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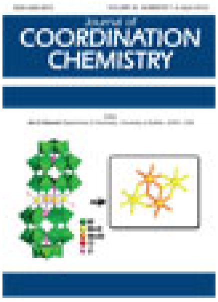

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Multi-wall carbon nanotube supported manganese(III)tetraphenylporphyrin: efficient catalysts for epoxidation of alkenes with $NaIO_4$ under various reaction conditions

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Multi-wall carbon nanotube supported manganese(III)tetraphenylporphyrin: efficient catalysts for epoxidation of alkenes with $NaIO_4$ under various reaction conditions

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Manganese(III)tetraphenylporphyrin supported on multi-wall carbon nanotubes (MWCNTs) were developed as efficient catalysts for epoxidation of alkenes with sodium periodate under mild conditions. The catalysts were prepared by axial ligation of manganese to 2-aminobenzimidazole and 2-aminothiazole preanchored to MWCNTs. The formation of these heterogenized catalysts was followed using elemental analysis, FT-IR spectroscopy, diffuse reflectance UV-Vis spectrophotometry, and scanning electron microscopy. The reactivity of these catalysts under both magnetic stirring and ultrasonic irradiation and also their reusability were investigated.

Keywords: Manganese(III)tetraphenylporphyrin; Alkene epoxidation; Sodium periodate; Multi-wall carbon nanotubes; Heterogeneous catalyst

1. Introduction

The cytochrome P-450 family of monooxygenase enzymes has attracted much attention [1–3]. P-450 enzymes catalyze a wide range of oxidation reactions *via* oxygen atom insertion. Metalloporphyrins, which mimic the action of cytochrome P-450 enzymes, can serve as catalysts for oxidation and particularly epoxidation of a large variety of substrates. Since the synthetic metalloporphyrins readily undergo decomposition through self-oxidation, several efforts have been made to immobilize them onto solid supports [4]. Homogeneous metalloporphyrins have been heterogenized using organic polymers [5–14], ion-exchange resins [15–17], zeolites [18–21], silica [22–25], MCM-41 [26], clay [25, 27], and carbon nanotubes (CNTs) [28].

Recently, metalloporphyrins and metallophthalocyanines have been applied as catalyst for oxygenation of hydrocarbons using iodine(III) or iodine(V) compounds as single oxygen donor [29–32].

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The use of ultrasound to improve the catalytic activity of metalloporphyrins has been reported [33–38]. The ability of ultrasound to create highly reactive surfaces and to increase mass transfer makes it a particularly elegant technique for activation of the catalyst.

Among all the supports multi-wall CNTs (MWCNTs) are considered to be most effective because of their unique structural, mechanical, thermal, optical, and electronic properties. Functionalization of nanotubes is extremely important because of coincidence of its extraordinary properties with catalytic ability of manganese porphyrin. The nanometric particle size and extremely large surface area of CNTs can easily overcome mass transfer limitations of supported catalysts [39–43].

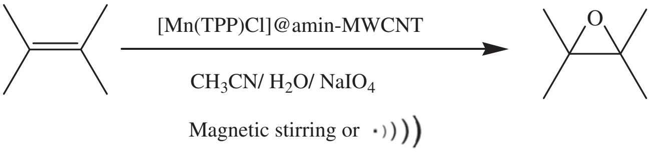
In this study, the preparation, characterization, and investigation of catalytic activity of [Mn(TPP)Cl] supported on MWCNTs modified with 2-aminobenzimidazole and 2-aminothiazole are reported. These new heterogenized catalysts were used as efficient catalysts for alkene epoxidation with sodium periodate (scheme 1).

2. Experimental

All materials were of commercial reagent grade and purchased from Merck and Fluka. All alkenes were passed through a column containing active alumina to remove peroxidic impurities. Tetraphenylporphyrin was prepared and metallated according to the literature [44, 45]. FT-IR spectra were obtained with potassium bromide pellets from 400 to 4000 cm^{-1} with a Perkin-Elmer version 10.00 spectrophotometer. Scanning electron micrographs (SEMs) of catalysts were taken on a Philips XL 30 SEM instrument. Gas chromatography (GC) experiments were performed with a Shimadzu GC-16A instrument using a 2 m column packed with silicon DC-200 or Carbowax 20 m. In the GC experiments, *n*-decane was used as an internal standard. Inductively coupled plasma (ICP) analyses were performed on an ICP-Spectrociros CCD instrument. The diffuse reflectance ultraviolet-visible spectrum was determined by solid UV-Vis on a Shimadzu model 265 spectrophotometer. MWCNTs (containing –COOH groups, purity 96%) were purchased from Shenzen NTP Factory (China). The products were identified by comparison of their retention times with known samples.

2.1. *Preparation of MWCNT supported manganese tetraphenylporphyrin*

2.1.1. Modification of MWCNT-COCl with amines. The carboxylic acid groups (MWCNT-COOH) in MWCNTs were converted to acid chloride (MWCNT-COCl) as reported [27]. In a 100 mL round-bottom flask equipped with a magnetic stirring (MS) bar, MWCNT-COCl (5 g) and Et_3N (10 mL) were added to a solution of 2-aminobenzimidazole (ABI) or 2-aminothiazole (AT) (2.0 g) in dimethylformamide



Scheme 1. Epoxidation of alkenes with $NaIO_4$ in the presence of [Mn(TPP)Cl@amin-MWCNT].

(DMF) (100 mL) and heated at 80°C for 72 h. Then, the reaction mixture was filtered, washed with Et_2O, and dried at 60°C. CHN analysis of ABI-MWCNT (%): C: 87.25, H: 1.86, N: 3.11, and of AT-MWCNT (%): C: 86.59, H: 1.84, N: 2.75.

2.2. *Preparation of the catalysts, [Mn(TPP)Cl@ABI-MWCNT] and [Mn(TPP)Cl@AT-MWCNT]*

To a solution of Mn(TPP)Cl [43, 44] (1.0 g) in toluene (100 mL), ABI-MWCNT or AT-MWCNT (5 g) was added and refluxed for 72 h. At the end of the reaction, the mixture was cooled and the catalysts were filtered and washed thoroughly with toluene, methanol, and ether, consecutively, and dried in vacuum for several hours.

2.3. *General procedure for alkene epoxidation with $NaIO_4$ catalyzed by [Mn(TPP)Cl@ABI-MWCNT] and Mn(TPP)Cl@AT-MWCNT]*

All of the reactions were carried out at room temperature under air in a 25 mL flask equipped with a magnetic stirrer bar. To a mixture of alkene (0.5 mmol), [Mn(TPP)Cl@ABI-MWCNT] (250 mg) or [Mn(TPP)Cl@AT-MWCNT] (300 mg) and CH_3CN (5 mL) was added a solution of $NaIO_4$ (1 mmol) in H_2O (5 mL). The progress of the reactions was monitored by GC. Since different alkenes have different reactivity toward oxidation, the reactions were continued until no further progress was observed. At the end of the reaction, the reaction mixture was diluted with Et_2O (20 mL) and filtered. The catalysts were thoroughly washed with Et_2O and the combined washings and filtrates were purified on a silica gel plate to obtain the pure product.

2.4. *General procedure for alkene epoxidation with $NaIO_4$ catalyzed by prepared catalysts under ultrasonic irradiation*

All reactions were carried out at room temperature in a 40 mL glass reactor. A UP 400S ultrasonic processor equipped with a 3 mm wide and 140 mm long probe, which was immersed directly into the reaction mixture, was used for sonication. The operating frequency was 24 kHz and the output power was adjustable manually at 0–400. The total volume of the solution was 10 mL. The temperature was adjusted at 25°C during sonication. A solution of $NaIO_4$ (1 mmol in 5 mL H_2O) was added to a mixture of alkene (0.5 mmol) in CH_3CN (5 mL). After addition of catalyst ([Mn(TPP)Cl@ABI-MWCNT] (250 mg) or [Mn(TPP)Cl@AT-MWCNT] (300 mg)), the mixture was sonicated. Progress of the reaction was followed by GC. At the end of reaction, the reaction mixture was diluted with Et_2O (20 mL) and filtered. The catalysts were thoroughly washed with Et_2O and the combined washings and filtrates were purified on a silica gel plate to obtain the pure product.

2.5. *Reusability of the catalysts*

The reusability of the catalysts was studied by multiple sequential epoxidation of cyclooctene as described above. At the end of each reaction, the catalysts were separated from the reaction mixture by simple filtration, washed thoroughly with Et_2O, and dried carefully before using in the next run.

3. Results and discussion

3.1. *Preparation and characterization of the catalysts, [Mn(TPP)Cl@ABI-MWCNT] and [Mn(TPP)Cl@AT-MWCNT]*

The specifications of MWCNTs containing carboxylic acid groups, MWCNT-COOH, which was used as support, are listed in table 1. Scheme 2 shows the preparation route for MWCNT-supported manganese porphyrin catalysts. The modified MWCNT, ABI-MWCNT, and AT-MWCNT were prepared by covalent attachment of 2-aminobenzimidazole and 2-aminothiazole to MWCNT-COCl *via* an amide linkage. Then, Mn(TPP)Cl was reacted with amine-MWCNT to obtain the catalysts. The [Mn(TPP)Cl@ABI-MWCNT] and [Mn(TPP)Cl@AT-MWCNT] catalysts were characterized by elemental analysis, SEM, FT-IR, and diffuse reflectance UV-Vis spectroscopic methods. The nitrogen content of the supports was determined by CHN analysis which showed values of 3.11% and 2.75% for ABI-MWCNT and AT-MWCNT. Based on these values, the amount of available nitrogen sites for coordination of [Mn(TPP)Cl] were 0.74 and 0.98 $mmol\,g^{-1}$ of the ABI-MWCNT and AT-MWCNT, respectively. The metal loading of the catalysts, measured by ICP, obtained 0.065 and 0.061 $mmol\,g^{-1}$ for [Mn(TPP)Cl@ABI-MWCNT] and [Mn(TPP)Cl@AT-MWCNT], respectively (table 2).

The most informative spectroscopic data, which confirmed the anchoring of the Mn(TPP)Cl on the functionalized MWCNT, were obtained by FT-IR spectra of ABI-MWCNT, AT-MWCNT, [Mn(TPP)Cl@ABI-MWCNT], and [Mn(TPP)Cl@AT-MWCNT] (Supplementary material and table 2). In the FT-IR spectrum of ABI-MWCNT, the C=O stretching band of the amide appeared at 1633 cm^{-1}. The C–N and N–H stretches of amides were observed at 1397 and 3445 cm^{-1}, respectively, confirming the anchoring of 2-aminobenzimidazole to acylated MWCNT. FT-IR spectrum of 2-aminothiazole modified MWCNT showed bands of the amide linkage at 1632, 1398, and 3449 cm^{-1}, respectively. The FT-IR spectra of the synthesized catalysts exhibited the characteristic absorptions of porphyrin units (table 2). These observations prove coordination of [Mn(TPP)Cl] to ABI-MWCNT and AT-MWCNT [46–48].

Because of the insolubility of supported catalysts, UV-Vis spectroscopy was employed in the diffuse reflectance mode which can be used for qualitative analysis of chemical compounds in solids. The diffuse reflectance of the MWCNT-bound porphyrin resembles the solution counterpart spectrum (figure 1), but with a slight shift. The difference between baselines is due to variation of analyzed sample's concentration. The presence of Soret and Q bands of manganese porphyrin in the supported catalysts clearly indicate the

Table 1. The specifications of MWCNT-COOH used in this study.

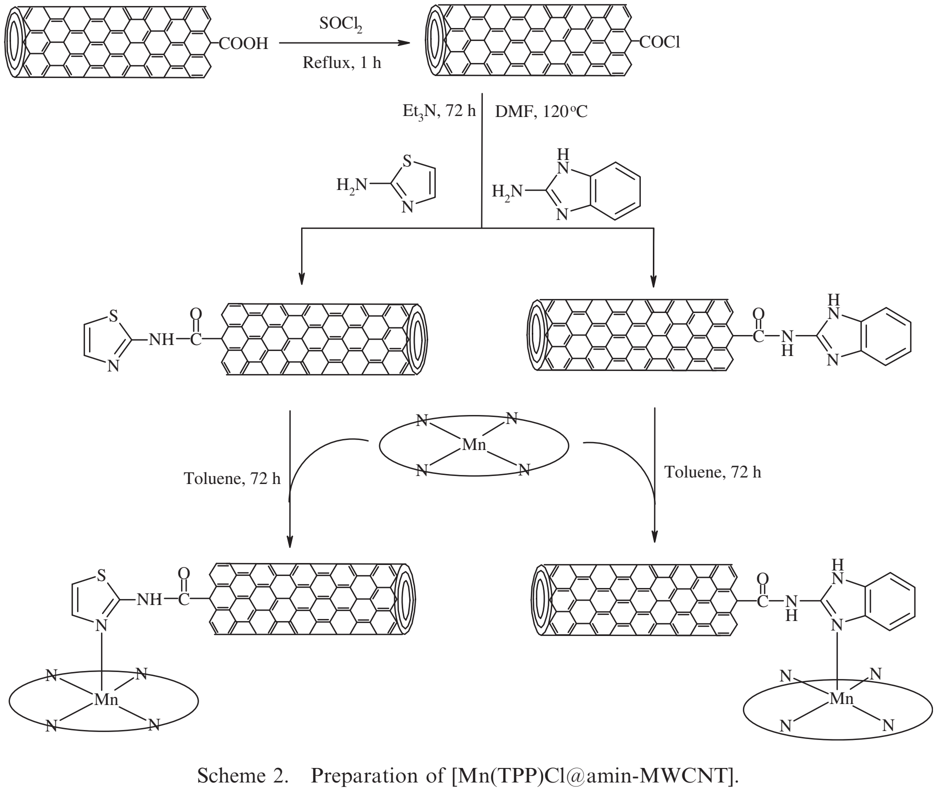
MWCNT-COOH				
Outside diameter	Inside diameter	Length	COOH content	Specific surface area
20–30 nm	5–10 nm	30 μm	1.5%	>110 $m^2\,g^{-1}$

presence of metalloporphyrin on the surface of the MWCNT (figure 2 and table 2). Since the MWCNT shows no absorption in its diffuse reflectance spectrum, [Mn(TPP)Cl] has been supported on the MWCNT. The SEM images of the [Mn(TPP)Cl@ABI-MWCNT] and [Mn(TPP)Cl@AT-MWCNT] prove the nanometric size of the catalysts and show that the nanotubes are aggregated and have retained their tubular nature (figure 3). The image exhibits the inner porosity of the MWCNTs. Due to their geometrical shape (empty cylinders with high surface area) they provide better catalytic performance.

3.2. *Catalytic experiments*

The prepared catalysts were used for epoxidation of olefins with sodium periodate at room temperature. Reaction parameters such as catalyst amount and kind of solvent were optimized in the epoxidation of cyclooctene. Different solvents were used to optimize reaction media. The results showed that higher catalytic activity was observed in 1 : 1 acetonitrile : water (table 3). The higher catalytic activity in acetonitrile/water mixture can be attributed to polarity of solvent and solubility of $NaIO_4$ in this medium. The oxidation activities were found to be extremely affected by solvent polarity. The environments of the porphyrins having the axial ligand are generally hydrophilic. On the other hand, all substrates are soluble in this solvent.

Different amounts of catalysts were used to optimize catalyst amount. The best results were obtained in the presence of 0.016 mmol (250 mg) of [Mn(TPP)Cl@ABI-MWCNT]



Scheme 2. Preparation of [Mn(TPP)Cl@amin-MWCNT].

Table 2. Characteristics of the prepared catalysts.

			FT-IR spectrum (cm^{-1})							UV-Vis peak (nm)	
						Porphyrin units					
Catalyst	N (%)	Mn content (mmol g^{-1})	C=O	C–N	N–H	C–H$_{\text{pyrrol}}$	C–H$_{\text{Ph}}$	C=N	C–H$_{\text{Ph}}$	Soret band	Q band
ABI-MWCNT	3.11	–	1633	1397	3445	–	–	–	–	–	–
AT-MWCNT	2.75	–	1632	1398	3449	–	–	–	–	–	–
[Mn(TPP)Cl]	–	–	–	–	–	752	1176	1240	2920	477.5	582, 617
[Mn(TPP)Cl@ABI-MWCNT]	3.15	0.065	1630	1397	3445	798	1120	1218	2921	465	569, 616
[Mn(TPP)Cl@AT-MWCNT]	2.81	0.061	1628	1397	3449	799	1134	1220	2923	470	580, 612

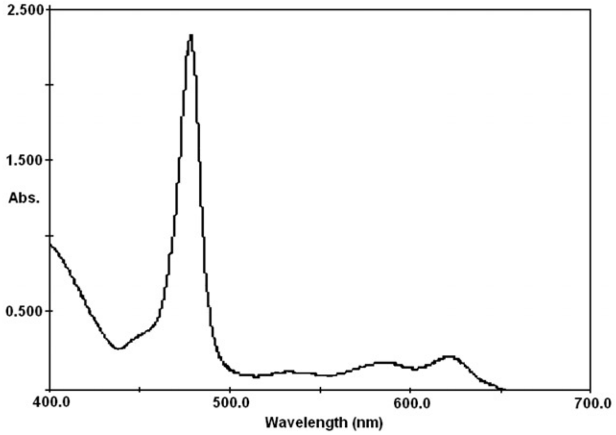


Figure 1. The UV-Vis spectrum of homogeneous [Mn(TPP)Cl].

and 0.018 mmol (300 mg) of [Mn(TPP)Cl@AT-MWCNT]. Control experiments in the absence of catalysts were also performed showing less than 5% epoxide (table 4).

3.3. *Epoxidation of alkenes with $NaIO_4$ catalyzed by [Mn(TPP)Cl@ABI-MWCNT] and [Mn(TPP)Cl@AT-MWCNT] under mechanical stirring*

The supported catalysts were used for epoxidation of olefins with $NaIO_4$ under optimized conditions. During the reaction, the catalysts are suspended in the solvent. This is due to the bundled agglomerates of MWCNT that aggregate slowly (this is due to the presence of functional groups and also the weak π–π interactions) and make the catalyst suspend in the reaction mixture for a long period of time. While, other heterogeneous catalysts were aggregated more rapidly in comparison with CNTs. These catalysts were efficient catalysts for epoxidation of alkenes with $NaIO_4$ (tables 5 and 6). In these heterogenized catalytic systems, cyclooctene was oxidized in 92–96% and cyclohexene was oxidized in high yield and selectivity to cyclohexene oxide and no by-product was observed. In the epoxidation of styrene and α-methylstyrene, styrene oxide and α-methylstyrene oxide were produced as major products with only small amounts of benzaldehyde and acetophenone produced, respectively. In the case of linear alkenes, such as 1-octene and 1-dodecene, the corresponding epoxides were obtained in high yields with 100% selectivity.

3.4. *Epoxidation of alkenes with $NaIO_4$ catalyzed by [Mn(TPP)Cl@ABI-MWCNT] and [Mn(TPP)Cl@AT-MWCNT] under ultrasonic irradiation*

The chemical effect of ultrasonic (US) irradiation is due to cavitation phenomena. The acoustic cavitation has some enormous effects such as local increasing in temperature and pressure, the propagation of oxidation catalysts, and the formation of intense liquid microflows [49]. The mechanical effects of ultrasound offer an opportunity to overcome problems associated with conventional solid/metal reactions such as break up of the surface structure allowing penetration of reactants and/or release of materials from the surface, degradation of large solid particles due to shear forces

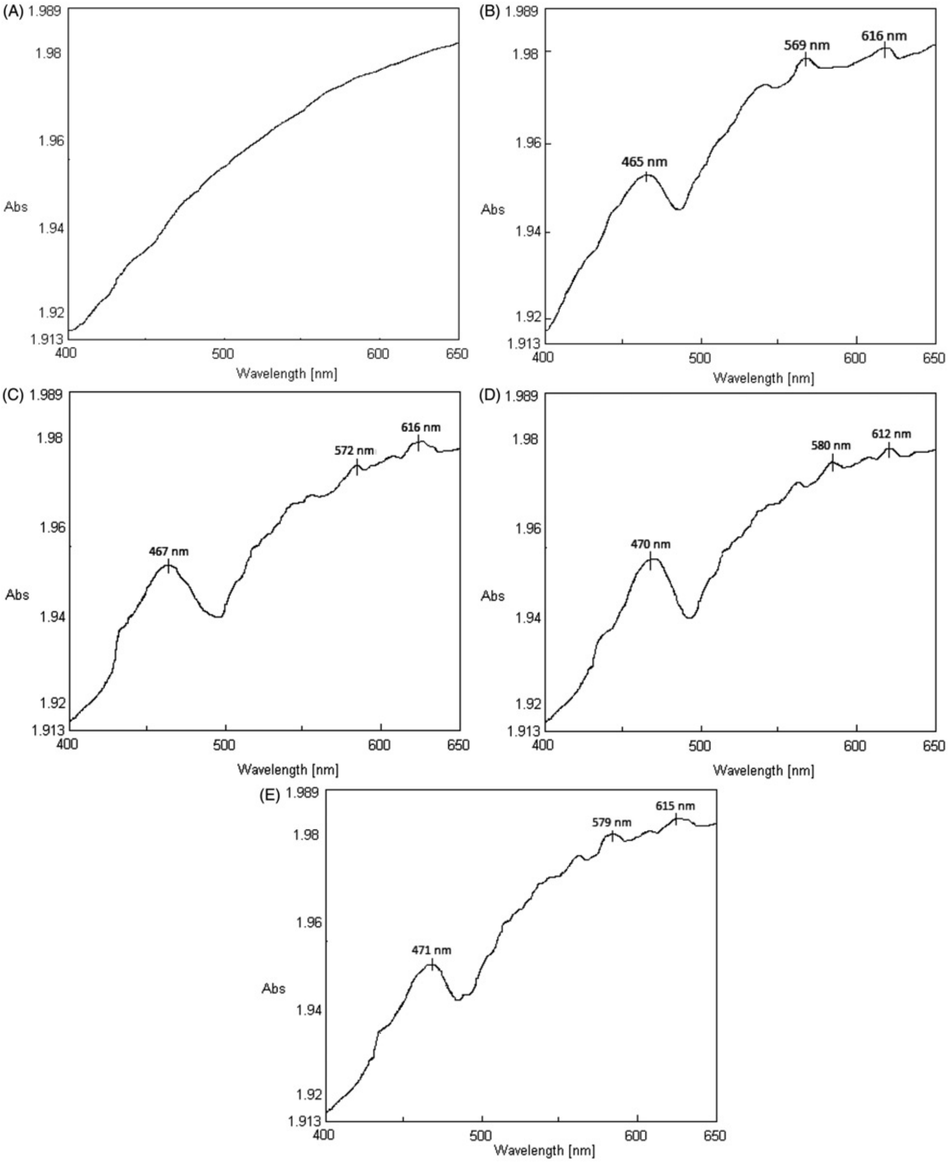


Figure 2. Diffuse reflectance UV-Vis spectra of: (A) MWCNT, (B) [Mn(TPP)Cl@ABI-MWCNT], (C) recovered [Mn(TPP)Cl@ABI-MWCNT], (D) [Mn(TPP)Cl@AT-MWCNT], and (E) recovered [Mn(TPP)Cl@AT-MWCNT].

induced by shock waves and microstreaming leads to reduction of particle size and increase of surface area and accelerated motion of suspended particles leads to better mass transfer [50].

Therefore, all reactions were exposed to US irradiation. The obtained results are summarized in tables 5 and 6. These results clearly show reduced reaction times and increased TOFs in the systems under US irradiation.

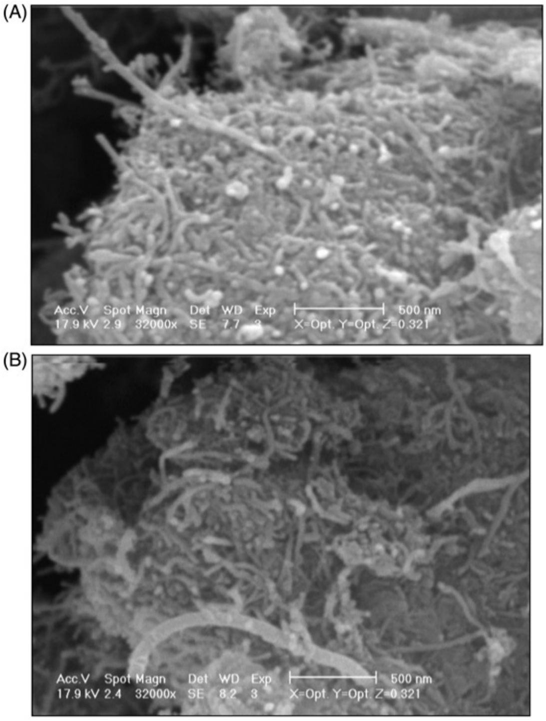


Figure 3. The SEM image of: (A) [Mn(TPP)Cl@ABI-MWCNT] and (B) [Mn(TPP)Cl@AT-MWCNT].

In alkene epoxidation with $NaIO_4$ in the presence of [Mn(TPP)Cl@ABI-MWCNT] and [Mn(TPP)Cl@AT-MWCNT] cyclooctene was epoxidized in 95% and 94% yield with 100% selectivity, but the reaction time decreased to 20 min. The yields in the case of linear alkenes increased since the reaction time was extremely decreased. To confirm break up of the agglomerates by US irradiation, a sample [Mn(TPP)Cl@ABI-MWCNT] catalyst was sonicated for 30 min and used in epoxidation of cyclooctene with $NaIO_4$ under agitation with MS. It was observed that the reaction times reduced from 150 min to 95 min. The blank experiment in the absence of catalysts under US irradiation showed that the US irradiation is much less efficient in oxidation reactions with sodium periodate. When these reactions were carried out under reflux conditions, the reaction times decreased. On the other hand, US waves may degrade the agglomeration of CNT in the solution, and also could lead the increase of local temperature on the particle surface which may accelerate the reaction speed.

Figure 4 shows a comparison between systems under US irradiation and under agitation with MS, which indicates the effect of US irradiation on the catalytic activity of [Mn(TPP)Cl@ABI-MWCNT] in the epoxidation of cyclooctene with $NaIO_4$.

3.5. *Catalyst reuse and stability*

The reusability of [Mn(TPP)@ABI-MWCNT] and [Mn(TPP)Cl@AT-MWCNT] was investigated in multiple sequential epoxidations of cyclooctene with $NaIO_4$. At the end

Table 3. The effect of solvent on epoxidation of cyclooctene catalyzed by [Mn(TPP)Cl@ABI-MWCNT] and [Mn(TPP)Cl@AT-MWCNT] at room temperature.[a]

		Epoxide yield (%)[b] after 2.5 h	Epoxide yield (%)[b] after 3 h
Row	Solvent	[Mn(TPP)Cl@ABI-MWCNT][c]	[Mn(TPP)Cl@AT-MWCNT][d]
1	CH_3CN/H_2O (1 : 1)	99	92
2	CH_3CN/H_2O (1 : 2)	86	84
3	CH_3CN/H_2O (2 : 1)	67	64
4	CH_3COCH_3/H_2O	28	49
5	CH_3OH/H_2O	35	56
6	CH_3CH_2OH/H_2O	55	43
7	CH_2Cl_2/H_2O	90	74
8	CCl_4/H_2O	15	12

[a] Reaction conditions: cyclooctene (0.5 mmol), $NaIO_4$ (1 mmol), solvent/H_2O (5 mL/5 mL).
[b] GC Yield based on the starting alkene.
[c] 250 mg (0.016 mmol) of the catalyst.
[d] 300 mg (0.018 mmol) of the catalyst.

Table 4. Optimization of the catalyst amount in epoxidation of cyclooctene with $NaIO_4$.[a]

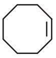
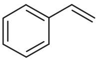
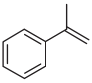
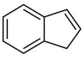
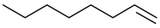
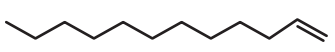
Catalyst amount (mg)	Epoxide yield (%)[b] after 2.5 h	Epoxide yield (%)[b] after 3 h
	[Mn(TPP)Cl@ABI-MWCNT]	[Mn(TPP)Cl@AT-MWCNT]
0	4	3
100	20	41
200	63	70
250	99	83
300	99	92
350	–	92

[a] Reaction conditions: cyclooctene (0.5 mmol), oxidant, catalyst, CH_3CN/H_2O (5 mL/5 mL).
[b] GC yield based on the starting alkene.

of each reaction, the catalysts were separated by simple filtration, washed with Et_2O, and dried carefully before using in the next run. After using catalysts five consecutive times, the epoxide yields were 88% and 80% for [Mn(TPP)Cl@ABI-MWCNT] and [Mn(TPP)Cl@AT-MWCNT], respectively (table 7). The filtrates were collected for determination of Mn leaching. The results showed that after two runs, no manganese was detected in the filtrates by atomic absorption spectrometry. The nature of the recovered catalyst was followed by FT-IR (Supplementary material) and DR UV-Vis (figure 2C and E). The results indicate that the catalysts show no change in their structure after reusing several times. The catalytic activity of the separated solution was also investigated. In this manner, after separation of each catalyst, fresh cyclooctene and oxidant were added to the solution. Continuation of the oxidation reaction under the same reaction conditions, as with catalyst, showed that the obtained results were the same as the result of blank experiments.

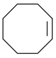
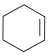
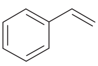
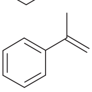
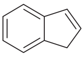
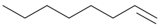
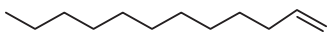
CNT is highly recommended for the catalyst's support because of its nanometric size, high surface area, chemical inertness, poor solubility and processability. Therefore, it is

Table 5. Epoxidation of alkenes with $NaIO_4$ catalyzed by [Mn(TPP)Cl@ABI-MWCNT] under agitation with MS and under US irradiation.[a]

	Conversion (%)[b]		Epoxide yield (%)[b]		Time (min)		TOF (h^{-1})	
Alkene	MS	US	MS	US	MS	US	MS	US
	99	98	96	98	150	15	12.38	120.98
	97	100	97	100	120	15	14.97	123.45
	80[c]	84[d]	66	65	210	20	7.05	78.56
	76[e]	80[e]	63	59	210	20	6.70	74.82
	62	67	62	67	210	25	5.38	49.71
	61	63	61	63	240	30	4.71	38.89
	52	54	52	54	240	30	4.01	33.33

[a] Reaction conditions: alkene (0.5 mmol), $NaIO_4$ (1 mmol), catalyst (250 mg), CH_3CN/H_2O (5 mL/5 mL).
[b] GLC yield based on starting alkene.
[c] 14% benzaldehyde was produced.
[d] 19% benzaldehyde was produced.
[e] The by-product is acetophenone.

Table 6. Epoxidation of alkenes with $NaIO_4$ catalyzed by [Mn(TPP)Cl@AT-MWCNT] under agitation with MS and under US irradiation.[a]

	Conversion (%)[b]		Epoxide yield (%)[b]		Time (min)		TOF (h^{-1})	
Alkene	MS	US	MS	US	MS	US	MS	US
	92	94	92	94	180	20	8.29	78.99
	96	97	96	97	150	15	10.38	104.8
	79[c]	81[d]	64	63	210	20	6.10	66.34
	73[e]	79[e]	59	58	210	20	5.64	64.70
	56	69	56	69	180	25	5.04	44.83
	57	67	57	67	240	30	3.85	36.22
	43	53	43	53	240	30	2.90	28.65

[a] Reaction conditions: alkene (0.5 mmol), $NaIO_4$ (1 mmol), catalyst (300 mg), CH_3CN/H_2O (5 mL/5mL).
[b] GLC yield based on starting alkene.
[c] 15% benzaldehyde was produced.
[d] 18% benzaldehyde was produced.
[e] The by-product is acetophenone.

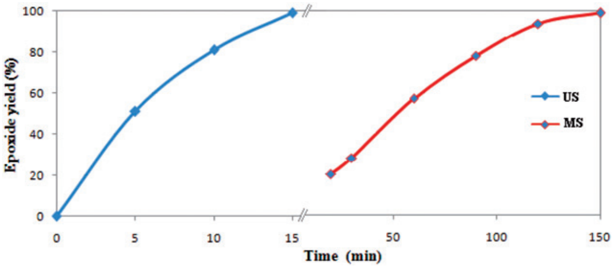


Figure 4. Comparison of systems under US irradiation and MS in the epoxidation of cyclooctene with $NaIO_4$ catalyzed by [Mn(TPP)Cl@ABI-MWCNT].

Table 7. The results of catalyst recovery and the amounts of manganese leached in epoxidation of cyclooctene with sodium periodate.[a]

	[Mn(TPP)Cl@ABI-MWCNT][b]		[Mn(TPP)Cl@AT-MWCNT][c]	
Run	Yield (%)[d]	Mn leached (%)[e]	Yield (%)[d]	Mn leached (%)[e]
1	99	0.8	92	0.7
2	96	0.4	90	0.5
3	94	0	89	0
4	91	0	83	0
5	88	0	80	0

[a] Reaction conditions: alkene (0.5 mmol), $NaIO_4$ (1 mmol), CH_3CN/H_2O (5 mL/5 mL).
[b] 250 mg (0.016 mmol) of the catalyst.
[c] 300 mg (0.018 mmol) of the catalyst.
[d] GLC yield based on the starting alkene.
[e] Determined by atomic absorption spectroscopy.

easily recovered and recycled without significant lose of its unique properties, while the homogeneous catalyst cannot be recovered even one time.

4. Conclusion

In this work, epoxidation of alkenes with $NaIO_4$ catalyzed by tetraphenylporphyrinatomanganese(III) chloride supported on MWCNTs modified with 2-aminobenzimidazole and 2-aminothiazole is reported. These heterogenized catalysts were efficient catalysts for epoxidation of a wide range of alkenes including cyclic and linear ones under MS and US irradiation. The reaction times decreased significantly under ultrasonic waves and product yields increased. The catalysts could be recovered and reused several times by simple filtration.

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