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Liquid-phase epoxidation of olefins by manganese oxide octahedral molecular sieves

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Abstract

Manganese oxide octahedral molecular sieves with a cryptomelane structure (OMS-2) were used to catalyze the oxidation of cyclic olefins and benzylic double bonds with *tertiary*-butyl hydroperoxide (TBHP) as the oxidant. OMS-2 showed good catalytic activity with high selectivity under mild conditions (substrate:oxidant molar ratio of 1:1) for the oxidation of different substrates that were studied. Cyclooctene gets oxidized to cyclooctene epoxide selectively in the presence of OMS-2 among the different substrates used for oxidation. The order of reaction with respect to cyclooctene was determined to be pseudo-first order using OMS-2 and excess TBHP. The effects of time, reaction temperature, solvents, and amount of catalyst were investigated. Various reaction conditions and conversion of cyclooctene were maximized at 60 °C using acetonitrile as the solvent.

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Keywords: OMS-2; Epoxidation; Cyclic olefins; Cyclooctene

1. Introduction

Recently there has been an increasing interest in the development of heterogeneous catalysts for the oxidation of olefins in the liquid phase with molecular oxygen, aqueous hydrogen peroxide, or organic peroxides. Besides oxygen, aqueous hydrogen peroxide or alkyl peroxides prove to be very efficient and environmentally friendly oxidants as the by-products are only water or alkyl alcohols, respectively. Heterogeneous catalytic oxidations of olefins find wide chemical and biological applications besides synthetic applications in pharmaceutical industries. The selective oxidation products serve as the starting materials for the production of several fine chemicals and polymers [1]. Due to the ease in separation, recovery, recycling, and amenability for continuous processing, heterogeneous catalytic oxidation is a more acceptable pathway compared to homogeneous counterparts.

Many different transition metal complexes are available that can utilize a variety of oxygen sources for the oxidation of olefins. The catalytic decomposition of alkyl hydroperoxides as a source of oxygen has been investigated in numerous environments, being one of the well-established routes considered for the formation of alcohols and carbonyl groups by the autooxidation of alkanes and alkenes. Titanium silicate (TS-1) was found to be an effective heterogeneous catalyst for the selective oxidation of olefins [2] using dilute hydrogen peroxide as an oxidizing agent under mild conditions, after which titanium silicate (TS-2) [3] and Ti-ZSM-48 [4] followed in effectiveness. Other interesting results have also been obtained with Ti, V, Cr, and Sn containing zeolites or aluminophosphates [5–9]. Pyridines as bifunctional cocatalysts in the chromium oxide-catalyzed oxidation of olefins by *tertiar*y-butyl hydroperoxide have also been reported [10]. However, only a small amount of work in heterogeneous catalytic oxidation has been reported using manganese as transition metal complexes. Manganese coordination complexes [11–13], which are capable of effective oxidation, have structures that often contain bulky ligands necessitating a multistep synthetic process.

Octahedral molecular sieves (OMS-2), used in this research, are microporous tunnel-structured manganese oxide materials. These are mixed valent materials, which are good

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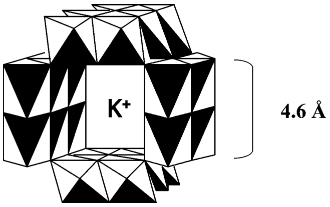

Fig. 1. Structure of OMS-2, which is synthetic cryptomelane $KMn_8O_{16} \cdot nH_2O$.

semiconductors and oxidation catalysts [14–18]. These synthetic mixed valent manganese oxide materials have been modeled after naturally occurring manganese nodules. Manganese is the tenth most abundant element in the earth's crust. Due to the easy availability of the manganese precursors, preparation of OMS-2 is essentially inexpensive and easy, and leads to a purer material compared to the natural mineral.

The K^+ ion form of hollandite, which is known as cryptomelane, has a composition of $KMn_8O_{16} \cdot nH_2O$ [19]. Synthetic cryptomelane (OMS-2) has the structural units of MnO_6 octahedra, edge and corner shared, similar to the hollandite structure with K^+ as the predominant cation in the tunnel. The structure contains 4.6 × 4.6 Å tunnels because of the 2 × 2 arrangement of octahedral and K^+ ion with a small amount of water present in the tunnel. The average manganese oxidation state OMS-2 is 3.8 due to the presence of a mixture of Mn^{4+}, Mn^{3+}, and Mn^{2+} ions [20–22]. The mixed valency of OMS-2 along with the one-dimensional tunnel structure is capable of exhibiting interesting oxidation properties [14–18]. Pore-size distribution studies show that a wide range of micropores are present with the diameters of the pores ranging from ∼ 4.5 to 6.5 Å [23].

In comparison to other manganese coordination complexes [11–13] manganese oxides having a cryptomelane structure is very easy and inexpensive to prepare and this led to the examination of this material for the olefin oxidation. These materials have already shown good catalytic activity in the case of alcohol oxidations [18,24] and cyclic alkane oxidation [17]. In this paper the catalytic behavior of manganese oxide having a cryptomelane structure (Fig. 1) was studied in the presence of *tertiary*-butyl hydroperoxide (TBHP, 70 wt% in water) as the oxidant and acetonitrile as the solvent for the oxidation of various cyclic olefins. For the kinetic study of oxidation, cyclooctene was chosen as a representative substrate.

2. Experimental

2.1. Reagents

All chemicals were purchased from Aldrich unless otherwise noted and were of analytical grade, unless otherwise noted.

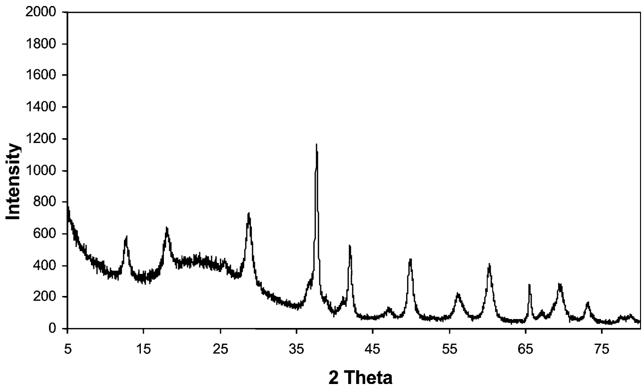

Fig. 2. X-ray diffraction pattern of OMS-2. The XRD pattern shows that OMS-2 formed was crystalline and comprised one single phase.

2.2. Synthesis of catalyst

OMS-2 was prepared by the precipitation method [25]. A 0.4 M solution of $KMnO_4$ (13.3 g in 225 mL of distilled, deionized water, DDW) was added to a mixture of a 1.75 M solution of $MnSO_4 \cdot H_2O$ (19.8 g in 67.5 mL DDW) and 6.8 mL of concentrated HNO_3. The resulting black precipitate was stirred vigorously and refluxed at 373 K for 24 h. The precipitate was filtered and washed with DDW until neutral pH and dried at 393 K. This gave the K^+ form of OMS-2.

2.3. Catalyst characterization

2.3.1. X-ray powder diffraction studies

The OMS-2 catalyst was characterized by XRD methods. The XRD patterns were obtained using a Scintag 2000 PDS instrument with Cu-K_α radiation with a beam voltage of 45 kV and 40 mA beam current. The X-ray pattern of the catalyst (Fig. 2) was compared with that of OMS-2 standard material and was found to be pure.

2.3.2. Surface area measurements

The surface area of OMS-2 was measured using the Braunuer–Emmet–Teller (BET) method on a Micromeritics ASAP 2010 instrument. Using N_2 as the adsorbent and a multipoint method the area determined was $\sim 50\ m^2\ g^{-1}$.

2.3.3. Transmission electron microscopy

The TEM bright-field micrograph was taken with a JEOL 2010 FAS TEM (200 kV) equipped with an EDAX Phoenix EDX detector and a Gatan GIF/EELS system. The sample was made by grinding using mortar and pestle, dispersed in *n*-butanol, sonicated, and dropped into a wholly carbon-coated copper grid. The transmission electron microscopy shows that the fiber lengths mostly range from 20 to 200 nm in size (Fig. 3).

2.3.4. Scanning electron microscopy

SEM photographs were taken on a Zeiss DSM 982 Gemini field emission scanning microscope with a Schottky

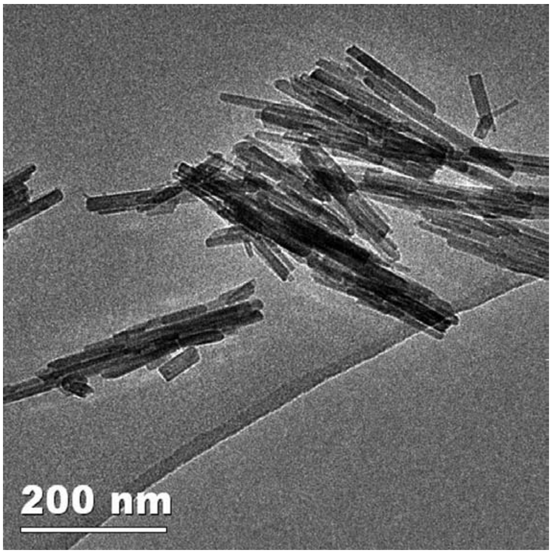

Fig. 3. TEM picture of OMS-2.

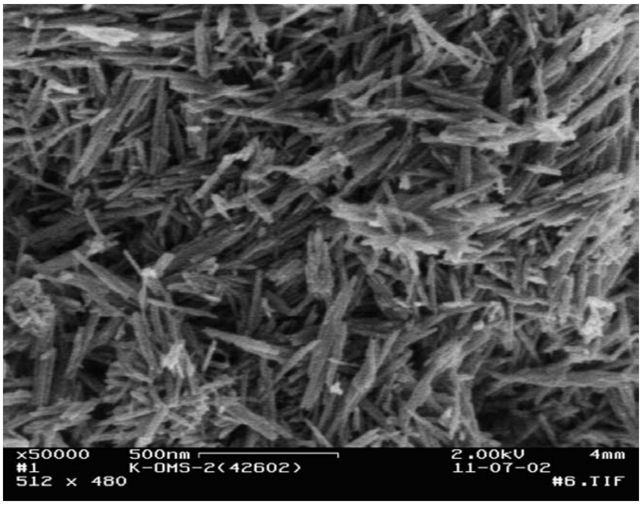

Fig. 4. SEM picture of OMS-2.

Emitter at an accelerating voltage of 2 kV with a beam current of 1 μA (Fig. 4). The picture shows the characteristic fibers of the OMS-2.

2.4. Catalytic reactions

All experiments were carried out at 60 °C, open to atmosphere, in a round-bottomed flask equipped with a condenser and magnetic stirrer and placed in an isothermal paraffin oil bath. A typical reaction mixture was composed of OMS-2 0.0625 mmol (50 mg), olefinic substrate 5 mmol, TBHP 5 mmol (70 wt% in water), and acetonitrile 15 mL as solvent. The reactions were carried out for 24 h. Cyclooctene was the olefin and excess TBHP (20 mmol) was used for kinetic studies and reactions were carried for long period of time (for 48 h at 60 °C). The OMS-2 was pretreated at $\sim$ 100–120 °C overnight before being used in the reaction. For all product analysis purposes, cyclohexyl benzene was used as an internal standard.

2.5. Analytical procedure

Gas chromatography-mass spectrometry (GC-MS) was used for the identification and the quantification of the reaction products. The analyses were done in a HP 5890 Series II gas chromatograph coupled with an HP 5971 mass detector. The column used was an HP-1 (nonpolar cross-linked siloxane) with dimensions of 12.5 m × 0.2 mm × 0.33 μm.

3. Results

3.1. Effect of substrates on oxidation

Experiments on various selected cyclic olefins (with and without benzylic group) were performed and the comparisons with respect to conversion and product selectivity are represented in Table 1. High conversions were obtained for olefins, on OMS-2 catalyst using TBHP. The reactivity of the olefin toward oxidation with TBHP and OMS-2 depends on the particular structure of the substrate. The type of substrate also influences the product distribution. Cyclohexene gets oxidized mainly at the allylic position to give alcohol and ketone as the primary products besides a dimer. Cycloheptene shows some formation of the cycloheptene epoxide along with cycloheptenone while cyclooctene forms the cyclooctene epoxide selectively. The reactivity of the double bond is expected to be similar for cyclohexene, cycloheptene, and cyclooctene but the product distributions do not show such behavior. Cyclohexene and cycloheptene shows oxidation at the allylic position whereas cyclooctene solely undergoes double bond oxidation. For double bonds attached to benzylic rings the double bond either gets oxidized to epoxide or undergoes further oxidation to aldehydes (refer to the reactions with styrene and stilbene in Table 1). Oxidation of *trans*-stilbene gave *trans*-stilbene epoxide stereoselectively. In the case of *trans*-stilbene the oxidative cleavage product, viz. benzaldehyde was formed in only 7% yield. No isomeric product, such as *cis*-stilbene epoxide, was detected.

As cyclooctene was the substrate that selectively gave the epoxide, among the substrates that have been used so far, cyclooctene was chosen as the representative substrate for kinetic studies. Comparisons of the turnover frequencies (TOF) have been represented in Table 2 for a particular oxidant to substrate ratio. However, a higher oxidant to substrate ratio (4/1 mmol/mmol) and longer reaction times (for 48 h at 60 °C) were used for cyclooctene, keeping all other conditions constant, in order to predict the order of the oxidation reaction with respect to cyclooctene.

Table 1
Distribution of oxidation products for selected substrates[a]

Substrate	Conversion[c] (%)	Selectivity[e] (%)			
		Alcohol	Aldehyde/ketone	Epoxide	Others
Cyclohexene	65	2-Cyclohexen-1-ol (20%)	2-Cyclohexen-1-one (49%)	–	Cyclohexenylcyclohexene (31%)
Cycloheptene	49	–[d]	Cycloheptenone (69%)	Cycloheptene epoxide (17%)	Others (14%)
Cyclooctene	59	–	–	Cyclooctene epoxide (100%)	–
Styrene	48	–	Benzaldehyde (69%)	Styrene epoxide (31%)	–
trans-Stilbene[b]	68	–	Benzaldehyde (7%)	*trans*-Stilbene epoxide (93%)	–

[a] All reactions were done at 60 °C for 24 h with 0.0625 mmol of the catalyst and 5 mmol of the substrate and 5 mmol of the *tertiary*-butyl hydroperoxide (70 wt% in water).

[b] Reaction was done at 60 °C for 24 h with 0.0625 mmol of the catalyst and 5 mmol of the *trans*-stilbene substrate and 2.5 mmol of the *tertiary*-butyl hydroperoxide (70 wt% in water).

[c] Conversion (%) based on substrate = [1 − (concentration of substrate left after reaction/initial concentration of substrate)] × 100.

[d] (–) Signifies no such product formation.

[e] Selectivity (%) of product A = (concentration of product A/total concentration of all products) × 100.

Table 2
Catalytic oxidation of olefins using OMS-2[a]

Substrate	Eq. of oxidant vs substrate	Conversion[b] (%)	TOF[c] (h^{-1})
Cyclohexene	1.0	65	2.17
Cycloheptene	1.0	49	1.63
Cyclooctene	1.0	59	1.97
Styrene	1.0	48	1.6
trans-Stilbene[d]	0.5	68	2.27

[a] All reactions were done at 60 °C for 24 h with 0.0625 mmol of the catalyst and 5 mmol of the substrate and 5 mmol of the *tertiary*-butyl hydroperoxide (70 wt% in water).

[b] Conversion (%) based on substrate = [1 − (concentration of substrate left after reaction/initial concentration of substrate)]×100.

[c] TOF = turnover frequency = moles of converted substrate/(moles of catalyst × reaction time in hours).

[d] Reaction was done at 60 °C for 24 h with 0.0625 mmol of the catalyst and 5 mmol of the *trans*-stilbene substrate and 2.5 mmol of the *tertiary*-butyl hydroperoxide (70 wt% in water).

3.2. Oxidation of cyclooctene with TBHP and OMS-2 as catalyst

Oxidation of cyclooctene was studied exclusively for kinetic measurements and the results of the study are as follows.

3.2.1. Kinetics of reaction

In this kinetic study the depletion of cyclooctene concentration in the presence of excess TBHP was monitored and plotted with respect to time (Fig. 5). The reaction was carried out at 60 °C in a two-necked round-bottom flask and ∼ 0.5 mL of sample was drawn out at regular intervals. The rate expression [26] may be written as

$$\text{Rate} = k[\text{Cy8}]^{\alpha}[\text{TBHP}]^{\beta} \quad \text{and} \tag{1}$$

$$\text{Rate} = -\mathrm{d}(\text{Cy8})/\mathrm{d}(t), \tag{2}$$

where Cy8 stands for cyclooctene concentration, α is the order of reaction with respect to cyclooctene, β is the order of reaction with respect to TBHP, and k is the rate constant. In order to find α, the rate expression (1) may be rewritten as

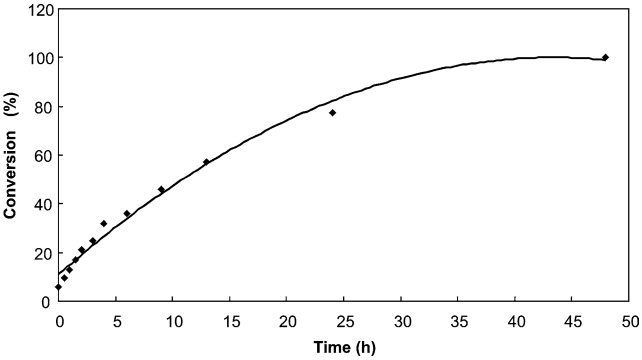

Fig. 5. Conversion of cyclooctene as a function of time at 60 °C with OMS-2 catalyst in the presence of excess TBHP.

$$\text{Rate} = k'[\text{Cy8}]^{\alpha} \quad \text{if } [\text{TBHP}]^{\beta} = \text{constant, because it is in excess.} \tag{3}$$

Combining expressions (2) and (3) gives rise to

$$-\mathrm{d}(\text{Cy8})/\mathrm{d}(t) = k'[\text{Cy8}]^{\alpha}. \tag{4}$$

If $\alpha = 1$ on integrating expression (4), from the initial concentration at initial time to the final concentration at the final time t, the expression (4) can be written as

$$-\ln(1 - X) = k'(t), \tag{5}$$

X = conversion of cyclooctene after time t.

A plot of $-\ln(1 - X)$ (where X is the conversion of cyclooctene) with respect to time gives a linear relationship showing a pseudo-first-order dependence on the cyclooctene (Fig. 6).

3.2.2. Effect of reaction time

The change in conversion of 5 mmol of cyclooctene at 60 °C with excess TBHP was studied with time over a period of 48 h. The conversion of cyclooctene increases continuously until 100% as time increases (Fig. 5) and no inhibitory effect was observed. Similar experiments were done at 40 and 50 °C (Fig. 7).

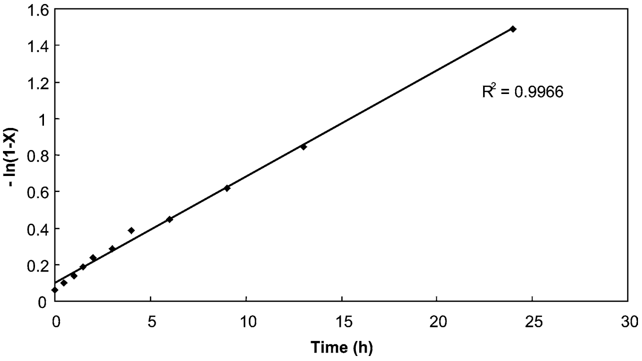

Fig. 6. Pseudo-first-order kinetics of cyclooctene oxidation at 60 °C with OMS-2 catalyst in the presence of excess TBHP.

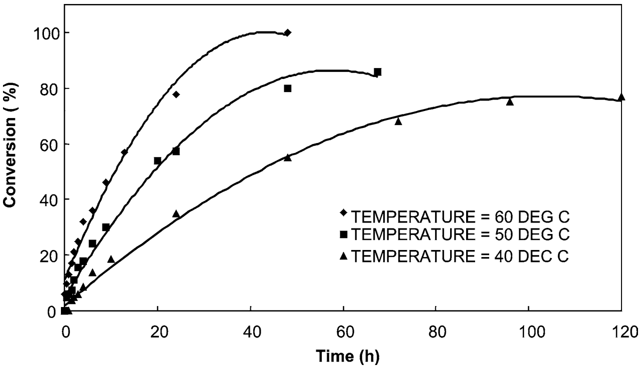

Fig. 7. Conversion of cyclooctene as a function of time at 40, 50, and 60 °C with OMS-2 catalyst in the presence of excess TBHP.

3.2.3. *Effect of temperature on the oxidation of cyclooctene*

Oxidation of 5 mmol of cyclooctene was carried out at various temperatures starting from room temperature in the presence of 5 mmol of TBHP and 0.0625 mmol of the catalyst for 24 h. The results are tabulated (Table 3) and there is a drastic increase in conversion of cyclooctene with an increase in temperature without any loss in selectivity to the epoxide. From kinetic studies, the rate constants of reaction for a typical mixture of 5 mmol cyclooctene, 20 mmol of TBHP, 0.0625 mmol of the catalyst, and 15 mL of acetonitrile as solvent were found by conducting the reaction at 40, 50, and 60 °C (refer to Figs. 6 and 8). From the pseudo-first-order rate constants, the plot of ln (rate constant) vs $1/T$ (Arrhenius plot) was drawn (Fig. 9) and the value of activation energy (E_a) was evaluated from the slope of the plot to be 14.0 kcal mol^{-1}.

3.2.4. *Effect of the amount of the catalyst*

Catalyst amounts were varied from 12.5 to 50.0 mg for reactions carried out at 60 °C, for 24 h, and other reaction conditions remaining the same. The results are shown in Table 4. There is a general trend of increasing conversion of cyclooctene with higher catalyst amounts. However when the catalyst amount was increased higher than 75 mg, with the same reaction conditions, the conversion decreased.

Table 3

Catalytic oxidation of olefins using OMS-2 at different temperatures[a]

Temperature	Conversion (%)
Room temperature (23 °C)	10
30 °C	12
40 °C	22
50 °C	41
60 °C	59
70 °C	54

[a] The reactions were done with 0.0625 mmol of the catalyst and 5 mmol of the *tertiary*-butyl hydroperoxide (70 wt% in water) and with 5 mmol of the cyclooctene, respectively, for 24 h.

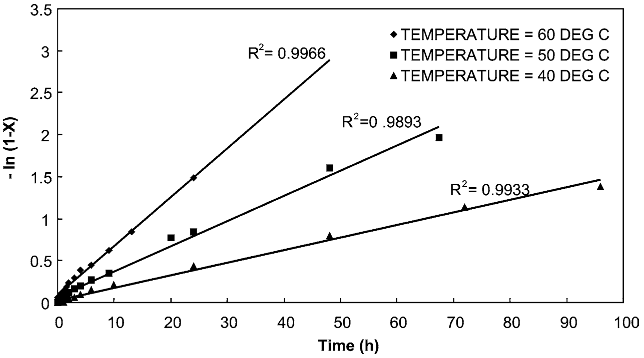

Fig. 8. Pseudo-first-order kinetics of cyclooctene oxidation at 40, 50, and 60 °C with OMS-2 catalyst in the presence of excess TBHP.

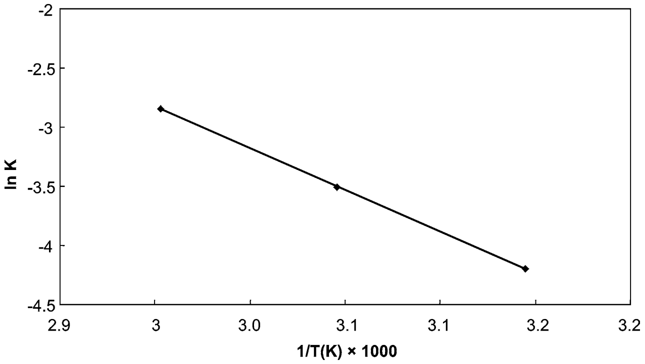

Fig. 9. Effect of temperature on the rate of cyclooctene oxidation (Arrhenius plot).

Table 4

Effect of catalyst amount for cyclooctene oxidation at 60 °C[a]

Catalyst amount (mg)	Conversion (%)
12.5	17
22.5	29
50	59
75	25
100	37

[a] The reaction mixture had 5 mmol of cyclooctene, 5 mmol of TBHP, and 15 ml of the solvent acetonitrile and reaction was continued for 24 h in which the catalyst amount was varied for each run.

Table 5
Effect of solvents on epoxidation of cyclooctene[a]

Solvent	Protic/aprotic	Dielectric constant	Dipole moment (*D*)	Conversion (%)
Acetonitrile	Aprotic	37.5	3.92	57%
Toluene	Aprotic	2.4	0	13%
THF	Aprotic	7.52	3.89	No conversion
Ethanol	Protic	24.5	1.69	No conversion

[a] All reactions were done at 60 °C for 24 h with 0.0625 mmol of the catalyst and 5 mmol of the cyclooctene and 5 mmol of the *tertiary*-butyl hydroperoxide (70 wt% in water).

3.2.5. *Effect of solvents*

In these experiments the solvent was changed for each run while keeping the other conditions the same, i.e., 0.05 g of the OMS-2 and 5 mmol of cyclooctene and temperature maintained at 60 °C under reflux for 24 h. The solvent has been varied from polar protic solvent to polar nonprotic solvent and also extended to nonpolar solvent. Table 5 gives the results of conversion of cyclooctene with the various solvents.

4. Discussion

4.1. *Catalytic reactions*

Based on the XRD results all catalytic reactions for the study were carried out on a pure crystalline OMS-2 material. Although the BET surface area for OMS-2 was small ($\sim 50\ \mathrm{m^2\,g^{-1}}$), considerable activity of the catalyst was observed based on the experimental results. The results of SEM and TEM micrographs show that the catalysis has essentially been carried out on OMS-2 fibers, which are in the nanometer range.

Metal-catalyzed oxidation involving alkyl peroxides may proceed either through a homolytic or heterolytic mechanism. Transition metal salts of Co, Mn, Fe, Cu, or the metal oxides are normally involved in homolytic cleavage [1]. Sheldon et al. [27] have noted that strong (one-electron) oxidants, e.g., later and/or first row transition elements such as Cr^{+6}, Mn^{+3}, Co^{+3}, and Fe^{+3}, favor oxo-metal pathways and/or homolytic decomposition of TBHP. Since OMS-2 exhibits variable oxidation states of +2, +3, and +4, it may be possible for the reaction to follow both a homolytic decomposition pathway for the TBHP along with the formation of the oxo-catalyst species.

When the oxidation reaction of cyclooctene with OMS-2 was carried out in the presence of 4-Oxo Tempo (4-oxo-2,2,6,6-tetramethylpiperidine-1-oxyl), which is a radical inhibitor/ scavenger, the conversion was reduced from 59 to 37%. A similar experiment was also carried out in the presence of IONOL (2,6-di-*tert*-butyl-4-methylphenol) also a radical inhibitor/scavenger, and the conversion of cyclooctene was only 22.5%. This inhibition also shows, to a certain extent, a homolytic pathway being involved. Oxo-metal or free radical autoxidation pathways may carry out allylic, benzylic, and double bond oxidations, which are difficult to distinguish. The possible oxidation pathway may be as shown in Eqs. (6)–(16).

Oxo-metal formation,

$$\begin{aligned}\text{OMS-2}^{n+} + t\text{-butOOH} &\xrightarrow{(-)t\text{-butOH}} \text{OMS-2}^{n+2}{=}\text{O}\\ &\xrightarrow{\text{S}} \text{SO} + \text{OMS-2}^{n+},\end{aligned} \tag{6}$$

where S = substrate and SO = epoxide.

Homolytic pathway,

$$\text{OMS-2}^{n-1} + t\text{-butOOH} \rightarrow t\text{-butO}^{\bullet} + \text{OMS-2}^{n}\text{OH}, \tag{7}$$

$$t\text{-butOOH} + \text{OMS-2}^{n} \rightarrow t\text{-butOO}^{\bullet} + \text{OMS-2}^{n-1} + \text{H}^{\bullet}, \tag{8}$$

$$t\text{-butOO}^{\bullet} + \text{RH} \rightarrow \mathbf{RHO} + t\text{-butO}^{\bullet}, \tag{9}$$

$$2t\text{-butOO}^{\bullet} \rightarrow 2t\text{-butO}^{\bullet} + \text{O}_2, \tag{10}$$

$$t\text{-butO}^{\bullet} \xrightarrow{\text{RH}} \text{R}^{\bullet} + t\text{-butOH}, \tag{11}$$

$$\text{R}^{\bullet} + \text{O}_2 \rightarrow \text{ROO}^{\bullet}, \tag{12}$$

$$\text{ROO}^{\bullet} \xrightarrow{\text{RH}} \mathbf{RHO} + \text{RO}^{\bullet}, \tag{13}$$

$$\text{R}^{\bullet} + \text{R}^{\bullet} \rightarrow \text{R–R}, \tag{14}$$

$$\text{RO}^{\bullet} + \text{H}^{\bullet} \rightarrow \mathbf{ROH}, \tag{15}$$

$$\text{ROH} \xrightarrow{\text{OMS-2}} \mathbf{RO}, \tag{16}$$

where RH = olefin substrate, R–R = dimer, RO = aldehyde/ ketone, ROH = alcohol, and RHO = epoxide.

OMS-2 is capable of oxiding alcohols [18,24] to ketones, so conversion of the product alcohol formed, as a result of the oxidation at the allylic position, in case of cycloheptene and cyclohexene, is a faster process once the allylic position gets oxidized. Different product distribution is mainly due to the difference in activity of the double bond due to the different ring sizes of different cyclic olefins. There is competition between oxidation of the allylic position and oxidation of the double bond in the case of cyclic olefins, which is dependent on the type of the substrate [1,28,29]. Cyclohexene was predominantly oxidized at the allylic position, while cycloheptene showed a mixed result involving both the allylic oxidation and the double bond oxidation and cyclooctene predominantly showed only the double bond oxidation. These results are in accordance to the work of Kaneda et al. [28] and Van Sickle et al. [29].

In the case of cyclohexene oxidation, the formation of the cyclohexyl dimer further concludes the formation of radicals in the process. Some of the cyclic olefins react partly or entirely through addition of peroxy radicals to the double bonds of the substrate rather than via hydrogen abstraction. The allylic hydrogen of cyclohexene and cycloheptene is abstracted easily because the removal of hydrogen allows an allylic radical system, which has the geometry suitable for maximum overlap of the n and π molecular orbitals. On the other hand, it is not so easy for the allylic radical from cyclooctene to attain maximum overlap because of the conformational constraint of the ring system.

In the case of cyclohexene the formation of cyclohexyl dimer leads to the conclusion that allylic H gets abstracted very fast compared to the double bond attack. For cycloheptene there is a mixed result of both epoxide and cycloheptenone formation. The intermediate formed due to the abstraction of the allylic H of cyclohexene and cycloheptene may be considered more stable than the intermediate formed for the epoxide formation by double bond attack (as supported from the experimental results). Hence, the stability of the intermediate for allylic oxidation may be as $C6 \gg C7 \ggg C8$ and the stability of the intermediate for the double bond oxidation for epoxide formation follows a reverse order of $C8 \gg C7 > C6$.

The peroxy radical formed in association with the OMS-2 [refer to Eqs. (8) and (9)] may be the source of the epoxide, in the case of cyclooctene [29]. As for styrene and stilbene, they showed predominantly double bond oxidation, possibly by forming the epoxide first followed by cleavage to give the next higher oxidized product. In the case of the double bonds in conjugation with a benzene ring there is no allylic hydrogen present for abstraction. As a result, such double bonds get predominantly oxidized. The formation of benzaldehyde and styrene epoxide from styrene also suggests that styrene epoxide may be the intermediate product for the formation of benzaldehyde. The same discussion also holds when stilbene is oxidized to stilbene epoxide and benzaldehyde. The oxidation of the double bond in case of the styrene and stilbene may be by the oxo-metal complex or the peroxy radical (free radical) but the epoxidation of the *trans*-stilbene formed only the *trans*-stilbene epoxide, whereas in a free radical reaction some *cis*-stilbene epoxide would also have been expected. This further proved that a nonradical nature of reaction, like formation of an oxo-metal complex might be prevailing. CrO_3-catalyzed oxidation reactions [10] also showed similar results.

The large differences in the turnover frequencies (Table 2) represent to a certain extent how reactive a substrate is to the particular oxidation environment. Based on the results of Table 2, *trans*-stilbene is most active to oxidation under the prevailing experimental conditions and styrene the least active. The higher TOF may be attributed to the structure of the substrate, which is favorable for oxidation, and easy formation of the reaction intermediate, thus enabling higher conversion.

4.2. Cyclooctene oxidation and overall possible pathway of cyclooctene oxidation

Figs. 5–8 represent the kinetics of oxidation of cyclooctene. The pseudo-first-order kinetics of oxidation of cyclooctene have also been established by Rao et al. [30] in the case of cyclooctene air oxidation in the presence of [MoO_2(salicylidene salicyloyl hydrazinato-)(solv)] as a catalyst. No marked reaction inhibition has been observed over a long time (Fig. 7), only after a 72-h period the conversion of cyclooctene seems to level off as has been observed in the case of 40 and 50 °C (Fig. 7). The behavior of these results is in accordance with the results of alkane oxidation over OMS catalyst as reported by Wang et al. [17] where the reaction continued for a long period of time ($\sim$ 85 h). The cyclooctene epoxidation therefore seems to continue for a long period with a conversion as high as $\sim$ 100% being observed after 48 h of reaction time at 60 °C. With increasing temperature the conversion of cyclooctene increases while still retaining 100% selectivity to the epoxide, although at around 70 °C the conversion flattens out (Table 3). This may be due to the decrease in efficiency of TBHP with increase in temperature. The decomposition of peroxide is faster at higher temperatures, which may not allow the TBHP to remain chemisorbed on the active sites of OMS-2 for the formation of oxo-metal species.

The results of the effect of catalyst amounts shown in Table 4 demonstrate clearly that OMS-2 is very active in this reaction system, and that even small amounts (0.5 eq) can lead to significant conversion. However with higher amounts of the catalyst the conversion of cyclooctene falls drastically. Sheldon [1] observed that sometimes metal complexes of transition metals, especially in media of low polarity such as neat hydrocarbons, often behave as catalysts at low concentrations but as inhibitors at high concentration. This phenomenon is often referred to as catalyst-inhibitor conversion. At high OMS-2 concentrations the catalyst may compete effectively with the cyclooctene for the t-butyl peroxy radicals, which may be formed from the TBHP decomposition. High concentrations of the catalyst may actually favor the homolytic decomposition of the TBHP at a faster rate instead of the oxo-metal complex formation, as a result of which less cyclooctene epoxide is formed. If more radicals are formed due to higher concentrations of the catalyst in a similar reaction mixture, a higher percentage of the radicals may also combine with each other to terminate the radical chain process. More radicals may also decompose peroxide than at a lower radical concentration when the cyclooctene concentrations are the same. Due to these side reactions, the efficiency of radicals toward oxidation may be lower at higher concentrations of radicals than at lower concentrations.

The kinetics of cyclooctene oxidation at temperatures of 40, 50, and 60 °C (Fig. 8) also followed a pseudo-first order with respect to cyclooctene, and their apparent reaction rate constants have been used in obtaining an Arrhenius plot.

The apparent activation energy (Fig. 9) was estimated from the slope of the Arrhenius plot to be 14.0 $\mathrm{kcal\,mol^{-1}}$ which is low compared to the reported value of 25.8 $\mathrm{kcal\,mol^{-1}}$ by Rao et al. [30] for the air epoxidation of cyclooctene using *cis*-[MoO_2(salicylidene salicyloyl hydrazinato-)(solv)] in the same temperature range while Abrantes et al. [31], however, reported a lower value of 5 $\mathrm{kcal\,mol^{-1}}$ with peroxide as the oxidant in the presence of [$(n\text{-}Bu_3Sn)_2MoO_4$].

The behavior of cyclooctene oxidation in various solvents is very strikingly different as demonstrated by Table 5. Acetonitrile gives the best conversion results (Table 5), followed by toluene. Selectivity toward epoxide as the only product was maintained in both the solvents. However, there was no conversion at all in THF and ethanol as the solvent. This may be due to lone electron pairs on the oxygen in THF and ethanol that gets attached to the strong Lewis acid sites of the OMS-2. The decrease in conversion in toluene may be explained by the low solubility of TBHP in a nonpolar solvent as a result of which the reaction cannot proceed. Acetonitrile although being polar and having a very high dielectric constant readily dissolves TBHP along with the cyclooctene and helps in proper contact of the reactants on the catalyst surface allowing efficient conversion.

Experiments without TBHP and in the presence of other oxidants were also tried. When the reaction having the same batch composition was carried out at room temperature in the presence of 5 mmol of hydrogen peroxide (30%), a brisk effervescence was observed at the beginning of the reaction. However, after 24 h of reaction time there was no conversion of cyclooctene. This may be due to the fact that the rate of decomposition of hydrogen peroxide is very fast on OMS-2 compared to the decomposition of TBHP even at room temperature. The decomposition of H_2O_2 on OMS-2 has been explained by Zhou et al. [32] where the initial step involved adsorption of H_2O_2 at the active sites on the surface of OMS-2, followed by activation and decomposition to water and the formation of atomic oxygen on the OMS-2 surface and finally desorption of gaseous oxygen. The size of the H_2O_2 molecule is comparable to the pore size of the OMS-2. H_2O_2 gets easily decomposed in the presence of OMS-2, as a result of which the cyclooctene substrate does not produce a catalytically active site ready for oxygen transfer for epoxidation. The cyclooctene epoxide formation may follow an oxo-metal complex, which may not be formed when H_2O_2 is the oxidant. TBHP, being a very bulky oxidant, does not get into the channels of OMS-2 as readily as H_2O_2 because the decomposition is slow and there could be a chance for the formation of the oxo-metal complex, which provides the necessary catalytic active sites for oxidation of cyclooctene. The OMS-2 material has Lewis acid sites, which are mainly caused by vacancies of oxygen atoms, located at vertices of octahedral structural units of OMS-2 [16–33]. Lewis base sites are due to the lone electron pairs on the oxygen atoms of TBHP. Due to the presence of a positive inductive effect due to t-butyl groups, TBHP will be a stronger Lewis base than H_2O_2. Control experiments with cyclooctene without TBHP in the presence of OMS-2 and without OMS-2 in the presence of TBHP showed no cyclooctene epoxide in both cases. This further suggests that neither OMS-2 nor TBHP by itself can carry out oxidation of cyclooctene. Both are necessary to form a complex intermediate, which leads to the formation of cyclooctene epoxide.

In order to see if a similar oxidation reaction can be carried out in the presence of other radical initiators, a reaction was carried out with 0.1 g of α,α'-azobis(isobutyronitrile) (AIBN), having the same batch composition but without TBHP for 24 h at 60 °C. The conversion of cyclooctene was found to be approximately 22%. When 0.01 g of the AIBN was used, however, only 3% of the conversion was observed. When the reaction with the AIBN was carried out in the absence of air in a nitrogen atmosphere, no oxidation product was observed. Reactions with radical initiators like AIBN (> 0.01 mmol) showed a low conversion of cyclooctene to the epoxide in the presence of OMS-2, which suggests that cyclooctene epoxidation may not be a totally free radical mechanism. Instead an oxo-metal complex may be involved. When 4-oxo-Tempo was used as a radical scavenger the decrease in cyclooctene conversion was only 22%, which is not a substantial decrease in the case of a free radical reaction.

5. Conclusions

OMS-2 materials are active in catalyzing the oxidation of various olefinic substrates with good yields of useful products by using TBHP as the oxidant. Depending on the substrates, allylic oxidation products or epoxides were formed. For environmental reasons, all chlorinated solvents were avoided for all reactions, which were carried out in alternative solvents. The cyclooctene epoxidation gives very high yield after a 48-h period in the presence of excess TBHP at 60 °C. Substrates of different sizes gave reasonably good conversion of products. Only a small amount of the catalyst is able to carry out the oxidation reaction successfully. Epoxidation in these systems may not be purely a free radical-type mechanism. Further work is in progress, on the epoxidation of linear olefins, and details of the mechanism are under study in this laboratory.

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