



Silica supported Mn(Br₈TPP)Cl and Mn(TPP)Cl as efficient and reusable catalysts for selective hydrocarbon oxidation under various reaction conditions: The effect of substituted bromines on the catalytic activity and reusability

Majid Moghadam^{a,*}, Valiollah Mirkhani^{a,**}, Shahram Tangestaninejad^a,
Iraj Mohammadpoor-Baltork^a, Hadi Kargar^b

^a Department of Chemistry, Catalysis Division, University of Isfahan, Isfahan 81746-73441, Iran

^b Payame Noor University (PNU), Ardakan, Yazd, Iran

ARTICLE INFO

Article history:

Received 22 October 2007

Received in revised form 18 March 2008

Accepted 27 March 2008

Available online 8 April 2008

Keywords:

Epoxidation

Hydroxylation

Silica

Ultrasonic irradiation

Metalloporphyrin

ABSTRACT

The imidazole-modified silica (SiIm) was used for immobilization of octabromotetraphenylporphyrinatomanganese(III) chloride, Mn(Br₈TPP)Cl and tetraphenylporphyrinatomanganese(III) chloride, Mn(TPP)Cl. SiIm is not only a heterogeneous axial base but also a support for immobilization of manganese porphyrins. [Mn(Br₈TPP)Cl-SiIm] and [Mn(TPP)Cl-SiIm] as biomimetic oxidation catalysts catalyze alkene epoxidation and alkane hydroxylation with NaIO₄ under agitation with magnetic stirring. Ultrasonic irradiation enhanced the catalytic activity of these catalysts in alkene epoxidation and alkane hydroxylation and this led to shorter reaction times and higher product yields. These new heterogenized catalysts could be reused several times without significant loss of their catalytic activity.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

An iron porphyrin surrounded by proteins is known to be the active site of the enzyme P-450 monooxygenase, which can selectively catalyze the oxidation in particular the epoxidation of a wide range of substrates [1]. Synthetic metalloporphyrins have been used as cytochrome P-450 models and have been found to be highly efficient homogeneous catalysts for alkene epoxidation and alkane hydroxylation [2–8]. Several simple oxidants such as PhIO, ClO⁻, H₂O₂, ROOH and IO₄⁻ have been extensively studied in oxygenation reactions catalyzed by metalloporphyrins in order to understand the mechanism of cytochrome P-450 monooxygenation enzyme [9–14]. However, the synthesis of metalloporphyrins is challenging and low-yielding. Immobilization onto a solid support can counteract this problem, enabling the easier recovery and reuse of the catalysts, which makes them cost-effective. Moreover, the support can also reduce the instability of the metalloporphyrins during the epoxidation reaction, *i.e.* self-oxidation leading to the formation of a catalytically inactive μ-oxo porphyrin dimer in solution [15–19].

* Corresponding author. Tel.: +98 311 7932705; fax: +98 311 6689732.

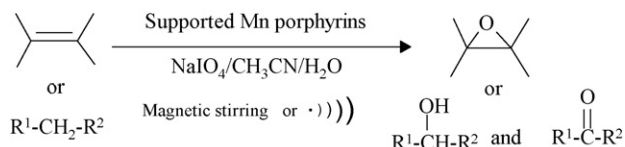
** Corresponding author. Tel.: +98 311 7932713; fax: +98 311 6689732.

E-mail addresses: moghadamm@chem.ui.ac.ir, majidmoghadamz@yahoo.com (M. Moghadam), mirkhani@sci.ui.ac.ir (V. Mirkhani).

Over the last two decades, several homogeneous and heterogenized metalloporphyrins have been developed for alkene epoxidation and alkane hydroxylation [20–44]. Previously, we have reported the use of supported manganese(III) porphyrins in the oxidation of organic compounds with NaIO₄ [45–54]. Here, we report the use of silica-supported octabromotetraphenylporphyrinatomanganese(III) chloride, [Mn(Br₈TPP)Cl]-SiIm, and tetraphenylporphyrinatomanganese(III) chloride, Mn(TPP)Cl in alkene epoxidation and alkane hydroxylation with NaIO₄ under mechanical stirring and ultrasonic (US) irradiation conditions (Scheme 1).

2. Experimental

All materials were of the commercial reagent grade. Alkene, alkane 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. Tetraphenylporphyrin was prepared, brominated and metallated according to the literature [55–57]. FT-IR spectra were obtained with potassium bromide pellets in the range 400–4000 cm⁻¹ with a Nicolet Impact 400D spectrometer. Scanning electron micrographs of the catalyst and silica were taken on a Philips XL 30 SEM. Gas chromatography (GC) experiments were performed with a Shi-



Scheme 1. Alkene epoxidation and alkane hydroxylation catalyzed by silica-supported manganese porphyrins.

madzu GC-16A instrument using a 2 m column packed with silicon DC-200 or Carbowax 20 m. ^1H NMR spectra were recorded on a Bruker-Arance AQS 300 MHz spectrometer.

2.1. Preparation of silica-supported manganese porphyrins, $\text{Mn}(\text{Br}_8\text{TPP})\text{Cl-Silm}$ and $\text{Mn}(\text{TPP})\text{Cl-Silm}$

3-Chloropropylsilica gel functionalized imidazole, as support, was prepared according to the reported procedure [27]. IR and elemental analysis were in accordance with those previously described. To a solution of 0.5 g manganese porphyrins in toluene (100 ml), was added 3-chloropropylsilica gel functionalized imidazole (5 g). The mixture was vigorously stirred at 80°C for 24 h. After cooling, the green silica was collected by filtration, washed thoroughly with dichloromethane, methanol, and ether, successively, and dried in vacuum at room temperature for several hours. The manganese(III) porphyrin loading of silica support, which was calculated from the manganese content in heterogenized catalyst, was determined by neutron activation analysis (NAA).

2.2. General procedure for oxidation reactions catalyzed by $\text{Mn}(\text{Br}_8\text{TPP})\text{Cl-Silm}$ or $\text{Mn}(\text{TPP})\text{Cl-Silm}$ under agitation with magnetic stirring

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 or alkane (1 mmol), manganese porphyrins (30 μmol) and CH_3CN (10 ml) was added a solution of NaIO_4 (2 mmol) in H_2O (10 ml). The progress of reaction was monitored by GC. The reaction mixture was diluted with Et_2O (20 ml) and filtered. The catalyst was thoroughly washed with Et_2O and combined washings and filtrates were purified on a silica gel plates or a silica gel column. IR and ^1H NMR spectral data confirmed the identities of the products.

2.3. General procedure for oxidation reactions catalyzed by $\text{Mn}(\text{Br}_8\text{TPP})\text{Cl-Silm}$ or $\text{Mn}(\text{TPP})\text{Cl-Silm}$ 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 set at 0–400 W through manual adjustment. The total volume of the solution was 20 ml. The temperature reached to 40°C during sonication.

A solution of NaIO_4 (2 mmol in 10 ml H_2O) was added to a mixture of alkene or alkane (1 mmol) in CH_3CN (10 ml). After addition of manganese porphyrins (30 μmol), the mixture was sonicated. Progress of the reaction was followed by GC. At the end of reaction, the polymer beads were filtered off and the filtrates were extracted with Et_2O and were purified on a silica gel plate or a silica gel column (eluent: $\text{CCl}_4\text{-Et}_2\text{O}$). The identities of products were confirmed by IR and ^1H NMR spectral data.

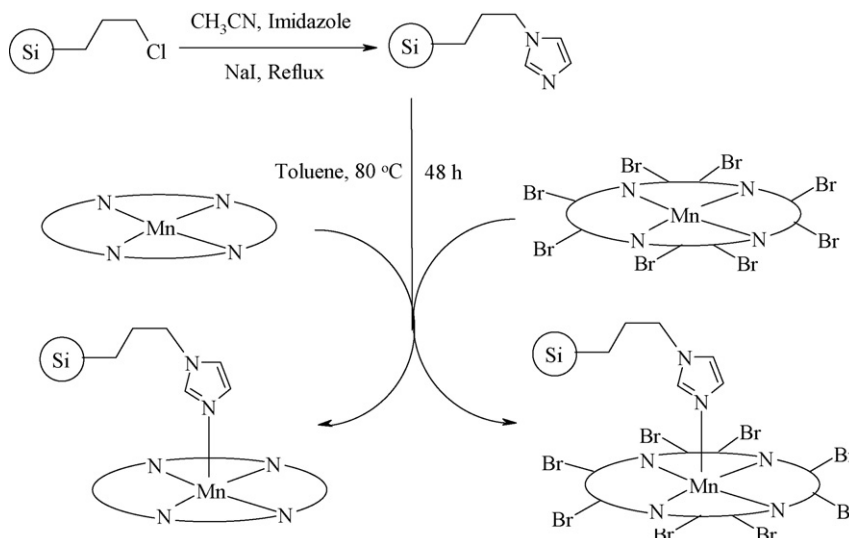
2.4. Catalyst reuse and stability

The reusability of $[\text{Mn}(\text{Br}_8\text{TPP})\text{Cl-Silm}]$ and $[\text{Mn}(\text{TPP})\text{Cl-Silm}]$ was studied in repeated epoxidation reactions. The epoxidation of cyclooctene was chosen as a model substrate for the study of catalyst reuse and stability. The catalyst was separated from the reaction mixture after each experiment by simple filtration, washed with methanol and dried carefully before using it in the subsequent run.

3. Results and discussion

3.1. Preparation of the catalysts, $[\text{Mn}(\text{Br}_8\text{TPP})\text{Cl-Silm}]$ and $[\text{Mn}(\text{TPP})\text{Cl-Silm}]$

Silica surface modification with imidazole to give the Si-Im was carried out through the method described by Cooke and Lindsay Smith [26]. The supported catalysts were prepared by the reaction of chloropropylated silica gel with imidazole in dichloromethane. The supported manganese catalysts, $[\text{Mn}(\text{Br}_8\text{TPP})\text{Cl-Silm}]$ and $[\text{Mn}(\text{TPP})\text{Cl-Silm}]$, were obtained by stirring a suspension of silica-modified imidazole in a solution of the manganese porphyrins in toluene (Scheme 2). The bonding of the silica and the manganese



Scheme 2. Preparation of silica-supported manganese porphyrins.

porphyrins is so strong that metalloporphyrins is not eluted from the silica with water and common organic solvents.

The imidazole bonded to silica was characterized by elemental analysis. The nitrogen content of this resin was 1.28%. According to this value, the degree of imidazole which was introduced into the silica was 0.457 mmol/g of support. This shows that only 64% of total chlorine was replaced with imidazole.

The amounts of manganese porphyrin on the supported catalysts were determined by NAA, which showed values of 5.26% (0.069 mmol/g) for [Mn(TPP)Cl-Silm] and 4.46% (0.032 mmol/g) for [Mn(Br₈TPP)Cl-Silm].

The catalysts were characterized by IR spectroscopy and SEM. The appearance of metalloporphyrin bands in the IR spectra of the supported catalysts confirmed [Mn(Br₈TPP)Cl] and [Mn(TPP)Cl-Silm] supported on the surface of silica *via* imidazole spacer. The SEM images of the catalysts and 3-chloropropylated silica are shown in Fig. 1. These images show that the morphology and the shape of silica particles were intact upon attachment of metalloporphyrins.

3.2. The effect of oxidant on the epoxidation of cyclooctene catalyzed by [Mn(Br₈TPP)Cl-Silm] and [Mn(TPP)Cl-Silm]

The effect of different oxidants on the epoxidation of cyclooctene catalyzed by [Mn(Br₈TPP)Cl-Silm] and [Mn(TPP)Cl-Silm] was investigated. NaIO₄, KHSO₅, H₂O₂, NaOCl, *tert*-BuOOH and *n*-Bu₄NIO₄ were chosen as oxygen source. The results obtained at room temperature are summarized in Table 1. The results show 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. We have reported that in the oxidation of hydrocarbons with NaIO₄ catalyzed by supported metalloporphyrins, imidazole plays a co-catalytic role [45–54]; the co-catalyst is *t*-butylpyridine (BuPy) for NaOCl, imidazole or ammonium acetate for H₂O₂ and pyridine (Py) for oxone. In the investigation of the effect of different oxidants on the epoxidation of cyclooctene, we added the suitable co-catalyst to the reaction mixture. The observed

Table 1

The effect of oxidant on the epoxidation of cyclooctene catalyzed by Mn(Br₈TPP)Cl-Silm and Mn(TPP)Cl-Silm at room temperature under agitation with magnetic stirring^a

Oxidant	Solvent	Epoxide yield (%) after 7 h ^b	
		Mn(Br ₈ TPP)Cl-Silm	Mn(TPP)Cl-Silm
NaIO ₄ (2 mmol)	CH ₃ CN/H ₂ O	100	100
NaIO ₄ (1 mmol)	CH ₃ CN/H ₂ O	72	67
NaIO ₄ (2 mmol)/imidazole	CH ₃ CN/H ₂ O	84	87
Oxone (KHSO ₅) (2 mmol)	CH ₃ CN/H ₂ O	91	95
Oxone (KHSO ₅) (1 mmol)	CH ₃ CN/H ₂ O	58	47
Oxone (KHSO ₅) (2 mmol)/pyridine	CH ₃ CN/H ₂ O	89	91
H ₂ O ₂ (2 mmol)	CH ₃ CN	15	30
H ₂ O ₂ (1 mmol)	CH ₃ CN	10	16
H ₂ O ₂ (2 mmol)/imidazole	CH ₃ CN	10	23
H ₂ O ₂ (2 mmol)/NH ₄ Ac	CH ₃ CN	18	29
NaOCl (2 mmol)	CH ₃ CN	10	15
NaOCl (1 mmol)	CH ₃ CN	9	12
NaOCl (2 mmol)/4- <i>tert</i> -butylpyridine	CH ₃ CN	12	16
<i>tert</i> -BuOOH (2 mmol)	CH ₃ CN	20	25
Bu ₄ NIO ₄ (2 mmol)	CH ₃ CN	10	15
No oxidant	CH ₃ CN	5	8

^a Reaction conditions: cyclooctene (1 mmol), oxidant (1 or 2 mmol based on the active oxygen content), catalyst (0.03 mmol), CH₃CN/H₂O (10 ml/10 ml).

^b GLC yield based on starting alkene.

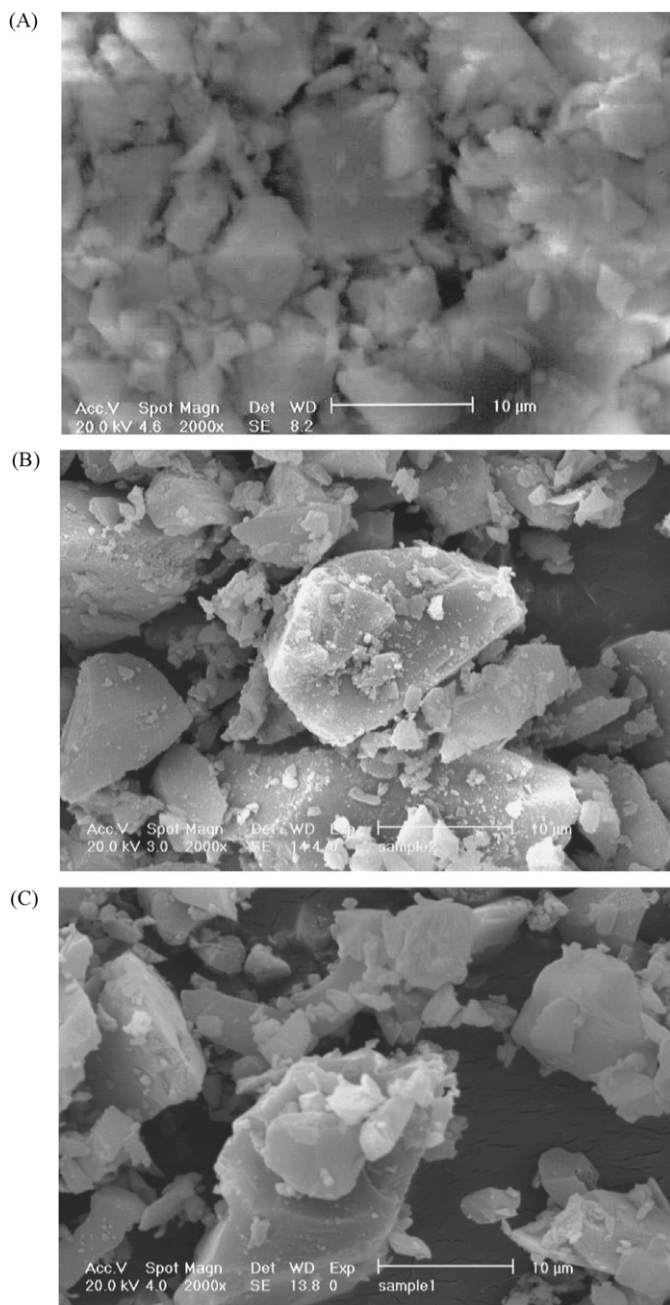


Fig. 1. Scanning electron micrograph of (A) silica-bounded imidazole, (B) Mn(Br₈TPP)Cl-Silm, and (C) Mn(TPP)Cl-Silm.

results showed that no progress was observed in the presence of *t*-BuPy for NaOCl, AcNH₄ for H₂O₂ and Py for oxone. But addition of imidazole to the epoxidation reaction of cyclooctene, the yields reduced to 82% and 85% for [Mn(Br₈TPP)Cl-Silm] and [Mn(TPP)Cl-Silm], respectively. This may due to the strong coordination of imidazole to the sixth coordination position of the metalloporphyrins, which will reduce the epoxide yield.

3.3. The effect of solvent on the epoxidation of cyclooctene catalyzed by [Mn(Br₈TPP)Cl-Silm] and [Mn(TPP)Cl-Silm]

In the catalytic epoxidation of alkenes the choice of reaction media is crucially important. Among the mixture of acetonitrile, acetone, methanol, ethanol (single phase systems),

Table 2

The effect of solvent on the epoxidation of cyclooctene with NaIO₄ catalyzed by Mn(Br₈TPP)Cl-Silm and Mn(TPP)Cl-Silm at room temperature under agitation with magnetic stirring^a

Solvent	Epoxide yield (%) after 7 h ^b	
	Mn(Br ₈ TPP)Cl-Silm	Mn(TPP)Cl-Silm
CH ₃ CN/H ₂ O (1:1)	100	100
CH ₃ CN/H ₂ O (1:2)	82	85
CH ₃ CN/H ₂ O (2:1)	40	45
CH ₃ COCH ₃ /H ₂ O	65	80
CH ₃ OH/H ₂ O	58	70
CH ₃ CH ₂ OH/H ₂ O	43	50
CHCl ₃ /H ₂ O	18	20
CH ₂ Cl ₂ /H ₂ O	20	25
CCl ₄ /H ₂ O	10	15

^a Reaction conditions: cyclooctene (1 mmol), NaIO₄ (2 mmol), catalyst (0.03 mmol).

^b GLC yield based on starting alkene.

dichloromethane, chloroform and carbontetrachloride (two phase systems with Bu₄NBr as phase transfer catalyst) with water, the 1:1 acetonitrile/water mixture was chosen as the reaction medium, because the higher catalytic activity was observed. The higher catalytic activity in acetonitrile/water mixture is attributed to polarity of solvent and solubility of NaIO₄ in it. The results are shown in Table 2. Different ratios of acetonitrile/water mixture were also examined to find the ratio between solvents. The results showed that the 1:1 mixture of acetonitrile/water is the best.

Blank experiment in the presence of oxidant and in the absence of catalyst was also investigated in the epoxidation of cyclooctene. The results showed that NaIO₄ has poor ability to oxidize the cyclooctene. No cyclooctene oxide was detected in the absence of oxidant in the reaction mixture either.

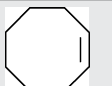
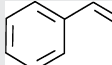
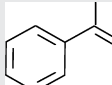
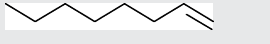
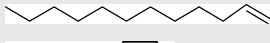
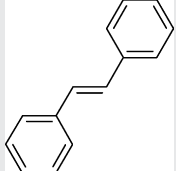
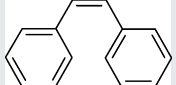
3.4. Alkene epoxidation with NaIO₄ catalyzed by Mn(Br₈TPP)Cl-Silm and [Mn(TPP)Cl-Silm] under mechanical stirring

First, the epoxidation of cyclooctene with NaIO₄ was chosen as a model substrate to investigate the catalytic activity of [Mn(Br₈TPP)Cl-Silm] and [Mn(TPP)Cl-Silm]. The obtained results (Tables 3 and 4) showed that this substrate was oxidized to the corresponding epoxide in 100% yield with 100% selectivity in the presence of manganese porphyrins. The optimum conditions used for the epoxidation of cyclooctene were catalyst, oxidant, and substrate in a molar ratio of 1:66:33. Under the same reaction conditions a range of alkenes were oxidized in this catalytic system in the presence of these two heterogenized catalysts.

In the case of [Mn(Br₈TPP)Cl-Silm] catalyst, oxidation of styrene produced 74% of styrene oxide and 13% benzaldehyde. Oxidation of α -methylstyrene produced 76% α -methylstyrene oxide and 11% acetophenone. In the case of 1-octene and 1-dodecene, the corresponding epoxides were produced in 88% and 41% yields with 100% selectivity, respectively. In the case of stilbenes, *trans*-stilbene was epoxidized in a stereospecific manner with complete reten-

Table 3

Epoxidation of alkenes with NaIO₄ catalyzed by Mn(Br₈TPP)Cl-Silm under agitation with magnetic stirring (MS) and under ultrasonic irradiation (US)^a

Entry	Alkene	Conversion (%) ^b		Epoxide yield (%) ^b		Time (min)		Epoxide selectivity (%)		TOF (h ⁻¹)	
		MS	US	MS	US	MS	US	MS	US	MS	US
1		100	100	100	100	420	15	100	100	4.76	133
2		97 ^c	98 ^d	74	72	420	30	76	75.5	4.62	65.3
3		97 ^e	97 ^e	76	67	300	50	78	69	6.47	26.9
4		88	90	88	90	420	15	100	100	4.19	120
5		41	58	41	58	180	15	100	100	4.56	77.3
6		37	52	37 (<i>trans</i> -epoxide) ^f	52 (<i>trans</i> -epoxide) ^f	300	120	100	100	2.47	8.67
7		95	90	53 (<i>cis</i> -epoxide) ^f , 42 (<i>trans</i> -epoxide) ^f	72 (<i>cis</i> -epoxide) ^f , 18 (<i>trans</i> -epoxide) ^f	300	120	100	100	6.33	15

^a Reaction conditions: alkene (1 mmol), NaIO₄ (2 mmol), catalyst (0.03 mmol), CH₃CN/H₂O (10 ml/10 ml).

^b GLC yield based on starting alkene.


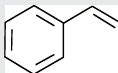
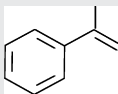


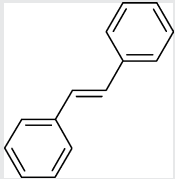
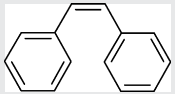
^c 23% benzaldehyde was produced.

^d 26% benzaldehyde was produced.

^e The by-product is acetophenone.

^f Both ¹H NMR and GLC data approved the reported yields.

Table 4
Epoxidation of alkenes with NaIO₄ catalyzed by Mn(TPP)Cl-Silm under agitation with magnetic stirring (MS) and under ultrasonic irradiation (US)^a

Entry	Alkene	Conversion (%) ^b		Epoxide yield (%) ^b		Time (min)		Epoxide selectivity (%)		TOF (h ⁻¹)	
		MS	US	MS	US	MS	US	MS	US	MS	US
1		100	100	100	100	240	15	100	100	8.33	133
2		100 ^c	100 ^d	92	91	210	25	92	91	9.52	80.0
3		100 ^e	98 ^e	76	80	180	20	76	82	11.11	98.0
4		90	100	90	100	300	15	100	100	6.00	133.3
5		62	85	62	85	180	15	100	100	6.89	113.3
6		70	71	70 (<i>trans</i> -epoxide) ^f	71 (<i>trans</i> -epoxide) ^f	300	120	100	100	4.67	11.8
7		98	99	70 (<i>cis</i> -epoxide) ^f , 28 (<i>trans</i> -epoxide) ^f	66 (<i>cis</i> -epoxide) ^f , 33 (<i>trans</i> -epoxide) ^f	300	120	100	100	6.53	16.5

^a Reaction conditions: alkene (1 mmol), NaIO₄ (2 mmol), catalyst (0.03 mmol), CH₃CN/H₂O (10 ml/10 ml).

^b GLC yield based on starting alkene.

^c 8% benzaldehyde was produced.

^d 9% benzaldehyde was produced.

^e The by-product is acetophenone.

^f Both ¹H NMR and GLC data approved the reported yields.

tion of configuration (37% yield). In contrast, the epoxidation of *cis*-stilbene was associated with some loss of stereochemistry and afforded 53% *cis*-stilbene and 42% *trans*-stilbene oxides, respectively. In the case of stilbenes, the crude mixture was analyzed by ¹H NMR and only stilbene oxide was observed as product; neither deoxybenzoin nor diphenylacetaldehyde was detected as products.

In the presence of [Mn(TPP)Cl-Silm], styrene was epoxidized with 92% selectivity and 8% benzaldehyde was also produced as by-product. In the oxidation of α -methylstyrene, 76% α -methylstyrene oxide and 24% acetophenone were produced. In the case of 1-octene and 1-dodecene, the corresponding epoxides were produced in 90% and 62% yields with 100% selectivity, respectively. In the case of stilbenes, *trans*-stilbene was epoxidized into *trans*-epoxide in 70% yield. In contrast, the epoxidation of *cis*-stilbene was associated with some loss of stereochemistry and afforded 70% *cis*-stilbene and 28% *trans*-stilbene oxides. The low yield for *trans*-stilbene in comparison with *cis*-stilbene may be due to the steric hindrance between phenyl groups in *trans*-stilbene and the substituted bromines in the porphyrin ring.

3.5. Alkene epoxidation with NaIO₄ catalyzed by Mn(Br₈TPP)Cl-Silm and [Mn(TPP)Cl-Silm] under ultrasonic irradiation

The main effect of ultrasonic irradiation in liquids is a cavitation phenomenon, which is accompanied by a few extreme

effects, such as a local increase in temperature, a local high pressure, the propagation of oxidation catalysts, and the formation of intense liquid microflows [58]. These effects may enhance liquid–solid mass transfer and cause physicochemical change in the processed medium considerably [59,60]. On the other hand, ultrasonic irradiation can also be used to influence selectivity and yields of reactions. These features prompted us to explore the effect of ultrasonic waves on this catalytic system. Therefore, all reactions were exposed to ultrasonic irradiation. The obtained results are summarized in Tables 3 and 4. These results clearly showed that the reaction times reduced and the TOFs increased in the system under US irradiation. In the alkene epoxidation with NaIO₄ in the presence of Mn(Br₈TPP)Cl-Silm and [Mn(TPP)Cl-Silm] cyclooctene was epoxidized in 100% yield with 100% selectivity, but the reaction time decreased to 15 min. The yields in the case of linear alkenes increased. In the epoxidation of *trans*-stilbene in the presence of Mn(Br₈TPP)Cl-Silm, the yields increased to 57%, while in the case of *cis*-stilbene, the *cis/trans* ratio increased from 1.26 to 4 under ultrasonic irradiation. In the epoxidation of *cis*-stilbene catalyzed by [Mn(TPP)Cl-Silm], the *cis/trans* ratio changed from 2.5 to 2 for system under ultrasonic irradiation.

The effect of irradiation intensity on the epoxidation of cyclooctene was also investigated.

Fig. 2 shows a comparison between systems under ultrasonic irradiation and under agitation with magnetic stirring, which indicates the effect of ultrasonic irradiation on the catalytic activity.

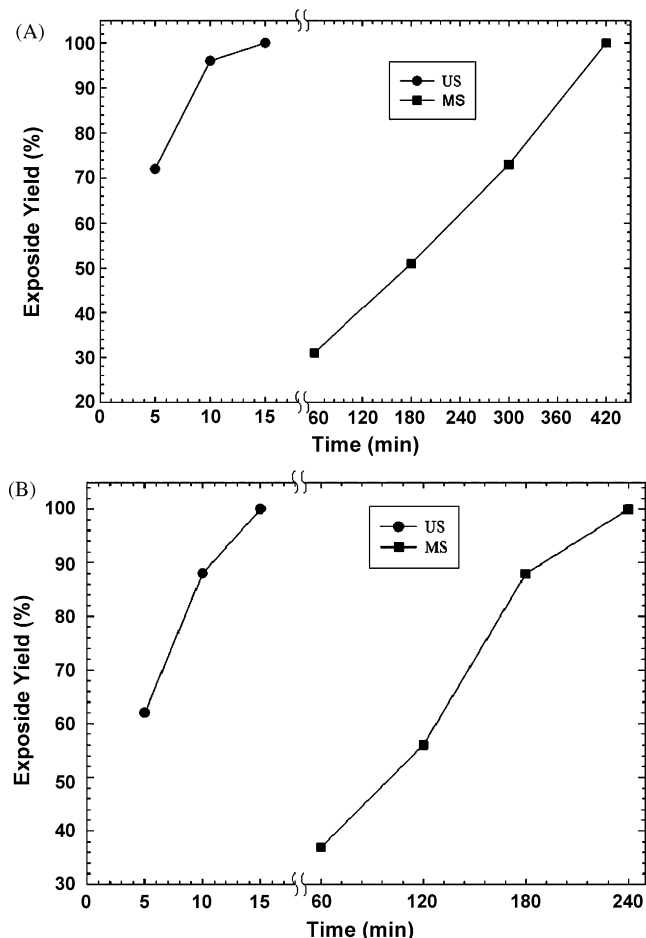


Fig. 2. Comparison of ultrasonic irradiation and magnetic agitation in the epoxidation of cyclooctene with NaIO_4 catalyzed by (A) $\text{Mn}(\text{Br}_8\text{TPP})\text{Cl-Silm}$ and (B) $\text{Mn}(\text{TPP})\text{Cl-Silm}$.

In order to show the effect of ultrasonic irradiation on the catalytic activity enhancement, the particle size distribution of the catalysts was determined before and after sonication. The results of $\text{Mn}(\text{TPP})\text{Cl-Silm}$ showed (Fig. 3) that the catalyst agglomerates break-up during the sonication process. It seems that a part of ultrasonic irradiation effect is due to this phenomenon. To stress this point, the catalytic activity of a sonicated sample catalyst was studied in the epoxidation of cyclooctene under conventional mechanical stirring. It was found that the reaction time reduced from 4 to 3 h for complete conversion of cyclooctene to its corresponding epoxide. These results show that in addition to break-up of the agglomerates, other factors such as thorough mixing of the reactants and producing of hot spots are the main reasons for catalytic enhancement by ultrasonic irradiation. On the other hand, when the epoxidation reactions were carried out under reflux conditions, the reaction times decreased, which confirms the effect of producing the hot spots on the enhancement of catalytic activity.

The blank experiment in the absence of catalysts under ultrasonic irradiation showed that the ultrasonic irradiation is much less efficient in the oxidation reactions with NaIO_4 .

3.6. Alkane hydroxylation with NaIO_4 catalyzed by $\text{Mn}(\text{Br}_8\text{TPP})\text{Cl-Silm}$ and $\text{Mn}(\text{TPP})\text{Cl-Silm}$ under mechanical stirring

Direct oxidation of hydrocarbons is also one of the typical reactions of cytochrome P-450 [61]. Therefore, the ability of

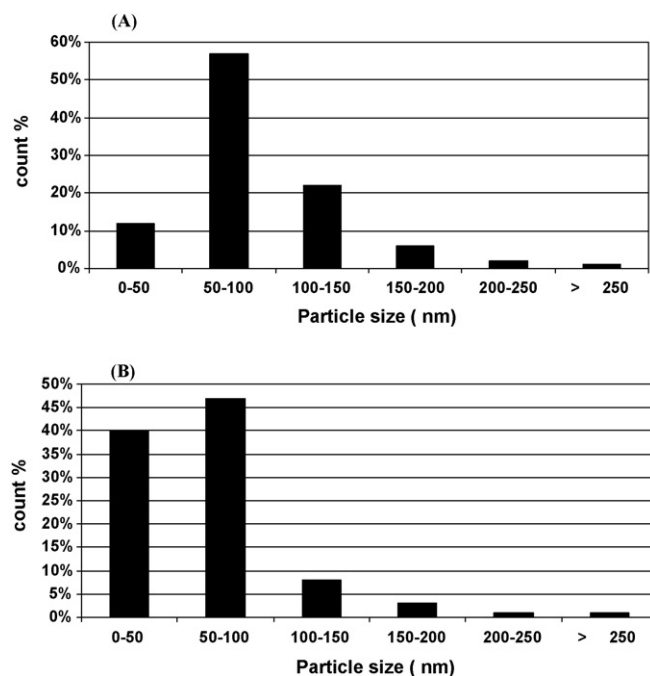


Fig. 3. The particle size distribution of (A) $\text{Mn}(\text{TPP})\text{Cl-Silm}$ before sonication and (B) $\text{Mn}(\text{TPP})\text{Cl-Silm}$ in the epoxidation of cyclooctene under ultrasonic irradiation.

these catalytic systems in the alkane hydroxylation with NaIO_4 catalyzed by $[\text{Mn}(\text{Br}_8\text{TPP})\text{Cl-Silm}]$ and $[\text{Mn}(\text{Br}_8\text{TPP})\text{Cl-Silm}]$ was investigated. In both catalytic systems, cyclooctane, cyclohexane, and 1,2,3,4-tetrahydronaphthalene were converted to their corresponding alcohols and ketones. In the case of $[\text{Mn}(\text{Br}_8\text{TPP})\text{Cl-Silm}]$, the alcohol/ketone ratio were 2.11, 2.33, and 0.86 for cyclooctane, cyclohexane, and 1,2,3,4-tetrahydronaphthalene, respectively.


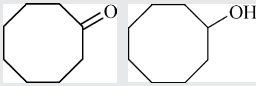

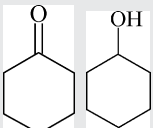
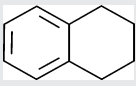
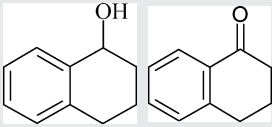
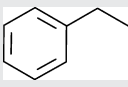
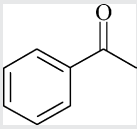

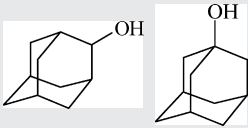
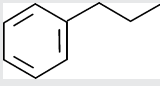
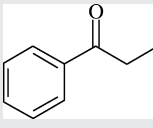
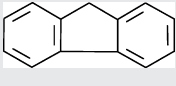
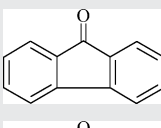
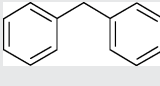
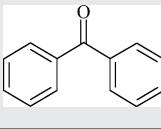
In the $[\text{Mn}(\text{TPP})\text{Cl-Silm}]/\text{NaIO}_4$ catalytic system, the alcohol/ketone ratio were 1.08, 4.00, and 1.00 for cyclooctane, cyclohexane, and 1,2,3,4-tetrahydronaphthalene, respectively. Note that in the case of 1,2,3,4-tetrahydronaphthalene only the α -position was oxidized. In both catalytic systems ethylbenzene, propylbenzene, diphenylmethane and fluorene only were oxidized to their corresponding ketones. Oxidation of adamantane produced a mixture of 1-adamantanol/2-adamantanol in 5.5:1 and 4.5:1 ratio for $[\text{Mn}(\text{Br}_8\text{TPP})\text{Cl-Silm}]$ and $[\text{Mn}(\text{TPP})\text{Cl-Silm}]$, respectively (Tables 5 and 6).

Comparison of the data for $[\text{Mn}(\text{TPP})\text{Cl-Silm}]$ with $[\text{Mn}(\text{Br}_8\text{TPP})\text{Cl-Silm}]$ in alkane hydroxylation showed that the hydroxylation yields for bulky substrate such as cyclooctane, diphenylmethane and fluorene were higher in the case of unsubstituted catalyst. This effect can be attributed to the bulky substituted bromines on the porphyrin ring.

3.7. Alkane hydroxylation with NaIO_4 catalyzed by $[\text{Mn}(\text{TPP})\text{Cl-Silm}]$ and $[\text{Mn}(\text{Br}_8\text{TPP})\text{Cl-Silm}]$ under ultrasonic irradiation

A mixture of alkane, NaIO_4 , and catalyst was exposed to ultrasonic waves to investigate the effect of ultrasonic irradiation on the catalytic activity of $[\text{Mn}(\text{TPP})\text{Cl-Silm}]$ and $[\text{Mn}(\text{Br}_8\text{TPP})\text{Cl-Silm}]$ in the alkane hydroxylation. The products from all alkanes were the same as for the system under agitation with magnetic stirring. But the reaction times were reduced and the product yields were increased in all cases.

Table 5
Hydroxylation of alkanes with NaIO₄ catalyzed by Mn(Br₈TPP)Cl-Silm under agitation with magnetic stirring (MS) and under ultrasonic irradiation (US)^a

Entry	Alkane	Product	Conversion (%) ^b		Ketone (%) ^b		Alcohol (%) ^b		Time (h)	
			MS	US	MS	US	MS	US	MS	US
1			84	93	27	32	57	61	10	0.5
2			100	100	30	18	70	82	10	0.5
3			69	86	37	31	32	55	10	1
4			68	93	68	93	–	–	10	1
5			88	92	–	–	88 ^c	92 ^c	10	1
6			45	87	45	87	–	–	10	1
7			70	71	70	71	–	–	10	1
8			30	68	30	68	–	–	10	1

^a Reaction conditions: alkane (1 mmol), NaIO₄ (2 mmol), catalyst (0.03 mmol), CH₃CN/H₂O (10 ml/10 ml).

^b GLC yield based on starting alkane.

^c The products are 72% 1-ol and 16% 2-ol for magnetic stirring (MS) and 69% 1-ol and 23% 2-ol for ultrasonic irradiation (US).

In the case of [Mn(TPP)Cl-Silm], the alcohol/ketone ratio increased from 4.00 to 7.33 and 1.00 to 1.59 for cyclohexane and 1,2,3,4-tetrahydronaphthalene, respectively. In the case of adamantane, the 1-adamantanol/2-adamantanol ratio decreased to 2.92.

In the presence of [Mn(Br₈TPP)Cl-Silm], the alcohol/ketone ratio increased from 2.33 to 4.55 and 0.86 to 1.77 for cyclohexane and 1,2,3,4-tetrahydronaphthalene, respectively. In the case of adamantane, the 1-adamantanol/2-adamantanol ratio decreased to 3.

3.8. Catalyst reuse and stability


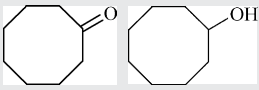

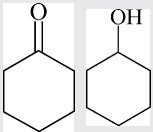
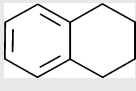
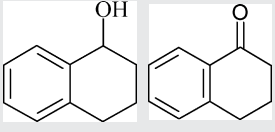
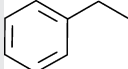
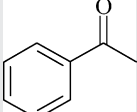

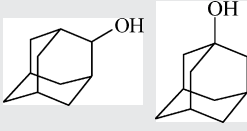
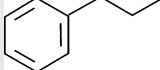
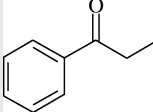
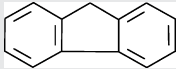
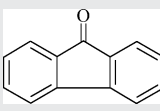
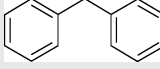
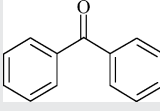
The catalysts reuse and stability were checked using multiple sequential epoxidation of cyclooctene with NaIO₄ under agitation with magnetic stirring or under ultrasonic irradiation. The catalysts were separated from the reaction mixture after each experiment by simple filtration, washed with methanol and dried carefully before using it in the subsequent run.

[Mn(Br₈TPP)Cl-Silm] could be reused for seven consecutive runs and the epoxide yields were 94% and 96% for systems under agitation with magnetic stirring and under ultrasonic irradiation, respectively (Table 7).

[Mn(TPP)Cl-Silm] was reused for four consecutive runs, the epoxide yields were 94% and 95% for systems under agitation with magnetic stirring or under ultrasonic irradiation, respectively. For both catalysts, the filtrates were collected for determination of the Mn leached out. After the first run, no manganese was detected in the filtrates by atomic absorption spectrometry (Table 8). The nature of the recovered catalysts has been followed by IR. The results indicated that the catalysts after reusing several times showed no change in their IR spectra.

It is clear that introduction of electron-withdrawing substituents increases the catalyst robustness toward destruction and that the catalytic activity may decrease. These are in accordance with a comparison of the data obtained in the oxidation reactions by [Mn(Br₈TPP)Cl-Silm] and [Mn(TPP)Cl-Silm]. In the case

Table 6Hydroxylation of alkanes with NaIO₄ catalyzed by Mn(TPP)Cl-Silm under agitation with magnetic stirring (MS) and under ultrasonic irradiation (US)^a

Entry	Alkane	Product	Conversion (%) ^b		Ketone (%) ^b		Alcohol (%) ^b		Time (h)	
			MS	US	MS	US	MS	US	MS	US
1			100	99	48	53	52	46	6	0.25
2			100	100	20	12	80	88	3.5	0.25
3			74	88	37	34	37	54	6	0.5
4			63	100	63	100	–	–	6	0.5
5			85	98	–	–	85 ^c	98 ^c	6	0.6
6			50	100	50	100	–	–	6	0.75
7			76	84	76	84	–	–	6	0.75
8			57	76	57	76	–	–	6	0.75

^a Reaction conditions: alkane (1 mmol), NaIO₄ (2 mmol), catalyst (0.03 mmol), CH₃CN/H₂O (10 ml/10 ml).^b GLC yield based on starting alkane.^c The products are 72% 1-ol and 13% 2-ol for magnetic stirring (MS) and 73% 1-ol and 25% 2-ol for ultrasonic irradiation (US).

of [Mn(Br₈TPP)Cl-Silm] the TOFs has been decreased, but the catalyst robustness has been increased and the catalyst can be reused seven times while [Mn(TPP)Cl-Silm] could be reused four times.

Table 7The results of [Mn(Br₈TPP)Cl-Silm] catalyst recovery and the manganese leached in the epoxidation of cyclooctene with NaIO₄ with magnetic stirring and under ultrasonic irradiation

Run	Conversion (%) ^a		Epoxide yield (%) ^a		Mn leached (%) ^b	
	MS	US	MS	US	MS	US
1	100	100	100	100	1	1.5
2	98	99	98	99	0	0
3	96	97	96	97	0	0
4	95	97	95	97	0	0
5	95	97	95	97	0	0
6	95	96	95	96	0	0
7	94	96	94	96	0	0

^a GLC yield based on starting alkene.^b Determined by atomic absorption spectroscopy.**Table 8**The results of [Mn(TPP)Cl-Silm] catalyst recovery and the manganese leached in the epoxidation of cyclooctene with NaIO₄ with magnetic stirring and under ultrasonic irradiation

Run	Conversion (%) ^a		Epoxide yield (%) ^a		Mn leached (%) ^b	
	MS	US	MS	US	MS	US
1	100	100	100	100	1.5	1.7
2	98	99	98	99	0	0
3	96	97	96	97	0	0
4	94	95	94	95	0	0

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

4. Conclusion

In conclusion, the [Mn(Br₈TPP)Cl-Silm] and [Mn(TPP)Cl-Silm] catalysts have been used as highly active and heterogeneous biomimetic oxidation catalysts. The catalysts could be recovered and reused by simple filtration. In the case of [Mn(Br₈TPP)Cl-Silm],

the catalyst stability and robustness increased by introduction of electron-withdrawing substituents on the porphyrin rings. The irradiation of ultrasonic waves increased the performance of the catalysts.

Acknowledgements

We are thankful to the Center of Excellence of Chemistry of University of Isfahan (CECU) for financial support of this work.

References

- [1] M.C. Feiters, A.E. Rowan, R.J.M. Nolte, *Chem. Soc. Rev.* 29 (2000) 375.
- [2] R.A. Sheldon, in: B. Meunier (Ed.), *Biomimetic Oxidations Catalyzed by Transition Metal Complexes*, Imperial College Press, London, 2000.
- [3] B. Meunier, *Chem. Rev.* 92 (1992) 1411.
- [4] D. Mansuy, P. Battioni, J.P. Battioni, *Eur. J. Biochem.* 184 (1989) 267.
- [5] D. Mansuy, *Pure Appl. Chem.* 59 (1987) 759.
- [6] J.R. Lindsay-Smith, in: R.A. Sheldon (Ed.), *Metalloporphyrins in Catalytic Oxidations*, Marcel Dekker, New York, 1994, p. 325 (Chapter 11).
- [7] D. Mansuy, *Coord. Chem. Rev.* 125 (1993) 129.
- [8] B.A. Arndtsen, R.G. Bergman, T.A. Mobley, T.H. Peterson, *Acc. Chem. Res.* 28 (1995) 154.
- [9] M.J. Coon, R.E. White, in: T.G. Spiro (Ed.), *Dioxygen Binding and Activation by Metal Centers*, Wiley, New York, 1980.
- [10] J.T. Groves, T.E. Nemo, *J. Am. Chem. Soc.* 105 (1983) 5786.
- [11] O. Bortolini, B. Meunier, *J. Chem. Soc., Perkin Trans. 2* (1984) 1967.
- [12] B. Meunier, E. Guilmet, M.E. De Carvalho, R. Poilblanc, *J. Am. Chem. Soc.* 106 (1984) 6668.
- [13] D. Mohajer, S. Tangestaninejad, *J. Chem. Soc., Chem. Commun.* (1993) 240.
- [14] D. Mohajer, S. Tangestaninejad, *Tetrahedron Lett.* 35 (1994) 945.
- [15] C.K. Chang, T.G. Traylor, *Proc. Natl. Acad. Sci. U.S.A.* 70 (1973) 2647.
- [16] J.P. Collman, C.A. Reed, *J. Am. Chem. Soc.* 97 (1973) 2132.
- [17] O. Leal, D.L. Anderson, R.C. Bowman, F. Basalo, R.L. Burwell, *J. Am. Chem. Soc.* 97 (1975) 5125.
- [18] L.D. Rollman, *J. Am. Chem. Soc.* 97 (1975) 2132.
- [19] J.H. Wang, *Acc. Chem. Res.* 3 (1970) 90.
- [20] M. Nakamura, T. Tatsumi, H. Tominaga, *Bull. Chem. Soc. Jpn.* 63 (1990) 3334.
- [21] T. Tatsumi, M. Nakamura, H. Tominaga, *Chem. Lett.* (1989) 419.
- [22] W. Nam, H.J. Han, S.Y. Oh, Y.J. Lee, M.H. Choi, S.Y. Han, C. Kim, S.K. Woo, W. Shin, *J. Am. Chem. Soc.* 122 (2000) 8677.
- [23] R. Naik, P. Joshi, S. Umbarkar, R.K. Deshpande, *Catal. Commun.* 6 (2005) 125.
- [24] F.S. Vinhadó, P.R. Martins, A.P. Masson, D.G. Abreu, E.A. Vidoto, O.R. Nascimento, Y. Iamamoto, *J. Mol. Catal. A: Chem.* 188 (2002) 141.
- [25] P.R. Cooke, J.R. Lindsay Smith, *Tetrahedron Lett.* 33 (1992) 2737.
- [26] P.R. Cooke, J.R. Lindsay Smith, *J. Chem. Soc., Perkin Trans. 1* (1994) 1913.
- [27] C. Gilmartin, J.R. Lindsay Smith, *J. Chem. Soc., Perkin Trans. 2* (1995) 243.
- [28] H.C. Sacco, Y. Iamamoto, J.R. Lindsay Smith, *J. Chem. Soc., Perkin Trans. 2* (2001) 181.
- [29] C.M.C. Prado-Manso, E.A. Vidoto, F.S. Vinhadó, H.C. Sacco, K.J. Ciuf, P.R. Martins, A.G. Ferreira, J.R. Lindsay Smith, O.R. Nascimento, Y. Iamamoto, *J. Mol. Catal. A: Chem.* 150 (1999) 251.
- [30] Z. Li, C.-G. Xia, X.-M. Zhang, *J. Mol. Catal. A: Chem.* 185 (2002) 47.
- [31] J. Poltowicz, E.M. Serwicka, E. Bastardo-Gonzalez, W. Jones, R. Mokaya, *Appl. Catal. A* 218 (2001) 211.
- [32] M.A. Schiavon, Y. Iamamoto, O.R. Nascimento, M.D. Assis, *J. Mol. Catal. A: Chem.* 174 (2001) 213.
- [33] F.G. Doro, J.R. Lindsay Smith, A.G. Ferreira, M.D. Assis, *J. Mol. Catal. A: Chem.* 164 (2000) 97.
- [34] M.A. Martínez-Lorente, P. Battioni, W. Kleemiss, J.F. Bartoli, D. Mansuy, *J. Mol. Catal. A: Chem.* 113 (1996) 343.
- [35] P. Battioni, O. Brigaud, H. Desvaux, D. Mansuy, T.G. Traylor, *Tetrahedron Lett.* 32 (1991) 2893.
- [36] T.G. Traylor, Y.S. Byun, P.S. Traylor, P. Battioni, D. Mansuy, *J. Am. Chem. Soc.* 113 (1991) 7821.
- [37] M. Benaglia, T. Danelli, G. Pozzi, *Org. Biomol. Chem.* 1 (2003) 454.
- [38] G.R. Geier III, T. Sasaki, *Tetrahedron* 55 (1999) 1859.
- [39] G.R. Geier III, T.P. Lybrand, T. Sasaki, *Tetrahedron* 55 (1999) 1871.
- [40] E. Brule, K.K. Hii, Y.R. de Miguel, *Org. Biomol. Chem.* 3 (2005) 1971.
- [41] E. Brule, Y.R. de Miguel, K.K. Hii, *Tetrahedron* 60 (2004) 5913.
- [42] R. Zhang, W.-Y. Yu, H.-Z. Sun, W.-S. Liu, C.-M. Che, *Chem. Eur. J.* 8 (2002) 2495.
- [43] X.-Q. Yu, J.-S. Huang, W.-Y. Yu, C.-M. Che, *J. Am. Chem. Soc.* 122 (2000) 5337.
- [44] J.-L. Zhang, C.-M. Che, *Org. Lett.* 4 (2002) 1911.
- [45] S. Tangestaninejad, V. Mirkhani, *J. Chem. Res. (S)* (1998) 788.
- [46] S. Tangestaninejad, M. Moghadam, *J. Chem. Res. (S)* (1998) 242.
- [47] S. Tangestaninejad, M. Moghadam, *Synth. Commun.* 28 (1998) 427.
- [48] S. Tangestaninejad, M.H. Habibi, V. Mirkhani, M. Moghadam, *J. Chem. Res. (S)* (2001) 444.
- [49] M. Moghadam, S. Tangestaninejad, M.H. Habibi, V. Mirkhani, *J. Mol. Catal. A: Chem.* 217 (2004) 9.
- [50] M. Moghadam, S. Tangestaninejad, V. Mirkhani, H. Kargar, H. Komeili-Isfahani, *Catal. Commun.* 6 (2005) 688.
- [51] S. Tangestaninejad, M.H. Habibi, V. Mirkhani, M. Moghadam, *Molecules* 7 (2002) 264.
- [52] S. Tangestaninejad, V. Mirkhani, *Chem. Lett.* 12 (1998) 1265.
- [53] V. Mirkhani, S. Tangestaninejad, M. Moghadam, B. Yadollahi, *J. Chem. Res. (S)* (2000) 515.
- [54] S. Tangestaninejad, M. Moghadam, V. Mirkhani, H. Kargar, *Ultrason. Sonochem.* 10 (2006) 32.
- [55] A.D. Adler, F.R. Long, J.D. Finarelli, J. Goldmacher, J. Assour, L. Korsakoff, *J. Org. Chem.* 32 (1967) 476.
- [56] A.D. Adler, F.R. Long, F. Kampas, J. Kim, *J. Inorg. Nucl. Chem.* 32 (1970) 2443.
- [57] P. Bhyrappa, V. Krishnan, *Inorg. Chem.* 30 (1991) 239.
- [58] K.S. Suslick, *Annu. Rev. Mater. Sci.* 29 (1999) 295.
- [59] M. Margulis, *Sonochemistry and Cavitation*, Gordon and Breach, New York, 1995.
- [60] M. Run, S. Wu, G. Wu, *Micropor. Mesopor. Mater.* 74 (2004) 37.
- [61] R. Ortiz de Montellano, *Cytochrome P-450, Structure, Mechanism and Biochemistry*, 2nd ed., Plenum Press, New York, 1995.