Biomimetic epoxidation of alkenes with sodium periodate catalyzed by tetraphenylporphyrinatomanganese(III) chloride supported on multiwall carbon nanotubes

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Abstract The biomimetic epoxidation of alkenes catalyzed by tetraphenylporphyrinatomanganese(III) chloride, [Mn(TPP)Cl], immobilized on multiwall carbon nanotubes modified with 4-aminopyridine and 4-aminophenol is reported. These heterogenized catalysts were used as efficient and reusable catalysts for epoxidation of a variety of cyclic and linear alkenes with sodium periodate under mild conditions. The catalysts, [Mn(TPP)Cl@amine-MWCNT], were characterized by physico-chemical and spectroscopic methods. The effect of ultrasonic irradiation on these catalytic systems was also investigated. The catalysts were reused several times without loss of their activity.

Introduction

Catalytic oxidation of hydrocarbons in organic liquid phase by oxo metalloporphyrins, in which the metal possesses high oxidation number, has attracted much attention by mimicking the function of monooxygenase enzymes like cytochrome P-450. In the presence of single oxygen donors such as iodosylbenzene [1, 2], hypochlorites [3, 4], amine *N*-oxides [5], alkyl hydroperoxides [6], hydrogen peroxide [7, 8] and sodium periodate [9, 10], natural cytochrome P-450 and metalloporphyrin complexes are able to oxidize organic compounds.

Homogenous metalloporphyrins readily undergo decomposition during the oxidation reaction, which leads to the formation of μ -oxo catalytically inactive dimers in solvent. Hence, immobilizing these expensive catalysts on to a solid organic or inorganic support can overcome this problem [11, 12]. Although the reactivity of this heterogenized catalyst is often lower than the homogenized counterpart, recovery and reusability of the catalyst makes it cost-effective.

Manganese porphyrins can be immobilized on variety of supports via different methods, including coordination bonding, covalent anchorage, electrostatic interactions, encapsulation and intercalation. In the last two decades, several manganese porphyrins have been successfully attached to different supports and investigated for catalytic activity in organic reactions. Previously, our research group reported the catalytic activity of manganese porphyrins immobilized on silica, polystyrene, ion-exchange resins and zeolite. Recently, we reported the preparation of *tetrakis*(*p*-aminophenyl)porphyrinatomanganese(III) chloride, [Mn(TNH₂PP)CI], supported on multiwall carbon nanotubes via covalent attachment. All of them were used for alkene epoxidation with NaIO₄ [9, 10, 13–22].

Carbon nanotubes (CNTs) offer an ideal opportunity as a support because of their large specific surface area, water insolubility and chemical inertness. These long tubes have attracted a lot of attention from researchers around the world [23–25].

The use of ultrasound to improve the catalytic activity of metalloporphyrins has been reported [26–30]. 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. The main effect of

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$$(Mn(TPP)Cl@amin-MWCNT] \rightarrow (CH_3CN/H_2O/NaIO_4) \rightarrow (Magnetic stirring or .))))$$

Scheme 1 Epoxidation of alkenes with NaIO₄ in the presence of [Mn(TPP)Cl@amin-MWCNT]

ultrasound in liquids is cavitation, which involves numerous tiny gas bubbles called cavitation bubbles. The collapse of the bubbles generates high temperature and pressures at the center of the bubbles. These local effects produce a variety of radicals and highly active intermediates, which initiate other secondary chemical reactions in the bulk liquid. These radicals can react with contaminants to form by-products [31].

In the present work, the preparation, characterization and investigation of catalytic activity of [Mn(TPP)Cl] supported on functionalized multiwall carbon nanotubes in the epoxidation of alkenes with sodium periodate is reported (Scheme 1).

Experimental

All materials were of the commercial reagent grade. Alkenes were obtained from Merck chemical company and passed through a column containing active alumina to remove the peroxidic impurities. Tetraphenylporphyrin was prepared and metallated according to the literature [32, 33]. FT-IR spectra were obtained with potassium bromide pellets in the range 400–4,000 cm^{-1} with a Perkin Elmer version 10.00 spectrometer. Scanning electron micrographs of MWCNT were taken on a Philips XL 30 SEM instrument. Gas chromatography experiments (GC) 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. The ICP analyses were performed on an ICP-Spectrociros CCD instrument. The diffuse reflectance ultraviolet-visible spectra of solids were determined on a UV-Vis Shimadzu model 265 spectrophotometer. MWCNTs (multiwall carbon nanotubes with diameters between 20 and 30 nm 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.

Chlorination of MWCNT-COOH

The MWCNT-COOH (1 g) and $SOCl_2$ (10 mL) were mixed and refluxed for 1 h. Then the reaction mixture was cooled and the $SOCl_2$ was evaporated. The resulting

precipitate was assumed to be the chlorinated multiwall carbon nanotubes, MWCNT-COCl, and used without further purification.

Modification of MWCNT-COCl with amines

The MWCNT-COCl (1 g) and Et_3N (3 mL) were added to a solution of 4-aminopyridine (Apy) or 4-aminophenol (AP) (0.5 g) in dimethylformamide (DMF) (20 mL) and heated at 80°C for 72 h. Then, the solid was filtered off, washed with CH₃CN and dried at 60°C. CHN analysis for Apy-MWCNT: C:87.8%, H:1.8%, N:2.9% and of AP-MWCNT: C:89.2%, H:1.9%, N:1.8%.

Supporting of Mn(TPP)Cl on amine modified MWCNTs

To a solution of Mn(TPP)Cl (1 g) in toluene (50 mL), amine modified MWCNTs (5 g) was added and refluxed for 72 h. At the end of the reaction, the mixture was cooled; the catalysts were filtered off and washed thoroughly with toluene, methanol, and ether, successively, and dried in vacuum for several hours.

General procedure for alkene epoxidation with NaIO₄ catalyzed by [Mn(TPP)Cl@amine-MWCNT] under agitation with magnetic stirring

All of the reactions were carried out at room temperature under air. To a mixture of alkene (0.5 mmol), [Mn(TPP)-Cl@APy-MWCNT] (250 mg) or [Mn(TPP)Cl@AP-MW-CNT] (300 mg) and CH₃CN (5 mL), a solution of NaIO₄ (1 mmol) in H₂O (5 mL) was added. The progress of the reaction 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 Et₂O (20 mL) and filtered. The catalysts were thoroughly washed with Et₂O and the combined washings and filtrate were purified on a silica gel plate to obtain the pure product.

General procedure for alkene epoxidation with NaIO₄ catalyzed by [Mn(TPP)Cl@amin-MWCNT] 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 from 0 to 400 W manually. The total volume of the solution was 10 mL. The

temperature was maintained at 25 °C during sonication. A solution of NaIO₄ (1 mmol in 5 mL H₂O) was added to a mixture of alkene (0.5 mmol) in CH₃CN (5 mL). After addition of catalyst, [Mn(TPP)Cl@APy-MWCNT] (250 mg) or [Mn(TPP)Cl@AP-MWCNT] (300 mg), the mixture was sonicated. Progress of the reaction was followed by GC. At the end of reaction, the reaction mixture was thoroughly washed with Et₂O (20 mL) and filtered. The catalyst was thoroughly washed with Et₂O and the combined washing and filtrates were purified on a silica gel plate to obtain the pure product.

Catalyst reuse and stability

The reusability of the catalysts was investigated in the multiple sequential epoxidation of cyclooctene as described above. At the end of each reaction, the catalyst was separated from the reaction mixture by simple filtration,

Table 1 The specification 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			

washed with Et_2O and dried carefully before using it in the next run.

Results and discussion

Preparation and characterization of the catalysts, [Mn(TPP)Cl@APy-MWCNT] and [Mn(TPP)Cl@AP-MWCNT] and investigation of their catalytic activity in the epoxidation of alkenes with NaIO₄ under agitation with magnetic stirring and ultrasonic irradiation

The specifications of multiwall carbon nanotubes containing carboxylic acid groups, MWCNT-COOH, which was used as support, are listed in Table 1. Scheme 2 shows the preparation procedure for immobilization of [Mn(TPP)Cl] on amine modified MWCNTs. The amine modified MWCNT, amine-MWCNT, was prepared by covalent attachment of 4-aminopyridine and 4-aminophenol to MWCNT-COCl via an amide linkage. In the next step, the Mn(TPP)Cl was reacted with amine-MWCNT to obtain the catalysts via axial ligation. The prepared catalysts were characterized by elemental analysis, scanning electron microscopy, and FT-IR and diffuse reflectance UV-vis spectroscopic methods. The nitrogen content of the supports was determined by CHN analysis which showed



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

Table 2	Characteristics	of	the	prepared	catalysts
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Catalyst	N (%)	Mn content (mmol/g)	FT-IR spectrum (cm ⁻¹)						UV-Vis peak (nm)		
			C=O	C–N	N–H	Porphyrin units				Soret band	Q bands
						C-H _{pyrrol}	$C\text{-}H_{Ph}$	C=N	C-H _{Ph}		
APy-MWCNT]	2.92	-	1655	1397	3439	_	_	_	_	_	_
AP-MWCNT]	1.79	-	1633	1395	3446	-	_	-	_	-	_
[Mn(TPP)Cl]	_	-	-	-	-	752	1176	1240	2920	477.5	582,617
[Mn(TPP)Cl@APy-MWCNT]	2.94	0.076	1653	1397	3448	797	1160	1226	2923	466	574,612
[Mn(TPP)Cl@AP-MWCNT]	1.	0.069	1634	1400	3444	799	1173	1232	2921	469	570,610

values of 2.92% and 1.79% for APy-MWCNT and AP-MWCNT, respectively. Based on these values, the nitrogen contents of the supports, which were available for attachment of manganese porphyrin, were obtained as about 1.04 and 1.28 mmol per gram of the APy-MWCNT and AP-MWCNT, respectively. The Mn content of the catalysts, measured by ICP analysis, were obtained 0.076 and 0.069 mmol/g of catalyst for [Mn(TPP)@APy-MWCNT] and [Mn(TPP)@AP-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, [Mn(TPP)Cl], amine-MWCNT and [Mn(TPP)Cl@amine-MWCNT] Fig. S1 (see the Supplementary Data). In the FT-IR spectrum of APy-MWCNT, the C=O stretching band of the amide group was observed at 1,655 cm^{-1} . The C–N and the N-H stretching bands of amide groups present at 1,397 and $3,439 \text{ cm}^{-1}$, respectively (Fig. S1B), which confirmed the anchoring of 4-aminopyridine to acylated multiwall carbon nanotubes. The FT-IR spectrum of the supported catalyst, [Mn(TPP)Cl@APy-MWCNT], exhibits the characteristic bands of the porphyrin units at 797 (C-H_{Pyrrole}), 1160 (C-H_{Ph}), 1226 (C = N) and 2923 cm⁻¹ (C-H_{Ph}) (Fig. S1C). These observations proved the coordination of [Mn(TPP)Cl] to MWCNT. The FT-IR spectrum of 4-aminophenol modified MWCNT (Fig. S1D) shows the bands of the amide linkage at 1,633, 1,395 and 3,446 cm^{-1} corresponding to C=O, C-N and N-H stretching bands, respectively. The porphyrin units of the catalyst, [Mn(TPP) Cl@AP-MWCNT], are observed at 799, 1,173, 1,232 and $2,921 \text{ cm}^{-1}$ (Fig. S1E). The UV-vis spectroscopy was employed in the diffuse reflectance mode for characterization of the supported catalysts. The diffuse reflectance of the MWCNT-bound porphyrin resembles the solution counterpart spectrum (Fig. 1) with a slight shift. The presence of Soret and Q bands of manganese porphyrin in the supported catalysts clearly indicated the presence of the metalloporphyrin on the surface of the MWCNT (Fig. 2; Table 2). Since the MWCNT shows no absorption peak in its diffuse reflectance spectrum, it is confirmed that [Mn(TPP)Cl] has been supported on the MWCNT. The SEM images of the



Fig. 1 The UV–Vis spectrum of homogeneous [Mn(TPP)Cl]

[Mn(TPP)Cl@APy-MWCNT] and [Mn(TPP)Cl@AP-MWCNT] showed that the nanotubes are aggregated and have retained their nanotube nature (Fig. 3).

The prepared catalysts were used for the epoxidation of olefins with sodium periodate at room temperature. First, the reaction parameters such as catalysts amount, kind of solvent and oxidant were optimized in the epoxidation of cyclooctene.

In order to optimize the catalysts amount, different quantities of each catalyst were used in the epoxidation of cyclooctene (0.5 mmol) with NaIO₄ (1 mmol). The best results were obtained with 250 mg (0.019 mmol) of [Mn(TPP)Cl@APy-MWCNT] and 300 mg (0.020 mmol) of [Mn(TPP)Cl@AP-MWCNT] catalysts (Table 3).

The ability of different single oxygen donors such as NaIO₄, H₂O₂, NaOCl, *tert*-BuOOH and *n*-Bu₄NIO₄ was investigated in the epoxidation of cyclooctene. The results, which are summarized in Table 4, showed that NaIO₄ is the best oxygen source because this oxidant, which is inert in the absence of catalyst, can give good oxidation conversion in CH₃CN/H₂O.

In order to choose the reaction media, different solvents were checked in the epoxidation of cyclooctene with NaIO₄. Among the different mixtures of acetonitrile, acetone, methanol, ethanol (single phase systems),



Fig. 2 Diffuse reflectance UV–Vis spectra of: a MWCNT b [Mn(TPP)Cl@APy-MWCNT], c [Mn(TPP)Cl@AP-MWCNT]

dichloromethane and chloroform (two phase systems with n-Bu₄NBr as phase transfer catalyst), the 1:1 mixture of acetonitrile: water was chosen as the reaction medium, because the higher catalytic activity was observed in this experimental condition (Table 5). The higher catalytic activity in acetonitrile/water mixture is attributed to polarity of solvent and solubility of NaIO₄ and alkene in this medium.

The supported catalysts were used for epoxidation of olefins with NaIO₄ under optimized conditions. During the reaction, the catalysts were suspended in the solvent. This



Fig. 3 The SEM image of: a [Mn(TPP)Cl@APy-MWCNT] and b [Mn(TPP)Cl@AP-MWCNT]

Table 3 Optimization of the catalysts amount in the epoxidation of cyclooctene with $NaIO_4$

Catalyst amount (mg)	Epoxide yield (%) ^a after 2.5 h [Mn(TPP)Cl@APy-MWCNT]	Epoxide yield (%) ^a after 3 h [Mn(TPP)Cl@AP-MWCNT]
0	4	2
100	68	49
200	76	67
250	98	80
300	98	94
350	_	94

Reaction conditions: cyclooctene (0.5 mmol), oxidant, catalyst, CH₃CN/H₂O (5 mL/5 mL)

^a GC yield based on the starting alkene

is due to the bundled agglomerates of MWCNT that aggregate slowly and let the catalysts to suspend without setting down for a long period of time. The [Mn(TPP)Cl@APy-MWCNT] and [Mn(TPP)Cl@AP-MWCNT] were found as efficient catalysts for epoxidation of alkenes with NaIO₄ (Tables 6 and 7). In these heterogenized catalytic systems, the oxidation of cyclooctene

Row	Oxidant	Solvent	Epoxide yield (%) ^a after 2.5 h [Mn(TPP)Cl@APy-MWCNT] ^b	Epoxide yield (%) ^a after 3 h [Mn(TPP)Cl@AP-MWCNT] ^c
1	NaIO ₄	CH ₃ CN/H ₂ O	98	94
2	Oxone (KHSO ₅)	CH ₃ CN/H ₂ O	90	89
3	NaOCl	CH ₃ CN	25	45
4	tert-BuOOH	CH ₃ CN	74	67
5	$(n-Bu)_4NIO_4$	CH ₃ CN	35	28
6	H_2O_2	CH ₃ CN	36	42
7	No oxidant	CH ₃ CN	5	6

Table 4 The effect of oxidant on the epoxidation of cyclooctene catalyzed by [Mn(TPP)Cl@amine-MWCNT] at room temperature

Reaction conditions: cyclooctene (0.5 mmol), oxidant (1 mmol), CH₃CN/H₂O (5 mL/5 mL)

^a GC Yield based on the starting alkene

^b 250 mg (0.019 mmol) of the catalyst

^c 300 mg (0.020 mmol) of the catalyst

 Table 5
 The effect of solvent on the epoxidation of cyclooctene catalyzed by [Mn(TPP)Cl@amine-MWCNT] at room temperature

Row	Solvent	Epoxide yield (%) ^a after 2.5 h [Mn(TPP)Cl@ APy-MWCNT] ^b	Epoxide yield (%) ^a after 3 h [Mn(TPP)Cl@ AP-MWCNT] ^c
1	CH ₃ CN/H ₂ O (1:1)	98	96
2	CH ₃ CN/H ₂ O (1:2)	87	90
3	CH ₃ CN/H ₂ O (2:1)	64	67
4	CH ₃ COCH ₃ /H ₂ O	75	73
5	CH ₃ OH/H ₂ O	63	59
6	CH ₃ CH ₂ OH/H ₂ O	46	52
7	CH ₂ Cl ₂ /H ₂ O	27	32
8	CCl ₄ /H ₂ O	18	14

Reaction conditions: cyclooctene (0.5 mmol), NaIO₄ (1 mmol), solvent/H₂O (5 mL/5 mL)

^a GC Yield based on the starting alkene

^b 250 mg (0.019 mmol) of the catalyst

^c 300 mg (0.020 mmol) of the catalyst

produced 94–96% of cyclooctene oxide. The 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, the major products were styrene oxide and α -methylstyrene oxide and only small amounts of benzaldehyde and acetophenone were 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.

The results obtained by this method were compared with some of those reported previously in the oxidation of cyclohexene with NaIO₄. As can be seen in Table 8, the present method is superior in term of selectivity while the TOFs are comparable with the others.

Ultrasonic irradiation can alter the reactivity observed during the heterogeneous catalysis of a variety of reactions. The chemical effect of ultrasonic irradiation is due to several acoustic phenomena, of which cavitation is the most important. The acoustic cavitation has important effects such as local increasing in temperature and pressure, the propagation of oxidation catalysts, and the formation of intense liquid microflows [34]. The mechanical effects of ultrasound offer an opportunity to overcome the following types of problem associated with conventional solid/metal reactions: break-up of the surface structure allows penetration of reactants and/or release of materials from surface, degradation of large solid particles due to shear forces 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 [35].

Therefore, all the reactions were exposed to ultrasonic irradiation. The obtained results are summarized in Tables 6 and 7. These results clearly showed that the reaction times were reduced and the TOFs increased in the system under US irradiation.

In the alkene epoxidation with NaIO₄ in the presence of [Mn(TPP)Cl@APy-MWCNT] and [Mn(TPP)Cl@AP-MWCNT], cyclooctene was epoxidized in 99 and 95% yield with 100% selectivity, but the reaction time decreased to 15 and 20 min, respectively. The yields in the case of linear alkenes increased and the reaction times were greatly decreased.

To confirm the break-up of the agglomerates by US irradiation, a sample of each catalyst was sonicated for 30 min and used in the epoxidation of cyclooctene with NaIO₄ under agitation with magnetic stirring. It was observed that the reaction times reduced from 150–180 min to 90–100 min. The blank experiment in the

Entry

1

2

3

4

5

6

Alkene

Conversion $(\%)^a$

US

99

100

89^c

86^d

78

72

MS

98

100

87^b

85^d

71

73

Epoxide yield (%)^a

US

99

100

72

76

78

72

MS

98

100

70

67

71

73

Table 6 Epoxidation of

alkenes with NaIO₄ catalyzed by [Mn(TPP)Cl@APy-

MWCNT] under agitation with magnetic stirring (MS) and

under ultrasonic irradiation

(US)

(0.5 mmol), NaIO₄ (1 mmol), catalyst (250 mg), CH₃CN/H₂O (5 mL/5 mL) ^a GC yield based on starting alkene ^b 17% benzaldehyde was produced

Reaction conditions: alkene

- ^c 18% benzaldehyde was produced
 ^d The by-product is
- acetophenone

Table 7Epoxidation ofalkenes with NaIO4 catalyzedby [Mn(TPP)Cl@AP-MWCNT]under agitation with magneticstirring (MS) and underultrasonic irradiation (US)

7	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	60	56	60	56	180	30	5.23	29.32
Entry	Alkene	Conve	rsion (%) ^a	Epoxid	e yield (%) ^a	Time	e/min	TOF (I	n^{-1})
		MS	US	MS	US	MS	US	MS	US
1		94	95	94	95	180	20	7.56	69.53
2	\bigcirc	98	98	98	98	120	15	11.83	94.63
3		85 ^b	83 ^c	66	67	180	25	6.84	48.19
4		82 ^d	79 ^d	65	58	180	25	6.60	45.87
5		68	71	68	71	180	25	5.47	41.22
6	$\sim\sim\sim\sim$	64	68	64	68	210	30	4.42	32.85
7	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	52	56	52	56	210	30	4.19	27.05

Reaction conditions: alkene (0.5 mmol), NaIO4 (1 mmol), catalyst (300 mg), CH3CN/ H2O (5 mL/5 mL) ^a GC yield based on starting alkene ^b %19 benzaldehyde was

produced ^c % 16 benzaldehyde was produced ^d The by-product is acetophenone US

103.66

163.61

70.60

68.22

49.08

37.69

TOF (h^{-1})

MS

10.26

13.04

7.50

7.42

6.19

6.37

Time/min

MS

150 15

120 10

180 20

180 20

180 25

180 30

US

Table 8 The comparison of the results obtained for the oxidation of cyclohexene with NaIO₄ catalyzed by manganese porphyrins with those obtained by the recently reported catalysts

Row	Catalyst	Selectivity (%)	TOF (h ⁻¹)	Ref.
1	MnTPPS-PSMP	83	17.5	[36]
2	MnTPyP-CMP	85	9.4	[13]
3	Mn(Br ₈ TPPS)-Ad-400	83	14.09	[37]
4	MnTPPS-Ad	79	15.71	[38]
5	Mn(TNH ₂ PP)-PSA	77	6.5	[39]
6	Mn(TPP)-PSI	64	16.6	[30]
7	MnP-NaY	53	9.10	[2]
8	[Mn(TNH ₂ PP)Cl-MWCNT]	74	18.4	[<mark>9</mark>]
9	Mn(TPP)Cl-APy-MWCNT	100	13.04	Present work
10	Mn(TPP)Cl-AP-MWCNT	100	11.83	Present work



Fig. 4 Comparison of systems under US irradiation and MS in the epoxidation of cyclooctene with NaIO₄ catalyzed by [Mn(TPP)Cl@ APy-MWCNT]

absence of catalysts, under ultrasonic irradiation, showed that the ultrasonic irradiation is much less efficient in the oxidation reactions with sodium periodate. When these reactions were carried out under reflux conditions, the reaction times decreased. These observations showed that another part of the ultrasonic effect is production of hot spots due to cavitation phenomenon.

Figure 4 shows a comparison between systems under US irradiation and under agitation with magnetic stirring, which indicates the effect of ultrasonic irradiation on the catalytic activity of [Mn(TPP)Cl@APy-MWCNT] in the epoxidation of cyclooctene with NaIO₄.

The reusability of a heterogeneous catalyst is of great importance from synthetic and economical points of view. The homogeneous [Mn(TPP)Cl] cannot be recovered even one time, in contrast, the MWCNT supported catalysts can be filtered and reused several times without significant loss of its activity. The reusability of [Mn(TPP)@Apy-MWCNT]
 Table 9 The results of catalysts recovery and the amount of manganese leached in the epoxidation of cyclooctene with sodium periodate

Run	[Mn(TPP APy-MW	P)Cl@ /CNT] ^a	[Mn(TPP)Cl@ AP-MWCNT] ^b			
	Yield (%) ^c	Mn leached $(\%)^d$	Yield (%) ^c	Mn leached (%) ^d		
1	98	1.4	94	1.4		
2	96	0.5	92	0.4		
3	96	0	88	0		
4	90	0	85	0		
5	90	0	85	0		

Reaction conditions: alkene (0.5 mmol), NaIO₄ (1 mmol), CH_3CN/ H_2O (5 mL/5 mL)

^a 250 mg (0.019 mmol) of the catalyst

^b 300 mg (0.020 mmol) of the catalyst

^c GC yield based on the starting alkene

^d Determined by atomic absorption spectroscopy

and [Mn(TPP)@AP-MWCNT] was investigated in the multiple sequential epoxidation of cyclooctene with NaIO₄. At the end of the each reaction, the catalysts were separated by simple filtration, washed with Et₂O and dried carefully before using in the next run. After using of the catalysts for five consecutive times, the epoxide yields were 90 and 85% [Mn(TPP)@Apy-MWCNT] and [Mn(TPP)@APfor MWCNT], respectively (Table 9). The filtrates were collected for determination of Mn leaching. The results showed that after two first runs, no manganese was detected in the filtrates by atomic absorption spectrometry. The nature of the recovered catalysts has been followed by FT-IR (Fig S2) and DR UV-Vis (Fig. S3). The results indicated that the catalysts after reusing several times, showed no change in their structures. The catalytic activity of the separated solution was also investigated. In this manner, after separation of the each catalyst, fresh cyclooctene and oxidant were added to the solution. Execution of the oxidation reaction under the same reaction conditions, as with catalyst, showed that the obtained results were the same as those for blank experiments.

Conclusion

In conclusion, manganese(III)tetraphenylporphyrin immobilized on MWCNTs modified with amines were used as heterogenized catalysts for efficient epoxidation of alkenes with NaIO₄ under mechanical stirring and ultrasonic irradiation. The ultrasonic irradiation increased the performance of the catalysts. The catalysts could be recovered several times by simple filtration and reused without significant loss of their catalytic activity. Acknowledgments We acknowledge the support of this work by Center of Excellence of Chemistry of University of Isfahan (CECUI).

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