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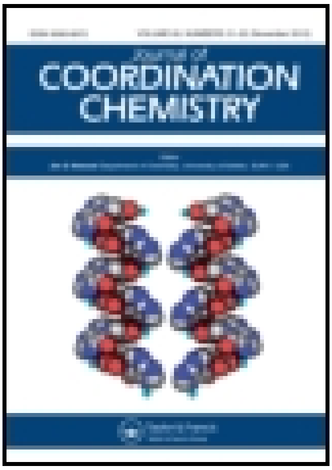

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Synthesis and characterization of NaY zeolite-encapsulated Mn-hydrazone Schiff base: an efficient and reusable catalyst for oxidation of olefins

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Synthesis and characterization of NaY zeolite-encapsulated Mn-hydrazone Schiff base: an efficient and reusable catalyst for oxidation of olefins

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The Mn-hydrazone Schiff base has been prepared, characterized, and encapsulated into NaY to prepare a new heterogeneous catalyst. Elemental analysis, UV-Vis, infrared spectroscopic analysis, diffuse reflectance spectroscopy, thermal analysis, small angle X-ray diffraction, and N_2 sorption indicate the presence of Mn-hydrazone Schiff base within the nanocavity pores of zeolite-Y. The catalysts showed excellent catalytic efficiency in epoxidation with various olefinic compounds including cyclooctene, using tert-BuOOH as oxidant. Cyclooctene showed high conversion (97%) as well as epoxide selectivity (89%) with tert-BuOOH. Moreover, the encapsulated complex showed good recoverability without significant loss of activity and selectivity within successive runs.

Keywords: Hydrazone Schiff base; Zeolite; Epoxidation; tert-Butyl hydroperoxide

1. Introduction

Heterogenization of homogeneous catalysts on supports through non-covalent immobilization in zeolite [1–4], tethering of a ligand to support, covalent grafting on to inorganic supports such as silica and MCM-41 [5–11], and co-polymerization of a functionalized Salen monomer into an organic polymer [12–17] provide easy separation of products from reaction medium, thermal stability, recovery, recycling of the catalysts, etc.

Zeolites are excellent candidates for encapsulation of homogeneous catalysts in that the metal complex can be physically trapped in nanopores of the zeolite and not bound to the oxide surface. Synthesis of zeolite-entrapped metal complexes has followed three approaches: template synthesis [18, 19], a zeolite synthesis method [20–23], and a flexible-ligand method [24–26].

Schiff-base complexes play important roles in biological, clinical, analytical, and industrial areas in addition to important roles in catalysis and organic synthesis [27–31]. Their properties depend on the metal ion and nature of the ligand. Hydrazone Schiff-base metal complexes have biological and pharmacological applications [32–34].

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Hydrazones have been shown to possess antimicrobial, anticonvulsant, analgesic, anti-inflammatory, and antitumor properties [35–37]. Due to tautomerism in hydrazones, the amide oxygen can be in neutral keto or enolic forms and can coordinate in neutral, mono-anionic, di-anionic, or tetra-anionic forms to metal ions depending on the metal ion concentration, the pH, and the nature of the hydrazones [38–40].

Here, we describe the synthesis and characterization of neat and zeolite-Y-encapsulated Mn(II) complexes and test the catalytic activities of these complexes on epoxidation reactions in different media using tert-butyl-hydroperoxide as oxidant.

The heterogenized catalyst has comparable activity to the corresponding homogeneous one. The lifetime of the heterogenized catalyst has been examined by repeated use of the complex leading to similar yields of cyclooctene oxide without noticeable loss of metal.

2. Experimental

2.1. *Materials and methods*

All reagents were supplied by Merck and employed without purification. NaY zeolite with Si : Al ratio of 2.53 was purchased from Aldrich. Hydrazone (H_2sal-bhz) was synthesized according to published procedures [41]. FT-IR spectra were recorded on a Unicam Matson 1000 FT-IR paragon 1000 spectrophotometer. ^{1}H and ^{13}C NMR spectra of the ligand and products of epoxidation were recorded on a Bruker FT-NMR 500 MHz spectrometer. Electronic spectra of the neat complex in the UV-Vis region were recorded in methanol using a Shimadzu UV-Vis scanning spectrophotometer. Diffuse reflectance spectra (DRS) were taken on a Shimadzu UV/3101 PC spectrophotometer from 1500 to 200 nm using MgO as reference. The loading of complex encapsulated in zeolite was determined by atomic absorption spectroscopy (AAS) recorded on a Perkin-Elmer AA-300 spectrophotometer. X-ray diffraction (XRD) patterns were recorded by a Rigaku D-max C III, X-ray diffractometer using Ni-filtered Cu-Kα radiation. Thermogravimetric analysis (TGA) was carried out using a Perkin-Elmer TGA-7 instrument at a heating rate of $10^\circ\mathrm{C\,min^{-1}}$ under air. Nitrogen adsorption measurements were performed at 77 K using a Coulter Omnisorb 100CX instrument. The samples were degassed at 150°C until a vacuum better than 10^{-3} Pa was obtained. Gas chromatographic (GC) analyses were performed on an Agilent Technologies 6890N, 19 019J-413 HP-5, 5% phenyl methyl siloxane, capillary $60.0\,\mathrm{m} \times 250\,\mu\mathrm{m} \times 1.00\,\mu\mathrm{m}$.

2.2. *Sample preparation*

2.2.1. Preparation of Mn-hydrazone Schiff base, $\mathbf{Mn^{II}(Hsal\text{-}bhz)_2}$. The ligand was prepared in a manner similar to reported procedures [41]. A solution of salicylaldehyde (1 mmol) was added dropwise to a stirred solution of benzhydrazide (2 mmol) in methanol (10 mL) and the mixture was refluxed for 2 h. The solvent was removed under vacuum to produce yellow crystals, which were washed with 5 mL of cooled methanol and then dried in air (97% yield).

To prepare the complex, 20 mL of a methanolic solution of H_2sal-bhz (2 mmol) was added dropwise to a methanolic solution of $Mn(CH_3COO)_2 \cdot 4H_2O$ (1 mmol) at room temperature. A yellow precipitate formed immediately upon addition and stirring was continued for 30 min, after which the yellow solid was filtered, washed with methanol, and dried under vacuum (yield: 93%). Anal. Calcd for $C_{28}H_{22}N_4O_4Mn$ (%): C, 62.98; H, 4.12; N, 10.49. Found (%): C, 62.95; H, 3.93; N, 10.47. IR (KBr): ν(C=N), 1614 cm^{-1}. UV-Vis (CH_3OH): λ_{max}: 240, 297, 395 nm.

2.2.2. Preparation of the metal-exchanged zeolite (Mn(II)-Y). Mn(II)@NaY was prepared by ion-exchange. Typically, 1.1 mmol of $Mn(CH_3COO)_2$ salt was first dissolved in 150 mL deionized water. Then, 1 g NaY was added to the solution and further stirred for 24 h at ambient temperature. Then, the solid fraction was filtered, twice washed with deionized water, and dried at 120°C for 12 h [42].

2.2.3. Preparation of zeolite-encapsulated Mn(II) complex, Mn^{II}(Hsal-bhz)$_2$/Y. Mn(II)@NaY was mixed with an excess of H_2sal-bhz and the reaction mixture was refluxed for 24 h on an oil bath with stirring. Uncomplexed ligand and the complex adsorbed on the exterior surface were removed by full Soxhlet extraction with DMF and acetonitrile. The unreacted Mn(II) present in the zeolite was removed by stirring with aqueous 0.1 mol L^{-1} NaCl solution (200 mL) for 8 h. The resulting solid was washed with deionized water until no Cl^- could be detected with $AgNO_3$ aqueous solution. Finally, it was dried at 120°C in an air oven for several hours.

2.3. *Catalytic reaction*

Catalytic reactions were carried out at 75°C in a 25 mL glass reactor. In a typical procedure, to a solution of cyclooctene (1 mmol), either Mn^{II}(Hsal-bhz)$_2$ (0.001 mmol) or Mn^{II}(Hsal-bhz)$_2$/Y (0.001 mmol, 0.005 g) and chlorobenzene (1 mmol) as internal standard in acetonitrile (1 mL) was added 1 mmol tert-butyl hydroperoxide as oxidant. The reaction was followed by GC and results are summarized in table 1; assignments of products were made by comparison with authentic samples. All the reactions were run at least in duplicate.

3. Results and discussion

3.1. *Synthesis and characterization*

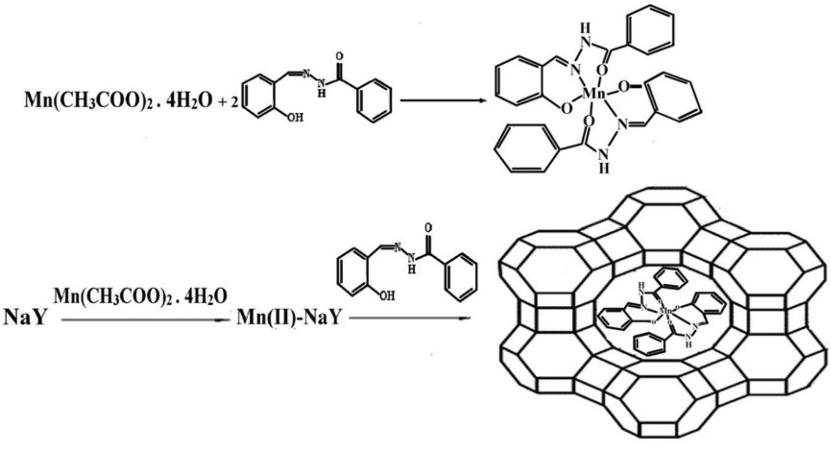
The neat complex was prepared in good yield by condensation of H_2sal-bhz with metal salt. It was slightly soluble in common solvents such as ethanol, acetone, acetonitrile, and chloroform, but soluble in DMF and DMSO. Elemental analysis confirmed that two molecules of hydrazone are chelated to metal as mono-anionic ligand with carbonyl-oxygen, azomethine-nitrogen and phenolic-oxygen as ONO, coordination forming non-electrolytic octahedral metal complexes (scheme 1).

The encapsulation was achieved by a flexible ligand method in which ligand enters slowly into the cavity through the zeolite pores due to its flexible nature and reacts with

Table 1. Optimized reaction condition in oxidation of cyclooctene with t-BuOOH catalyzed by neat and encapsulated complexes.[a]

Run	Catalyst (mmol)	Solvent	Temperature (°C)	Conversion[c] (%)[d]	Selectivity to epoxide[c] (%)[d]	Turnover number[b, c] ( )[d]
1	0.005	CH_3OH	75	58 (43)	88 (87)	116 (86)
2	0.005	DMF	75	33 (32)	93 (93)	66 (64)
3	0.005	CH_2CL_2	75	76 (69)	80 (89)	152 (138)
4	0.005	DCE	75	86 (85)	89 (75)	172 (170)
5	0.005	CH_3CN	75	95 (98)	87 (87)	182 (196)
6	0.01	CH_3CN	75	97 (98)	88 (87)	97 (98)
7	0.001	CH_3CN	75	91 (89)	89 (90)	910 (890)
8	0.0005	CH_3CN	75	88 (88)	89 (89)	1760 (1760)
9	0.005	CH_3CN	65	71 (65)	89 (89)	142 (130)
10	0.005	CH_3CN	55	69 (57)	90 (90)	138 (114)
11	0.005	CH_3CN	40	34 (21)	98 (98)	68 (42)
12	0.005	CH_3CN	R.T	20 (18)	98 (98)	40 (36)

[a] Reaction condition: 1 mmol cyclooctene, 1 mmol t-BuOOH, time: 14 h.
[b] Turnover number is moles of products per mole catalyst. GC conversion based on starting cyclooctene.
[c] Neat complex as catalyst.
[d] Encapsulated complex as catalyst.



Scheme 1. Preparation of neat and encapsulated Mn-hydrazone Schiff-base complexes.

previously exchanged metal ions. The complexation of Mn(II) with H_2sal-bhz was accompanied by a color change from light pink of exchanged zeolite to pale yellow. Soxhlet extraction using DMF and acetonitrile purified the impure materials. The remaining uncomplexed metal ions in the zeolite were removed by exchanging back with aqueous $0.1\,mol\,L^{-1}$ NaCl solution (scheme 1). The analytical analysis of solid catalyst sample showed that it contained 2.72 wt% of manganese, which is similar to that estimated by atomic absorption. Analytical and physical data of the $Mn^{II}(Hsal\text{-}bhz)_2$ complex and isolated zeolite-encapsulated complex as well as the parent NaY zeolite are listed in table 2. To characterize the resulting materials and to assess the efficiency of the encapsulation process, the parent zeolite, neat complex, and sample of

Table 2. Physical and analytical data.

Compound	Color	C (%)	H (%)	N (%)	C/N (%)	Mn (%)	S_{BET} ($m^2 g^{-1}$)	V_P ($cm^3 g^{-1}$)
Mn^{II}(Hsal-bhz)$_2$	Yellow	62.98	4.12	10.49	6.00	10.11	–	–
Zeolite	White	–	–	–	–	–	438.16	0.1765
Mn^{II}(Hsal-bhz)$_2$/Y	Pale yellow	16.93	1.11	2.76	6.13	2.72 (2.68)[a]	356.36	0.1514

[a] Determined by ICP.

Mn^{II}(Hsal-bhz)$_2$/Y were studied by several techniques and the obtained results compared.

The textural properties (surface area (S_{BET}), pore volume (V_P)) of the encapsulated complex were determined from N_2 absorption carried out at 77 K (table 2). A noticeable reduction in surface area, pore volume, and adsorption capacity of the zeolite was observed upon encapsulation of metal complexes in the supercages of zeolite-Y, indicating the presence of the Mn^{II}(Hsal-bhz)$_2$ complex within the zeolite cages and not on the external surface.

FT-IR spectra of zeolite, Hsal-bhz, Mn^{II}(Hsal-bhz)$_2$, and zeolite-encapsulated complex are presented in the "Supplementary material" section. The IR spectra of the complex show a significant change in some bands from free Schiff base. For example the free ligand exhibits ν(C=N) at 1673 cm^{-1}. In the complex, this band shifts to 1614 cm^{-1}, indicating coordination of azomethine nitrogen. The IR spectrum of the hydrazone contains a strong C–O absorption at 1621 cm^{-1} and an N–H absorption at 3005 and 3050 cm^{-1}. Both of these bands appear on complexation, indicating that the hydrazone has not undergone deprotonation on complexation. The appearance of two or three bands between 420 and 540 cm^{-1} indicates coordination of phenolic oxygen in addition to azomethine nitrogen. The presence of several bands of medium intensity at 2700–2950 cm^{-1} indicates C–H of the tridentate Schiff-base ligand. The ν O–H as a medium band at 3270 cm^{-1} disappears in spectra of the neat complex. These data give evidence for coordination of H_2sal-bhz to Mn(II) *via* two nitrogen atoms and one oxygen atom. The intensities of the peaks of the encapsulated complex are weak due to low concentration of the complex in zeolite. Spectra of encapsulated complex and neat complex show similar bands, indicating encapsulating of the complex in NaY zeolite.

The zeolite-Y-encapsulated metal complex is confirmed by UV-Vis spectra shown in figure 1. The complex shows bands at *ca* 230, 283, 296, 325 corresponding to the ligand and a band at 396 nm having a molar extinction coefficient of 9277 $(mol\,L^{-1})^{-1}\,cm^{-1}$ that can be attributed to ligand-to-metal charge transfer originating from the azomethine [43]. For the encapsulated complex, bands corresponding to the intraligand π–π*, n–π* transitions and ligand-to-metal charge transfer are visible at 230, 283, 296, 325, and 396, respectively.

The powder XRD patterns of Na-Y and encapsulated metal complex were recorded at 2θ values between 4° and 70°. The XRD pattern of zeolite-encapsulated metal complex along with Na-Y is presented in the "Supplementary material" section. The diffraction patterns of Mn^{II}(Hsal-bhz)$_2$ and Na-Y are similar except slight changes in the intensity of the bands in the encapsulated complex. These observations indicate that the framework of the zeolite has not undergone significant structural change during encapsulation. This is expected as the flexible ligand enters slowly through pores of the

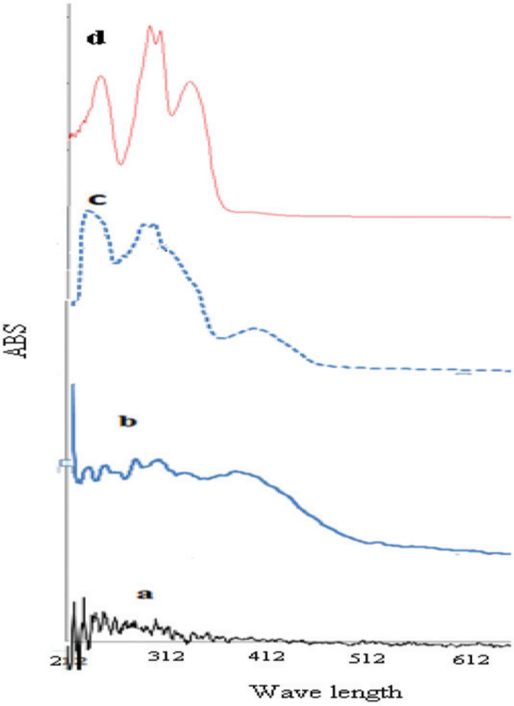


Figure 1. UV-Vis spectra of the samples: (a) NaY, (b) encapsulated complex, (c) neat complex, and (d) hydrazone ligand.

zeolite and fits nicely in the cavity upon coordination with the metal ions. Our data show the relative peak intensities of the (220) and (311) reflections in the XRD pattern vary upon inserting the complexes. I_{220} at $2\theta = 10^\circ$ is greater than I_{311} at 12° for NaY, but I_{220} is lower than I_{311} for zeolite-encapsulated metal complex, clear evidence for formation of a complex within the supercage of zeolite [44, 45].

The TG patterns of $Mn^{II}(Hsal\text{-}bhz)_2$ and $Mn^{II}(Hsal\text{-}bhz)_2/Y$ are presented in the "Supplementary material" section. The thermograms of the neat complex indicate decomposition in two steps. The first at 300–350°C and the second step between 400 and 470°C are associated with decomposition of the complex. There is no peak at 100–120°C, indicating the absence of water or solvent in the structure. The encapsulated complex exhibits an exothermic weight loss of *ca* 20% attributed to removal of intra-zeolite water up to 150°C. Weight loss of *ca* 2.7% extends to 560°C, indicating that thermal stability is greatly enhanced. This very small percentage of weight loss is in agreement with small amounts of metal content obtained for encapsulated complex, as estimated by AAS.

3.2. *Catalytic oxidation of cyclooctene with t-BuOOH*

Catalysis of the neat and encapsulated complexes was studied in oxidation of cyclooctene, a model substrate, with t-BuOOH as the oxygen donor (table 1). The results show a similarity between the catalytic activity of the encapsulated complex and that of the dissolved complex in solution. Control experiments show that zeolite-Y

Table 3. Recycling studies of catalyst in oxidation of cyclooctene with t-BuOOH.[a]

Run	Conversion (%)[b]	Selectivity to epoxide	Leaching of Mn (%)[c]
1	98	87	0.039
2	97	90	0.004
3	91	91	0.007
4	91	88	–
5	90	91	0.004

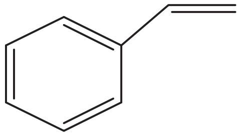
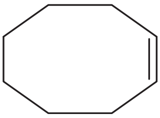
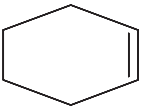
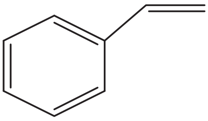
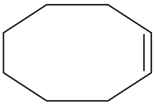
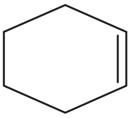
[a] Reaction condition: The molar ratio for catalyst: cyclooctene: t-BuOOH are 1 : 200 : 200. The reactions were run for 14 h at 75°C temperature in 1 mL acetonitrile.
[b] GC conversion based on starting cyclooctene.
[c] Determined by AAS.

is inactive, under the operating conditions. Also, use of metal/NaY zeolite showed lower conversion than $Mn^{II}(Hsal\text{-}bhz)_2/Y$, confirming that the Schiff-base complex played a role. The effect of various reaction media on the oxidation of cyclooctene has been studied. Efficiency of the catalysts in different solvents decreases in the order, acetonitrile > dichloroethane > dichloromethane > methanol > DMF. The effect of catalyst amount on the conversion and selectivity is illustrated in table 1. Four different amounts of catalyst, namely 0.01, 0.005, 0.001, 0.0005 mmol, were examined while keeping a fixed amount of cyclooctene (1 mmol) and t-BuOOH (1 mmol). Increasing of catalyst from 0.005 to 0.01 mmol does not have a significant effect on the percent of conversion under the reaction conditions (table 1, entries 5, 6). With a further decrease in the catalyst amount from 0.005 to 0.0005 mmol, the conversion shows a small reduction from 98 to 88 (table 1, entries 5, 8). The effect of reaction temperature on cyclooctene oxidation was also investigated. As expected, conversion of cyclooctene increased with increasing reaction temperature to 75°C for neat and encapsulated complexes, while low conversion was detected when the reaction temperature was below 40°C (table 1, entries 5, 9–12).

The major advantages of heterogeneous catalysis over its homogeneous counterpart are ease of the recovering and reusability of the catalyst. The stability and recyclability of the catalyst were examined by using it in several reaction cycles. Before reuse, the solid was separated from the reaction medium by filtration, washed several times with diethyl ether, dried, and subjected to catalytic reactions under similar conditions as in the first cycle. The heterogenized catalyst could be reused several times with a conversion ranging from 98% at the beginning to 90% in the fifth run, with unchanged selectivity (table 3).

This was also supported by the AAS analysis and by using UV-Vis in the reaction solution after filtration of the encapsulated complex that a trace amount of Mn complex was observed in the reaction liquid, indicating slight leaching of the complex from the interior of the zeolite host to the solution. To verify further that the observed catalysis was truly heterogeneous, the solid was filtered from the reaction mixture and the fresh alkene and oxidant was added to the reaction mixture. The conversion of oxidation is comparable to the blank experiment, in accord with the leaching data. Moreover, heterogeneity can be confirmed by filtering the catalysts at the reaction temperature before completion of the reaction and performing the AAS analysis of the hot filtration. The results show the amounts of leached Mn are 0.025, 0.030, 0.039, and 0.039 wt% at 2, 6, 10, and 14 h, respectively. Thus the observed catalysis is truly heterogeneous in nature.

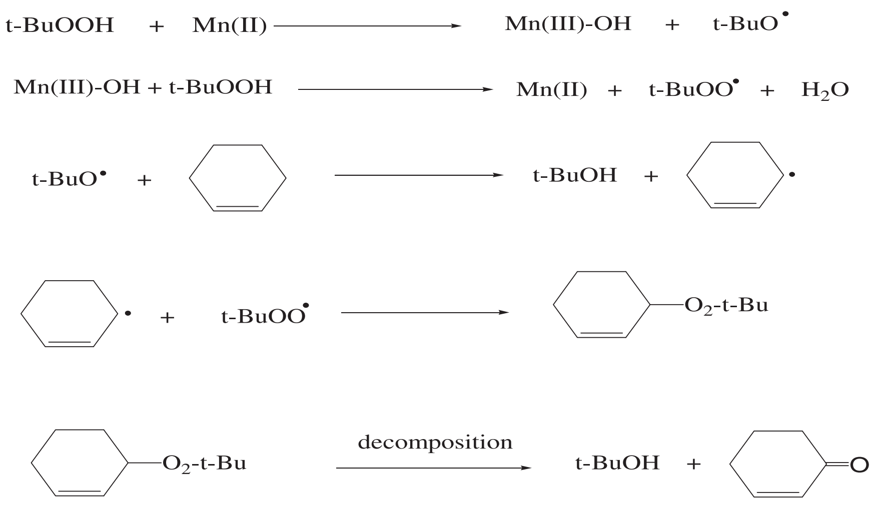
Table 4. Catalytic oxidation of various alkenes with t-BuOOH by neat and encapsulated catalysts.[a]

Catalyst	Substrate	Conversion (%)[b]	Product	Product selectivity (%)[b]
$Mn^{II}(Hsal\text{-}bhz)_2$		97	Epoxide	32
			Benzaldehyde	54
			Benzoic acid	8
			Other	6
		95	Epoxide	87
			Other	12
		92	Ketone	91
			Other	9
		56	Epoxide	20
			Alcohol	36
			Ketone	41
			Other	3
$Mn^{II}(Hsal\text{-}bhz)_2/Y$		98	Epoxide	33
			Benzaldehyde	28
			Benzoic acid	35
			Other	4
		98	Epoxide	87
			Other	13
		94	Ketone	93
			Other	7
		57	Epoxide	21
			Alcohol	35
			Ketone	40
			Other	4

[a] Reaction condition: The molar ratio for catalyst: alkene: t-BuOOH are 1 : 200 : 200. The reactions were run for 14 h at 75°C in 1 mL acetonitrile.

[b] GC conversion based on starting alkene.

Manganese(V)-oxo, manganese(IV)-oxo, and/or radical species have been known as reactive intermediates in reactions mediated by compounds of manganese [46–52]. Formation of oxomanganese(V) species in the Mn(III)Salen catalysis of cyclohexene oxidation with iodosylbenzene (PhIO) was reported by Kochi *et al.* [46]. In this system cyclohexene is oxygenated to cyclohexene oxide with high selectivity. A typical radical reaction has been demonstrated by Busch [47] in which two distinct reactive intermediates, the alkyl peroxy radical, $ROO^\bullet$, and the Mn(IV)/alkyl peroxo adduct,



Scheme 2. Proposed mechanism for oxidation of cyclohexene with Mn-hydrazone Schiff-base complex in the presence of t-BuOOH.

$Mn(IV)(Me_2\text{-}EBC)(O)(OOR)^+$, serve as epoxidizing reagents in $Mn(Me_2\text{-}EBC)Cl_2$-mediated oxygen-transfer reaction using alkyl hydroperoxide as the terminal oxidant. Epoxidation of cyclohexene provided a 32.4% yield of cyclohexen-1-one and a 1.4% yield of cyclohexene oxide as the minor product. In the cyclohexene oxidation with t-butyl hydroperoxide-pyridine catalyzed by Mn(III)Salen complexes, Kochi *et al.* suggested dual pathways leading to allylic substitution (cyclohexenyl t-butyl peroxide) and olefin oxidation (cyclohexene oxide) [48]. Allylic peroxidation corresponded to a hemolytic chain process in which free radicals and one-electron redox changes of MnSalen played important roles. Olefin epoxidation on the other hand represented the two-electron interconversion of manganese(III) and oxomanganese(V) species.

In the present catalytic system, the epoxidation of different substrates has been examined and the results are given in table 4. The cyclohexene oxidation in table 4 shows excellent conversion of 94% to form 2-cyclohexen-1-one as the major product with 93% selectivity. These results strongly suggest a radical pathway involving alkoxy (t-BuO$^\bullet$) or alkylperoxy (t-BuOO$^\bullet$) radicals which are produced from redox reactions (Haber-Weiss process, Mn(II)/Mn(III)) as expected on the basis of earlier literature reports [49, 53]. The oxidation of cyclohexene in the presence of $Mn^{II}(Hsal\text{-}bhz)_2$ with tert-butyl hydroperoxide is proposed to occur as in scheme 2.

Epoxidation of styrene with tert-BuOOH gives styrene oxide, benzaldehyde, 1-phenylethane-1,2-diol, and benzoic acid. The selectivity of various reaction products in the homogeneous system follows the order, benzaldehyde > styrene oxide > benzoic acid, whereas selectivity of the reaction products in the presence of encapsulated complex varies in the order, benzoic acid > styrene oxide > benzaldehyde. The conversion of benzaldehyde to benzoic acid was probably catalyzed by the Bronsted acid sites originating from Si–OH–Al in the zeolite framework.

The catalytic potential of the encapsulated complex presented here compares well with similar encapsulated complexes (table 5). For example, $[Mn(H_4C_6N_6S_2)]$-Y exhibited as high as 90.3% conversion of cyclohexene with tert-BuOOH, where no

Table 5. Comparison of the results obtained for oxidation of olefins catalyzed by $Mn^{II}(Hsal\text{-}bhz)_2/Y$ with some of those reported in the literature.

Catalyst	Oxidant	Substrate	Conversion (%)	Ref.
$Mn^{II}(Hsal\text{-}bhz)_2/Y$	t-BuOOH	Cyclohexene	94	This work
		Cyclooctene	98	
$[Mn(H_4C_6N_6S_2)]$-Y	t-BuOOH	Cyclohexene	90.3	[54]
$Mn(salen)^+$-Y	$KHSO_3$	Cyclohexene	8	[55]
		Cyclooctene	6.8	
$Mn(salen)^+$-clay	t-BuOOH	Cyclohexene	25	[50]
		Cyclooctene	7	
[Mn(sal-1,3-phen)]-NaY	t-BuOOH	Cyclohexene	84.6	[56]
[Ni(L)]@Mont	t-BuOOH	Cyclooctene	69	[57]

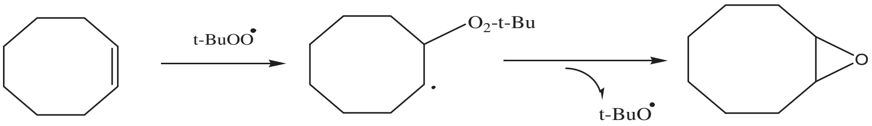
Table 6. Oxidation of olefins catalyzed by neat and encapsulated complexes at the presence of ionol (2,6-di-tert-butyl-p-cresol) as radical scavenger.[a]

Catalyst	Substrate	Conversion (%)[b]	Product	Yield to product (%)
$Mn^{II}(Hsal\text{-}bhz)_2$	Cyclooctene	49 (>95)[c]	Epoxide	2
			Alcohol	–
	Styrene	4 (>97)[c]	Epoxide	–
			Benzaldehyde	1
			Benzoic acid	–
$Mn^{II}(Hsal\text{-}bhz)_2/Y$	Cyclooctene	46 (98)[c]	Epoxide	–
			Alcohol	–
	Styrene	4 (>98)[c]	Epoxide	–
			Benzaldehyde	–
			Benzoic acid	–

[a] Reaction condition: The molar ratio for catalyst: alkene: TBHP: ionol are 1 : 200 : 200 : 200. The reactions were run for 14 h at 75°C in 1 mL acetonitrile.
[b] GC conversion based on starting alkene.
[c] GC conversion in the absence of the radical scavenger.

formation of cyclohexene epoxide was observed and the selectivity of the other oxidation products varied in the order, 2-cyclohexene-1-one (87.5%) > 2-cyclohexene-1-ol (11.5%) > 1-(tert-butylperoxy)-2-cyclohexene (1%) [54]. Cyclohexene and cyclooctene oxidation catalyzed by the $Mn(salen)^+$-Y proceeded with 8% and 6.8% conversion and 100% selectivity toward the corresponding epoxides, respectively, with $KHSO_3$ [55]; catalytic oxidation of cyclohexane by $Mn(salen)^+$-clay with tert-BuOOH in the presence of imidazole was 25% with selectivity of products, 1-(tert-butylperoxy)-2-cyclohexene (14%) > cyclohexene epoxide (6.8%) > cyclohexenone(1.2%) > cyclohexenol (1%). Cyclooctene was oxidized by TBHP and only 7% conversion was obtained with selectivity to cyclooctene epoxide [50]. Cyclohexene was oxidized by tert-butylhydroperoxide using similar catalyst [Mn(sal-1,3-phen)]-NaY with 84.6% conversion obtained with selectivity of products, 2-cyclohexene-1-one (84.2%) > 2-cyclohexene-1-ol (14.7%) > 1-(tert-butylperoxy)-2-cyclohexene (1.1%) [56]. Oxidation of cyclooctene with tert-butylhydroperoxide in the presence of [Ni(L)]@Mont catalyst proceeds with 62.3% selectivity for epoxidation with 69% conversion [57].

To explore *in situ* formation of radicals in the oxidation reaction, ionol (2,6-di-tertbutyl-p-cresol) was used as a radical trap in oxidation of styrene and cyclooctene



Scheme 3. Proposed mechanism for oxidation of cyclooctene with Mn-hydrazone Schiff-base complex in the presence of t-BuOOH.

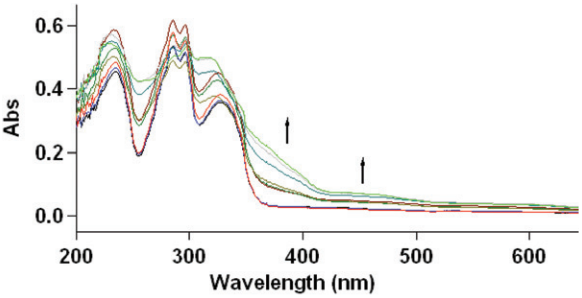


Figure 2. Spectral changes observed during titration of solution of Mn(II)(Hsal-bhz)$_2$ in dichloroethane (2.5×10^{-3} mol L^{-1}) with t-BuOOH dissolved in dichloroethane.

with t-BuOOH catalyzed by Mn^{II}(Hsal-bhz)$_2$ and Mn^{II}(Hsal-bhz)$_2$/Y. The results are shown in table 6. Oxidation of styrene is strongly inhibited in the presence of ionol. The effective inhibition of oxidation by ionol is achieved by interception of the radical intermediate. In the case of cyclooctene, substrate is consumed, but no oxidation products can be detected. The findings with cyclooctene reveal that cyclooctene oxide formation may occur *via* a free-radical pathway, shown in scheme 3 [50].

To understand the mechanism of the catalytic reaction, we have studied the interaction of Mn^{II}(Hsal-bhz)$_2$ with t-BuOOH in dichloroethane by electronic absorption spectroscopy (figure 2). The addition of one-drop portions of t-BuOOH dissolved in dichloroethane to 2 mL of *ca* 2.5×10^{-3} 1 mol L^{-1} solution of Mn^{II}(Hsal-bhz)$_2$ in dichloroethane causes a band and shoulder to appear at 450 and 380 nm. This change in spectra may correspond to formation of [Mn^{III}(Hsal-bhz)$_2$]$^+$ [58]. In UV-Vis spectrophotometer, no new absorption band appeared at 550 nm, showing the existence of Mn(V) = O species [46]. So the reaction does not proceed *via* the oxometal route.

4. Conclusion

We have synthesized Mn-hydrazone Schiff base and zeolite-encapsulated Mn-hydrazone Schiff base. The nature of the encapsulated manganese complex in the supercages of zeolite-Y was confirmed with various characterization techniques such as FT-IR, DRS, UV–Vis, and TGA. The results showed that the homogeneous and heterogeneous complexes are active and highly selective catalysts for cyclooctene epoxidation with the oxidizing agent t-BuOOH in CH_3CN. The oxidation of styrene gives at least four different products, benzaldehyde, styrene oxide, benzoic acid, and 1-phenylethane-1,2-diol. The reaction of cyclohexene with tert-butyl hydroperoxide in the presence of both catalysts gives 2-cyclohexene-1-one formed by the decomposition of cyclohexenyl-tert-butyl peroxide. The reaction products suggest the catalytic reactions proceed through a radical mechanism in which t-BuOO$^\bullet$ and t-BuO$^\bullet$ are the reactive intermediates. Addition of ionol (2,6-di-tertbutyl-p-cresol) as a radical-scavenging species quenched formation of oxidation product, confirming the proposed radical mechanism. The encapsulated catalyst was reusable for epoxidation of cyclooctene with t-BuOOH with a conversion ranging from 98% at the beginning to 90% in the fifth run.

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