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# **CHAPTER-VI**

**Molybdate and Tungstate-intercalated Mg-Al  
Layered Double Hydroxides: Synthesis,  
Characterization and Catalytic Activity towards  
Epoxidation of Alkenes**

# **CHAPTER VI**

## **Molybdate and Tungstate-intercalated Mg-Al Layered Double Hydroxides: Synthesis, Characterization and Catalytic Activity towards Epoxidation of Alkenes**

### **Abstract**

Polyoxometalate ( $M_7O_{24}^{6-}$ , M = Mo or W) intercalated layered double hydroxides (LDHs) with  $Mg^{2+}$  and  $Al^{3+}$  cations in the brucite-like layer have been prepared by direct anion exchange, starting from the corresponding terephthalate precursor. The solids have been characterized by various instrumental techniques such as elemental chemical analysis, powder XRD, IR spectroscopy, TGA, SEM and TEM. The  $M_7O_{24}^{6-}$  intercalated LDHs have been explored as catalysts for the epoxidation of a series of alkenes at room temperature using environmentally benign hydrogen peroxide ( $H_2O_2$ ) as oxidant. The effect of different reaction parameters such as nature of solvent, amount of catalyst and concentration of substrate on the catalytic activity of intercalated LDHs has also been investigated. The selectivity of epoxidation by the present catalytic system is found to be dependent on the nature of the intercalated anions and the reaction medium. Recycling of the catalyst shows that it is used up to three more cycles without significant loss of performance.

## VI.1 Introduction

Layered double hydroxides (LDHs), also called anionic clays or “hydrotalcite-like” clays, are host-guest layered materials [1]. These compounds exhibit the property of intercalation, the incorporation of guest species between the sheets of a layered host. Most of LDHs are available as synthetic materials and their structure resembles the naturally occurring mineral Hydrotalcite  $[Mg_6Al_2(OH)_{16}]CO_3 \cdot 4H_2O$ , discovered in 1842. LDH was first prepared as a synthetic material in 1942 by Feitknecht [2]. However, the detailed structural features of LDH were not understood until the late 1960’s by Allmann [3], Taylor [4] and their co-workers.

### VI.1.1 Chemical composition and structure

LDH materials are mostly described by the general formula  $[M^{2+}_{1-x}M^{3+}_x(OH)_2]A^{n-}_{x/n} \cdot mH_2O$ , where  $M^{2+}$  and  $M^{3+}$  are divalent and trivalent cations respectively;  $x$  is equal to the ratio  $M^{3+}/(M^{2+} + M^{3+})$  and  $A$  is an interlayer anion of valence  $n$ .

The structure of LDH is similar to that of brucite,  $Mg(OH)_2$ , which consists of  $Mg^{2+}$  ions coordinated octahedrally by hydroxyl groups. The octahedral units share edges to form infinite, charge neutral layers. These layers are stacked on top of each other and held together by weak hydrogen bonds. The isomorphic substitution of some of the magnesium(II) ions by higher valent cations of similar size develops excess positive charge in these brucite-like sheets and to maintain electroneutrality, anions are introduced between the layers [5], as shown in Figure VI.1. The remaining free space of the interlayer is occupied by water molecules.

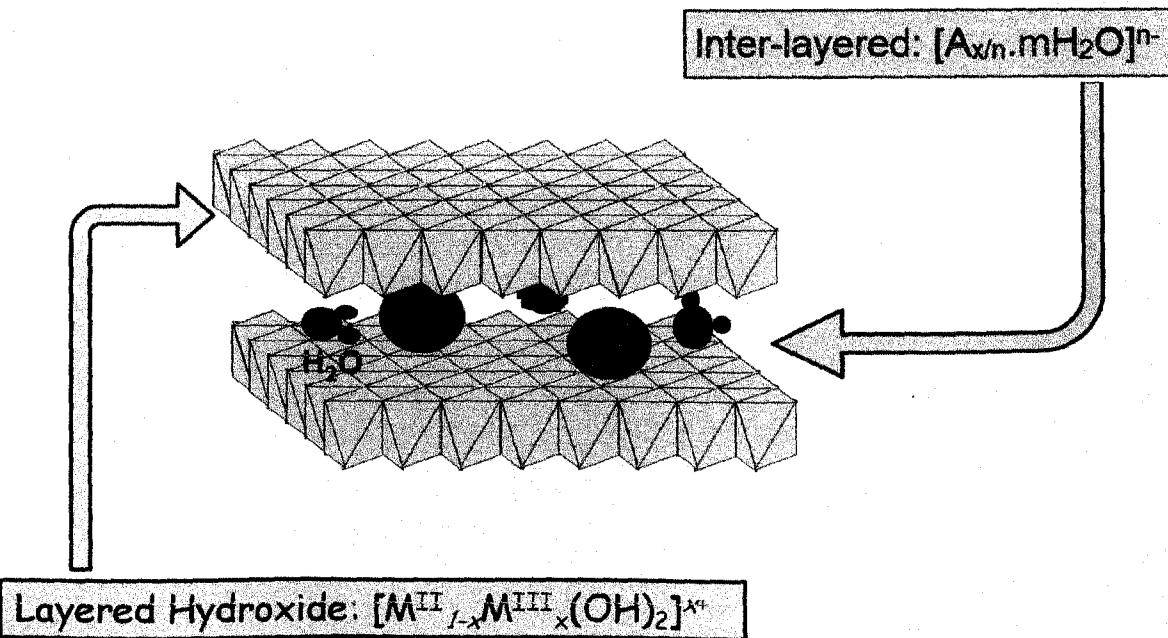


Figure VI.1 General structure of layered double hydroxide [Ref. 6].

### **VI.1.2 Nature of cations**

Many different metal cations may be located in the brucite-like layers. The most commonly found are  $Mg^{2+}$ ,  $Zn^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$  or  $Mn^{2+}$  as divalent cations and  $Al^{3+}$ ,  $Cr^{3+}$ ,  $Co^{3+}$ ,  $Fe^{3+}$ ,  $V^{3+}$ ,  $Ga^{3+}$  or  $Mn^{3+}$  among the trivalent ones. In addition to these cations, other LDHs containing monovalent and tetravalent metal cations within the brucite-like layers have also been synthesized [7]. Although most of the systems reported so far contain only two different metal cations in the layers, other systems containing three or even four different metal cations have also been described [8]. In terms of ionic radii, divalent positive metal ions with an ionic radius in the range 0.65-0.80 Å and trivalent metal ions with an ionic radius in the range 0.62-0.69 Å (with the exception of  $Al^{3+}$  for which the radius is 0.50 Å) facilitate their accommodation in the holes of close-packed OH groups in the hydroxide layers for the LDH formation. The compositional flexibility of the layer structure is illustrated in Figure VI.2.

Li												
Na	Mg									Al	Si	
Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	
	Y	Zr				Ru	Rh	Pd		Cd	In	Sn
							Ir	Pt				

Figure VI.2 Metals incorporated into LDH layers (literature reports) [Ref. 9].

### **VI.1.3 Nature of interlayer anions**

Regarding the anions in the interlayer, there is no restriction on the nature of anions and systems with different anionic species are well-known. Simple inorganic anions (carbonate, nitrate, halides *etc.*) [10], organic anions (terephthalate, acrylate, lactate *etc.*) [11], coordination compounds [12], polyoxometalates [13], biomolecules such as nucleoside monophosphates (AMP, CMP, GMP or ATP) or even DNA fragments [14] have been successfully intercalated between the brucite-like layers.

#### 7.1.4 Applications of LDHs

ayered double hydroxides (LDHs) being typical intercalation compounds are of considerable interest due to their unique ion exchange intercalation properties [15].

method to produce the desired LDH-guest molecule compound as shown in Figure VI.3. In general, ion exchange is performed by dispersion of LDH precursor in the solution with the excess of the guest anion. The requirement for the anion to be intercalated is its stability at the exchange pH.

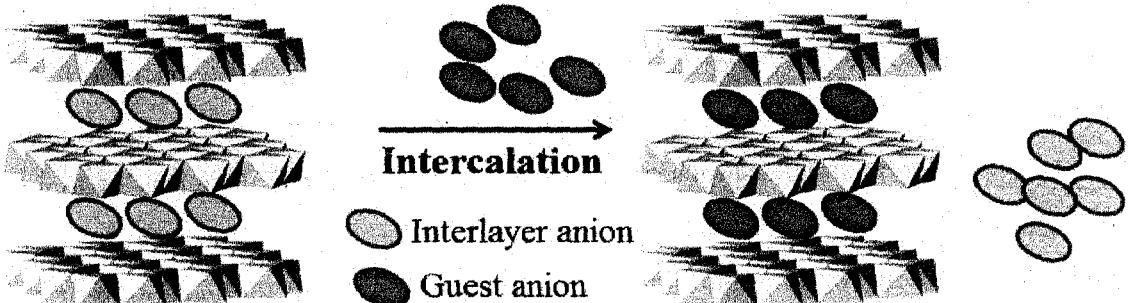


Figure VI.3 Schematic representation of an anion exchange reaction.

Moreover, convenient synthetic method and low cost of the materials have made them attractive candidates for industrial applications. These materials are of current interest because of their applications in polymer stabilizers, adsorbents, pharmaceutical industry and catalysis as well as electrochemistry and photochemistry [11a, 16].

#### VI.1.5 *Applications in catalysis*

LDHs find most of their applications in the area of catalysis. The ease to incorporate a wide number of metal ions dispersed with controlled proportions allows the synthesis of tailored catalysts. Moreover, the cations in the brucite-like layers of LDHs are evenly-distributed and so in principle catalytic activity can be finely tuned by the incorporated metal ions and their ratio within the layer structure. The catalytic properties of LDHs and their applications as catalyst supports, catalyst precursors or actual catalysts are well-known [17]. LDHs have been reported as catalysts in base-catalyzed reactions, hydrogenation and oxidation reactions [18]. It is also used as supports for Ziegler-Natta catalysts [15b]. Other applications of LDH includes the hydroxylation of phenol to diphenol [19], oxidation of toluene to benzaldehyde [20], Suzuki-Miyaura cross-coupling reactions (Pd (II) supported on MgAl-LDH) [21], aldol condensations [22], Claisen-Schmidt condensation and Knoevenagel condensations [23].

#### VI.1.6 *Polyoxometalates in catalysis*

Polyoxometalates (POMs) are the polyoxoanions of the early transition metals, especially tungsten, molybdenum and vanadium in their highest oxidation state. They have a wide range of molecular structural diversity, existing in a variety of shapes, sizes and compositions. The versatility and accessibility of polyoxometalates have led to

various applications in the fields of medicine, material science and catalysis [24]. Especially, the catalytic function of polyoxometalates has attracted much attention because their chemical properties such as redox and acidic properties can be controlled at atomic or molecular levels. In addition, POMs are stable under thermal and oxidative conditions. Therefore, POMs have received much attention in the field of oxidation catalysis. Examples of POM chemistry applied to catalysis include the oxidation of alkanes, phenols and olefins, C-C bond cleavage of vic-diols, the epoxidation of alkenes, allylic acetoxylations *etc.* [25] as well as in water decontamination process through photocatalytic decomposition of organic pollutants [26].

#### **VI.1.7 Solid supported polyoxometalates**

The POMs suffer from the limitation of poor recyclability and low density of active sites. One way to overcome this problem is to intercalate POMs into different solid supports like LDHs, forming hybrid materials [27]. Upon intercalation of POMs between the layers of LDHs, thermal stability, acidic and redox behavior of POMs are modified, which make them suitable catalyst in oxidation reactions.

The first example of pillared LDH derivatives based on  $V_{10}O_{28}^{6-}$  and  $XM_{12}O_{40}^{n-}$  Keggin ions as the pillarating anion was synthesized by an ion exchange reaction between a simple LDH-chloride/nitrate and the pillarating POM [28]. Since then several strategies for the intercalation of POMs have been developed. The incorporation of inorganic polyoxometalate anions, such as  $V_{10}O_{28}^{6-}$  and  $Mo_7O_{24}^{6-}$ , into LDHs has received considerable attention. Such polyoxometalate LDHs represent a class of pillared materials for selective adsorption and oxidation catalysis. Although the direct synthesis of an LDH containing POM anions has been reported [29], earlier work by Drezdzon [30] demonstrated that the incorporation of these POM anions could be achieved *via* an intermediate intercalation of large organic anions such as terephthalate (TA). The use of LDH-TA intermediate avoids the problems that may be associated with exchanging a small anion such as  $NO_3^-$  with a large POM anion.

#### **VI.1.8 Epoxidation of alkenes**

The epoxidation of alkenes deserves special attention not only from an academic viewpoint, but also from an industrial perspective. Epoxides are useful intermediates in various organic syntheses and are widely used as raw materials for epoxy resins, paints, surfactants. Consequently, the epoxidation of alkenes has received great attention. Although a number of homogeneous catalysts have been developed for this purpose [31], there is still a demand for solid supported catalysts for epoxidation with easily available

oxidants, such as hydrogen peroxide or organic peroxides. Solids such as Amberlite, MCM-41 or  $\text{SiO}_2$  loaded with different metal cations (e.g., Ti, Mn, W, V, Mo etc.) have been tested and showed high selectivities for the epoxidation of several alkenes and/or unsaturated alcohols [11a].

The advantages of different LDHs intercalated with POMs as heterogeneous catalysts in some epoxidation reactions have been reported [32]. Tatsumi *et al.* reported the epoxidation of 2-hexene by LDH catalysts interlayered by POM (heptamolybdate or paratungstate B) and found that both intercalates were better catalysts in terms of selectivity than the unsupported POMs [32a, 33]. Watanabe *et al.* examined  $\text{Zn}_3\text{Al-SiW}_{11}\text{O}_{39}$  and  $\text{Zn}_3\text{Al-SiW}_{12}\text{O}_{40}$  LDHs in the epoxidation of cyclohexene using  $\text{H}_2\text{O}_2$  or  $\text{O}_2$  as oxidant and observed higher selectivity of the epoxides using  $\text{Zn}_3\text{Al-SiW}_{11}\text{O}_{39}$  with  $\text{H}_2\text{O}_2$ ; but  $\text{O}_2$  as oxidant showed loss of selectivity [32c]. Carrizo *et al.* studied the LDH systems ZnAl, MgAl and NiAl-heptamolybdate in the epoxidation of bicycloalkenes and reported that these materials are suitable catalysts for this process. The selectivity is found to depend on the hydrotalcite composition as well as on the nature of the solvent [32d].

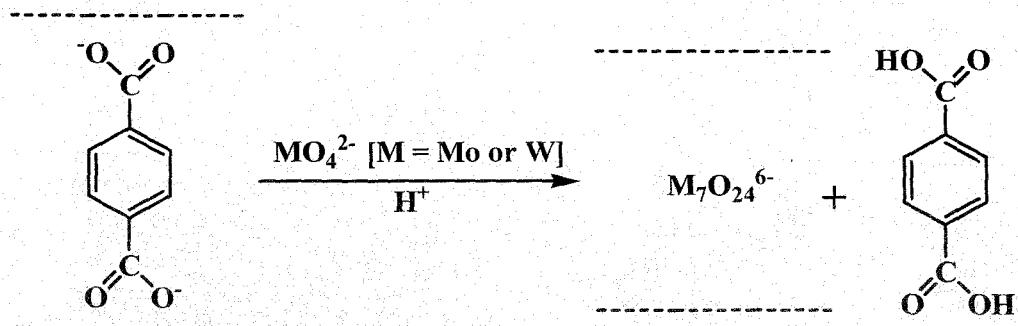
In this chapter, we wish to report the synthesis of LDHs containing Mg/Al within the layers and  $\text{Mo}_7\text{O}_{24}^{6-}$  and  $\text{W}_7\text{O}_{24}^{6-}$  anions in the interlayers, following the exchange method, starting from the corresponding LDH containing terephthalate anion in the interlayer. Characterization of the synthesized LDHs have been done using elemental analysis, powder X-ray diffraction, FT-IR spectroscopy, SEM, TEM and thermogravimetric analysis. The synthesized polyoxometalate intercalated LDHs have been examined as catalysts in the epoxidation of alkenes using mild  $\text{H}_2\text{O}_2$  at room temperature. The effect of different reaction parameters on the catalytic activity of intercalated LDHs has also been tested.

## VI.2 Results and discussion

### VI.2.1 Synthesis

The LDH-POM catalysts have been synthesized following a reported method, developed by Drezdon [30]. The method involves intercalation of terephthalate ion into the interlayer space of hydrotalcite to facilitate the subsequent incorporation of POMs. In case of LDH- $\text{Mo}_7\text{O}_{24}$ , acidifying the organo-LDH in the presence of  $\text{MoO}_4^{2-}$  ions leads to the simultaneous polymerization of the monomolybdate and displacement of the terephthalate from the interlayer, resulting in the incorporation of the polyoxometalate,  $\text{Mo}_7\text{O}_{24}^{6-}$ . Acidification weakens the electrostatic interaction between the organic species

and the brucite layers by protonation of the terephthalate anion and hence allows migration of the organic species out of the clay interlayer forming LDH-POM catalysts (Scheme VI.1).



Scheme VI.1 Intercalation of POM in LDH-TA.

### VI.2.2 Characterization

#### VI.2.2.1 Chemical analysis

The results obtained from the element chemical analysis for the prepared catalysts are summarized in Table VI.1.

Table VI.1 Element data for the various samples studied<sup>a</sup>.

Sample	% Mg	% Al	% C	% M (Mo/W)	1-x	x	Mg/Al
LDH-TA	7.92	4.11	13.8		0.67	0.33	2.03
LDH-Mo <sub>7</sub> O <sub>24</sub>	5.13	2.68		12.08	0.66	0.34	1.94
LDH-W <sub>7</sub> O <sub>24</sub>	5.53	2.97		23.9	0.65	0.35	1.86

<sup>a</sup>Assuming a formula [M<sup>2+</sup><sub>1-x</sub> M<sup>3+</sup><sub>x</sub>(OH)<sub>2</sub>]A<sup>n-</sup><sub>x/n</sub>.

The Mg/Al ratio in the LDH-TA precursor is close to 2 and it does not change significantly in the intercalated LDHs containing Mo<sub>7</sub>O<sub>24</sub><sup>6-</sup> and W<sub>7</sub>O<sub>24</sub><sup>6-</sup> as the intercalating anion with the values 1.94 and 1.86 respectively.

#### VI.2.2.2 Powder X-ray diffraction

The powder X-ray diffraction (PXRD) pattern of the LDH-TA precursor is shown in Figure VI.4. The PXRD pattern shows the basal spacing of LDH-TA of 14.2 Å (2θ = 6.2 degree), which is in agreement with the reported data [30]. Assuming the thickness of brucite layer is approximately 4.8 Å [34], the gallery height is close to 9.4 Å. Given that the size of the TA anion is approximately 9.0 Å, this value has been described to the presence of the terephthalate anion adopting a vertical arrangement within the gallery [35].

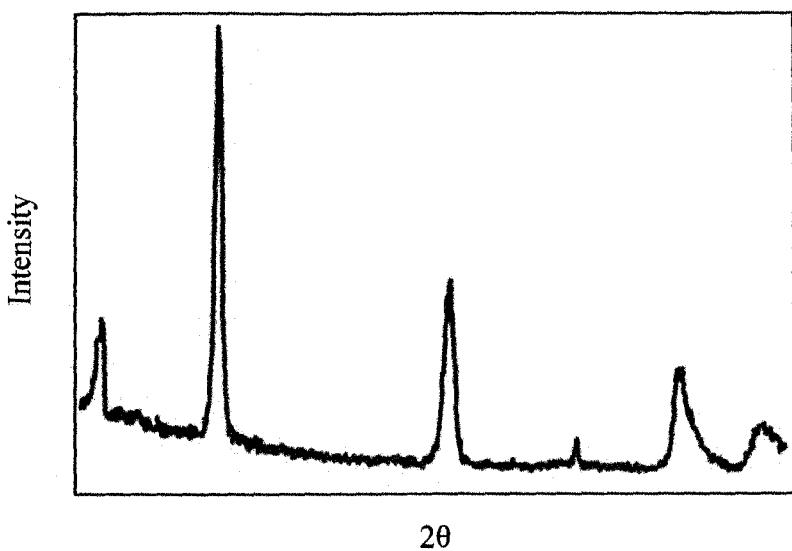


Figure VII.4 Powder X-ray diffraction pattern of LDH-TA.

The PXRD patterns of LDH-Mo<sub>7</sub>O<sub>24</sub> and LDH-W<sub>7</sub>O<sub>24</sub> are shown in Figure VI.5. The basal spacing of LDH-Mo<sub>7</sub>O<sub>24</sub> is recorded at 12.2 Å ( $2\theta = 7.2$  degree) [30] and that of LDH-W<sub>7</sub>O<sub>24</sub> is 12.1 Å ( $2\theta = 7.3$  degree), which are in agreement with those reported in literature [32b].

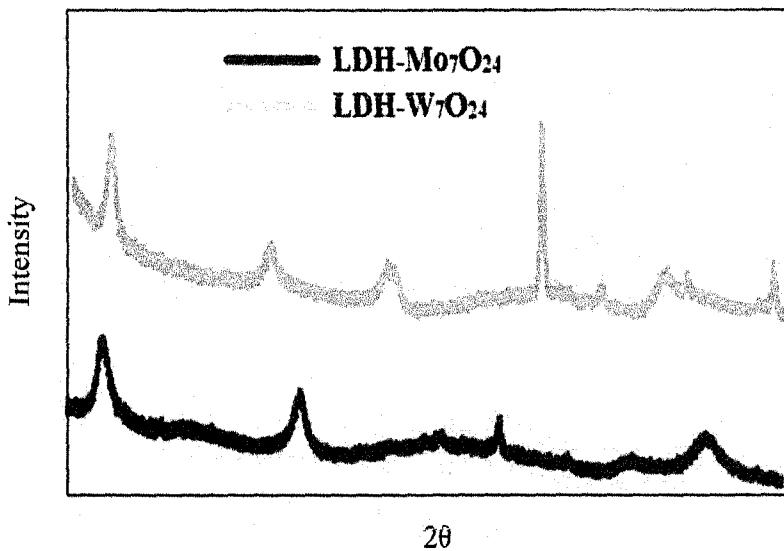


Figure VI.5 Powder X-ray diffraction pattern of POM intercalated LDH.

### VI.2.2.3 Infrared spectroscopy

The infrared spectra of the LDH-samples show a broad absorption band between 3400-3450 cm<sup>-1</sup> which is associated with the stretching mode of the layer hydroxyl groups and of the interlayer water molecules and other of medium intensity at 1630-1632 cm<sup>-1</sup> due to the bending mode of the same species, characteristic of hydrotalcite-type solids [36].

#### **VI.2.2.4 Thermogravimetric (TGA) analysis**

The TG curves of the LDH-samples exhibited two important stages of weight loss. The mass loss in the range from the room temperature to around 250 °C can be attributed to the removal of interlayer water molecules and adsorbed water molecules [37]. The second one corresponds to dehydroxylation of the brucite-like layers in the range of 250-500 °C [37]. For LDH-TA, the third loss, above 500 °C corresponds to the elimination and combustion of the terephthalate anion [34, 38].

#### **VI.2.2.5 SEM and TEM micrographs**

The scanning electron micrographs for both parent sample and the exchanged ones show slightly flattened beadlike particles with a diameter ranging between 5-20 µm. Examination of these samples by TEM at high magnification reveals the layered structure of these materials. TEM micrographs indicate the existence of lamellar particles with rounded hexagonal shape, typical of hydrotalcite-like materials [38]. The SEM micrographs of LDH-TA, LDH-Mo<sub>7</sub>O<sub>24</sub> and LDH-W<sub>7</sub>O<sub>24</sub> have been shown in Figures VII. 6 (a-c) and their TEM micrographs are shown in Figures VI.6 (d-f) respectively.

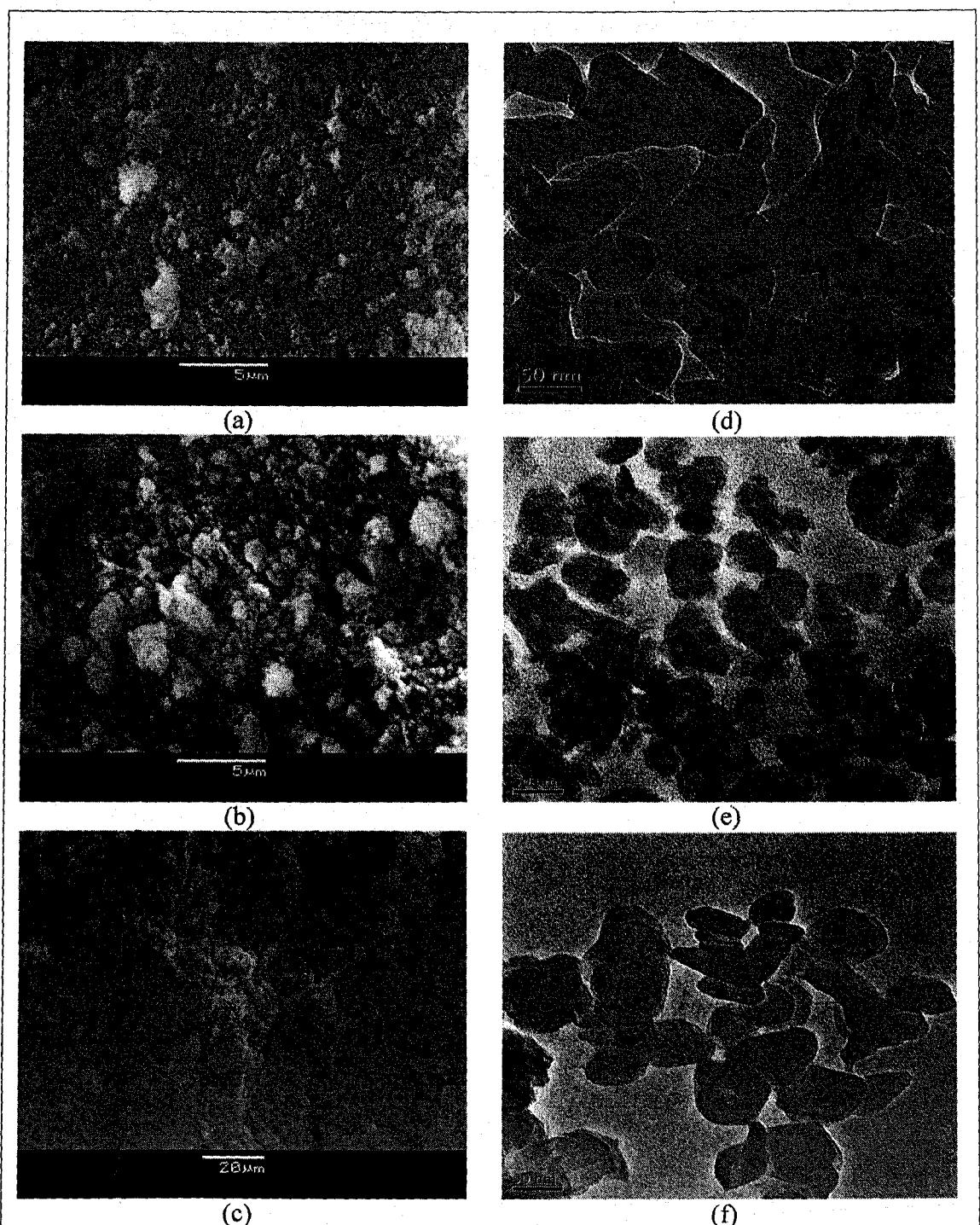


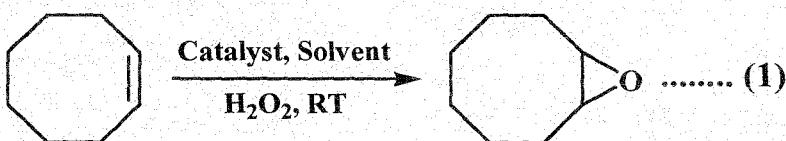
Figure VI.6: SEM micrographs (a-c) and TEM micrographs (d-f) of LDH-TA, LDH-Mo<sub>7</sub>O<sub>24</sub> and LDH-W<sub>7</sub>O<sub>24</sub> respectively.

### VI.2.3 Epoxidation of alkenes with H<sub>2</sub>O<sub>2</sub>

The M<sub>7</sub>O<sub>24</sub><sup>6-</sup> intercalated LDHs have been explored as catalysts for the epoxidation of a group of alkenes at room temperature under anaerobic condition. Detailed experimental procedure and analysis process are given in the experimental section. The results obtained have been discussed in the following section.

#### VI 2.3.1 Epoxidation of cyclooctene

The catalytic activities of the intercalated LDHs have been examined initially in the epoxidation of cyclooctene by mild H<sub>2</sub>O<sub>2</sub> as oxidant at room temperature according to equation 1.



In order to obtain suitable reaction conditions to achieve the maximum yield, the effect of different reaction parameters such as nature of the solvent, amount of catalyst and concentration of substrate have been studied in details using LDH-Mo<sub>7</sub>O<sub>24</sub> as catalyst.

##### VI.2.3.1.1 Effect of solvent

In order to achieve the maximum yield, solvent effects on the reaction have been studied with three different solvents *viz.* acetonitrile (CH<sub>3</sub>CN), dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) and mixture of acetonitrile and dichloromethane (1:1, *v/v*) under the same reaction conditions. The results are summarized in Table VI.2.

Table VI.2 Influence of the solvent on the epoxidation of cyclooctene with time<sup>a</sup>.

Solvent	Yield (%) <sup>b</sup>			
	6 h	12 h	18 h	24 h
CH <sub>3</sub> CN	18%	27%	38%	46%
CH <sub>2</sub> Cl <sub>2</sub>	42%	57%	69%	76%
1:1 CH <sub>3</sub> CN/CH <sub>2</sub> Cl <sub>2</sub>	29%	41%	52%	58%

<sup>a</sup>Reaction condition: cyclooctene (200 mM), catalyst (50 mg), H<sub>2</sub>O<sub>2</sub> (2 mM) in 2 mL solvent.

<sup>b</sup>Yields are reported with respect to the concentration of the oxidant.

The catalytic activity of LDH-Mo<sub>7</sub>O<sub>24</sub> towards epoxidation of cyclooctene in three solvents with time is shown in Figure VI.7. The results reveal that cyclooctene conversion strongly depends on the nature of the solvent. The order of efficiency of the catalyst in terms of yield in three solvents follows the order: CH<sub>2</sub>Cl<sub>2</sub> > CH<sub>3</sub>CN/CH<sub>2</sub>Cl<sub>2</sub> (1:1, *v/v*) > CH<sub>3</sub>CN.

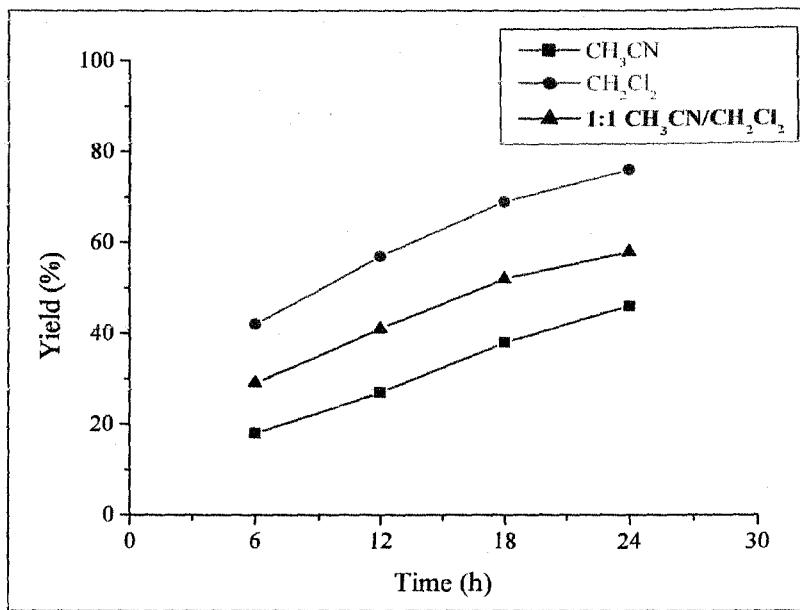


Figure VI.7 Effect of solvent on the yield of LDH-Mo<sub>7</sub>O<sub>24</sub> catalyzed epoxidation of cyclooctene with H<sub>2</sub>O<sub>2</sub>.

#### VI.2.3.1.2 Nature of catalyst

The results obtained in the epoxidation of cyclooctene using LDH-Mo<sub>7</sub>O<sub>24</sub>, LDH-W<sub>7</sub>O<sub>24</sub> and LDH-TA as catalysts in three different reaction media *viz.* CH<sub>3</sub>CN, CH<sub>2</sub>Cl<sub>2</sub> and mixture of CH<sub>3</sub>CN/CH<sub>2</sub>Cl<sub>2</sub> (1:1, *v/v*) are summarized in Table VI.3. The reaction was also carried out in the presence of Mo<sub>7</sub>O<sub>24</sub><sup>6-</sup> (without intercalation) and very low epoxide yield (less than 4%) is obtained.

Table VI.3 Influence of nature of catalyst in the epoxidation of cyclooctene<sup>a</sup>.

Catalyst	Yield (%) <sup>b</sup>		
	CH <sub>3</sub> CN	CH <sub>2</sub> Cl <sub>2</sub>	1:1 CH <sub>3</sub> CN/CH <sub>2</sub> Cl <sub>2</sub>
LDH-TA	Nil	4%	2%
LDH- Mo <sub>7</sub> O <sub>24</sub>	46%	76%	58%
LDH-W <sub>7</sub> O <sub>24</sub>	20%	55%	28%

<sup>a</sup>Reaction condition: cyclooctene (200 mM), catalyst (50 mg), H<sub>2</sub>O<sub>2</sub> (2 mM) in 2 mL solvent, 24 h. <sup>b</sup>Yields are reported with respect to the concentration of the oxidant.

The LDH-TA precursor affords very low epoxide yield (2-4%) in comparison to exchanged LDH materials. This suggests that the intercalated Mo<sub>7</sub>O<sub>24</sub><sup>6-</sup> and W<sub>7</sub>O<sub>24</sub><sup>6-</sup> have significant contribution to the epoxidation of cyclooctene. Moreover, the catalytic activity depends on the nature of the interlayer anion. The LDH-Mo<sub>7</sub>O<sub>24</sub> exhibits better catalytic efficiency in terms of yield than LDH-W<sub>7</sub>O<sub>24</sub>. The effect of nature of catalyst together with the LDH-TA precursor is presented in Figure VI.8.

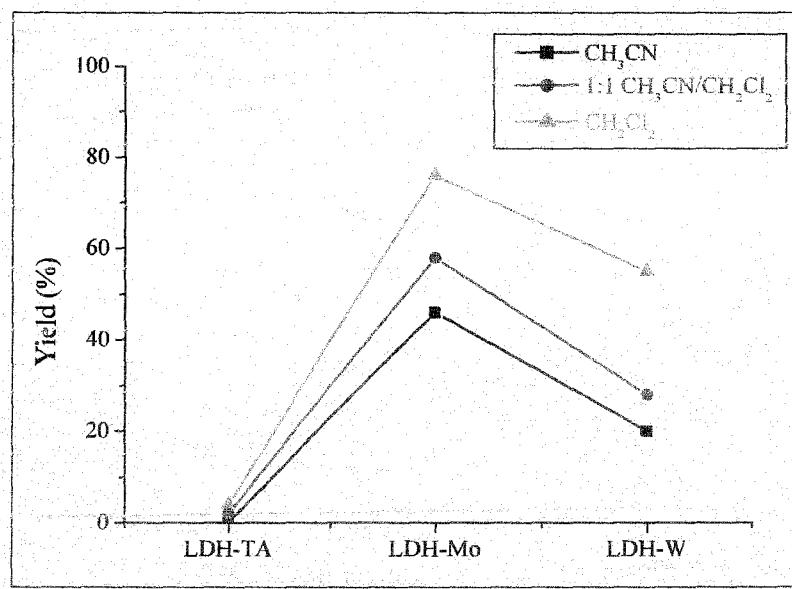


Figure VI.8 Influence of nature of catalyst in the epoxidation of cyclooctene with  $\text{H}_2\text{O}_2$ .

#### VI.2.3.1.3 Optimization of catalyst amount

The optimization of catalyst ( $\text{LDH-Mo}_7\text{O}_{24}$ ) amount has been undertaken on the basis of epoxide yield. Five different amounts of catalyst (0.02 g, 0.03 g, 0.04 g, 0.05 g and 0.06 g) have been used (Table VI.4, Figure VI.9). The results indicate that an amount of 0.05 g is most effective in terms of epoxide yield for the fixed amount of oxidant and substrate in three different solvent systems.

Table VI.4 Effect of amount of catalyst in the epoxidation of cyclooctene<sup>a</sup>.

Solvent	Amount of catalyst ( $\text{LDH-Mo}_7\text{O}_{24}$ )				
	0.02 g	0.03 g	0.04 g	0.05 g	0.06 g
$\text{CH}_3\text{CN}$	20%	27%	31%	38%	40%
$\text{CH}_2\text{Cl}_2$	48%	54%	67%	69%	70%
$1:1 \text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$	27%	33%	39%	52%	54%

<sup>a</sup>Reaction condition: cyclooctene (200 mM), catalyst (0.02-0.06 g),  $\text{H}_2\text{O}_2$  (2 mM) in 2 mL solvent, 18 h.

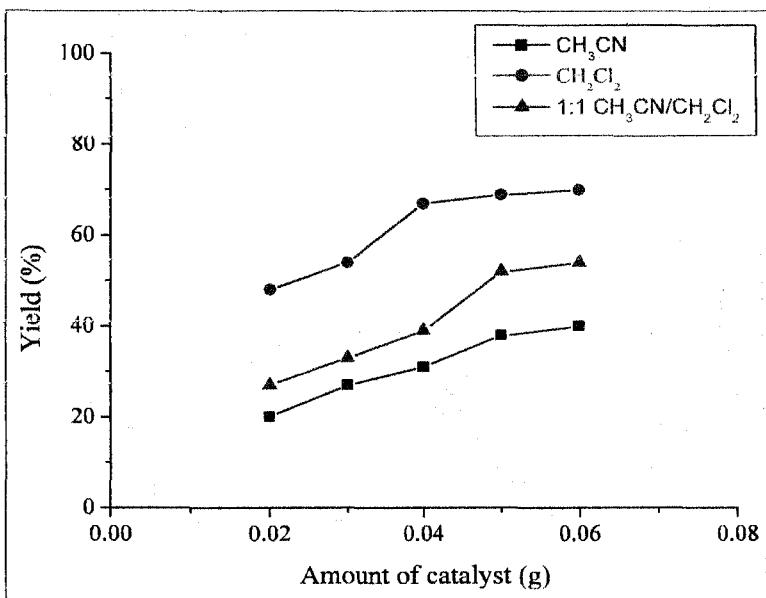


Figure VI.9 Optimization of catalyst amount in cyclooctene epoxidation.

#### VI.2.3.1.4 Optimization of substrate concentration

The effect of variation of substrate concentration keeping oxidant concentration (2 mM) constant on epoxidation of cyclooctene has also been studied. Five different concentration of cyclooctene (10 mM, 20 mM, 50 mM, 100 mM and 200 mM) has been used using LDH-Mo<sub>7</sub>O<sub>24</sub> as catalyst in a mixture of CH<sub>3</sub>CN/CH<sub>2</sub>Cl<sub>2</sub> (1:1, v/v). The results reveal that 200 mM concentration of cyclooctene is most effective in terms of epoxide yield with 2 mM of oxidant concentration. The results are compiled in Figure VI.10.

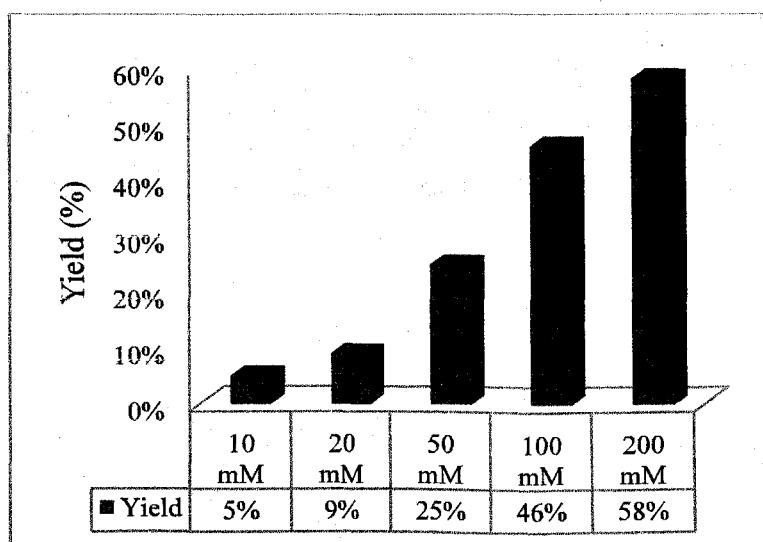
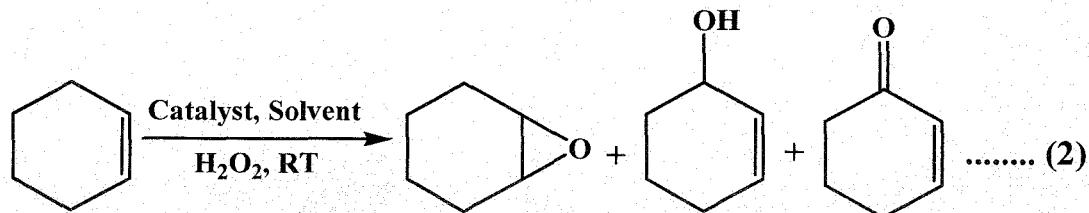


Figure VI.10 Optimization of substrate concentration for LDH-Mo<sub>7</sub>O<sub>24</sub> catalyzed epoxidation of cyclooctene.

### VI.2.3.2 Oxidation of cyclohexene

The oxidation of cyclohexene has also been studied with  $H_2O_2$  by LDH catalysts at room temperature. The oxidation products are epoxide, cyclohexene-1-ol and cyclohexene-1-one as shown in equation 2.



The results of cyclohexene oxidation with  $H_2O_2$  catalyzed by LDH-TA precursor and exchanged LDH materials in different solvents [ $CH_3CN$ ,  $CH_2Cl_2$  and mixture of  $CH_3CN/CH_2Cl_2$  (1:1, v/v)] are summarized in Table VI.5.

Table VI.5 Oxidation of cyclohexene with  $H_2O_2$  at room temperature<sup>a</sup>.

With LDH-TA precursor		Product Yield (%) <sup>b</sup>			Product selectivity (%) <sup>c</sup>		
Solvent	Yield (%) <sup>b</sup>	Epoxide	Ol	One	Epoxide	Ol	One
$CH_3CN$	33	6	6	21	18	18	64
1:1 $CH_3CN/CH_2Cl_2$	42	6	7	29	14	17	69
$CH_2Cl_2$	65	7	10	48	11	15	74
With LDH-Mo <sub>7</sub> O <sub>24</sub> catalyst		Product Yield (%) <sup>b</sup>			Product selectivity (%) <sup>c</sup>		
Solvent	Yield (%) <sup>b</sup>	Epoxide	Ol	One	Epoxide	Ol	One
$CH_3CN$	61	27	5	29	44	8	48
1:1 $CH_3CN/CH_2Cl_2$	72	31	6	35	43	8	49
$CH_2Cl_2$	83	51	5	27	61	6	33
With LDH-W <sub>7</sub> O <sub>24</sub> catalyst		Product Yield (%) <sup>b</sup>			Product selectivity (%) <sup>c</sup>		
Solvent	Yield (%) <sup>b</sup>	Epoxide	Ol	One	Epoxide	Ol	One
$CH_3CN$	51	19	6	26	37	12	51
1:1 $CH_3CN/CH_2Cl_2$	60	21	8	31	35	13	52
$CH_2Cl_2$	73	41	6	26	56	8	36

<sup>a</sup>Reaction condition: cyclohexene (200 mM), catalyst (50 mg),  $H_2O_2$  (2 mM) in 2 mL solvent, 24 h. <sup>b</sup>Yields are reported with respect to the concentration of the oxidant. <sup>c</sup>Selectivity is percentage expressed with respect to total yield.

The results reveal that cyclohexene is oxidized to afford mainly epoxide and cyclohexen-1-one along with minor amount of cyclohexen-1-ol with the exchanged LDH catalysts in all the solvents. In contrast, LDH-TA precursor affords cyclohexen-1-one as the major product. The total conversion of cyclohexene oxidation in different solvents decreases in the order  $CH_2Cl_2 > CH_3CN/CH_2Cl_2$  (1:1, v/v)  $> CH_3CN$  (Table VI.5). It has been found

that LDH-TA precursor gives lower yield of cyclohexene oxidation than POM intercalated LDHs in different solvents and the order of catalytic efficiency in terms of total yield is LDH-Mo<sub>7</sub>O<sub>24</sub> > LDH-W<sub>7</sub>O<sub>24</sub> > LDH-TA. The results are shown in Figure VI.11.

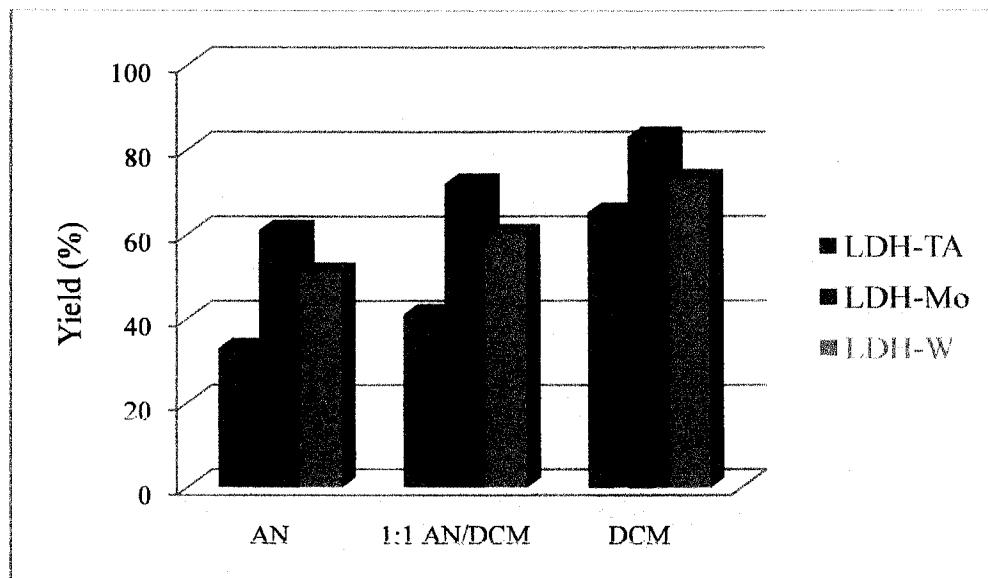


Figure VI.11 Total yield of cyclohexene oxidation in different solvents; AN: Acetonitrile, DCM: Dichloromethane; LDH-Mo: LDH-Mo<sub>7</sub>O<sub>24</sub>, LDH-W: LDH-W<sub>7</sub>O<sub>24</sub>.

The selectivity for epoxide also depends on the solvent used. Both LDH-Mo<sub>7</sub>O<sub>24</sub> and LDH-W<sub>7</sub>O<sub>24</sub> catalysts led to the highest selectivity to epoxide in CH<sub>2</sub>Cl<sub>2</sub> medium (61% and 56% respectively). The epoxide selectivity in cyclohexene oxidation using LDH-TA, LDH-Mo<sub>7</sub>O<sub>24</sub> and LDH-W<sub>7</sub>O<sub>24</sub> as catalysts in different reaction media is presented in Figure VI.12.

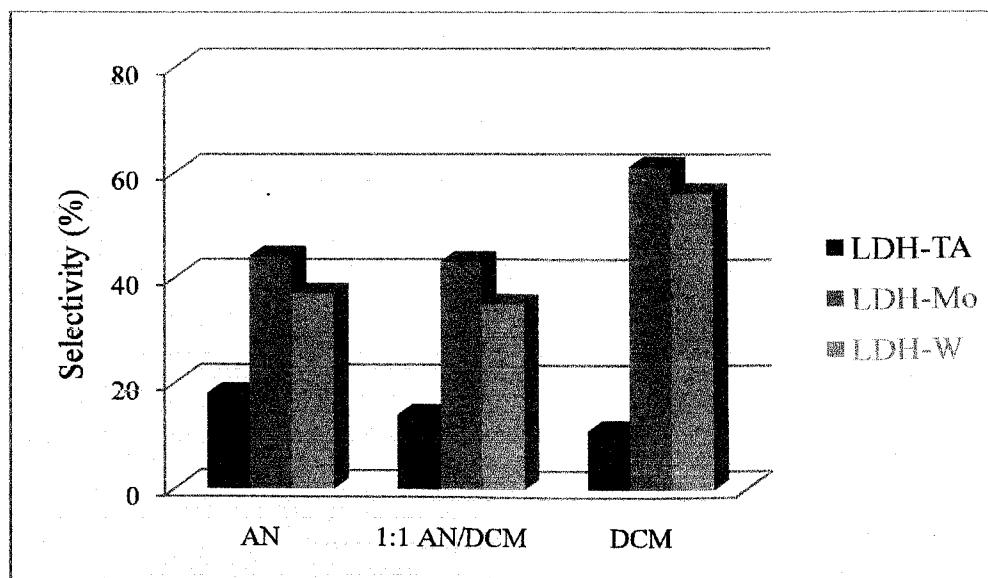


Figure VI.12 Selectivity of epoxide in cyclohexene oxidation in different solvents; AN: Acetonitrile, DCM: Dichloromethane; LDH-Mo: LDH-Mo<sub>7</sub>O<sub>24</sub>, LDH-W: LDH-W<sub>7</sub>O<sub>24</sub>.

### VI.2.3.3 Epoxidation of a series of alkenes

The epoxidation of a number of alkenes (1-octene, norbornene and dihydronaphthalene) has also been carried out with LDH-Mo<sub>7</sub>O<sub>24</sub> and LDH-W<sub>7</sub>O<sub>24</sub> as catalysts under an argon atmosphere using environmentally benign H<sub>2</sub>O<sub>2</sub> as oxidant at room temperature in different solvents. The results are summarized in Table VI.6.

Table VI.6 Epoxidation of alkenes by H<sub>2</sub>O<sub>2</sub> in different solvents<sup>a</sup>.

Entry	Substrate	Catalyst	Product	Yield (%) <sup>b</sup>		
				CH <sub>3</sub> CN	CH <sub>3</sub> CN / CH <sub>2</sub> Cl <sub>2</sub> (1:1, v/v)	CH <sub>2</sub> Cl <sub>2</sub>
1		LDH-Mo <sub>7</sub> O <sub>24</sub>		20	23	24
2		LDH-W <sub>7</sub> O <sub>24</sub>		20	22	25
3		LDH-Mo <sub>7</sub> O <sub>24</sub>		45	64	76
4		LDH-W <sub>7</sub> O <sub>24</sub>		35	47	63
5		LDH-Mo <sub>7</sub> O <sub>24</sub>		37	53	65
6		LDH-W <sub>7</sub> O <sub>24</sub>		29	43	58

<sup>a</sup>Reaction condition: Substrate (200 mM), catalyst (50 mg), H<sub>2</sub>O<sub>2</sub> (2 mM) in 2 mL solvent, 24 h. <sup>b</sup>Yields are reported with respect to the concentration of the oxidant.

As shown in Table VI.6, intercalated LDHs catalyze the epoxidation of 1-octene with H<sub>2</sub>O<sub>2</sub> as terminal oxidant to afford 1,2-epoxy octane with the yield of 20-25% (Entries 1, 2). No solvent dependence is observed in the epoxidation of 1-octene. Norbornene is regiospecifically oxidised to its *exo*-epoxide only. The Mo<sub>7</sub>O<sub>24</sub><sup>6-</sup> intercalated LDH catalyzes the oxidation of norbornene with the yield of 45-76% in different solvents; however, the conversion decreases to 35-63% when W<sub>7</sub>O<sub>24</sub><sup>6-</sup> intercalated LDH is used as catalyst (Table VI.6, entries 3, 4). In both cases, the epoxide yield in different solvents increases in the order CH<sub>2</sub>Cl<sub>2</sub> > CH<sub>3</sub>CN/CH<sub>2</sub>Cl<sub>2</sub> (1:1, v/v) > CH<sub>3</sub>CN. The present catalytic system is also effective in catalyzing the epoxidation of dihydronaphthalene at room temperature (Table VI.6, entries 5, 6). Here also LDH-Mo<sub>7</sub>O<sub>24</sub> appears as better catalyst than LDH-W<sub>7</sub>O<sub>24</sub>. Thus, at room temperature, Mo<sub>7</sub>O<sub>24</sub><sup>6-</sup> intercalated LDH exhibits better catalytic activity than W<sub>7</sub>O<sub>24</sub><sup>6-</sup> intercalated LDH towards the epoxidation of alkenes at room temperature in presence of H<sub>2</sub>O<sub>2</sub> as the terminal oxidant.

#### **VI.2.3.4 Catalyst recycling**

The recyclable tests of the catalysts have been undertaken by performing repeat reaction cycles under the similar reaction conditions as described above. At the end of each cycle, the catalyst was recovered by filtration, washed with solvent, dried and then placed into a fresh reaction mixture. The results of cyclooctene epoxidation with both the catalysts for three reaction cycles are given in Table VI.7.

Table VI.7 Recycling of the catalyst in the epoxidation of cyclooctene with  $\text{H}_2\text{O}_2^{\text{a}}$ .

Catalyst	No. of catalytic cycle	Yield (%) <sup>b</sup>
LDH-Mo <sub>7</sub> O <sub>24</sub>	1	58
	2	58
	3	56
LDH-W <sub>7</sub> O <sub>24</sub>	1	28
	2	27
	3	27

<sup>a</sup>Reaction condition: Cyclooctene (200 mM), catalyst (50 mg),  $\text{H}_2\text{O}_2$  (2 mM) in 2 mL  $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$  (1:1, v/v) solvent, 24 h. <sup>b</sup>Yields are reported with respect to the concentration of the oxidant.

No notable difference in the epoxide yield is observed irrespective of the number of cycles. These results suggest that the  $\text{M}_7\text{O}_{24}^{6-}$  containing LDH material is very stable under the catalytic reaction conditions.

### **VI.3 Conclusion**

1. LDHs containing  $\text{M}_7\text{O}_{24}^{6-}$  anions [M = Mo or W] in the interlayer has been prepared by ion-exchange from the corresponding LDH precursor containing terephthalate dianion and their intercalation has been ensured by different studies.
2. The intercalated LDHs exhibit good catalytic activity towards epoxidation of a series of alkenes with mild and environment friendly  $\text{H}_2\text{O}_2$  at room temperature.
3. Reaction conditions have been optimized considering different parameters to achieve maximum conversion.
4. Catalytic epoxidation reaction has been found to be dependent on the nature of the reaction medium. Remarkable improvement in epoxide yield has been observed in dichloromethane medium than in acetonitrile or mixture of acetonitrile/dichloromethane (1:1, v/v) medium.
5. The catalytic activities of the catalysts towards epoxidation are dependent on the nature of the anionic species in the interlayer gallery. The LDH-Mo<sub>7</sub>O<sub>24</sub> emerges as a better catalyst than LDH-W<sub>7</sub>O<sub>24</sub>.

6. The selectivity of cyclohexene epoxidation is found to be dependent on the nature of the interlayer anion and the solvent used.
7. Reactions with neat  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$  and LDH-TA precursor have shown much lower catalytic activity than exchanged LDHs. This confirms the significant role of intercalated molybdate and tungstate in the epoxidation reactions.
8. The catalysts are easily recovered and recycled without significant loss of their catalytic activity.

## VI.4 Experimental section

### VI.4.1 Materials

All chemicals used for the synthesis were reagent grade.  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$  were obtained from S. D. Fine Chemicals Ltd. All alkenes, reaction products and pentafluoroiodobenzene (internal standard) were procured from Sigma Aldrich and were used as received. Cyclohexene was distilled under argon and passed through a silica gel column prior to reaction. The solvents were distilled under argon and stored over molecular sieves (4 Å). The active oxygen content of the oxidant  $\text{H}_2\text{O}_2$  (as ~30% solution in water) was determined iodometrically prior to use.

### VI.4.2 Physical methods

All samples prepared have been characterized using different experimental techniques. The chemical compositions of synthesized samples were determined by EDXRF (PANalytical Epsilon 5). Powder X-ray diffraction patterns were recorded with Philips 1710 diffractometer (40 kV, 20 mA) with Cu-K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). Diffractograms were collected from  $2\theta = 5$  to 80 using steps of 0.02 ( $2\theta$ ) and a counting time of 0.5 s per step. FT-IR spectra were recorded with a Shimadzu model FTIR-8300 spectrometer. The morphologies and sizes of the specimen were examined by scanning electron microscopy (JSM-6360, Jeol) and transmission electron microscopy (JEM-2100, 200 kV, Jeol) techniques. The product analyses were done by Perkin Elmer Clarus-500 GC with FID (Elite-I, Polysiloxane, 15-meter column).

### VI.4.3 Preparation of LDHs

#### VI.4.3.1 Preparation of LDH-TA

LDH-TA was prepared according to the method used by Drezdzon [30] and stored as a suspension in deionized water.

#### **VI.4.3.2 Polyoxometalate intercalated LDHs**

The LDH-TA precursor was converted to the desired POM intercalated LDHs according to the procedure followed by Drezdzon [30]. To a 100 g portion of the preceding LDH-TA slurry was added a solution consisting of  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$  (10.0 g, 0.04 mol) or  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  (13.0 g, 0.04 mol) in 20 mL of deionized water. After stirring the mixture for 15 min, the pH was adjusted to 4.4 or 5.0 respectively with 4 N  $\text{HNO}_3$ . After 10 min of additional stirring, the product was filtered, washed several times by deionized water and dried at 125 °C overnight.

#### **VI.4.4 Catalytic epoxidation of alkenes**

Catalytic reactions were carried out under argon atmosphere in small screw capped vials fitted with PTFE septa. In a typical reaction, the solid catalyst (50 mg) and 200 mM of substrate were taken in 2 mL of argon saturated solvent. 2 mM of  $\text{H}_2\text{O}_2$  was then added and the contents were magnetically stirred at room temperature. After periodic time intervals standard solution of pentafluoroiodobenzene (PFIB) was added to this reaction mixture as an internal standard and an aliquot of (1  $\mu\text{L}$ ) was injected into a capillary column of a preheated GC. The identification and quantization of the products were done from the response factors of standard product samples as usual.

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