Efficient and Selective Hydrocarbon Oxidation with Sodium Periodate Catalyzed by Supported Manganese(III) Porphyrin

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Manganese(III) *tetrakis*(*p*-sulfonatophenyl)porphyrin was successfully bound to silica modified with zirconium. The heterogeneous catalyst, MnTPPS-silica, was characterized by SEM, FT-IR and diffuse reflectance UV-Vis spectroscopic techniques. MnTPPS-silica catalyzes alkene epoxidation and alkanes hydroxylation with sodium periodate under agitation with magnetic stirring and ultrasonic irradiation in the presence of imidazole as an axial ligand. This catalytic system shows a good activity in the epoxidation of linear alkenes. Alkyl aromatic and cycloalkanes were efficiently oxidized to their corresponding alcohols and ketones in the presence of this catalyst. This new heterogeneous catalyst is of high stability and reusability in the oxidation reactions and can be reused several times without loss of its activity.

Keywords: Supported metalloporphyrin, Sodium periodate, Heterogeneous catalyst, Ultrasonic irradiation, Silica gel

INTRODUCTION

Cytochrome P-450 enzymes catalyze various reactions such as aliphatic and aromatic hydroxylation, olefin epoxidation and *N-*, *O-* and *S*-oxidation [1,2]. In order to understand the mechanism of cytochrome P-450 monooxygenation enzyme, synthetic metalloporphyrins were used as cytochrome P-450 models [3-9]. Amongst them, manganese porphyrin complexes have been extensively used in homogeneous catalysis, mainly because of their high activity and selectivity. Various single oxygen atom donors such as PhIO, ClO$^-$, H$_2$O$_2$, ROOH and IO$_4^-$ have been used for oxidation reactions [10-15]. However, these homogeneous expensive catalysts suffer from three major drawbacks such as catalyst deactivation by irreversible dimerization, oxidative self-destruction of metalloporphyrins *via* an intermolecular process and non-reusable nature of the catalyst, which have

prevented progress with practical application for larger scale oxidation. One way to prepare commercial metalloporphyrin catalysts is to anchor them onto solid supports. Several homogeneous and heterogenized metalloporphyrin catalysts have been developed for oxidation of organic substrates [14-53].

Silica gel is one of the most frequently used supports in synthetic organic chemistry because of its inexpensiveness, ready availability, mechanical robustness, chemical inertness and facile functionalization. The immobilization of transition metals on silica gel supports offers a number of advantages over the traditional solution-phase chemistry. These heterogeneous catalysts can be recovered from the reaction media by simple filtration and reused. They do not contaminate the product solution, and increase the selectivity.

Here, we report the use of Mn(TPPS) supported on silica, [Mn(TPPS)-silica], in alkene epoxidation and alkane hydroxylation with sodium periodate in the presence of imidazole as an axial ligand under mechanical stirring and

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under ultrasonic irradiation conditions.

EXPERIMENTAL

All materials were commercial reagent grade. Silica gel 60 was a product of Merck. Alkenes, alkanes and alkylaromatic compounds were obtained from Merck or Fluka. All of these compounds were passed through a column containing active alumina to remove peroxidic impurities. Diffuse reflectance spectra were recorded on a Shimadzu UV-265 instrument using optical grade $BaSO_4$ as reference. Gas chromatography experiments (GC) were performed with a Shimadzu GC-16A instrument using a 2 m column peaked with silicon DC-200 or Carbowax 20 m. ^{1}H NMR spectra were recorded on a Bruker-Arance AQS 300 MHz spectrometer. FT-IR spectra were obtained as potassium bromide pellets in the range 400-4000 cm^{-1} with a Nicolet-Impact 400D instrument.

The tetraphenylporphyrin ligand was prepared, sulfonated and metallated according to the methods suggested in literature [56-58].

Preparation of Silica-Supported Manganese Porphyrin, [Mn(TPPS)-Silica]

To a solution of manganese(III) tetrakis (*p*-sulfonatophenyl)porphyrin (0.5 g, 0.05 mmol) in methanol (50 ml) was added surface modified silica gel (5 g). The mixture was vigorously stirred at room temperature for 6 h, the dark violet resin was collected by filtration, washed thoroughly with methanol and ethanol respectively, and dried in vacuum at room temperature. The content of mangenese(III) porphyrin on the silica support, which was calculated from manganese content in heterogenized catalyst, was determined by NAA.

General Procedure for Oxidation Reactions Catalyzed by [Mn(TPPS)-Silica] under Agitation with Magnetic Stirring

All of the reactions took place at room temperature under air in a 25-ml flask equipped with a magnetic stirrer bar. A solution of $NaIO_4$ (2 mmol) in H_2O (10 ml) was added to a mixture of alkene or alkane (1 mmol) and [Mn(TPPS)-silica] (0.026 mmol) in CH_3CN (10 ml). The progress of the reaction was monitored by GLC. At the end of the reaction, H_2O (20 ml) was added and the reaction mixture was diluted with Et_2O (20 ml) and filtered. The resin was thoroughly washed with Et_2O and combined washings and filtrates were purified on silica gel plates or silica gel column. IR and ^{1}H NMR spectral data confirmed the identities of the products.

General Procedure for Oxidation Reactions Catalyzed by [Mn(TPPS)-Silica] under Ultrasonic Irradiation

All reactions took place 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 in the reaction mixture, was used for sonication. To a solution of alkene or alkane (1 mmol) in CH_3CN (10 ml) was added Mn(TPP)-silica (0.026 mmol). After the addition of sodium periodate solution (2 mmol in 10 ml H_2O), the mixture was sonicated at room temperature. The progress of the reaction was followed by GLC. At the end of the reaction, the silica beads were filtered off and the filtrates were extracted with Et_2O and purified on a silica gel plate or silica gel column (eluent: CCl_4-Et_2O). The identities of the products were confirmed by IR and ^{1}H NMR spectral data.

RESULTS AND DISCUSSION

Preparation and Characterization of Silica Supported Manganese Porphyrin Catalyst [Mn(TPPS)-Silica]

Silica surface modification with 3-aminopropyl triethoxysilane, $POCl_3$ and $ZrOCl_2$, was carried out through the method described by Rodrigues and coworkers [54]. The supported catalyst was prepared by stirring a suspension of the support (silica) in a solution of Mn-porphyrin in methanol as solvent. The catalyst was washed with methanol, dichloromethane and acetone, consecutively to remove the free manganese porphyrin. The diffuse reflectance UV-Vis spectrum of the Mn(TPPS)-silica clearly indicated the presence of manganese(III) meso-*tetrakis*(*p*-sulfonatophenyl) porphyrin on the surface. The degree of incorporation of manganese porphyrin on the silica was also determined by neutron activation analysis (NAA), which showed a value of about 2.50% w/w. The electrostatic bonding of the silica and the metalloporphyrin was so strong that Mn-porphyrin could not be eluted from the silica with water and common organic

Scheme 1. Preparation of supported catalyst used in this study
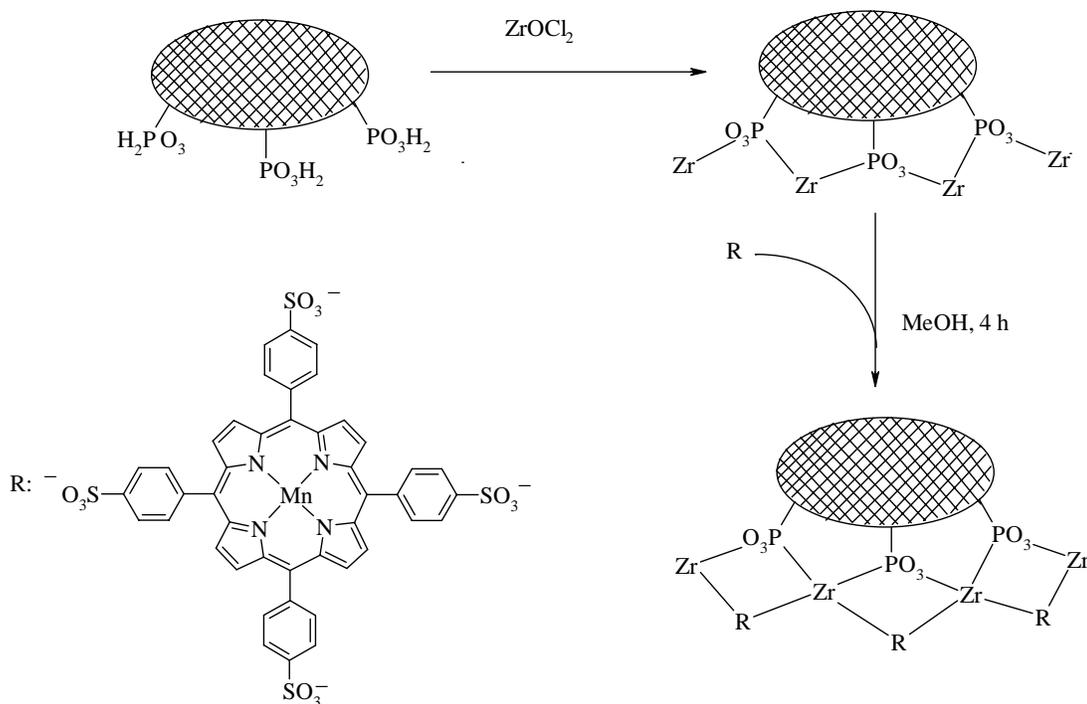
solvents.

The prepared [Mn(TPPS)-silica] catalyst was characterized by FT-IR, diffuse reflectance UV-Vis, SEM and elemental analysis.

The reflectance of the silica-bound porphyrin resembled the solution counterpart spectrum and the Soret band at 467 nm and Q bands at 526, 576 and 608 nm were observed, which clearly indicated the presence of metalloporphyrins on the surface (Fig. 1).

In order to ascertain the attachment of porphyrin to the silica support, FT-IR spectra were recorded in (4000-400 cm^{-1}) regions. The appearance of metalloporphyrin bands in the IR spectra of the supported catalyst confirmed that Mn(TPPS) had been supported on the surface of silica (Fig. 2).

Scanning electron micrograph, (SEM), was recorded to examine the morphological changes occurring on the surface of the silica. A clear change in the morphology of the silica, after the introduction of porphirin complex, was observed by SEM (Fig. 3).
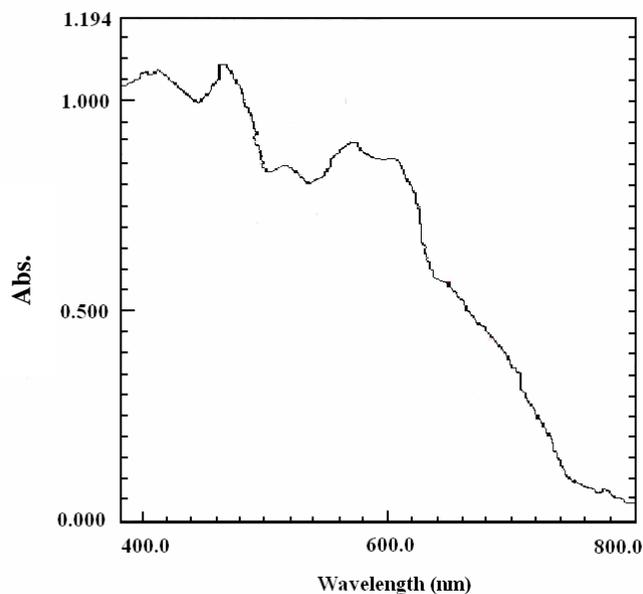
Fig. 1. Diffuse reflectance UV-Vis spectra of [Mn(TPPS)-Silica].

665
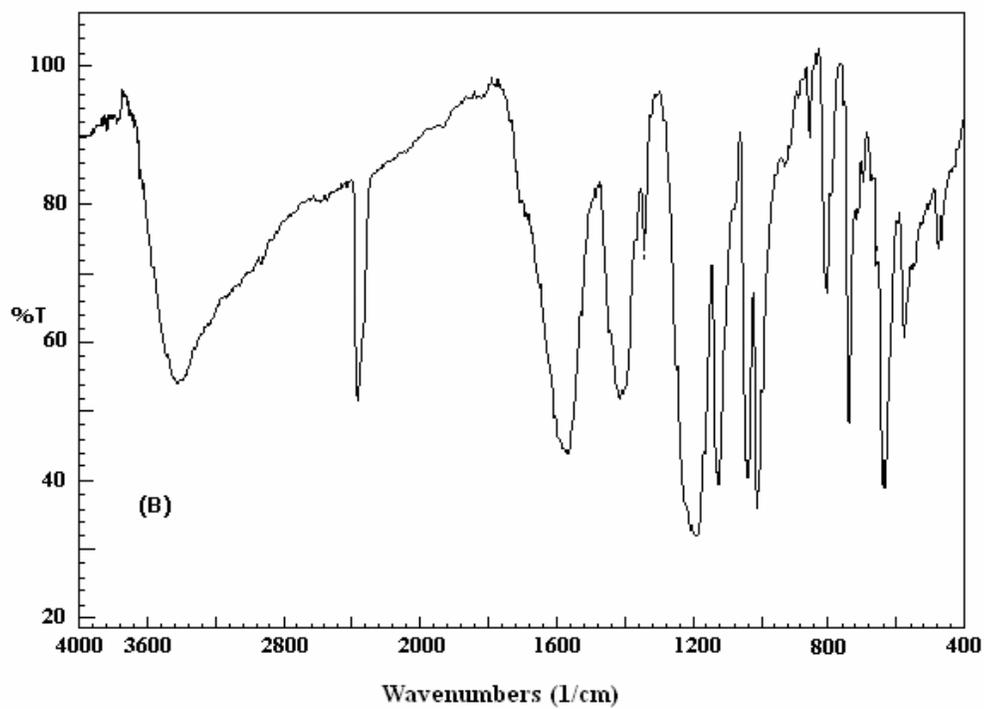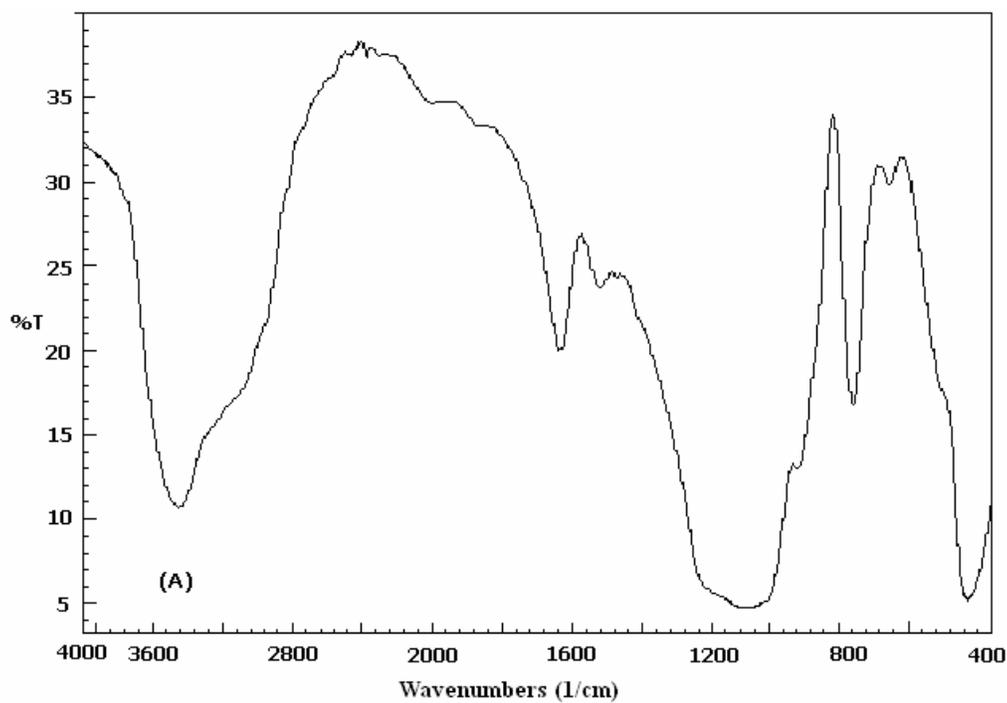
Fig. 2. FT-IR spectrum of: (A) silica and (B) [Mn(TPPS)-silica].
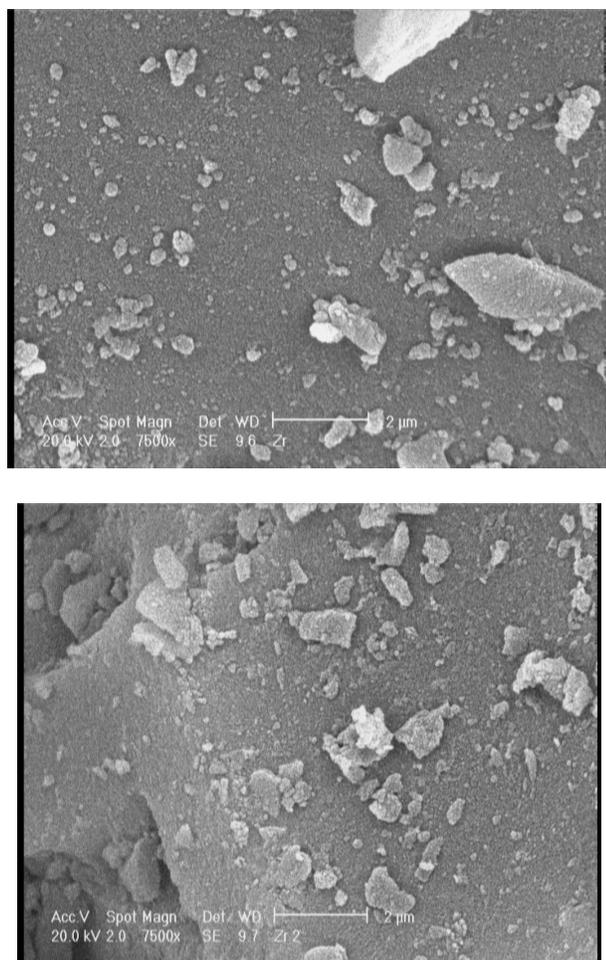
Fig. 3. Scanning electron micrograph of: (A) zircunated silica; (B) [Mn(TPPS)-silica].

The Effect of Oxidants on the Oxidation of Cyclooctene Catalyzed by [Mn(TPPS)-Silica]

In this study, we investigated the effect of different oxidants such as NaOCl, NaIO$_4$, H$_2$O$_2$, KHSO$_5$ *tert*-BuOOH and (*n*-Bu)$_4$NIO$_4$ on the epoxidation of cyclooctene, catalyzed by the heterogeneous Mn(III) porphyrin under agitation with magnetic stirring (MS) and under ultrasonic irradiation (US).

The results are summarized in Table 1. When, *tert*-BuOOH and (*n*-Bu)$_4$NIO$_4$ were used as the oxygen source in acetonitrile, only small amounts of cyclooctene oxide was detected in the reaction mixture. The use of Oxone (KHSO$_5$) was not favored because of the disadvantages such the need for a buffered medium and the bleaching of the metal catalysts during the oxidation reactions.

The results show that in the presence of the Mn(TPPS)-silica catalyst, NaIO$_4$ is the best oxygen source both under mechanical stirring and under ultrasonic irradiation, because of good oxidation conversion, inertness in the absence of the catalyst and high solubility in CH$_3$CN/H$_2$O mixture.

The Effect of Solvent on the Oxidation of Cyclooctene Catalyzed by [Mn(TPPS)-Silica]

The epoxidation of cyclooctene was studied in various solvents under agitation with magnetic stirring (MS) and under ultrasonic irradiation (US). Among the mixtures of methanol, ethanol, acetone, acetonitrile (single phase systems), chloroform, dichloromethane and carbontetrachloride (two phase systems with Bu$_4$NBr as a phase transfer catalyst) with water, the 1:1 mixture of acetonitrile/water was chosen as the

Table 1. The Effect of Oxidants on the Epoxidation of Cyclooctene Catalyzed by [Mn(TPPS)-Silica][a]

Entry	Oxidant	Solvent	Epoxide yield (%)	
			MS (8 h)[b]	US (30 min)[b]
1	NaIO$_4$	CH$_3$CN/H$_2$O	97	96
2	Oxone (KHSO$_5$)	CH$_3$CN/H$_2$O	90	86
3	H$_2$O$_2$	CH$_3$CN	81	64
4	NaOCl	CH$_3$CN	33	48
5	*tert*-BuOOH	CH$_3$CN	19	41
6	*n*-Bu$_4$NIO$_4$	CH$_3$CN	38	40

[a]Reaction conditions: cyclooctene (1 mmol), oxidant (2 mmol), catalyst (0.026 mmol), CH$_3$CN (10 ml), H$_2$O (10 ml). [b]GLC yield based on starting cyclooctene.

reaction medium because of its higher epoxidation yield (Table 2).

Catalytic Alkene Epoxidation with NaIO₄ Catalyzed by [Mn(TPPS)-Silica]

For the initial studies on the catalytic activity of [Mn(TPPS)-silica], the epoxidation of cyclooctene with NaIO₄ in the presence of imidazole as an axial ligand was chosen as a model substrate. The reaction took place at room temperature under mechanical stirring and under ultrasonisc irradiation in 1:1 CH₃CN/H₂O mixture. During the course of the epoxidation, the reaction solution remained colorless and there was no evidence of leaching of the catalyst from silica support into solution. This was further investigated by examining the UV-Vis spectrum of the filtered reaction mixture and determining the amount of manganese leached by atomic absorption spectroscopy. A wide range of substituted alkenes were oxidized with NaIO₄ in the presence of [Mn(TPPS)-silica] as a catalyst and imidazole as an axial ligand. The conditions used for epoxidation of other alkenes were identical to those for cyclooctene. The obtained results show that this catalyst is an efficient one for alkene epoxidation under agitation with magnetic stirring and ultrasonic irradiation (Table 3). Cyclooctene was oxidized in the presence of the catalyst in 98% and 99% yields under agitation with magnetic stirring and under ultrasonic irradiation, respectively. In the case of cyclohexene, only small amounts of allylic oxidation was observed. In the oxidation of styrene and α-methyl styrene, benzaldehyde and acetophenone were produced as by-products. The epoxidation of *trans*-stilbene under magnetic stirring led to *trans*-epoxide in 30% yield, while under ultrasonic irradiation 71% of *trans*-epoxide was produced. 1-Octene and 1-dodecene as linear alkenes were epoxidized efficiently through this heterogeneous system.

A blank experiment in the presence of oxidant using the same experimental conditions in the absence the catalyst was carried out for the epoxidation of cyclooctene. The obtained results showed that NaIO₄ had poor ability to oxidize the cyclooctene. Moreover, no cyclooctene oxide was detected in the absence of oxidant in the reaction mixture.

Oxidation of Alkanes with NaIO₄ Catalyzed by [Mn(TPPS)-Silica]

Direct oxidation of hydrocarbons is one of the typical reactions of cytochrome P-450 [55]. Therefore, catalytic oxidation of alkanes with oxygen sources under mild conditions is an especially justifieable attempt, since direct functionalization of inactivated C-H bonds in saturated hydrocarbons usually requires drastic conditions such as high pressure and high temperature. As shown in Table 4, we have found that the supported Mn(TPPS) is an efficient catalyst for the biomimetic functionalization of saturated hydrocarbons. In the oxidation of the alkanes, the hydroxylation product is highly dependent on the nature of the hydrocarbon itself. Cyclooctane, cyclohexane, 1,2,3,4-tetrahydronaphthalene and adamantane were converted in high yields to their

Table 2. The Effect of Solvent on the Epoxidation of Cyclooctene with NaIO₄ Catalyzed by [Mn(TPPS)-Silica][a]

Entry	Solvent	Epoxide yield (%)	
		MS (8 h)[b]	US (30 min)[b]
1	CH₃CN/H₂O	98	96
2	CH₃COCH₃/H₂O	56	76
3	CH₃OH/H₂O	32	45
4	CH₃CH₂OH/H₂O	20	18
5	CHCl₃/H₂O	12	17
6	CH₂Cl₂/H₂O	23	16
7	CCl₄/H₂O	9	8

[a]Reaction conditions: cyclooctene (1 mmol), oxidant (2 mmol), catalyst (0.026 mmol), CH₃CN (10 ml), H₂O (10 ml). [b]GLC yield based on starting cyclooctene.

Table 3. Epoxidation of Alkenes with $NaIO_4$ Catalyzed by [Mn(TPPS)-Silica] under Agitation with Magnetic Stirring (MS) and under Ultrasonic Irradiation (US)[a]

Entry	Alkene	Conversion (%)		Epoxide yield (%)[b]		Time (min)	
		MS	US	MS	US	MS	US
1		98	99	98	99	480	25
2		93	81	89	78	720	25
3		74[c]	87[d]	69	84	960	15
4		61[e]	69[e]	59	46	960	15
5		30	77	30 (*trans*-Epoxide)[f]	77 (*trans*-Epoxide)[f]	840	25
6		41	73	40	70	720	25
7		38	56	38	43	720	25
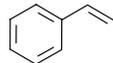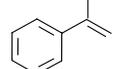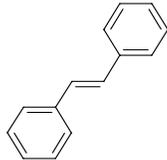
[a]Reaction conditions: alkene (1 mmol), oxidant (2 mmol), catalyst (0.026 mmol), CH_3CN (10 ml), H_2O (10 ml). [b]GLC yield based on starting alkene. [c]20% Benzaldehyde was produced. [d]23% Benzaldehyde was produced. [e]The by-product was acetophenone. [f]Both ^1H NMR and GLC data approved the reported yields.

corresponding alcohols and ketones. In contrast, ethylbenzene, propyl benzene and diphenylmethanene only produced the corresponding ketones. In the case of adamantane, 1-adamantanol and 2-adamantanone were produced in the reaction mixture.

Catalyst Reuse and Stability

To assess the long-term stability and reusability of [Mn(TPPS)-silica], cyclooctene was used as a model substrate, and recycling experiments were carried out with a single sample of the catalyst. After each experiment, the catalyst was separated from the reaction mixture by simple filtration,

washed with the methanol and dried carefully before being used in the subsequent run. After using the catalyst for four consecutive times, the epoxide yields were 83% and 79% for the systems under magnetic stirring and under ultrasonic irradiation. The amounts of manganese leached were measured by atomic absorption spectrometry (Table 5).

Comparison of Catalytic Activity of Homogeneous Mn(TPPS) and Heterogeneous [Mn(TPPS)-Silica] in Alkene Epoxidation and Alkane Hydroxylation with Sodium Periodate

In order to demonstrate the effect of supporting on the

Table 4. Epoxidation of Alkanes with NaIO$_4$ Catalyzed by [Mn(TPPS)-Silica] under Agitation with Magnetic Stirring (MS) and under Ultrasonic Irradiation (US)[a]

Entry	Alkane	Conversion (%)[b]		Ketone (%)[b]		Alcohol (%)[b]		Time (h)	
		MS	US	MS	US	MS	US	MS	US
1		54	71	22	40	32	31	8	0.5
2		48	62	15	31	30	31	9	0.5
3		63	74	37	54	37	40	11	0.75
4		36	53	36	43	-	-	11	0.75
5		39	51	14	30	25	21	11	0.75
6		13	44	44	13	13	-	11	0.75
7		31	56	31	56	-	-	11	0.75
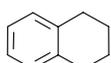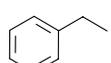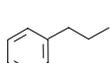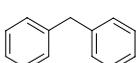
[a]Cyclooctene (1 mmol), oxidant (2 mmol), catalyst (0.026 mmol), CH$_3$CN (10 ml), H$_2$O (10 ml). [b]GLC yield based on starting alkene.

Table 5. The Results of [Mn(TPPS)-Silica] Catalyst Recovery and the Manganese Leached in the Epoxidation of Cyclooctene with Sodium Periodate under Agitation with Magnetic Stirring (MS) and under Ultrasonic Irradiation (US)[a]

Run	Time (h)		Epoxide yield (%)[a]		Mn leached (%)[b]	
	MS	US	MS	US	MS	US
1	8	0.4	98	97	1.2	1.5
2	8	0.4	90	90	0.9	1.1
3	8	0.4	87	85	0.5	0.7
4	8	0.4	83	79	0	0

[a]GLC yield based on starting alkene. [b]Determined by atomic absorption spectroscopy.

Table 6. Comparison of Catalytic Activity of Homogeneous Mn(TPPS) and Heterogeneous [Mn(TPPS)-Silica] in Alkene Epoxidation and Alkane Hydroxylation with Sodium Periodate

Entry	Substrate	Conversion (%)		Time (h)	
		Mn(TPPS)	[Mn(TPPS)-silica]	Mn(TPPS)	[Mn(TPPS)-silica]
1		21	98	8	8
2		9	54	8	8

catalytic activity of manganese(III) porphyrin in the oxidation reactions, the epoxidation of cyclooctene and hydroxylation of cyclooctane with sodium periodate were carried out under the same reaction conditions and with the same amounts of catalyst, substrate, NaIO$_4$ and imidazole as an axial ligand in a CH$_3$CN:H$_2$O mixture. The obtained results, which are summarized in Table 6, showed that the heterogeneous [Mn(TPPS)-silica] had a higher catalytic activity.

CONCLUSIONS

We have demonstrated that the silica supported manganese(III) porphyrin is an efficient catalyst both under agitation with magnetic stirring and under ultrasonic irradiation conditions. This catalytic system enjoys the following advantages: (i) easy preparation and handling of the tethered catalyst; (ii) increasing catalytic activity in comparison with the homogeneous counterpart; (iii) increasing product selectivity and (iv) facile and effective recovery and recycling of the catalyst.

ACKNOWLEDGEMENTS

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