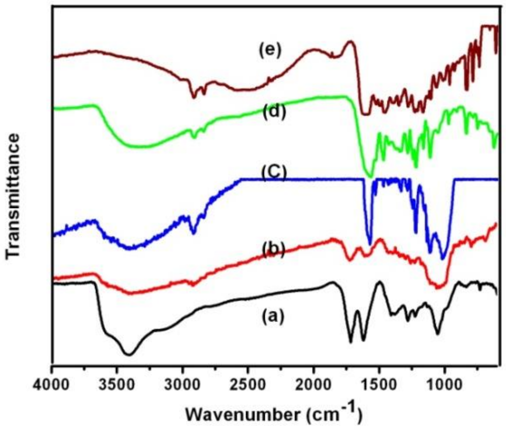


Figure 1. The FT-IR spectra of (a) GONs (b) CPGONs (c) heterogeneous catalyst (d) Mn (III) salen complex and (e) salen

The XRD patterns of GONs, CPGONs and heterogeneous catalyst were shown in Figure 2. Upon the oxidation of graphite to GONs, the basal reflection (002) peak (2θ = 26.6^0, d spacing = 0.335 nm) [27] shifts to the lower angle (2θ = 11.79^0, d spacing = 0.79 nm) (fig. 2 a) and the increase in d spacing is assigned to the formation of oxygen-containing functional groups and the intercalation of water molecules between the layers of the graphite. Decreasing in the intensity of 002 reflection peak of GONs as well as the appearance of a broad peak appeared at 2θ = 15–27◦ in the CPGONs indicated the immobilization of 3-chlorotrimetoxysilane on the GONs (Figure 2b). By grafting of the homogeneous Mn (III) msalen complex onto graphene oxide, the 002 reflections peak of GONs was completely disappeared (Figure 2c).

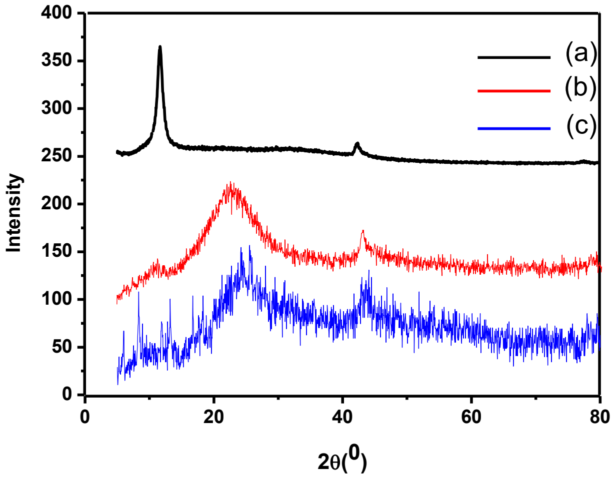


Figure 2. The XRD patterns of (a) GONs (b) CPGONs and (c) heterogeneous catalyst

Figure 3 shows the TGA curve of pure GONs, CPGONs and heterogeneous catalyst. At ca. 100 ^{0}C, a small mass loss (3 wt.%) was observed which is assigned to the loss of adsorbed water in the TGA curve of GONs (Figure 3a). A second degradation steps (165-250 ^{0}C) in GONs is due to the loss of epoxy functional groups, hydroxyl and remaining water molecules and the third degradation step (250–650 ^{0}C) depends on the pyrolysis of the remaining oxygen-containing groups as well as the burning of ring carbon. The TGA curve of CPGONs showed a weight loss over a wide range of temperature (170–600 ^{0}C) (Figure 3b). In addition, the TGA curve of heterogeneous catalyst showed three stepwise weight losses. The first step of weight loss (4.59% at 60-170 ^{0}C) is assigned to the loss of the surface or interstitial water. A second weight loss of 33% in the temperature range of 170-600 ^{0}C is corresponded to the decomposition of the appended organic groups. In comparison, a42.5% weight loss is experienced by pure GONs up to 600 ^{0}C. The loading of Mn (III) salen complex is calculated 0.45mmol g^{-1} based on the difference in the weight losses for GONs and heterogeneous catalyst. The contents of Mn are 0.34mmol g^{-1} estimated by AAS, respectively.

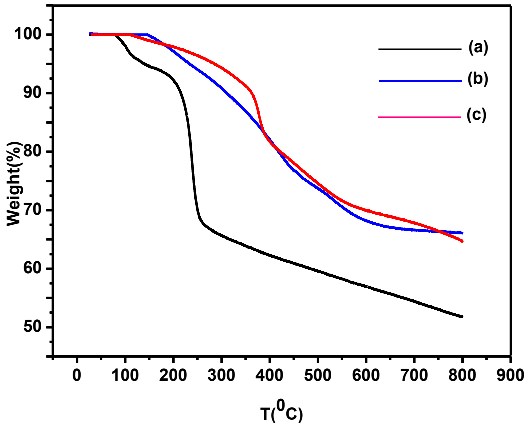


Figure 3. The TG curve of (a) GONs (b) CPGONs and (c) heterogeneous catalyst

A high magnification TEM image of GONs exhibits a completely amorphous and disordered structure (Figure 4). Figure 5 shows the nanoscopic features of the heterogeneous Mn (III) complex with amorphous nature.

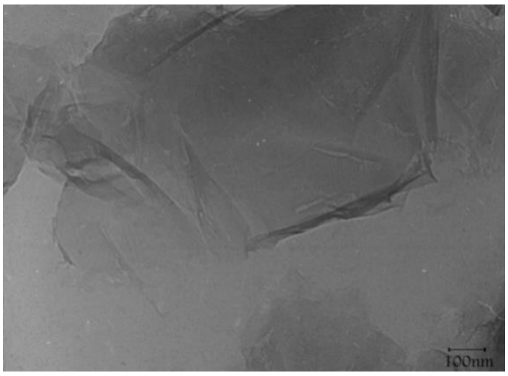


Figure 4. TEM image of GONs nanosheets

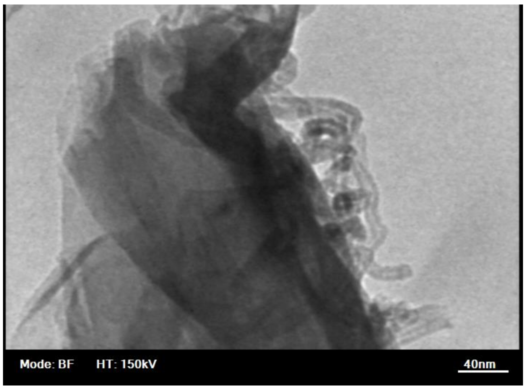
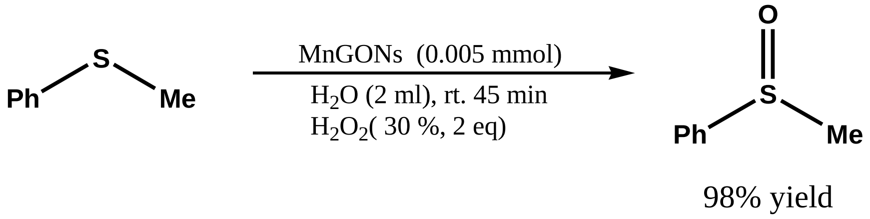


Figure 5. TEM image of heterogeneous catalyst

The BET specific surface area of the heterogeneous catalyst which is determined at room temperature by nitrogen physisorption was 18.6 m^2/g.

Catalytic activity studies

Man (III) selling complex was synthesized and supported onto the modified graphene oxide (MnGONs) according to the literature [37]. The catalytic activity of the freshly prepared MnGONs was initially evaluated in the oxidation of sulfides at ambient temperature. At first, the oxidation of methyl phenyl sulfide was selected as a model reaction in water with different oxidants (TBHP, UHP & H_2O_2) in the presence of MnGONs at room temperature (Scheme 2).



Scheme 2. Catalytic oxidation of sulfides at room temperature using hydrogen peroxide

It was observed that MnGONs was performed as a versatile nanocatalyst with H_2O_2 in the oxidation reaction of sulfide, furnishing the corresponding sulfoxide in 98% yield at 45 min. In addition, no considerable reaction progress was observed in the absence of MnGONs (Table 1, Entry 7).

We continued our investigation in the oxidation of methyl phenyl sulfide using different amounts of MnGONs and the results showed that the yield and selectivity of the reaction were affected crucially by the amount of catalyst (Table 1).

Table 1. The effect of different amounts of catalyst on oxidation of methyl phenyl sulfide catalyzed byMnGONs in water[a]

Entry	**MnGONs (mmol based on Mn element)**	**Yield[b]**	
		Sulfoxide %	**Sulfone %**
1	0.001	25	0
2	0.002	40	0
3	0.003	60	0
4	0.004	79	0
5	0.005	98	2
6	0.006	90	10
7	------	10	0

[a]Reaction conditions: methyl phenyl sulfide (1 mmol), H_2O_2 (2 mmol), water (2 mL), run under air at room temperature for 45 min.[b]GC yields based on the toluene as the internal standard.

As the results showed, methyl phenyl sulfoxide was achieved with excellent yield in the presence of 0.005 mmol MnGONs within 45 min using 2.0 eq. H_2O_2. Increasing the amount of catalyst leads to the over oxidation of sulfoxide to sulfone (Table 1, Entry 6). Also, in the absence of catalyst, only low conversion was observed in the presence of 2 eq. of H_2O_2 after prolonged reaction time. The effect of oxidant on the yield and selectivity of the product was also investigated. Various amounts of H_2O_2 affected on the conversion and selectivity of products and the best conversion and selectivity was achieved with 2 eq. H_2O_2 (Table 2, Entry 3). By increasing the molar ratio of hydrogen peroxide, decreasing in the selectivity of the products were achieved (Table 2, Entries 3-6).

Table 2. Effect of different amounts of H_2O_2 on the oxidation of thioanisole catalyzed by MnGONs in water[a]

Entry	**H_2O_2(mmol)**	**Yield[b]**	
		Sulfoxide %	**Sulfone %**
1	1	50	0
2	1.5	75	0
3	2	98	2
4	2.5	92	8
5	3	78	22
6	3.5	55	35

[a]Reaction conditions: methyl phenyl sulfide (1 mmol), MnGONs (0.005 mmol based on Mn element), water (2 mL), run under air at room temperature for 45 min.[b]GC yields based on the toluene as the internal standard.

The effect of different solvents ($CHCl_3$, DCM, THF, EtOAc, CH_3CN, EtOH, MeOH and water) was also investigated on the conversion and yield of the reaction and water gave the best result in the term of conversion and selectivity (Table 3, Entry 8). Furthermore, the reaction was studied in the presence of homogeneous Mn (III) complex and corresponding sulfoxide was achieved in 28 min with 97% yield (not listed).

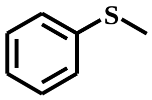
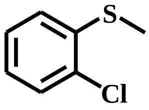
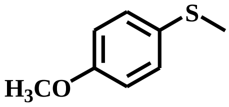
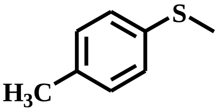
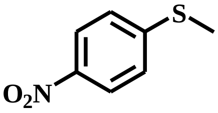
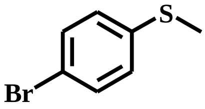
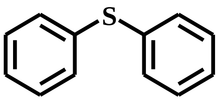
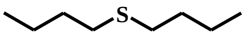
Table 3. Effect of different solvents on the oxidation of thioanisole catalyzed by MnGONs in water[a]

Entry	**Solvent**	**Yield[b]**	
		Sulfoxide %	**Sulfone %**
1	$CHCl_3$	40	0
2	DCM	43	0
3	THF	50	0
4	EtOAc	65	0
5	CH_3CN	68	0
6	EtOH	75	2
7	MeOH	81	2
8	water	98	2

[a]Reaction conditions: methyl phenyl sulfide (1 mmol), MnGONs (0.005 mmol based on Mnelement), Solvent (2 mL), run under air at room temperature for 45 min.
[b]GC yields based on the toluene as the internal standard.

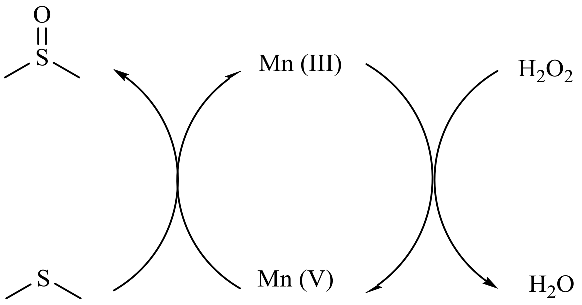
Under optimized conditions, the applicability of MnGONs was studied for the oxidation of different sulfides (Table 4). Different sulfides undergo selective oxidation to produce the corresponding sulfoxides with high conversion rates and excellent selectivity under mild conditions. The oxidation of sulfides to corresponding sulfoxides showed excellent efficiency in terms of conversion (95-99%), TOF (25333-26400) and selectivity (95-99%). Moreover, either electron-withdrawing or electron-releasing groups on the phenyl ring did not affect the yield of sulfoxide considerably (Table 4, Entries 3-6).

Table 4. Oxidation of different sulfides using H_2O_2 catalyzed by MnGONs[a]

Entry	**Substrate**	**Sulfoxide**[a]		
		Conv.[b] **(%)**	**Select.**[b]**%**	**TOF**[c] **(h^{-1})**
1		98	98	26133
2		95	95	25333
3		99	99	26400
4		99	99	26400
5		96	96	25600
6		97	97	25867
7		95	95	25333
8		96	96	25600

[a]Reaction conditions: sulfide (1 mmol), 30% H_2O_2 (2 equiv.), catalyst (0.005mmol based on Mn element), water (2 mL), 45 min., rt.[b]Conversion and selectivity were determined by GC, Conversion= [(initial moles of substrate - final moles of substrate)/initial moles of substrate] × 100, Selectivity to sulfoxide = [sulfoxide/(sulfoxide + sulfone)] × 100. [c]TOF = number of moles of substrate converted per mole of catalyst per hour.

A proposed mechanism for the oxidation of sulfides conducted in the presence of Mn(III) salen complex immobilized on graphene oxide with H_2O_2 as oxidant is presented by Scheme 3. At the first step, Mn (III) complex was reacted with H_2O_2 converted to Mn(V)complex (Mn-coordinated oxygen). In the presence of Mn (V) complex, sulfides were converted to sulfoxides. The coordination of oxygen to the main metal center may enhance the electrophilicity of Mn (V) complex.



Scheme 3. Proposed mechanism for the oxidation of sulfides

The efficiency of our method was also compared with some other published works for the oxidation of sulfides (Table 5). Despite of the advantages of these methods, some of them suffer from troubles, including the use of organic solvent (Entries 1, 2, 5, 6), long reaction time (Entries 1-4 and 6), as well as high reaction temperature (Entries 3 and 4).

Table 5. Oxidation of sulfides in the presence of different catalysts

Entry	**Catalyst**	**Condition**	**Solvent**	**Time (min)**	**Yield**	**References**
1	$CAN/NaBrO_3/SiO_2$	r.t.	CH_2Cl_2	150	96	[38]
2	Silica-based tungstate	r.t	$MeOH/CH_2Cl_2$	90	82	[39]
3	Fe_3O_4/ Cu (II) salen	60 ^{0}C	EtOH	180	83	[40]
4	Fe_2O_3/SBA-15	80 ^{0}C	Water	300	80	[41]
5	Co@SiO_2@Mn(III)SBC	45^{0}C	Ethyl acetate	40	92	[42]
6	Vanadium complex @ nano silica	r.t.	MeOH	120	97	[43]
7	MnGONs	r.t.	Water	45	97	This work

We also investigated the reusability of the recovered catalyst for new oxidation reactions. The MnGONs catalyst was separated in each run, washed with EtOH, dried and reused for a subsequent round of reaction with no significant loss of activity.

Table 6. The effect of recycling of catalyst on the oxidation of thioanisole[a]

Run	**Yield**	
	Sulfoxide %	**Sulfone %**
1	98	2
2	98	2
3	97	3
4	95	3
5	94	2
6	92	2

[a] Reaction conditions: methyl phenyl sulfide (1 mmol), MnGONs (0.005 mmol based on Mn element), water (2 mL), run under air at room temperature for 45 min.

In each run, no leaching of manganese was detected in the filtrates by AAS. As shown in Table 6, it is clear that the manganese worked well for oxidation of sulfide derivatives up to five cycles with no considerable decrease in reactivity and selectivity.

Conclusion

In conclusion, a versatile and efficient heterogeneous Mn (III) complex was synthesized by grafting of the Mn (III) salen complex onto GONs. The heterogeneous MnGONs were used in the oxidation of sulfide derivatives using H_2O_2 in aqueous media. The catalyst showed high catalytic activity in the oxidation of organic sulfides to the corresponding sulfoxides and 98 % yield was observed. The heterogeneous MnGONs catalyst exhibited comparable yields and selectivity than that of homogeneous counterpart for the oxidation of sulfide derivatives. This catalyst is an efficient nanocatalyst for green oxidation of various sulfides into sulfoxides at room temperature. In addition, short reaction times, no side reactions, easy and simple work-up, mild reaction conditions and excellent selectivity and yields are some advantages of this nanocatalyst. Furthermore, the catalyst is easily synthesized, cheap and reused without any noticeable loss of activity after several times.

Acknowledgments

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