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[Mn(TPPS)] immobilized on ionic liquid-modified silica as a heterogeneous and reusable catalyst for epoxidation of alkenes with NaIO₄ under ultrasonic irradiation

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Abstract Effective epoxidation of alkenes using sodium periodate was accomplished with Manganese (III) tetrakis(*p*-sulfonatophenyl)porphyrin, [C₄₄H₂₆N₄O₁₂S₄Na₄], supported on ionic liquids-modified silica, Im-SiO₂, under ultrasonic irradiation conditions is reported. This heterogeneous catalyst, [Mn(TPPS)@SiO₂-Im] was characterized by elemental analysis, scanning electron microscopy (SEM), FT-IR and UV-Vis spectroscopic methods. The synthesized hybrid catalyst was applied for efficient epoxidation of various alkenes with sodium periodate in acetonitrile under ultrasonic irradiation conditions. This solid catalyst can be easily recovered by simple filtration and reused several time without apparent loss of its catalytic activity.

Keywords Immobilized ionic liquid · Sodium periodate · Epoxidation · [Mn(TPPS)] · Heterogeneous catalyst · Ultrasonic irradiation

Introduction

Over the past three decades, epoxidation of alkenes catalyzed by metalloporphyrins catalyst with oxygen donors has been extensively studied to mimic the cytochrome P-450 chemistry [1–3]. The main target in this domain is designing selective, stable, and high turnover catalytic systems [4]. Among the metalloporphyrins, manganese porphyrins

Robabeh Hajian rhajian@yazd.ac.ir have been potentially employed as good catalysts for epoxidation of alkenes [5-7]. It was establish that when metalloporphyrins were used as catalysts, organic compounds could be oxidized by oxygen donors such as iodosylarenes, hypochlorites, alkylhydroperoxides, hydrogen peroxide and periodates [8–12]. However, the cost of synthesis and recovery of homogeneous porphyrins are drawbacks of these catalysts. Moreover, the intermolecular self-aggregation due to $\pi - \pi$ stacking and the tendency to oxidation led to deactivation, destruction of metalloporphyrin in such systems. One of the best manners to overcome these problems is their immobilization on solid supports [13-15]. Therefore, immobilization of metalloporphyrins on solid supports can provide catalysts, which are easier to handle, and may demonstrate improved selectivities and activities due to the support environment. Among various methods employed to anchor metalloporphyrins to supports, the one based on making use of electrostatic interactions between an ionic metalloporphyrin and counterionic groups on the surface of the carrier is of particular attraction. The main advantage of such an approach is the existence of strong interactions preventing leaching of the active centres from the support and a simplicity of the catalyst preparation, which is based on ion exchange procedures [16, 17].

Ionic liquids typically consist of organic nitrogen-containing heterocylic cations and inorganic anions and are liquid at room temperature. Due to their unique physicochemical properties such as negligible vapor pressure, wide liquid temperature range, excellent thermodynamic stability, wide electrochemical window, tunable polarity and amphiphilicity, good solvent behavior for inorganic, organic and even polymeric materials, excellent designable space through the changing of components, and so on, they have found many applications in the fields of synthesis, catalysis and extraction to function as new media and liquid materials [18, 19].

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Scheme 1 Epoxidation of alkenes with NaIO₄ catalyzed by $[Mn(TPPS)@SiO_2-Im]$

Supported ionic liquid catalyst consists of immobilized catalytic species residing in an ionic liquid layer immobilized on a solid support. On the other hand, supported ionic liquid catalysis is a concept that combines the advantages of ionic liquids with those of heterogeneous catalysts [20]. Ionic liquids supported catalysts supply the hydrophobic environment for organic reactions. Immobilization or supporting of ionic liquids can be performed in many different manners, such as simple impregnation, grafting, polymerization sol-gel method, encapsulation or pore trapping, among others and dilution with molecular solvent [21-23]. Some supported ionic liquid metalloporphyrins have been reported in the literature [24-26]. Previously, we have reported the use of supported manganese (III) porphyrins in the oxidation of organic compounds with NaIO₄ [10, 27, 28]. In addition, we have explored an ionic liquids supported porphyrin by immobilisation of [Mn(TPPS)] on poly(4-styrylmethyl)pyridinium chloride (PSMP) [29]. Ultrasound had been prosperously utilized in the past to improve the selectivity as well as conversion of the desired product by increasing the rates of the reactions by manifolds [30–34]. It also delays catalyst deactivation [33].

Herein, the preparation and characterization of [Mn(TPPS)] supported on ionic liquid-modified SiO₂, $[Mn(TPPS)@SiO_2-Im]$, and its catalytic activity in the alkene epoxidation with NaIO₄ under ultrasonic irradiation conditions are reported (Scheme 1).

Experimental

Measurement and analysis

All chemicals were commercial reagent grade and obtained from Merck and Fluka. Manganese (III) tetrakis(*p*-sulfonatophenyl)porphyrin was prepared according to the literature [35]. The prepared catalyst was characterized by elemental analysis, scanning electron microscopy (SEM), FT-IR and UV–Vis spectroscopic methods. FT-IR spectra were obtained as potassium bromide pellets in the range 400–4000 cm⁻¹ with a Jasco Impact 6300D spectrometer. Scanning electron micrographs (SEM) of the catalyst and support were taken on a SEM Philips XL 20 instrument. UV–Vis spectra were obtained in rang 200–800 cm⁻¹ with a Jasco V-670 spectrometer. Powder X-ray diffraction patterns were obtained on a D₈ Advanced Bruker using Cu K_{α} radiation (2 θ = 5°-60°). 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 GC experiments, *n*-decane was used as internal standard. 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.

Preparation of ionic liquid-modified silica, SiO₂-Im

The 3-chloropropyl functionalized silica, SiO_2 , was used as purchased. To a suspension of SiO_2 (1 g) in CH₃CN (20 mL), was added *N*-methylimidazole (10 mmol) and stirred under refluxed condition for 48 h. After the reaction was completed, the SiO₂-Im was filtered, washed consecutively with water and acetone, and dried under vacuum at 70 °C over night [36].

Preparation of Mn(TPPS) immobilized on ionic liquid-modified silica Mn(TPPS)@SiO₂-Im

To a solution of Mn(TPPS) (0.5 g) in acetone/water (v/v:1/1) was added SiO₂-Im (4 g) and refluxed for 24 h. Finally, the catalyst was filtered and dried at room temperature.

General procedure for epoxidation of alkenes with NaIO₄ catalyzed by [Mn(TPPS)@SiO₂-Im] under ultrasonic irradiation conditions

All of the reactions took place under ultrasonic irradiation in a 25 mL flask. A solution of NaIO₄ (460 mg, 2 mmol in 5 mL H₂O) was added to a mixture of alkene (1 mmol), imidazole (0.1 mmol) and the [Mn(TPPS)@SiO₂-Im] (330 mg, 0.02 mmol) in acetonitrile (5 mL). The mixture was exposed to ultrasonic irradiation. The progress of the reactions was monitored by GC. At the end of the reaction, the catalyst was filtered and washed with Et₂O (20 mL). The organic layer was separated, concentrated and after chromatography on a short column of silica gel the pure product was obtained. IR and ¹H-NMR spectral data confirmed the identities of the products.

Results and discussion

Preparation and characterization of catalyst, Mn(TPPS)@Im-SiO₂

The preparation route for catalyst is shown in Scheme 2. In the first step, 3-chloropropyl functionalized silica gel was reacted with N-methylimidazole at 80 °C to produce

the supported ionic liquid. Elemental analysis was carried out for ionic liquid support and respective catalyst. The nitrogen content of the SiO₂-Im was about 0.86 %. According to this value, 0.31 mmol of the ionic liquid fragment has been grafted per gram of the SiO₂-Im. The amount of Mn was measured by ICP. The value showed that the catalyst loading is about 0.06 mmol/g. The FT-IR spectrum of SiO₂-Im (Fig. 1) showed the characteristic band of the parent ionic liquid ($\nu_{C=N}$) at 1637 cm⁻¹. After anion exchange with metalloporphyrin anion, the C=N stretching band in supported catalyst (Fig. 2) is shifted to lower frequency (1633 cm^{-1}) by immobilisation of [Mn(TPPS)]. 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). Diffuse reflectance (DR) UV–Vis spectra of [Mn(TPPS)@SiO₂-Im] showed the Soret band at 474 nm and *Q* bands at 544, 580, 612 and 680 nm. This absorption bands were appeared in the UV–Vis spectra of [Mn(TPPS)@SiO₂-Im] and since pure SiO₂-Im shows no UV absorption peak in these area (Fig. 3). These observations clearly proved the presence of Mn(TPPS) on the



3000

10

4000

350

1095

2000 Wavenumber (1/cm) 1000



Fig. 4 Scanning electron micrographs of: **a** SiO₂-Im and **b** Mn(TPPS)@SiO₂-Im



support. The SEM images of SiO₂-Im and [Mn(TPPS)@ SiO₂-Im] are shown in Fig. 4. The SEM image of [Mn(TPPS)@SiO₂-Im] is clearly different from that of SiO₂-Im. This different can be attributed to the supporting of Mn(TPPS) on the surface of SiO₂-Im.

Catalytic activity

The catalytic activity of supported Mn(TPPS) metalloporphyrin was tested by investigating the conversion of cyclooctene to cyclooctene oxide in the presence of

Table 1 The effect of solvent on the epoxidation of *cis*-cyclooctenecatalyzed by $[Mn(TPPS)@SiO_2-Im]$ under ultrasonic irradiation conditions

Entry	Solvent	Epoxide (%) ^a	Time (min)
1	CH ₂ Cl ₂	20	10
2	CHCl ₃	15	10
3	(CH ₃) ₂ CO	67	10
4	CH ₃ OH	55	10
5	C ₂ H ₅ OH	60	10
6	CH ₃ CN	100	10

Reaction condition: *cis*-cyclooctene (1 mmol), catalyst (330 mg, 0.02 mmol), solvent (5 mL), NaIO₄ (2 mmol in 5 mL H_2O), imidazole (0.1 mmol)

^a GC yield based on the starting cyclooctene

and benzaldehyde was produced as by-product. In the oxidation of α -methylstyrene, the major product was α -methylstyreneoxide (62 %), while acetophenone was produced as minor products. Epoxidation of limonene with 100 % conversion and 100 % epoxide selectivity, was led to 67 % of 1,2-epoxide, 33 % of 8,9-epoxide. Control experiments indicate that in the absence of the catalyst was also investigated and it was observed that the amount of product is negligible.

Catalyst reuse and stability

The reusability of a supported catalyst is one of the most important benefits of heterogeneous catalysts,

Table 2	Oxidation of alkenes	with NaIO ₄ cataly	zed by [Mn(TPPS	S)@SiO ₂ -Im] under	r ultrasonic irradiatior	 conditions
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	Substrate	Product	Time (min)	Conversion (%) ^a	Epoxide selectivity (%)	TOF (h^{-1})
1			10	100	100	312.6
2			5	100	100	602.4
3			20	100	73	151.5
4			20	75	83	113.6
5	\rightarrow	$ \ \ \ \ \ \ \ \ \ \ \ \ \ $	22	100	(67 % exo) (33 % endo)	135.1
6			15	100	100	200

Reaction conditions: alkene (1 mmol), NaIO₄ (2 mmol in 5 mL H_2O), catalyst (330 mg, 0.02 mmol), imidazole (0.1 mmol), acetonitrile (5 mL) ^a GC yield based on the starting alkene

sodium periodate. The reactions were continued until no further progress was observed. In order to choose the reaction media, the various organic solvents were examined in the epoxidation of *cis*-cyclooctene. Among the dichloromethane, chloroform, acetonitrile, methanol, ethanol and acetone, acetonitrile was selected as reaction media because the highest epoxide yield was observed (Table 1). The catalytic activity of this catalyst was investigated in the epoxidation of different olefins (Table 2). The reactions were continued until no further progress was observed. In the epoxidation of *cis*-cyclooctene, indene and α -pinene were completely converted to their corresponding epoxides with 100 % selectivity. In the case of styrene, the major product was epoxide 73 %,

because metalloporphyrins are often expensive to purchase or prepare. Therefore, heterogenization of homogeneous catalysts makes them useful for commercial applications. In order to investigate the recyclability of the heterogeneous catalyst, we selected cyclooctene as a model substrate due to its relative unreactive alkene. The stability of the [Mn(TPPS)@SiO₂-Im] catalyst was monitored using multiple sequential oxidation of cyclooctene with sodium periodate under ultrasonic irradiation conditions. To assess stability and reusability, the catalyst was separated from the reaction mixture after each experiment, washed thoroughly with acetonitrile and *n*-hexane successively and dried before being



Fig. 5 The results obtained from catalyst reuse and stability in the oxidation of cyclooctene with $NaIO_4$ by $[Mn(TPPS)@SiO_2-Im]$ under ultrasonic irradiation conditions

Fig. 6 FT-IR spectrum of

recovered Mn(TPPS)@SiO₂-Im

the same reaction conditions [37]. As shown in Table 3, the TOF (h^{-1}) for supported ionic liquid catalyst, [Mn(TPPS)@ SiO₂-Im], were higher than that of supported catalyst [Mn(TPPS)-SiO₂].

Conclusion

In this summary, we have designed an efficient olefins epoxidation system with sodium periodate under ultrasonic irradiation conditions in which $[Mn(TPPS)-SiO_2]$ has been immobilized on ionic liquid-modified silica. The major advantage of ionic liquid-supported catalyst was recoverable and reusable.



used in the subsequent run. The catalyst was sequentially reused several times with some loss of its catalytic activity (Fig. 5). The filtrates were used for determination of the catalyst leaching by atomic absorption spectroscopy (AAS). The results showed that in two first runs some catalyst is leached from support (3.6 % in the first run and 0.95 % in the second run), but in the next runs no leaching was observed. The FT-IR spectroscopy of the recovered catalyst after using for ten times showed no change in its IR spectrum (Fig. 6), which illuminated the fact that the catalytic activity of the catalyst did not change significantly, as compared with fresh catalyst.

To demonstrate the effectiveness of ionic-liquid supporting on the catalytic activity of Mn(TPPS), some of the results obtained by [Mn(TPPS)@SiO₂-Im] was compared with our previously reported systems such as [Mn(TPPS)-SiO₂] under

Table 3 Comparison of TOF (h^{-1}) obtained in the presence of Mn(TPPS)@SiO₂-Im with Mn(TPPS)@SiO₂ for the epoxidation of olefins with NaIO₄ under ultrasonic irradiation conditions

Substrate	TOF (h^{-1})			
	Mn(TPPS)@SiO ₂ -Im ^a	Mn(TPPS)@SiO ₂ ^b		
Cyclooctene	312.6	90.7		
Styrene	151.5	133.8		
α -Methylstyrene	113.6	106.2		

^a Reaction conditions: alkene (1 mmol), catalyst (0.026 mmol), oxidant (2 mmol), CH₃CN (10 mL), H₂O (10 mL)

^b Reaction condition: alkene (1 mmol), catalyst(0.02 mmol), NaIO₄ (2 mmol), CH₃CN (5 mL), H₂O (5 mL), imidazole (0.1 mmol)

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