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Ultrasound promoted preparation of Mn(III)-porphyrin nanoparticles: An efficient heterogeneous catalyst for oxidation of alkenes, alkanes and sulfides

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ABSTRACT: In the present research *meso*-tetrakis(4-carboxyphenyl)porphyrinatomanganese(III) acetate (Mn(TCPP)OAc) nanoparticles have been prepared for the first time without any stabilizing agent or supporting matrix under ultrasonic irradiation. Scanning electron microscopy (SEM) was used to characterize and investigate the nanocatalyst. Rapid, efficient, facile and highly selective oxidation of a wide range of olefins by tetra-*n*-butylammonium hydrogen monopersulfate over the prepared manganese nanocatalyst was investigated. Also oxidation of sulfides and alkanes in the presence of the (Mn(TCPP)OAc) nanoparticles were studied. The catalyst is recovered by filtration and reused at least five times.

KEYWORDS: ultrasonic irradiation, oxidation, heterogeneous nanocatalyst, manganese porphyrin, nanoparticles.

INTRODUCTION

Inorganic nanoparticles with various capping groups or supported on mesoporous materials, polymers or carbon nanotubes are widely used as catalyst and many publications have been reported in the literature [1–7].

Synthetic metalloporphyrin complexes which are introduced to be as model of cytochrome P-450 enzyme have been used as homogeneous catalysts in oxidation reactions [8–12], but their high cost and difficult recovery from the reaction medium limited their use especially in industrial processes. Immobilization onto solid supports is a good strategy to overcome this problem [13–19]. On the other hand, the properties of nanoscaled particles are different from those of bulk materials composed of the same atoms or molecules. Gong and co-workers have reported the synthesis and characterization of porphyrin colloidal nanoparticles for the first time [20] and then production of porphyrin based nanoparticles using different stabilizers such as (polyethylene)glycol(PEG) has been reported by Drain [21]. They have investigated the effect of particle size on the catalytic activity and selectivity in the oxidation reactions, while they could not study the reusability of the catalyst [22–24].

In our present research, in order to overcome to this problem, we have used ultrasonic irradiation for production of Mn-porphyrin nanoparticles (Mn(TCPP)OAc) by a simple, rapid and cheap method without any supporting matrix. The prepared nanocatalyst has been used in oxidation of various alkenes, alkanes and sulfides with tetra-*n*-butylammonium hydrogen monopersulfate (TBAO).

RESULTS AND DISCUSSION

Characterization of the bulk and nano complexes by scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) was used for comparison of Mn(TCPP)OAc-nano and bulk complexes (Fig. 1). The results show that nanoparticles were well-distributed and the average particle size was from 30 to 60 nm for Mn(TCPP)OAc-nano (Fig. 2). These data confirms that sonication causes a significant decrease in the particle size. On the other hand, sonication may limited

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[◊] SPP full member in good standing

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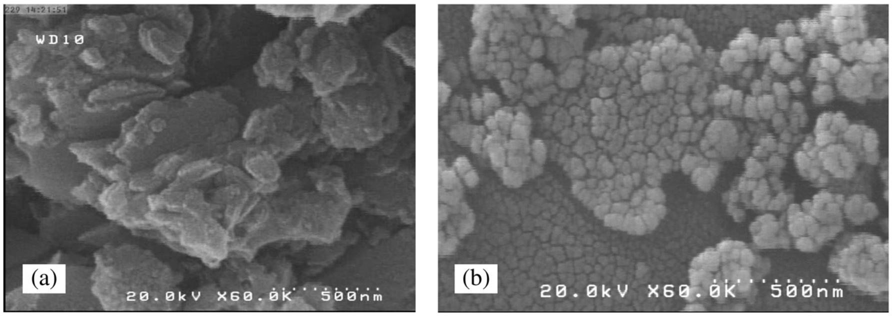


Fig. 1. The SEM images of (a) bulk, (b) nano-Mn(TCPP)OAc

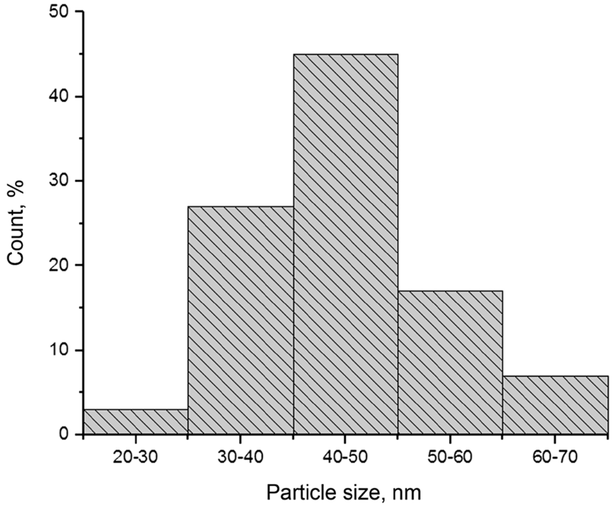


Fig. 2. The particle size distribution for Mn(TCPP)OAc nanoparticles

Table 1. Experiments on catalytic oxidation of cyclooctene[a]

Entry	Catalyst	Conversion, %	
		2 min	20 min
1	none	0	0
2	MnTCPP-bulk	11	33
3	MnTCPP-nano	18	65

[a] The molar ratio of the catalyst:ImH:cyclooctene:TBAO is: 1:30:70:70.

the tendency of Mn(TCPP)OAc molecules for aggregation which can definitely control Mn(TCPP)OAc particle size.

Heterogeneous catalytic epoxidation of olefins

The catalytic performance of Mn(TCPP)OAc was investigated in the epoxidation of olefins with TBAO at room temperature. Blank experiment shows that the existence of a catalyst is essential for oxidation reaction. Also catalytic efficiency of the nano-sized catalysts is considerably more than bulk ones (Table 1).

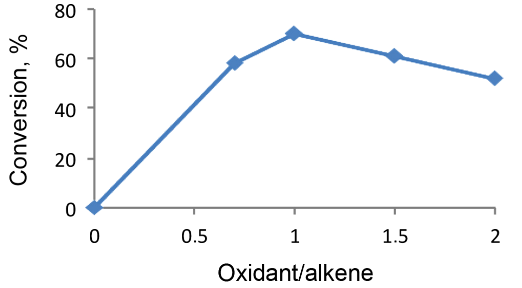


Fig. 3. The influence of the molar ratio of oxidant/alkene on the oxidation of cyclooctene. The molar ratio of Mn(TCPP)OAc-nano:ImH:cyclooctene:TBAO is 1:50:70:X. Time: 20 min

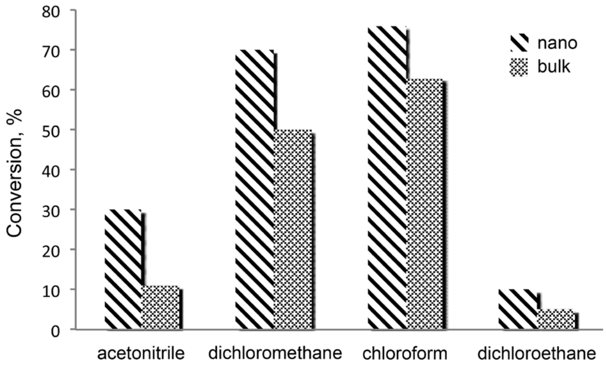
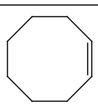
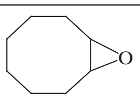
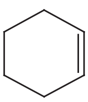
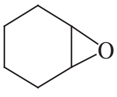
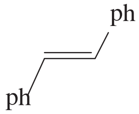
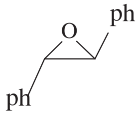
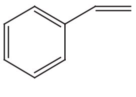
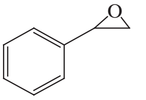
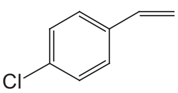
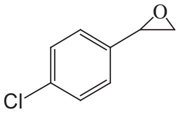
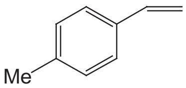
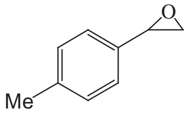
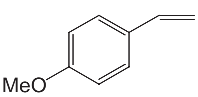
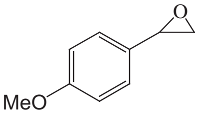
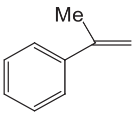
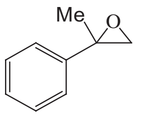
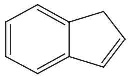
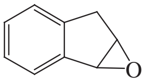
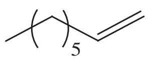
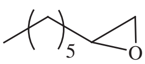


Fig. 4. The effect of solventon catalytic oxidation of cyclooctene with TBAO. The molar ratio of Mn(TCPP)OAc:ImH:alkene:TBAO is 1:50:70:70. Reaction time: 20 min

The effect of ultrasound irradiation on the particle size of Mn(TCPP)OAc confirmed by SEM (Fig. 1) and also the effect of particle size on the catalytic activity of Mn(TCPP)OAc investigated and presented in Table 1.

In order to find the suitable reaction conditions, the effect of different parameters that may affect the conversion of the reaction were studied. The molar ratio of the ImH/catalyst and oxidant/alkene and solvent are the factors that have been evaluated. The ImH/catalyst

Table 2. Epoxidation of olefins using TBAO catalyzed by Mn(TCPP)OAc in CH_2Cl_2[a]

Entry	Alkene	Product	Conversion (selectivity), %	
			Nano	Bulk
1			70 (100)	50 (100)
2			18 (100)	4 (100)
3			25 (93)	6 (70)
4			100 (100)	29 (100)
5			94 (100)	28 (100)
6			98 (85)	75 (86)
7			100 (100)	55 (100)
8			100 (64)	68 (50)
9			96 (100)	70 (100)
10			4 (100)	0

[a] The molar ratio of catalyst:ImH:Alkene:TBAO is 1:50:70:70. Reaction time: 20 min.

molar ratio is an important parameter that may affect the conversion of the reaction especially in the presence of Mn-porphyrins. In the absence of imidazole no significant product was observed. Higher conversions were obtained by increasing the amount of imidazole and the highest conversion was obtained in 1:50 Cat./ImH molar ratio. In order to investigate the effect of oxidizing agent in the oxidation of cyclooctene, different oxidant/alkene molar ratios were examined (Fig. 3). The highest conversion was obtained in 1:1 oxidant/alkene molar ratio. Lower conversion in higher molar ratios may be due to the catalyst degradation.

The influence of different solvents on the oxidation of cyclooctene was studied using Mn(TCPP)OAc-bulk and Mn(TCPP) OAc-nano as catalyst. The results which are presented in Fig. 4 show higher conversions for dichloromethane and chloroform while the oxidation reaction in dichloromethane shows the highest difference between bulk and nano complexes.

In order to establish the general applicability of this catalytic system, and also to determine the importance of particle size in the catalytic activity of Mn(TCPP)OAc, under the optimized conditions, different olefins were subjected to oxidation in the presence of the catalytic amount of Mn(TCPP)OAc (nano and bulk) with TBAO (Table 2). Cyclooctene, cyclohexene, 1-octene, *trans*-stilbene, styrene, indene, 4-chlorostyrene and 4-methoxystyrene converted to the related epoxide as the sole product. Nevertheless, in the oxidation of 4-methylstyrene and α-methylstyrene, some related benzaldehyde was obtained as by product.

Heterogeneous oxidation of alkanes

Oxidation of saturated hydrocarbons using Mn(TCPP)OAc/TBAO/ImH catalytic system has been studied (Table 3). However the product yield is not high, but comparison of the obtained conversion in Table 3, clearly demonstrate the effect of particle size on catalytic activity.

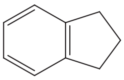
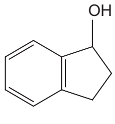
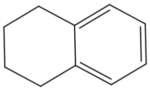
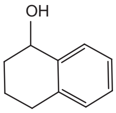
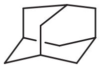
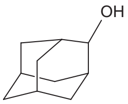
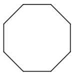
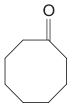
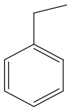
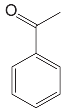
Heterogeneous oxidation of sulfides

In order to show the significance of particle size in the catalytic activity of Mn(TCPP)OAc on the oxidation of different substrate, oxidation of various sulfides with TBAO in the presence of Mn(TCPP)OAc nano and bulk complexes was investigated and the results are presented in Table 4.

Homogeneous epoxidation of cyclooctene

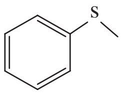
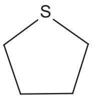
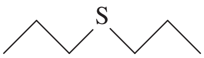
Homogeneous catalytic epoxidation of cyclooctene with TBAO in methanol led to only 38% conversion of cyclooctene to its corresponding epoxide. This may be due to the aggregation [27, 28] between Mn(TCPP)OAc molecules.

Table 3. Oxidation of alkanes using TBAO catalyzed by Mn(TCPP)OAc in dichloromethane[a]

Entry	Alkane	Product	Conversion (selectivity), %	
			Bulk	Nano
1			13 (83)	38 (95)
2			23 (100)	36 (100)
3			6 (80)	11 (62)
4			2 (100)	8 (100)
5			2 (100)	6 (55)

[a] The molar ratio of catalyst:ImH:Alkane:TBAO is 1:50:35:70. Reaction time: 20 min.

Table 4. Oxidation of various sulfides with TBAO catalyzed by Mn(TCPP)OAc

Entry	Sulfide	Conversion (selectivity to sulfoxide), %[a]	
		Bulk	Nano
1		52 (100)	71 (76)
2[b]		68 (88)	82 (90)
3[b]		83 (75)	96 (59)
4		49 (100)	61 (82)

[a] The molar ratio of catalyst:ImH:Alkene:TBAO is 1:50:70:70 based on 0.0015 mmol of catalyst. Reaction time: 2 min. [b] Temperature: 0 °C.

Catalyst reuse and stability

The reusability of a heterogeneous catalyst is significant in the catalytic systems. The homogeneous Mn(TCPP)OAc cannot be recovered even once while the heterogeneous Mn(TCPP)OAc nano particles can be separated easily and reused multiple times. For each of the repeated reactions, after the completion of the reaction, the solid catalyst was separated by centrifugation for 15 min, washed with dichloromethane (3 × 2 mL) and dried at 80 °C for 20 h and irradiated with ultrasonic waves for 40 min in dichloromethane and used for next run. The MnTCPP-nano was consecutively reused five times (Fig. 5). 40% conversion was obtained after five catalytic cycles which is valuable result especially in the presence of heterogeneous catalyst without any supporting matrix. A decrease in the conversion of cyclooctene after five times may be due to the catalyst degradation.

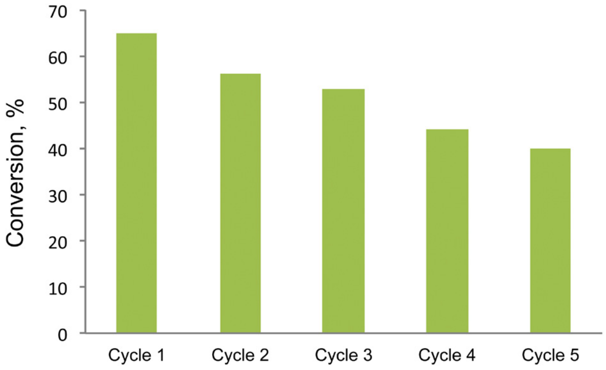


Fig. 5. Recycling of the catalytic system for the epoxidation of cyclooctene with TBAO by Mn(TCPP)OAc-nano complex. The molar ratio of Catalyst:ImH:Cyclooctene:TBAO is 1:30:70:70. Reaction time: 20 min

Comparison of this catalytic system with previously reported systems shows that the reaction conditions are much easier and this catalytic system is cheaper with respect to the heterogeneous catalysts with various capping groups or imbedded into polymers or other matrix [7, 14, 16].

Proposed mechanism

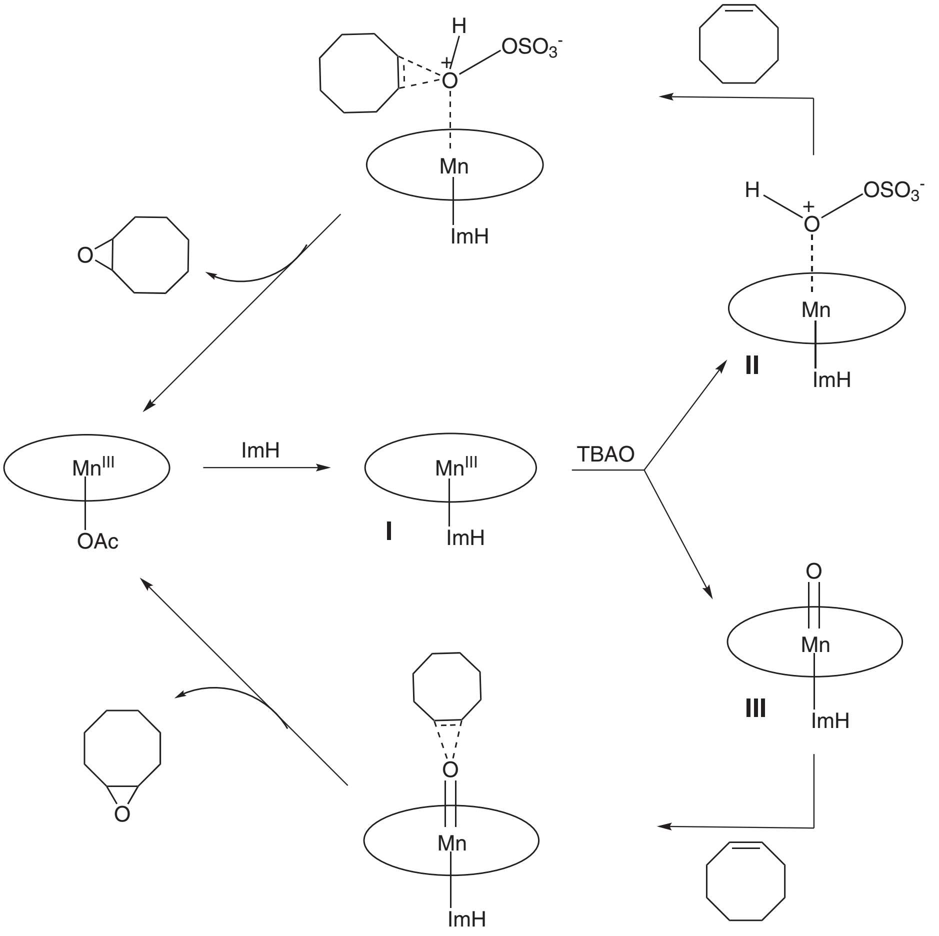
Although the difference in the catalytic activity of MnTCPP(OAc)-nano and bulk for oxidation of various substrate is completely clear, but the oxidation reactions show no significant differences in the selectivity of products (Tables 2, 3 and 4), which may be related to the same mechanism for both nano and bulk catalysts.

In the proposed catalytic cycle, TBAO will be activated by coordination to the Mn-center (Scheme 1, **I**) [29, 30]. It seems that a six coordinate species (Scheme 1, **II**) or a high-valent metal-oxo species (Scheme 1, **III**) as active oxidation species are responsible for an effective oxidation.

EXPERIMENTAL

Instruments and reagents

The reactions were irradiated with ultrasound 296 W (WUC-A03H, DAIHAN). Scanning electron microscopy



Scheme 1. Proposed mechanism for oxidation of cyclooctene

(SEM) images were obtained on a Hitachi S-1460 field emission scanning electron microscope using Acc voltage of 15 kV. The oxidation products were analyzed with a gas chromatograph (Shimadzu, GC-14B) equipped with a SAB-5 capillary column. ^{1}H NMR spectrum was obtained in dimethyl sulfoxide (DMSO) solutions with a Bruker FT-NMR 500 (500 MHz) spectrometer. The electronic absorption spectra were recorded on a single beam spectrophotometer (Cam Spec-M330) in DMF and CH_2Cl_2. Tetra-*n*-butylammonium hydrogen monopersulfate was prepared freshly according to the literature [25].

Synthesis

Preparation of the *meso*-tetrakis(4-carboxyphenyl) porphyrin (H_2TCPP). *Meso*-tetrakis(4-carboxyphenyl)-porphyrin was prepared and characterized by standard method [26]. Freshly distilled pyrrole (4.5 mmol) and terephthalaldehydic acid (4.5 mmol) were mixed in propionic acid (200 mL). The solution was refluxed for 2 h. Then the desired dark purple solution was cooled to room temperature and filtered to yield the purple crystals. The products were washed with warm water and methanol and finally dried in air. UV-vis (DMF): λ_{max}, nm 421, 515, 549, 592, 646. ^{1}H NMR (500 MHz; DMSO; Me_4Si): δ_H, ppm 8.69 (8H, br, β-pyrrole), 8.31–8.33 (8H, d, *o*-phenyl), 8.08–8.11 (8H, d, *m*-phenyl).

Preparation of the [Mn(TCPP)OAc]. The Mn(III)-porphyrincomplex was prepared according to the literature method [26]. In brief, H_2TCPP (0.3 mmol) and $Mn(OAc)_2.4H_2O$ (1.5 mmol) were added to 15 mL DMF and the reaction mixture was refluxed for 3 h. Then the solvent was evaporated under reduced pressure and the crude residue was washed with water and dried in air. UV-vis (DMF): λ_{max}, nm 477, 577, 609.

Preparation of the [Mn(TCPP)OAc] nanoparticles under ultrasonic irradiation. The Mn(TCPP)OAc (0.003 mmol or 0.0015 mmol for using in the catalytic experiment of hydrocarbon or sulfide respectively) was added to dichloromethane (1 mL) in a 5 mL test tube. The test tube was fixed in ultrasound batch and irradiated with ultrasonic waves for 40 min. Mn(TCPP)OAc is completely insoluble in dichloromethane and the suspension of Mn-porphyrins was observable during the irradiation. However because of the absence of any stabilizing agent, at the end of ultrasonic irradiation, Mn(TCPP)OAc quickly precipitated, while it is in nano scale. Mn(TCPP)OAc nanoparticles were used directly in the catalytic experiments. UV-vis spectra was used to checked and confirmed insolubility of Mn(TCPP)OAc in dichloromethane even after ultrasonic irradiation.

General heterogeneous oxidation procedure

General procedure for oxygenation of alkenes and alkanes. In a typical procedure for oxidation of alkenes or alkanes, substrate (0.21 mmol) and imidazole (0.15 mmol) were added to dichloromethane (1 mL) including Mn-porphyrin nanoparticles (0.003 mmol) and finally, freshly prepared TBAO (0.21 mmol or 0.42 mmol for alkenes or alkanes respectively) was added. The reaction mixture was stirred for 20 min at 25 °C. The resulting solution was directly analyzed by GC.

General procedure for oxygenation of sulfides. In a typical procedure for oxidation of sulfides, substrate (0.12 mmol) and imidazole (0.075 mmol) were added to a dichloromethane solution (3 mL) including Mn-porphyrin nanoparticles (0.0015 mmol) and finally, freshly prepared TBAO (0.11 mmol) was added. The reaction mixture was stirred for 2 min and was directly analyzed by GC.

CONCLUSION

In conclusion, use of this highly efficient catalytic system is a suitable path for biomimetic oxidation of alkenes, alkanes and sulfides with TBAO. Highly selective epoxidation of olefins such as cyclooctene, cyclohexene, 1-octene, indene and some substituted styrene were obtained. The use of ultrasonic irradiation conditions without any stabilizing agent to prepare heterogeneous nanocatalysts is of our interest. Finally, Mn(TCPP)OAc nanocatalyst is a reusable catalyst in oxidation reactions.

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