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Oxidation of Alkenes with *tert*-Butyl Hydroperoxide Catalyzed by Mn(II), Cu(II) and VO(IV) Schiff Base Complexes Encapsulated in the Zeolite-Y: A Comparative Study

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Oxovanadium(IV), manganese(II) and copper(II) complexes of a Schiff base ligand derived from 2,4-dihydroxyacetophenone and 1,2-diaminocyclohexane have been encapsulated in the nanocavity of zeolite-Y by flexible ligand method and characterized by metal analysis, IR spectroscopic studies and X-ray diffraction patterns. The encapsulated complexes abbreviated here as CuL-Y, MnL-Y and VOL-Y catalyze the oxidation of various olefins using *tert*-butyl hydroperoxide (TBHP) as oxidant in good yield (α-methyl styrene: 75%). The catalytic activity of the encapsulated Schiff base complexes decreased in the order CuL-Y > VOL-Y > MnL-Y.

Keywords: Nanostructures, Zeolite, Heterogenized catalyst, Olefin, Oxidation

INTRODUCTION

Catalytic oxidation of olefins in the presence of various metal complexes in homogeneous systems have been reported since many years ago. Because of the high degradation of the catalysts during the oxidation reactions, focusing on the homogeneous systems has been limited. One of the interesting methods for preparation of the reusable catalysts is encapsulation in the cavity of mesoporous materials. Zeolite could be introduced as an ideal solid support to prepare the heterogeneous catalyst because of the very regular pattern, pore structure and pore sizes [1]. Consequently, the product selectivity in the zeolite cages and the lifetime of the catalyst can also be improved by encapsulation. Therefore, many research groups investigate the catalytic properties of the complexes entrapped within the super cages of Y-zeolite. For example, oxidation of sulfides [2-3], olefins [4-8], phenols [9-11] alkanes [12-15], amine [16] and *p*-xylene [17] have been reported using various transition metal complexes encapsulated in zeolite.

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The present study describes the synthesis and characterization of manganese(II), copper(II) and oxovanadium(IV) Schiff base complexes encapsulated in the nanocavity of zeolite-Y. Also the catalytic activities of the prepared materials for oxidation of olefins with *tert*-butyl hydroperoxide (TBHP) were investigated and compared with each other.

EXPERIMENTAL

Materials and Methods

The infrared spectra were obtained as KBr pellets on an ABB FTLA 2000 instrument. Elemental CHN analysis is performed using a Heraeus Elemental Analyzer CHN-O-Rapid (Elemental-Analyse systeme KBr pellets, Gmbh, West Germany). ^{1}H NMR spectrum was recorded in $CDCl_3$ with a Bruker FT-NMR 500 (500 MHz) spectrometer. The residual $CHCl_3$ in conventional 99.8 atom% $CDCl_3$ gives a signal at δ = 7.26 ppm, has been used for calibration of the chemical shift scale. The UV-Vis spectra were recorded on a single beam spectrophotometer (Cam Spec-M330). Products were analyzed with a gas chromatograph (Shimadzu, GC-14B) equipped with a SAB-5 capillary

column (phenyl methyl siloxane 30 m × 320 mm × 0.25 mm) and a flame ionization detector.

2,4-Dihydroxyacetophenone, 1,2-diaminocyclohexane, and *tert*-butyl hydroperoxide (solution 80% in di-*tert*-butyl peroxide) were used as received. Solvents were dried and distilled by standard methods before use. Other chemicals were purchased from Merck or Fluka chemical companies

Preparation of the Heterogeneous Catalyst (ML-Y)

The heterogeneous catalysts were prepared according to literature by a multistep procedure as illustrated in Fig. 1.

Preparation of the bis(2,4-dihydroxyacetophenone)-1,2-cyclohexanediimine (H_2L). To a stirred ethanolic solution (20 mL), 1,2-diaminocyclohexane (0.114 g, 1 mmol) and 2,4-dihydroxyacetophenone (0.304 g, 2 mmol) was added. The bright yellow solution was stirred and heated to reflux for about 1 h. After 1 h, a red precipitate was obtained which was filtered off and washed several times with ethanol. Yield (92%), melting point 110 °C. Analysis calculated for $C_{22}H_{26}N_2O_4$ (382.45): C, 69.09; H, 6.85; N, 7.32. Found: C, 68.91; H, 7.01; N, 7.46%. Selected FT-IR data, υ (cm^{-1}): 3275 (O-H), 2865-2947 (C-H), 1601 (C=N), 1524 (C=C), 1052 (C-O). ^{1}H NMR (δ): 1.33 (s, 6H, *Me*C=N), 1.78-1.89 (m, 4H, $NCHCH_2(CH_2)_2CH_2CH$), 2.39-2.66 (m, 4H, $NCH\mathit{CH_2}(CH_2)_2CH_2CH$), 2.80-3.0 (m, 2H, $N\mathit{CH}CH_2(CH_2)_2CH_2\mathit{CH}$), 6.23-7.68 (m, 6H, ArH), 12.68 (s, 2H, OH). UV-Vis ($CHCl_3$): 310 nm (π→π*), 380 nm (n→π*).

Preparation of M-Y (M = Mn(II),Cu(II), VO(IV)). M-Y was prepared by ion-exchange method. Typically, 3 g manganese acetate, copper acetate or vanadyl acetylacetonate was dissolved in 300 mL deionized water. Then, 1.0 g NaY was added to the solution and stirred for 24 h at ambient temperature. The solid product was filtered out, washed with deionized water until the filtrate was free from any free metal ion on the surface of the zeolite, and dried at 120 °C for 12 h.

Preparation of ML-Y (M = Mn(II), Cu(II) and VO(IV)). The encapsulated complexes were prepared using general flexible ligand method (FLM) [18,19]. 1.0 g M-Y and 1.2 g of tetradentate Schiff base ligand (H_2L) were mixed in 100 mL methanol in a round-bottomed flask. The reaction mixture was heated at 250 °C for about 14 h in an oil bath with stirring. In order to remove the unreacted ligands and any metal complexes adsorbed onto the external surface of the zeolite crystallites, the resulting material was Soxhlet extracted using methanol for 24 h.

The uncomplexed metal ions present in the zeolite framework were removed by exchanging with 0.01 M aqueous solution of NaCl. The resulting solid was washed with hot distilled water until no precipitation of AgCl was observed on treating filtrate with $AgNO_3$ solution. The host-guest nanocomposite materials (HGNM) was dried at 150 °C for several hours to constant weight. The metal content of the supported catalysts was determined by atomic absorption spectroscopy.

General Heterogeneous Oxidation Procedure

In a typical procedure, 1 mmol cyclooctene, 0.055 g catalyst and 3 mmol TBHP were added in 5 ml solvent. The reaction mixture was refluxed for 6 h. After the desired reaction time, the reaction mixture was centrifuged, 1.0 μL of the filtrate was subjected to GC analysis and the products were identified by comparison with authentic samples.

RESULTS AND DISCUSSION

Characterization of the Catalysts

The metal exchanged M-Y zeolite (M = Mn(II), Cu(II) and VO(IV)) was prepared by exchanging Na^+ of the zeolite with the desired metal ion. In order to insert the Schiff base ligand in the cavity of the zeolite, an excessive amount of the ligand refluxed with M-Y zeolite in an oil bath with continuous stirring. The percentages of metal content of various catalysts estimated by atomic absorption spectrometer (AAS) as presented in Table 1.

In the IR spectra of the modified zeolites, a broad band in the range 3300-3700 cm^{-1} are due to the surface hydroxylic groups (Si-OH). The asymmetric stretching, symmetric stretching and bending bands ofthe Al-O-Si framework of the zeolite are presented in Table 2 [20].

No shift or broadening of zeolite vibrations is observed upon insertion of the complexes, which provides further evidence that the zeolite framework remains unchanged. The bands due to the complexes are weaker than the encapsulated ones (due to a low concentration of the complexes). A small shift in the IR bands of the [ML]-NaY with respect to those of corresponding free complexes [ML]

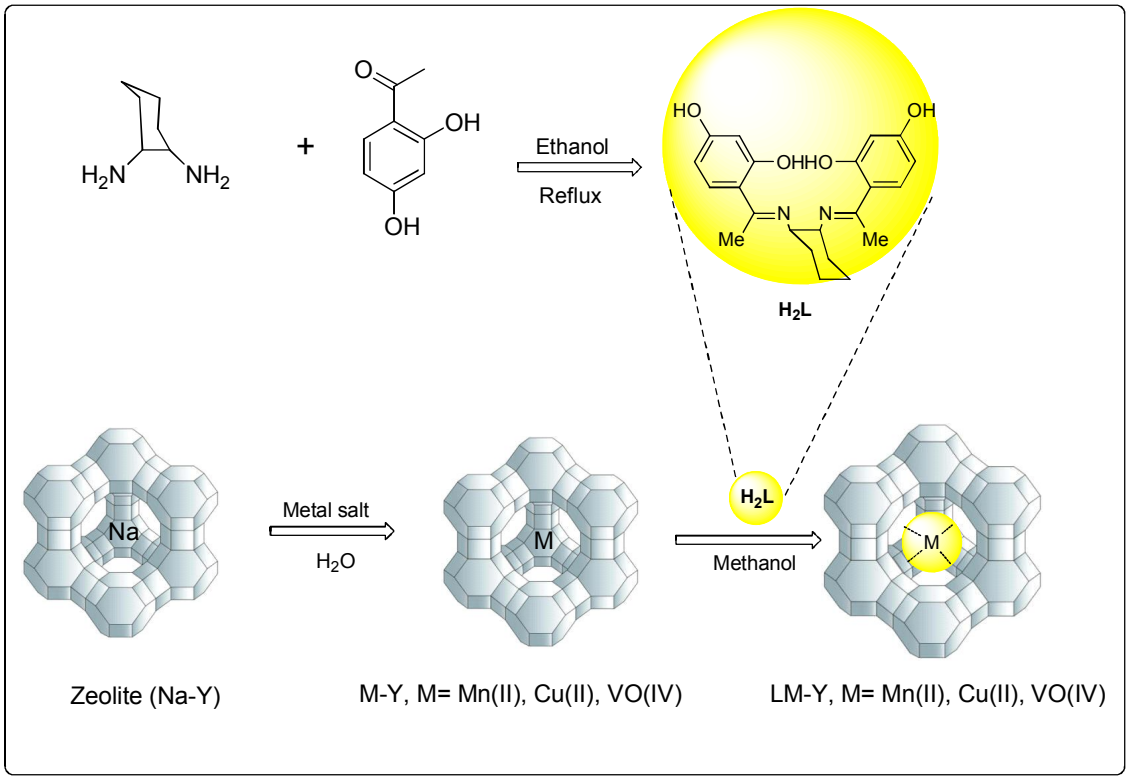


Fig. 1. Schematic preparation of the encapsulated catalyst.

Table 1. Metal Content of the Heterogeneous Catalysts

Catalyst	Metal content (wt.%)
CuL-Y	4.1
MnL-Y	3.9
VOL-Y	3.9

not only confirm the presence of the free complex in the porous of the zeolite, but also suggest that its structure is almost identical. These variations in band frequency can also be attributed to the interactions with the zeolitic matrix.

The X-ray diffraction (XRD) patterns of Na-Y, metal exchanged zeolite and the encapsulated metal complexes were recorded at 2θ values between 5° and 70°. The similarity of the XRD patterns of Na-Y, metal exchanged zeolite and the encapsulated complexes show that the framework and the crystallinity of zeolite-Y has not changed during encapsulation. Moreover, the detectable slight shift and change in the intensity of the peaks is due to the encapsulation of the metal complex. The XRD patterns of Na-Y, Cu-Y and CuL-Y are presented in Fig. 2.

Heterogeneous Catalytic Epoxidation of Olefins

The catalytic performance of metal complexes encapsulated in zeolite-Y was investigated in the

Table 2. IR Spectral Data of Ligand and its Neat and Encapsulated Complexes

Entry	Compound	C=C	C=N	Al-O-Si (Asymmetric stretching)	Al-O-Si (Symmetric stretching)	Al-O-Si (Bending)
1	H_2L	1524	1601	-	-	-
2	CuL	1540	1581	-	-	-
3	MnL	1540	1591	-	-	-
4	VOL	1529	1581	-	-	-
5	Cu-NaY	-	-	1021	795	453
6	Mn-NaY	-	-	1027	791	418
7	VO-NaY	-	-	1023	728	455
8	CuL-NaY	1548	1586	1021	795	453
9	MnL-NaY	1555	1596	1027	791	418
10	VOL-NaY	1541	1585	1023	728	455

Table 3. Epoxidation of Olefins Using TBHP Catalyzed by ML-Y[a]

Entry	Catalyst	Substrate	Conversion (%)[b]	Epoxide (%)	By product (%)[c]
1	CuL-Y	Cyclooctene	52	100	0
		Cyclohexene	62	18	13
		Styrene	55	21	78
		α-Methyl styrene	75	45	55
2	MnL-Y	Cyclooctene	20	100	0
		Cyclohexene	13	59	32
		Styrene	15	6	94
		α-Methyl styrene	41	49	51
3	VOL-Y	Cyclooctene	12	100	0
		Cyclohexene	42	29	26
		Styrene	47	0	100
		α-Methyl styrene	45	83	17

[a]Reaction conditions: olefin (1 mmol), catalyst (0.055 g ML-Y), solvent (5 mL), TBHP 3 mmol; The reactions were run for 6 h at reflux. [b]Based on the starting amount of substrate. [c]In the case of cyclohexene, 2-cyclohexene-1-ol, in the case of styrene, benzaldehyde, and in the case of α-Methyl styrene, acetophenone are by products.

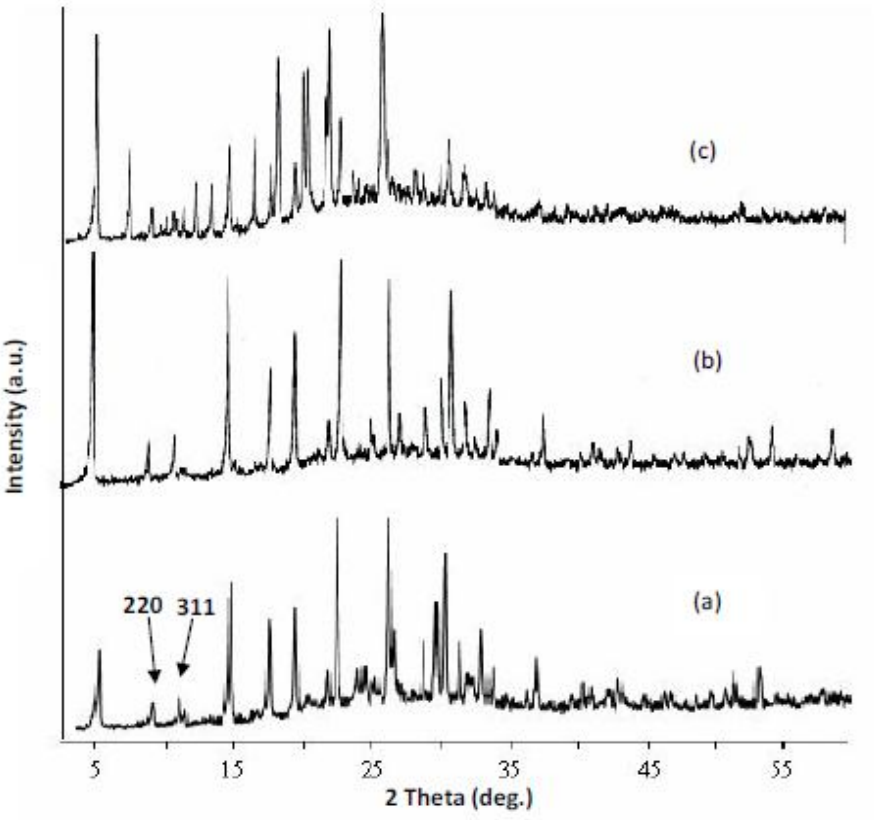


Fig. 2. XRD patterns of: (a) Na-Y, (b) Cu-Y and (c) CuL-Y.

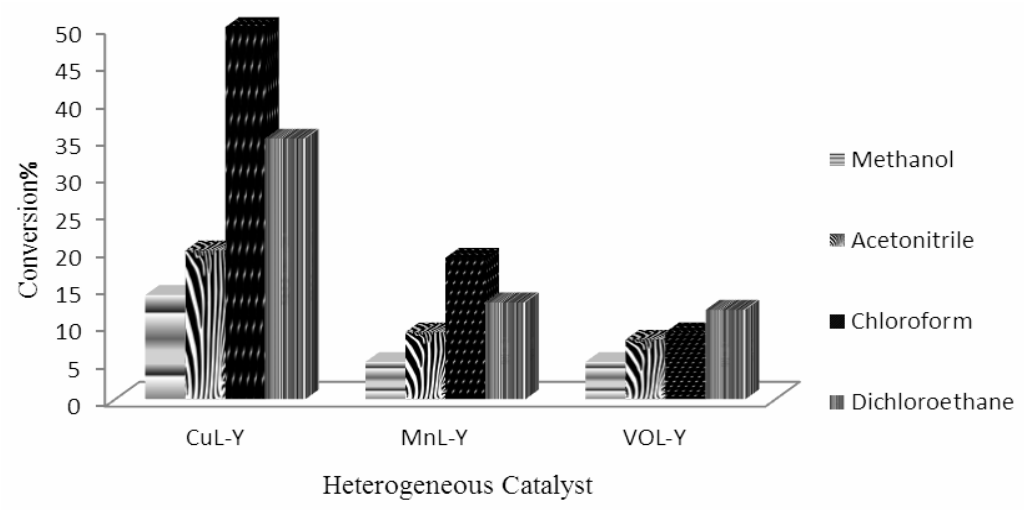


Fig. 3. The influence of different solvents on the oxidation of cyclooctene using TBHP catalyzed by ML-Y. Reaction conditions: catalyst (0.045 g), cyclooctene (1 mmol), TBHP (3 mmol), solvent (5 mL); The reactions were run for 6 h at reflux.

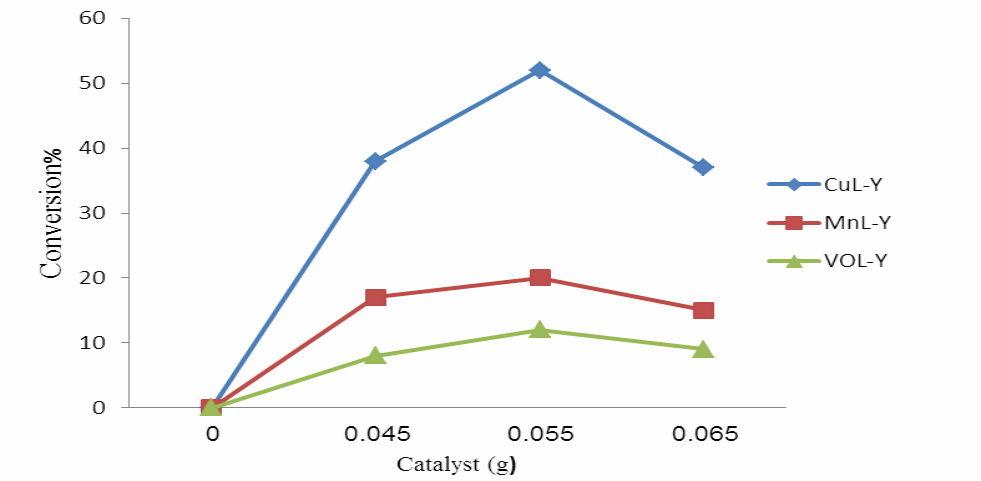


Fig. 4. The influence of catalyst concentration on the oxidation of cyclooctene using TBHP. Reaction conditions: cyclooctene (1 mmol), TBHP (3 mmol), solvent (5 mL); The reactions were run for 6 h at reflux.

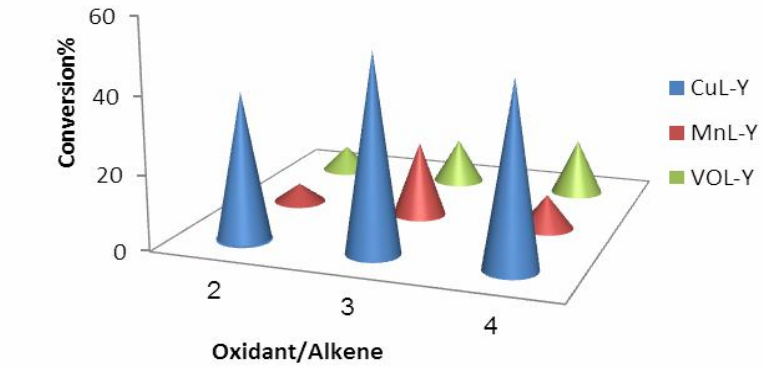
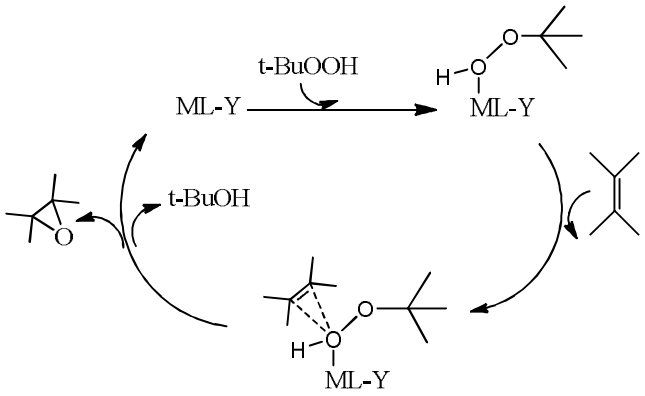


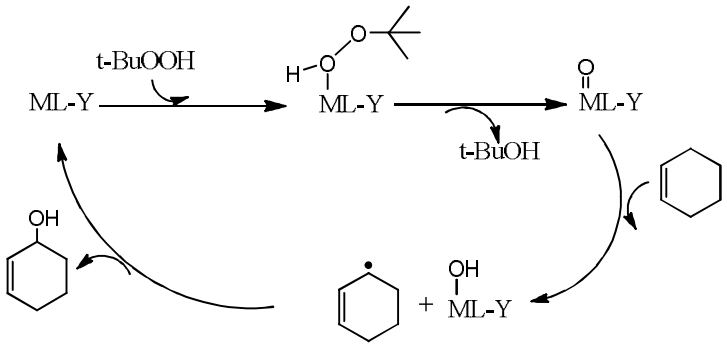
Fig. 5. The influence of oxidant concentration on the oxidation of cyclooctene using TBHP catalyzed by ML-Y. Reaction conditions: catalyst (0.055 g), cyclooctene (1 mmol), solvent (5 mL); The reactions were run for 6 h at reflux.

epoxidation of olefins with *tert*-butyl hydroperoxide (TBHP) as oxygen donor. A series of blank experiments revealed that the presence of catalyst and oxidant are essential for an effective catalytic oxidation. In order to find the best reaction conditions, the effect of various reaction parameters that may affect the conversion and selectivity of the reaction were also examined. Solvent, catalyst concentration, temperature, and concentration of oxidant are the factors that have been optimized.

Solvent effect. In order to obtain the highest conversion in the oxidation of cyclooctene with TBHP in the presence of ML-Y (M = Cu, Mn, VO), different solvents were tested and results have been shown in Fig. 3. It was found that in the oxidation reaction of cycloocetene with TBHP in the presence of VOL-Y, CuL-Y and MnL-Y, the highest conversion was achieved in chloroform while in the presence of VOL-Y, the maximum conversion was obtained



Scheme 1. Proposed catalytic cycle for oxidation of olefins with TBHP in the presence of ML-Y



Scheme 2. Proposed catalytic cycle for oxidation of cyclohexene with TBHP in the presence of ML-Y

in 1,2-dichloroethane. Accordingly, other optimizations were carried out in the best solvent for each catalyst.

Effect of the amount of catalyst. Different catalyst concentrations have been used in the oxidation of cyclooctene with TBHP and according to the results, maximum conversion of cyclooctene required 0.055 g of the catalyst (Fig. 4). A decrease in the conversion with higher amount of catalyst should be due to the degradation of the oxidant.

Effect of oxidant concentration. Different oxidant concentrations have been used in the oxidation of cyclooctene with TBHP (Fig. 5). It was observed that the highest conversion was achieved in the presence of 3 mmol TBHP in the oxidation of cyclooctene.

Oxidation of various olefins. In order to establish the general capability of this catalytic system, under the optimized conditions, oxidation of different olefins has been carried out in the presence of the catalytic amount of ML-Y (M:Cu, Mn, VO) and the results are presented in Table 3.

According to the data of Table 3, the Cu(II) complex is the most efficient catalyst among the three catalysts. Also, with the exception of cyclohexene, the catalytic activity of the Schiff base complexes decreased in the order CuL-Y > VOL-Y > MnL-Y. It seems that the higher Lewis acidity of copper relative to vanadium and manganese causes this observation.

Proposed catalytic cycle. TBHP will be activated by coordination to the metal center (Scheme 1). Consequently, nucleophilic attack of the olefin on the oxygen atom covalently bonded to the metal leading to the formation of epoxide product. In the case of styrene and α-methyl styrene, some benzaldehyde and acetophenone will be

achieved. This is due to the over oxidation of the epoxide product [21-22]. Also whenever cyclohexene used as substrate, allylic products has been obtained in addition to epoxide. This observation suggests a radical pathway for the reaction (Scheme 2) [23-24].

CONCLUSIONS

In summary, VO(IV), Mn(II) and Cu(II) complexes of a Schiff base ligand derived from 2,4-dihydroxyacetophenone and 1,2-diaminocyclohexane have been encapsulated in the nanocavity of zeolite-Y by flexible ligand method. These complexes were employed for the epoxidation of olefins with *tert*-butyl hydroperoxide. Excellent selectivity (100%) for epoxide formation was obtained in the case of cyclooctene. In the case of cyclohexene, styrene and α-methyl styrene, cyclohexene-1-ol, benzaldehyde and acetophenone are by products.

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