

# Catalytic air oxidation of cyclooctene using *cis*-[MoO<sub>2</sub>(SAL-SH)(DMF)] (SAL-SH = salicylidene salicyloyl hydrazinato-) and its zeolite-Y encapsulated composite

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## Abstract

Oxidation of cyclooctene to cyclooctene epoxide using *cis*-MoO<sub>2</sub>(SAL-SH)(DMF) and its zeolite-Y encapsulated composite as catalysts is reported. The percent conversion into epoxide was 68% at 60°C under 0.1 mmol of *cis*-MoO<sub>2</sub>(SAL-SH)(DMF), 0.3 mmol of cyclooctene and under oxygen saturated conditions. The turnover with respect to Mo in the complex is eight. The percent conversion improved to 75% and the turnover increased nine times when complex-NaY composite is used under the same conditions. The oxidation reaction showed first order dependence with respect to the concentrations of catalyst and cyclooctene. The reaction is endothermic with an activation energy of 25.8 kcal mol<sup>-1</sup>. A reaction scheme for oxidation of cyclooctene using *cis*-MoO<sub>2</sub>(SAL-SH)(DMF) is proposed and the higher activity observed with complex-NaY composite is attributed to absence of μ-oxo dimer formation in this case. The intermediate Mo(IV)O complex reacts with O<sub>2</sub>, regenerating the parent Mo(VI)O<sub>2</sub> complex, which participates cyclically in the reaction. © 1999 Elsevier Science B.V. All rights reserved.

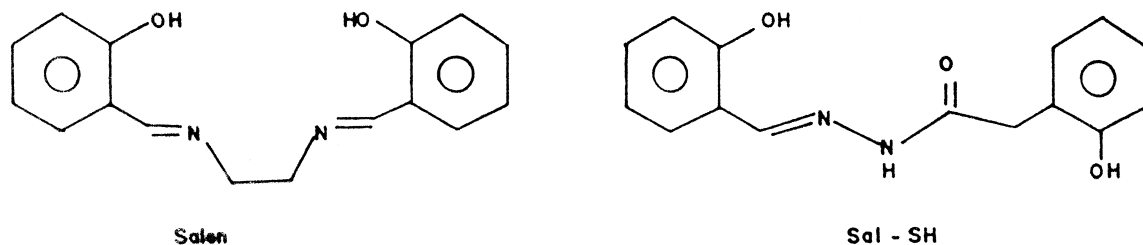
**Keywords:** Cyclooctene; Oxidation; Zeolite-Y encapsulated composite

## 1. Introduction

The role of the oxomolybdenum center in oxygen atom transfer enzymes in a biological environment is the subject of great interest [1–3]. In this context, investigations regarding synthesis, characterization and oxo-transfer activity of several dioxomolybdenum complexes in different Schiff base environments have been featured prominently in published literature [4–7]. Some of the dioxomolybdenum complexes with dithiocarbamates [8,9], stearily bulky tridentates [2,5] such as 2,6-bis(2,2-diphenyl-2-sulfidoethyl) pyridine (2-), 2-saliylideneamino phenolato (2-) and 2-salicylidene amino benzene thiolate (2-) have been shown to oxidize thiols, polyketones, tertiary phosphines, and some acyclic and cyclic olefins. Recently, we reported salicylidene salicyloyl hydrazinato-*cis*-oxo (solvato) molybdenum (VI), [*cis*-MoO<sub>2</sub>(SAL-SH) (solv)] to catalyze air oxidation of triphenyl

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phosphine into triphenylphosphine oxide [7]. In the present paper, we report oxidation of *cis*-cyclooctene using *cis*-MoO<sub>2</sub>(SAL-SH) (solv). This study interested us from two angles: (i) testing oxidation of some olefins using *cis*-MoO<sub>2</sub>(SAL-SH) (solv) as a natural consequence to knowing oxidation of PPh<sub>3</sub> using the same complex, and (ii) exploring encapsulation of *cis*-MoO<sub>2</sub>(SAL-SH) into Y-type zeolite through flexible ligand method for entrapping molecular species inside zeolite cavities [10–12] and examining cyclooctene oxidation. It may be reckoned here that Schiff bases other than salen (bis (salicylaldehyde) ethylenediimine) have seldom been used for complexation within zeolites. The SAL-SH (II) ligand may be expected to be flexible with minimum kinetic diameter of < 6.5 Å, comparable with that of salen (I).



The ligand, SAL-SH, has shown earlier [7] to undergo keto-imine tautomerisation during complexation with MoO<sub>2</sub> moiety and behaved as tridentate ligand. The –OH group on salicyloyl hydrazinato group abstained from complexation.

Apart from kinetic investigations on cyclooctene oxidation using *cis*-MoO<sub>2</sub>(SAL-SH) (solv), the characterisation of *cis*-MoO<sub>2</sub>(SAL-SH)-NaY and its use as a catalyst for epoxidation of *cis*-cyclooctene is reported in this paper. Our results on chemical composition analysis and diffuse reflectance data of complex-NaY composite supported the above referred rationale of intrazeolite complexation using SAL-SH ligand and the use of this composite enhanced the percent conversion of cyclooctene into epoxide, too.

## 2. Experimental

### 2.1. Materials

Ammoniummolybdate, (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub> · 4H<sub>2</sub>O; acetylacetone, salicylaldehyde were procured from BDH (UK). Salicylic acid hydrazide was purchased from Sisco Chem. Lab., Mumbai (India). Cyclooctene was procured from Aldrich (USA) and cyclooctene oxide as a standard from Lancaster. Acetone, ethanol and dimethyl formamide were of high purity (Spectra Pure). *cis*-MoO<sub>2</sub> (acac)<sub>2</sub> was synthesized and purified according to a reported method [13]. Y-zeolite (NaY, Koch-Light) was a gift from CSMCRI, Bhavnagar (India).

### 2.2. Preparation of *cis*-MoO<sub>2</sub>(SAL-SH) (solv)

This orange coloured complex was obtained by refluxing 1:1 mixture of SAL-SH and *cis*-MoO<sub>2</sub> (acac)<sub>2</sub> in acetone solvent for 6 h and by precipitation from excess of distilled water [7].

### 2.3. Preparation of $\text{MoO}_2(\text{SAL-SH}) (\text{solv})\text{-NaY}$

Initially, molybdate ion exchange was carried out by stirring NaY (2 g) in an aqueous solution (150 ml) of ammoniummolybdate (0.05 g, 0.047 mmol) at 90°C for 9–10 h. The powder was then filtered, washed several times with distilled water and dried in oven (80°C) for 24 h. The molybdate ion exchanged zeolite-Y was added to the hot ethanolic solution of SAL-SH ligand (0.1 g, 0.39 mmol) and heated with stirring at 90°C for 10 h to ensure complex formation. In order to remove the excess of ligand from the surface of zeolite, it was washed several times with hot ethanol and subjected to Soxhlet extraction using ethanol until no free ligand is detected in UV-VIS spectra of the extract. The zeolite composite was subsequently dried at 80°C for 24 h and stored in desiccator.

### 2.4. Physical measurements

FT-IR spectra of KBr discs were recorded on BioRad FTS-40 model FI-IR unit. Diffuse reflectance (FT-IR) spectra for zeolite composites were recorded on a ATI Mattson (Model Infinity) Fourier transform infrared spectrometer (4000–400  $\text{cm}^{-1}$ ). Atomic absorption data was obtained using Model GBC 932 AAS (Australia). The powder diffractograms of NaY and complex encapsulated zeolite composite were recorded on Philips PW 1140 Diffractometer with  $\text{Cu K}_\alpha$  radiation and  $2\theta$  varied from 2 to 70°.

### 2.5. Oxidation experiments

Oxidation of cyclooctene was carried out in a water-jacketed glass reactor fitted with a condenser, thermometer and a sampling port. Water from a constant temperature water bath was recirculated through a water jacket to attain the desired temperatures. In a typical oxidation experiment, 0.1 mmol *cis*- $\text{MoO}_2(\text{SAL-SH}) (\text{solv})$  was dissolved in 10 ml DMF and when the desired temperature was attained, 0.3 mmol cyclooctene was added and slow oxygen bubbling was commenced. The reaction was performed under stirring for a period of 5 h. Liquid samples were withdrawn from the reactor at chosen intervals of time and the progress of the reaction was monitored by gas liquid chromatography (Perkin-Elmer) using 8% Carbowax 20 M on Chromosorb (FID, column temperature 100–150°C; injection temperature 150°C; detector temperature 200°C;  $\text{N}_2$  carrier gas 10 ml/min). Similarly, 0.1 g of  $\text{MoO}_2(\text{SAL-SH})\text{-NaY}$  composite was used for the oxidation of cyclooctene and the membrane filtered (0.45  $\mu\text{m}$ ) samples were analyzed for conversion of cyclooctene.

## 3. Results and discussion

### 3.1. Characteristics of $\text{MoO}_2(\text{SAL-SH})\text{-NaY}$

The chemical composition of NaY and  $\text{MoO}_2(\text{SAL-SH})\text{-NaY}$  is given in Table 1. The Si/Al ratio in NaY is 4.18 indicating that it as a dealuminated sample. The Mo content of  $\text{MoO}_2(\text{SAL-SH})\text{-NaY}$

Table 1  
Elemental composition (weight percent) of NaY and  $\text{MoO}_2(\text{SAL-SH})\text{-NaY}$  composites

Sr. No.	Type of composite	%Si	%Al	%Na	%Mo	Si/Al
1	NaY	22.20	5.25	11.38	–	4.18
2	$\text{MoO}_2(\text{SAL-SH})\text{-NaY}$	21.87	4.98	10.56	1.2	4.40

Table 2

FT-IR transmittance data for *cis*-MoO<sub>2</sub>(SAL-SH) (H<sub>2</sub>O) and diffuse reflectance data for MoO<sub>2</sub>(SAL-SH)-NaY

<i>cis</i> -MoO <sub>2</sub> (Sal-SH) (H <sub>2</sub> O)		MoO <sub>2</sub> (Sal-SH) - NaY	
Peak, cm <sup>-1</sup>	Assignment	Peak, cm <sup>-1</sup>	Assignment
893 (S), 939 (m)	$\nu_{\text{asy}} \& \nu_{\text{sym}}$ of <i>cis</i> -MoO <sub>2</sub> moiety	537 (S)	$\nu_{\text{Al-O}}$ of Si<O>Al bridges
1157, 1260	$\nu_{\text{C-O}}$ (phenolic)	1024 (S)	$\nu_{\text{Si-O}}$ of Si<O>Al bridges
	$\nu_{\text{C-OH}}$ (phenolic)	1075 (m)	$\nu_{\text{Si-OH}}$
1527 (m), 1602 (S)	$\nu_{\text{sym}} \& \nu_{\text{asy}}$ of -C=N=N=C- group	878 (S), 926 (m)	$\nu_{\text{asy}} \& \nu_{\text{sym}}$ of <i>cis</i> -MoO <sub>2</sub> moiety
1618	Coordinated H <sub>2</sub> O	1182 (S)	$\nu_{\text{C-O}}$ (phenolic)
3000-3100	C-H stretching of aromatic ring	1260 (S)	$\nu_{\text{C-OH}}$ (phenolic)
		1514 (S)	$\nu_{\text{sym}} \& \nu_{\text{asy}}$ of -C=N=N=C-
		1608 (S)	
		1623	Coordinated H <sub>2</sub> O
		3000-3150	$\nu_{\text{C-H}}$ of aromatic rings
		3670-3784	$\nu_{\text{O-H}}$ of two different groups
			e.g.: AlO-H and SiO-H

is 1.2 wt.% which corresponds to about two Mo atoms per unit cell of zeolite-Y (i.e., one Mo atom per four super cages). The XRD patterns of the zeolite composite resembled that of NaY without any extra peaks that could be attributed to bulk molybdate or MoO<sub>2</sub>(SAL-SH) complex. The FT-IR data for the *cis*-MoO<sub>2</sub>(SAL-SH)(H<sub>2</sub>O) is compared with that of its zeolite composite in Table 2: the peaks at 893 and 939 cm<sup>-1</sup> due to *cis*-MoO<sub>2</sub>, at 1157, 1260 cm<sup>-1</sup> due to phenolic C–O stretching vibrations, at 1527 and 1602 cm<sup>-1</sup> due to coordinated H<sub>2</sub>O are characteristic of *cis*-MoO<sub>2</sub>(SAL-SH) (H<sub>2</sub>O) complex. These characteristic peaks, with a little or more displacement, are also found in the diffuse reflectance spectra of the complex-NaY zeolite composite. The stretching frequencies due to Al–O and Si–O of Si<O>Al bridges of zeolite matrix are found at 537 and 1024–1075 cm<sup>-1</sup>, respectively. Two peaks observed at 3670 and 3784 cm<sup>-1</sup> belong to  $\nu_{\text{AlO-H}}$  and  $\nu_{\text{SiO-H}}$  of zeolite matrix. Thus, the presence of MoO<sub>2</sub>(SAL-SH) complex within zeolite cages is confirmed.

### 3.2. Catalytic tests

Oxidation of cyclooctene in DMF medium using *cis*-MoO<sub>2</sub>(SAL-SH) (sol<sub>v</sub>) in the presence of O<sub>2</sub> is confirmed by identifying cyclooctene oxide peak in GLC by matching with that of an authentic cyclooctene epoxide sample. The epoxidation of cyclic olefins using hydroperoxides or H<sub>2</sub>O<sub>2</sub> in the presence of VO(acac)<sub>2</sub> and MoO<sub>2</sub>(acac)<sub>2</sub> has been reported to show high selectivity for epoxides [14].

At the end of 5-h run, a turn-over (in terms of Mo in the complex) of 8.0 was achieved using 0.1 mmol catalyst and 0.3 mmol substrate at 60°C, as the percent conversion was 68%. In the absence of

O<sub>2</sub>, the percent conversion was very poor (< 10%). Similarly, at temperatures lower than 50°C, the percent conversion was not significant. In the following kinetic studies, depletion of cyclooctene concentration was monitored and the rate dependence with respect to catalyst concentration and cyclooctene concentration were evaluated. Effect of temperature was examined in the range 50–70°C.

### 3.3. Effect of catalyst concentration

In a typical oxidation experiment, the concentration of catalyst was varied from 0.05 to 0.2 mmol at cyclooctene concentration of 0.3 mmol at 60°C and the rate at each concentration was estimated. The initial rates of cyclooctene oxidation showed first order dependence on *cis*-MoO<sub>2</sub>(SAL-SH) concentration (Fig. 1).

### 3.4. Effect of cyclooctene concentration

In these experiments, the concentration of cyclooctene is varied from 0.2–0.4 mmol keeping other conditions constant, i.e., 0.1 mmol *cis*-MoO<sub>2</sub>(SAL-SH) (solv) and 60°C. The initial rates of oxidation showed first order dependence on cyclooctene concentration (Fig. 2).

### 3.5. Effect of temperature

Typical oxidation run using 0.1 mmol *cis*-MoO<sub>2</sub>(SAL-SH) (solv) and 0.2 mmol cyclooctene was conducted at 50, 60 and 70°C; and the rate of reaction was estimated at each temperature. A plot of  $-\ln(\text{rate})$  vs.  $1/T$  (Arrhenius plot) was drawn (Fig. 3) and the value of activation energy ( $E_a$ ) was evaluated from the slope of the plot as 25.8 kcal mol<sup>-1</sup>.

### 3.6. Oxidation of cyclooctene using MoO<sub>2</sub>(SAL-SH)-NaY

In this experiment, 0.1 g MoO<sub>2</sub>(SAL-SH)-NaY catalyst was used for the oxidation of cyclooctene (0.3 mmol) in 10 ml DMF at 60°C and the reaction was continued for 5 h under oxygen bubbling. A

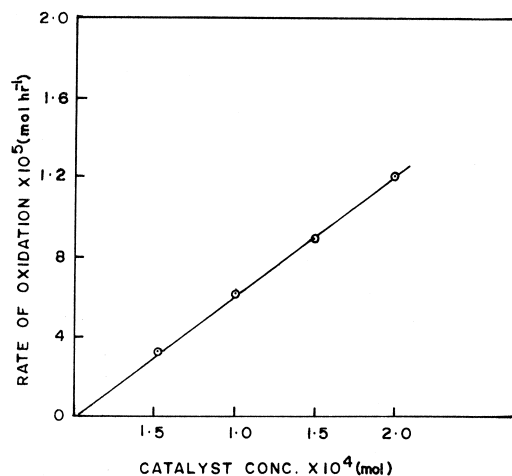


Fig. 1. Effect of catalyst concentration on the rate of cyclooctene oxidation.

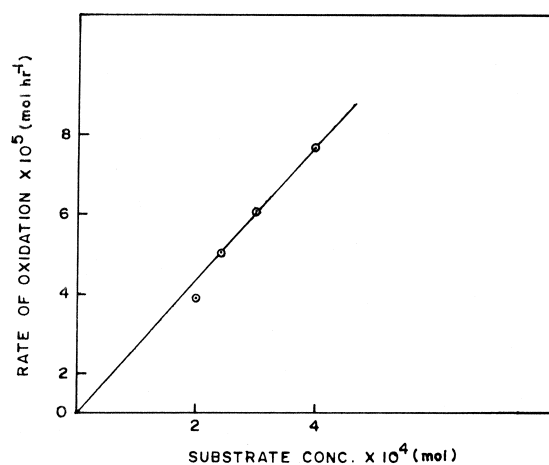


Fig. 2. Effect of cyclooctene concentration on the rate of cyclooctene oxidation.

total of 75% conversion was achieved during 5 h period and considering 1.2 wt.% Mo loading, the turn over worked out to be approximately 70. Thus, a nine-fold increase in turnover was observed due to encapsulation of metal complex within zeolite cavities. Further, the reaction rates in this case did not slacken during the 5-h reaction period in contrast to homogeneous reaction conditions. Oxidation of cyclooctene using *cis*-MoO<sub>2</sub>(SAL-SH) (H<sub>2</sub>O) approached saturation levels within 5-h reaction time.

The rates of oxidation of cyclooctene catalysed by *cis*-[MoO<sub>2</sub>(SAL-SH) (solv)] complex, exhibited first order dependence with respect to catalyst and substrate concentration. Taking into consideration the total catalyst concentration present in the form of different species *in situ* at steady state conditions, the final rate law can be written as:

$$\text{rate} = \frac{kK_1[\text{cat}]_T[S]}{1 + K_1[S]}, \quad (1)$$

where  $[\text{cat}]_T$  = total catalyst concentration,  $[S]$  = cyclooctene concentration,  $K_1$  is the pre-equilibrium constant and  $k$  is the rate constant.

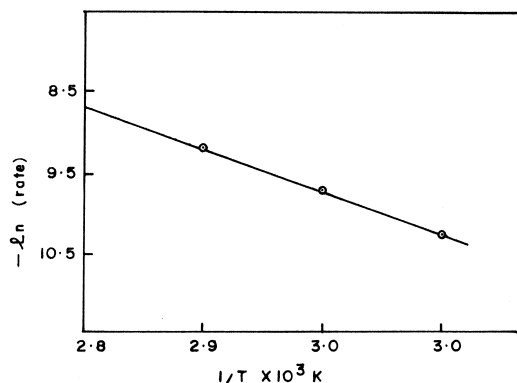


Fig. 3. Effect of temperature on the rate of cyclooctene oxidation.

To evaluate the kinetic constants, the above equilibrium (1) can be rearranged as:

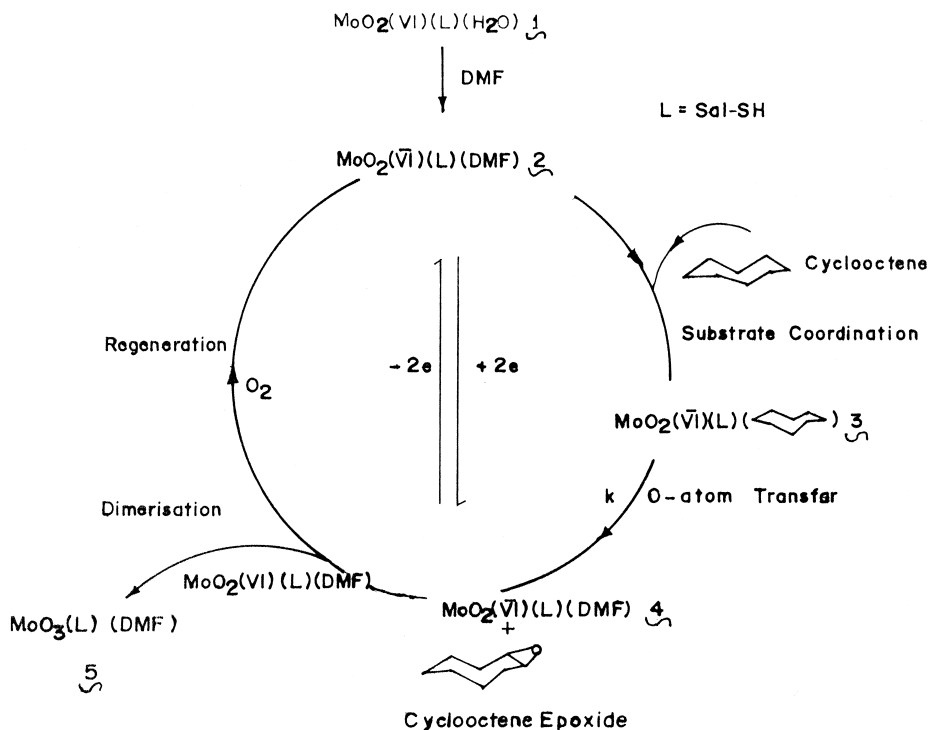
$$\frac{[\text{cat}]_T}{\text{rate}} = \frac{1}{[S]} \left( \frac{1}{kK_1} \right) + \frac{1}{k}. \quad (2)$$

From Eq. (2), the value of  $k$  was calculated from the intercept obtained by plotting the graph of  $[\text{cat}]_T/\text{rate}$  vs.  $1/[S]$ . By substituting the value of  $k$  in Eq. (2) and the value of the slope obtained from the above graph, the value of  $K_1$  was calculated. The values of kinetic constants obtained for the  $\text{MoO}_2(\text{SAL-SH})$  (solv) complex catalysed oxidation of cyclooctene to give cyclooctene oxide at  $60^\circ\text{C}$  are:  $K_1 = 7.66 \times 10^3 \text{ M}^{-1}$  and  $k = 4.35 \times 10^{-3} \text{ min}^{-1}$ .

The activation energy  $E_a$  was calculated from the temperature dependence of the rate of oxidation of cyclooctene in the range  $50\text{--}70^\circ\text{C}$  as  $25.8 \text{ kcal mol}^{-1}$ . The  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  values calculated at  $60^\circ\text{C}$  are  $25.2 \text{ kcal mol}^{-1}$  and  $+76 \text{ e.u.}$ , respectively. The  $\Delta H^\ddagger$  value of  $25.2 \text{ kcal mol}^{-1}$  observed in this study indicates that the oxidation of cyclooctene is endothermic. This is expected because of the bond cleavage in the transition state for the formation of the product.

### 3.7. Probable mechanistic route for cyclooctene oxidation

Oxidation of cyclooctene using  $\text{MoO}_2(\text{SAL-SH})$  (solv) as well as  $\text{MoO}_2(\text{SAL-SH})$  (solv)-NaY gave cyclooctene epoxide. The reaction rates showed first order dependence with respect to catalyst and substrate concentrations. Based on the above, a probable mechanism for oxidation of cyclooctene is presented in Scheme 1. The reaction proceeds through displacement of  $\text{H}_2\text{O}$  molecule in **1** by a solvent molecule, i.e., DMF. In an equilibrium step, cyclooctene participating in coordination through



Scheme 1.

$\eta^2$ -linkages formed between Mo centre and  $sp^2$  carbons of cyclooctene (complex **3**). Cyclooctene abstracts an oxogroup intra-molecularly to release Mo(IV)OL complex **4** and cyclooctene epoxide. Complex **4** is unstable and reverts back to the starting complex under  $O_2$  or undergoes dimerisation with the participation of  $MoO_2(SAL-SH)$  (solv) **1** to give  $\mu$ -oxo dimer  $Mo_2O_3(SAL-SH)_2$  (solv)<sub>2</sub>. The reaction mixtures recovered after 5-h reaction period were analysed for the presence of  $\mu$ -oxo dimer. In the case of oxidation of cyclooctene using *cis*- $MoO_2(SAL-SH)$  (solv); the reaction mixture at the end of 5 h showed additional IR bands at 956 and 802  $cm^{-1}$  which are characteristic of Mo=O and Mo–O–Mo bonds in  $\mu$ -oxo dimer. On the contrary, the formation of  $\mu$ -oxo dimer was absent in the case of cyclooctene oxidation using  $MoO_2(SAL-SH)$  (solv)-NaY composite as the reaction mixture in this case did not show characteristic peaks of  $\mu$ -oxo dimer. Since the rate of oxidation reached saturation under homogeneous conditions of reaction which indicates catalyst deactivation, the dimer formation could be imagined as the deactivation step. The absence of dimer formation in the case of oxidation using zeolite encapsulated metal complex could be due to siting of isolated metal complex molecules within the cavities of zeolite which kinetically prevent their interaction and dimer formation. Therefore, reversion of Mo(IV)OL **4** into  $MoO_2(VI)(L)$  **1** under air/oxygen is the regeneration pathway in the case of zeolite encapsulated metal complex. This is amply reflected through nine times higher turn over of cyclooctene oxidation found under catalysis using  $MoO_2(SAL-SH)$  (solv)-NaY composite. Concerning catalytic air oxidation of thiols mediated by bis(2-mercapto-2,2-diphenyl-ethanoate) dioxomolybdate (VI),  $MoO_2[(OCC(S)(C_6H_5)_2)_2]_2^-$ ; Corma et al. [15] reported that intercalation of this complex in layered double hydroxide inhibited the formation of Mo(V) dimer which are always formed under homogeneous conditions.

It may be concluded that while both *cis*- $MoO_2(SAL-SH)$  (solv) and  $MoO_2(SAL-SH)$ -NaY are useful for cyclooctene oxidation, the latter is more effective as zeolite host prevents the metal complex from participating in the deactivation step referred above and thereby increases the epoxide yield also.

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