

## Mn(II)-Schiff base complex immobilized onto MCM-41 matrix as a heterogeneous catalyst for epoxidation of alkenes

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### ABSTRACT

A heterogeneous catalyst containing manganese Schiff base complex (derived from 2,4-dihydroxybenzaldehyde and 1,2-phenylenediamine) is produced by covalent anchoring in MCM-41 matrix. The synthesized catalyst was characterized by X-ray diffraction pattern (XRD), inductivity coupled plasma (ICP), Fourier transform infrared (FT-IR) spectroscopy, N<sub>2</sub> sorption-desorption isotherm and by transmission electron microscopy (TEM). The obtained catalyst was used in the epoxidation of alkenes with hydrogen peroxide. Furthermore, the effect of various parameters such as reaction time, temperature, amount of catalyst, oxidant and imidazole has been investigated. The catalyst reusability was investigated. Our result reveals that this catalyst shows high catalytic activity in the epoxidation of alkenes.

**Keywords:** Alkene epoxidation, Heterogeneous catalyst, MCM-41, Schiff base.

### 1. Introduction

Epoxidation reaction with hydrogen peroxide that is one of the greenest oxidants has attracted a lot of attention because of the importance of epoxide in the industry. Hydrogen peroxide is preferred oxidant for epoxidation because of its low cost and safety at a low concentration. In addition, its by-product is the sole water and has high oxygen content [1-6].

Manganese Schiff base complexes have high catalytic activity for epoxidation of alkenes in a homogeneous phase but this homogeneous catalyst is not facile separated and recycled. Therefore, more attempts have been made for immobilization of homogeneous catalysts on the solid support such as MCM-41 [7-12].

Among different inorganic supports, MCM-41 materials are very favorable for researchers because of large surface area, uniform pore size distribution and high concentration of silanol groups allowing covalently attached metal complex [13,14].

Several approaches can be utilized to immobilize the heterogeneous Schiff base complex onto various supports [15]. Trialkoxysilane-based linking substrates were used to immobilize a Schiff base onto a support surface. Among these techniques, the formation of covalent bonds between the support and the Schiff base complex, lead to more resistant catalyst toward leaching during catalytic reaction.

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In this work, an anchoring Mn(II)-Schiff base complex on MCM-41 by forming urethane linkage between the surface hydroxyl groups of MCM-41 and one of the terminal isocyanate groups of 1,4-butanediisocyanate (DIC-4) were described, while another isocyanate ending was attached to the hydroxyl groups in the salen ligand [16]. The obtained heterogeneous catalyst was evaluated in the epoxidation of olefins with H<sub>2</sub>O<sub>2</sub> in ethanol as a solvent.

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## 2. Experimental

### 2.1. Materials and Instruments

Chemicals were purchased from Merck or Fluka and used as received without further purification. The solid samples were identified by X-ray powder diffraction (XRD) using asimens D500 diffractometer, Cu- $k_{\alpha}$  ( $\lambda=4541 \text{ \AA}$ ). Infrared spectra were recorded (KBr pellets) on a VECTOR-22 Bruker in the range of 400 to 4000  $\text{cm}^{-1}$ . The measurement of specific surface area for the prepared samples was performed through measuring  $\text{N}_2$  adsorption-desorption isotherms at 77 K with a Quanta-chrome NOVA-2200e system. Amount of loaded Mn(II) was determined by inductively coupled plasma (ICP-OESJobinYvon). Gas chromatography (GC) analysis was conducted on an Agilent chromatograph (model 7890B) equipped with the flame ionization detector (FID) and capillary column HP-5 (phenyl methyl siloxane 30 m  $\times$  0.32 mm  $\times$  0.25  $\mu\text{m}$ ).

### 2.2. Preparation of manganese Schiff base complex

The complexing agent N, N- bis (4- hydroxysalicyl aldehyde) phenylenediamine (4- OH salophen) was prepared by condensing the 1,2-phenylenediamine (3.9 mmol) and 2,4-dihydroxybenzaldehyde (7.8 mmol) in ethanol. A yellow-orange precipitate began to appear, however, the reaction required more than 1h for completion. The obtained precipitates were filtrated and dried under vacuum. The Mn(II) Schiff base complex (A) was prepared by refluxing 3 mmol of the prepared ligand and 3.3 mmol of manganese (II) acetate tetra hydrate was refluxed in an ethanolic solution for 2 h. The crystallization of Mn(II)-complex was performed in a solution of ethanol: acetonitrile (1:1). The obtained product was dried under vacuum, overnight [16] (Scheme 1).

### 2.3. Preparation of MCM-41

The MCM-41 was synthesized according to the procedure previously reported [17].

### 2.4. Complex anchoring

To anchor the prepared catalyst, 1g of the MCM-41 was refluxed as a support with 3 mmol of DiC-4 as a binder,

in dry toluene for 3 h under  $\text{N}_2$  atmosphere. After cooling down the solution to the room temperature, the Mn(II) complex was added and refluxed for 6 h under  $\text{N}_2$  atmosphere.

Then, the resulting product was extracted through soxhlet mode by ethanol for 24h and dried under vacuum [16]. The resulting material(B) was denoted as [Mn(4-OHsalophen) Dic] @MCM-41 (Scheme 2).

### 2.5. Catalytic experiment

Catalytic experiments were carried out in a 5 ml test tube. In a typical procedure, to an ethanolic solution (1 ml) of cyclooctene (13  $\mu\text{l}$ ), heterogeneous Schiff base catalyst (0.0046 g), imidazole (0.02 g) as a co-catalyst, and hydrogen peroxide (1 ml) as an environmental friendly oxidant were added. The reaction mixture was stirred for 30 min at room temperature and the catalyst was removed by centrifugation. Then, the reaction products were monitored at periodic time intervals using gas chromatography. The oxidation products were identified by comparison with authentic samples (retention times in GC).

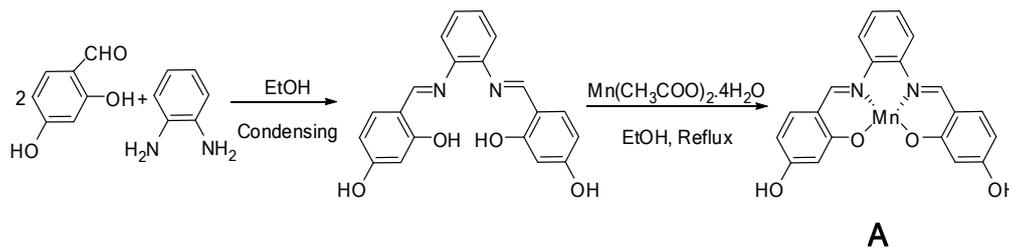
In recycling experiments, the solid catalyst was centrifuged, washed with distilled water and ethanol followed by acetone and used for the next time.

## 3. Results and Discussion

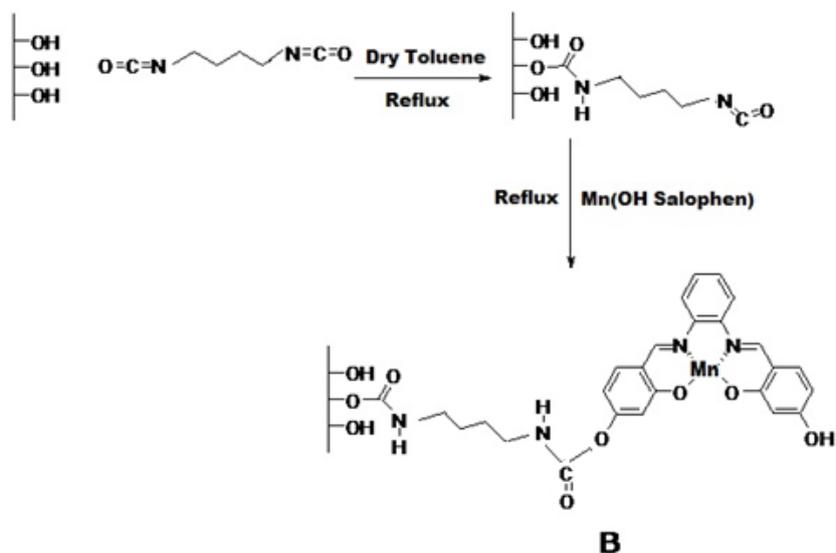
### 3.1. Catalyst characterization

The XRD pattern (Fig. 1) shows a very intense peak due to the (100) reflection that is due to the hexagonal pore structure of MCM-41 and two weaker peaks due to (110) and (200) reflections. The mentioned peaks were kept in the catalyst loaded MCM-41 sample; however, their intensity was decreased, this indicates disordering of plane arrangement during catalyst loading in the MCM-41 structure [18].

FT-IR spectra of the catalyst (Fig. 2) confirm that the MCM-41 framework was not changed during the modification. The bands at ranges of 3300-3770  $\text{cm}^{-1}$  are due to the surface hydroxyl groups and in the range of 1300-750  $\text{cm}^{-1}$  are due to the lattice vibrations.



**Scheme 1.** Preparation of manganese Schiff base complex.



Scheme 2. Anchoring of catalyst on MCM-41 support.

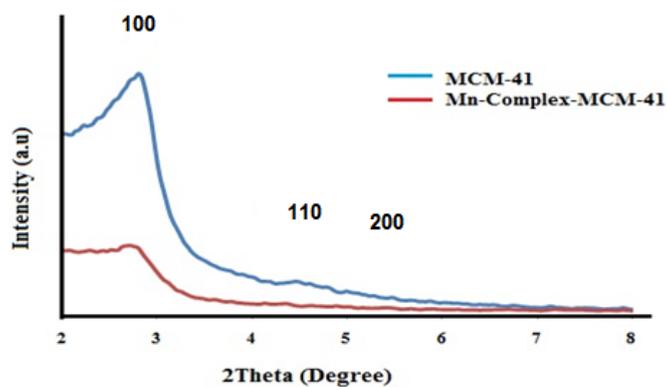


Fig. 1. XRD pattern of MCM-41 and catalyst [Mn(4-OHsalophen) Dic]@MCM-41.

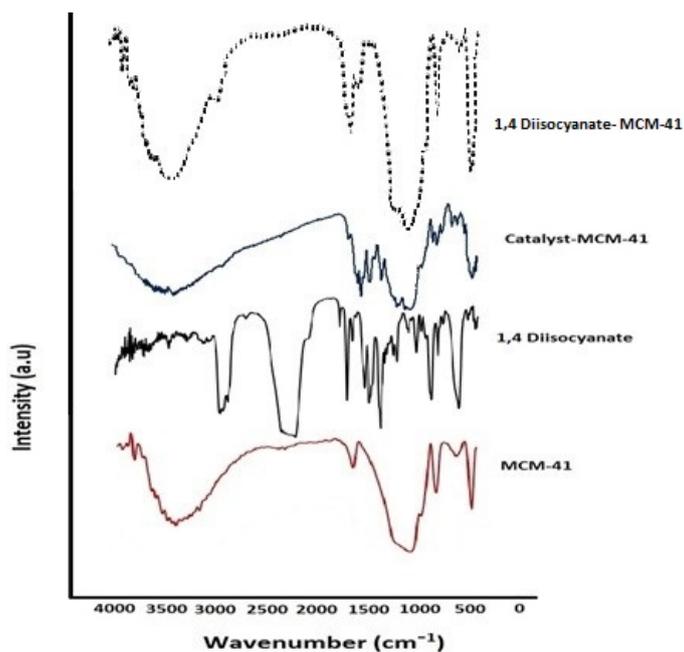


Fig. 2. FT-IR spectra of 1,4-diisocyanate, MCM-41, and heterogeneous catalyst [Mn(4-OHsalophen) Dic]@MCM-41.

Bands at 1070 and 802  $\text{cm}^{-1}$  are assignable to the asymmetric and symmetric stretching  $\nu(\text{Si-O-Si})$  and  $\nu_s(\text{Si-O-Si})$  of MCM-41 framework, the band present at about 960  $\text{cm}^{-1}$  is attributed to  $\nu(\text{Si-OH})$  vibrations. The observed peak at 1690  $\text{cm}^{-1}$  in the final product is assigned to the carbamate amide group. The spectrum of the modified MCM-41 (Fig. 2) as well as the spectra of the unmodified MCM-41 are dominated by a strong band characteristic of the support matrix, indicating the support framework remained unchanged. The peak observed in 1580–1600  $\text{cm}^{-1}$  is attributed to the stretching vibrations of the C=N bonds. A new peak was observed at 1440  $\text{cm}^{-1}$  can be attributed to the  $\text{CH}_2$  bending.

Disappearance of the-NCO characteristic peak at about 2275  $\text{cm}^{-1}$  in (DIC-4) indicates the reaction of both functional groups of 1,4-diisocyanatobutane [19].

The manganese content of heterogeneous catalyst was measured by ICP. Based on this analysis, the Mn content of the catalyst is about 3% (W/W).

Textural properties of the samples obtained by  $\text{N}_2$  isotherms are summarized in Table 1. The results

indicate that surface area, pore volume and diameter of MCM-41 decreased significantly after the catalyst modification. The decreased in surface area can be attributed to dispersion and deposition of catalyst particles into MCM-41 pore channels [20,21].

The TGA curve of the catalyst is presented in Fig. 3. The thermogram of catalyst shows two individual steps of weight loss. The first distinct weight loss in the region of 25–120  $^\circ\text{C}$  is associated with the desorption of water. Thereafter, a second (200–400  $^\circ\text{C}$ ) weight loss is observed, this is likely to be attributed to decomposition of Schiff base complex.

Fig. 4 shows the TEM images of MCM-41 and Schiff base catalyst loaded on MCM-41. The regular arrangement of pores can be clearly observed for materials. The loading of catalyst on MCM-41 did not change the original morphology of MCM-41.

SEM micrograph (Fig. 5), that shows the surface morphology, revealed that Schiff base particles were well dispersed in the porosity of MCM-41.

EDAX of the catalyst showed that the mass percents of Si, C, N, O, and Mn are 23%, 22/18%, 6/31%, 46/8% and 2/1% respectively (Fig. 6).

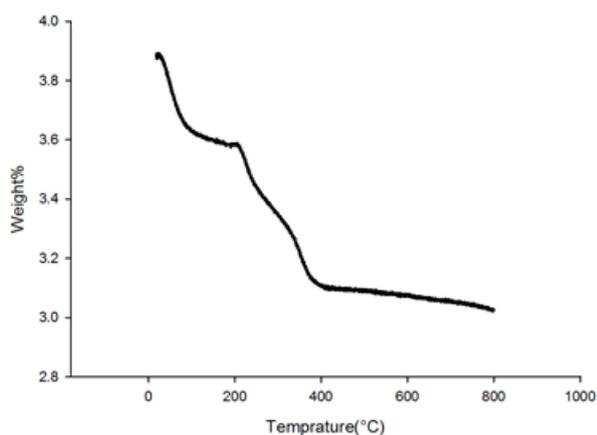
**Table 1.** Textural properties of samples obtained by  $\text{N}_2$  adsorption.

Sample Name	BET ( $\text{m}^2/\text{g}$ )	Average Pore Diameter (nm)	BJH Pore Volume ( $\text{cm}^3/\text{g}$ )
MCM-41	1500	3.52	1.2
Mn(4-OH Sallophen) Dic@MCM-41	480	2.67	0.31

**Table 2.** The optimum reaction conditions for the oxidation of cyclooctene.<sup>a</sup>

Entry	Catalyst:Im	Amount of catalyst (g)	Solvent (1 mL)	Temp. ( $^\circ\text{C}$ )	Time (h)	Conversion (%)
1	1:100	0.0046	EtOH	25	2	35
2	1:100	0.0046	EtOH	25	8	65
3	1:100	0.0046	EtOH	25	24	93
4	1:100	0.0046	EtOH	25	48	85
5	1:100	0.0046	$\text{CCl}_4$	25	24	3
6	1:100	0.0046	$\text{CHCl}_3$	25	24	8
7	1:100	0.0046	$\text{CH}_2\text{Cl}_2$	25	24	6
8	1:100	0.0046	MeOH	25	24	15
9	1:100	0.0046	EtOH	50	24	10
10	1:100	0.0030	EtOH	25	24	40
11	1:100	0.0069	EtOH	25	24	60
12	1:50	0.0046	EtOH	25	24	35
13	1:150	0.0046	EtOH	25	24	50

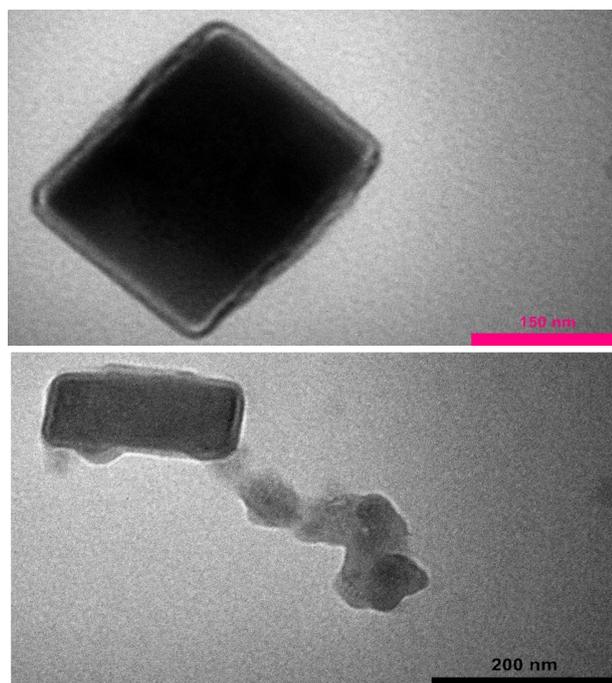
<sup>a</sup>Reaction conditions: Solvent: 1 mL,  $\text{H}_2\text{O}_2$  (1 mL), under magnetic stirrer.



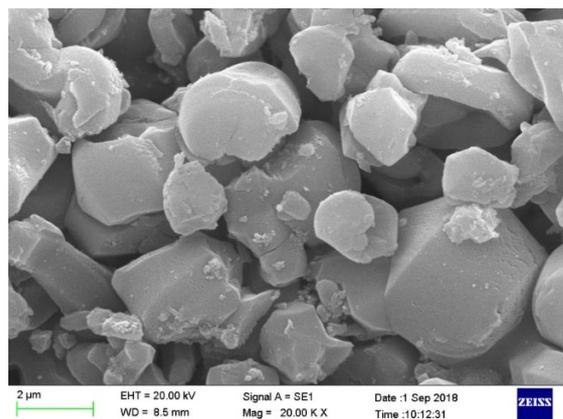
**Fig. 3.** The TGA thermograph of the heterogeneous catalyst [Mn(4-OHsalophen) Dic]@MCM-41.

### 3.2. Catalytic oxidation of cyclooctene

The heterogeneous catalyst was used for the oxidation of cyclooctene with  $H_2O_2$ . The effects of various parameters such as the time of reaction, amount of catalyst, oxidant and imidazole have been studied (Table 2). The effect of time on the oxidation reaction can be determined by varying the reaction time (Table 2, entries 1-4). Measuring of conversion value at different reaction times of 2, 8, 24, and 48 h clarified that the highest conversion was obtained after 24 h (Table, entry 3). The influence of different solvents ( $CCl_4$ ,  $CHCl_3$ ,  $CH_2Cl_2$ , methanol and ethanol) on the oxidation of cyclooctene was studied (Table 2, entries 5-8).



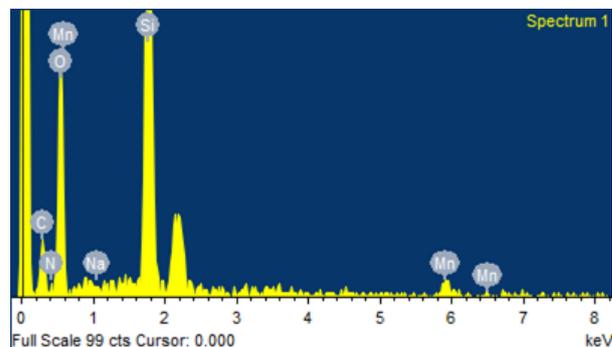
**Fig. 4.** TEM images of (a) MCM-41 and (b) catalyst [Mn(4-OHsalophen) Dic]@MCM-41.



**Fig. 5.** SEM image of the heterogeneous catalyst [Mn(4-OHsalophen) Dic]@MCM-41.

The highest conversion (93 %) was obtained in ethanol while 3%, 8%, 6% and 15% conversion were achieved in  $CCl_4$ ,  $CHCl_3$ ,  $CH_2Cl_2$  and methanol respectively. The reaction was carried out in 50 °C water bath and 10% conversion was achieved and it was much lower than room temperature (Table 2, entry 9). It can be due to the faster decomposition of  $H_2O_2$  in high temperatures. The effect of catalyst concentration was investigated in the presence of different amounts of the catalyst (0.003 g, 0.0046 g and 0.0069 g) in the oxidation of cyclooctene using  $H_2O_2$  as an oxidant (Table 2, entries 10-11). The highest conversion (93%) was obtained in the presence of 0.0046 g of catalyst, while 40% and 60% cyclooctene oxide were achieved in the presence of 0.0030 g and 0.0069 g catalyst respectively. To study the effect of the imidazole concentration on the oxidation of cyclooctene, different catalyst:imadazole molar ratios (1:50, 1:100 and 1:150) were examined (Table 2, entries 12-13). The highest conversion was achieved for the 1:100 catalyst:imadazole molar ratio.

All the results confirmed that the best reaction condition is when the reaction was carried out in the room temperature in the presence of 0.0046 g of a catalyst with the 1:100 (catalyst:imadazole) molar ratio (93% conversion).



**Fig. 6.** EDS of the surface of catalyst ([Mn(4-OHsalophen) Dic]@MCM-41).

The heterogeneous catalyst was used for the oxidation of various olefins with H<sub>2</sub>O<sub>2</sub> under optimized condition (Table 3). The higher reactivity of cyclooctene relative to cyclohexene is perhaps due to the greater flexibility of the cyclooctene (Table 3, entries 1, 2). Oxidation of indene and styrene led to 85% and 40% epoxide as the major product, respectively (Table 3, entries 3-4). In comparison to the aromatic hydrocarbons, linear alkenes such as 1-octene (which may be considered as an electron deficient alkene) is less desirous of involving in oxidation reactions and need longer times to complete the production. In this case, 50% conversion was obtained for 1-octene with an excellent selectivity (100%) (Table 3, entry 5).

### 3.3. Catalyst reusability and stability

The stability and reusability of a heterogeneous catalyst are of the most important factors in the catalytic systems. To this goal, the catalyst was subjected to oxidation of cyclooctene with H<sub>2</sub>O<sub>2</sub> under the optimized conditions. After completion of the reaction, the prepared catalyst was separated easily and reused several times. For each of the repeated reactions, after the completion of the reaction, the solid catalyst was removed by centrifugation for about 15 min, washed with acetone (2 × 1 mL), dried at 50 °C for about 20 h, and used for the next run. The catalyst showed remarkable results without noticeable loss of activity

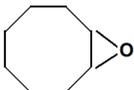
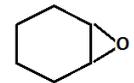
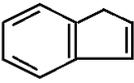
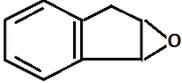
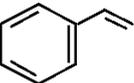
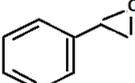
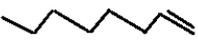
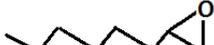
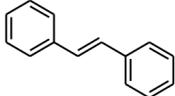
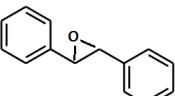
even after 5 runs indicating efficient recycling of the catalyst.

### 3.4. Proposed catalytic mechanism

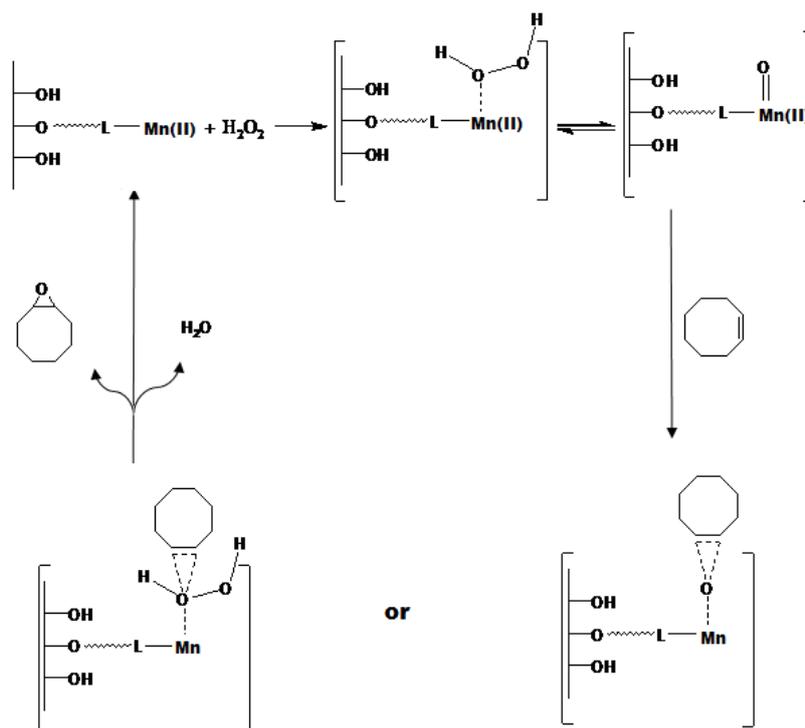
The mechanism proposed for the oxidation of cyclooctene with H<sub>2</sub>O<sub>2</sub> is presented in Scheme 3. [22]. In the catalytic cycle for oxidation reactions with hydrogen peroxide, two common intermediate species have been suggested in the literature. In this mechanism, hydrogen peroxide is activated with the manganese center followed by the generation of high valent Mn-oxido species. Both intermediates can produce epoxide products.

For verifying the activity of [Mn(4-OHsalophen) Dic]@MCM-41, the present study is compared with some other literature for oxidation of olefins. The results are shown in Table 4. Various heterogenized catalysts have been used for the oxidation of cyclohexene and cyclooctene with H<sub>2</sub>O<sub>2</sub>. However, none of the reported catalysts show such high activity as [Mn(4-OHsalophen) Dic]@MCM-41 used in this work. An exception is the Mn-Schiff base-Zeolite catalyst (entry 4) which shows a high conversion of cyclooctene oxide with H<sub>2</sub>O<sub>2</sub>. However, CH<sub>3</sub>CN is not a green solvent in comparison to EtOH, and the room temperature condition in this work is more cost-effective and environmentally benign than reflux used in entry 4.

**Table 3.** Oxidation of various olefins with hydrogen peroxide.

Entry	alkene	product	Yield(%) <sup>a</sup>
1			93
2			87
3			85
4			40
5			50
6			100

<sup>a</sup>GC yields are based on the starting alkenes. Catalyst: Imidazole: olefin molar ratio is 1: 100: 30. H<sub>2</sub>O<sub>2</sub> (30 %) 1ml, 24 h.



Scheme 3. Plausible reaction mechanism.

Table 4. Comparison of the activity of different complexes in the oxidation reaction.

Entry	Catalyst	Substrate	Oxidant	Solvent	Temp. (°C)	Time (h)	Yield (%)	Ref.
1	Na[SbW <sub>9</sub> O <sub>33</sub> ]+9[MTCA]+Cl	Cyclohexene	H <sub>2</sub> O <sub>2</sub>	Toluene	35	6	42	[23]
2	Mn(Br <sub>8</sub> TPP)Cl-PSI	Cyclooctene	H <sub>2</sub> O <sub>2</sub>	CH <sub>3</sub> CN	r.t.	5	10	[24]
3	FeTHPPCl-MWCNT	Cyclooctene	TBHB	CH <sub>3</sub> CN	r.t.	24	20	[25]
4	Mn Schiff base-Zeolite	Cyclooctene	H <sub>2</sub> O <sub>2</sub>	CH <sub>3</sub> CN	r.t.	4	70	[26]
5	VO Schiff base-Zeolite	Cyclooctene	H <sub>2</sub> O <sub>2</sub>	CH <sub>3</sub> CN	r.t.	4	26	[26]
6	Mn(II)-Complex-MCM-41	Cyclooctene	H <sub>2</sub> O <sub>2</sub>	EtOH	r.t.	24	88	[27]
7	[Mn(4-OHsalophen) Dic]@MCM-41	Cyclohexene	H <sub>2</sub> O <sub>2</sub>	EtOH	r.t.	24	47	This work
8	[Mn(4-OHsalophen) Dic]@MCM-41	Cyclooctene	H <sub>2</sub> O <sub>2</sub>	EtOH	r.t.	24	93	This work

#### 4. Conclusions

Oxidation of olefins by using hydrogen peroxide as a safe oxidant in ethanol media were efficiently enhanced in the presence of a Mn-Schiff base complex anchored in MCM-41 matrix. This, together with the use of ethanol as green solvents and a wide substrate range, makes this cost-effective, environmentally benign methodology suitable for applied goals.

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