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Mo- and W-containing layered double hydroxides: Mild and selective oxidation of alkenes with H_2O_2

Uday Sankar Agarwalla*
Department of Chemistry, P D Women's College, Jalpaiguri, West Bengal 735 101, India
*E-mail: udaygrwlla@gmail.com

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Molybdenum- and tungsten-containing ($M_7O_{24}^{6-}$, M = Mo or W) 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 X-ray diffraction, infrared spectroscopy, scanning electron microscopy, transmission electron microscopy and thermogravimetric analysis. The $M_7O_{24}^{6-}$ intercalated LDHs have been explored as catalysts for the selective oxidation of a series of alkenes at room temperature using safer, inexpensive and environmentally benign hydrogen peroxide as oxidant. Reaction conditions have been optimized considering different reaction parameters to achieve maximum conversion in the catalytic oxidation reaction. Recycling of the catalyst has shown that it can be reused up to three more cycles without significant loss of performance.

Keywords: Layered double hydroxide, Hydrotalcite, Polyoxometalate, Alkene, Oxidation, Hydrogen peroxide

Selective oxygen transfer to alkenes remains an important research objective in view of the industrial importance of epoxides, because epoxides play a significant role as flexible intermediate and precursor to many useful chemical products and are widely used as raw materials for epoxy resins, paints, and surfactants[1,2]. For example, cyclohexene oxide is a valuable organic intermediate, used in the synthesis of products such as chiral pharmaceuticals, pesticides, epoxy paints, rubber promoters and dyestuffs. The wide applicability of epoxy norbornene in polymer synthesis, pharmaceutical intermediates and general organic synthesis is also noteworthy. Consequently, the epoxidation of alkenes has gained much attention. Although a number of homogeneous catalysts have already proved their efficiency in this process, there is still a huge interest in the research of solid materials able to catalyze epoxidation under very mild reaction conditions, with the advantages of easy separation, better handling properties and facile recovery of the solid catalyst from the reaction mixture for recycling without tedious workup. Layered double hydroxides (LDHs) being typical intercalation compounds are of considerable interest due to their valuable and unique ion exchange intercalation properties[3,4]. This class of materials is defined by the general formula $M^{2+}_{1-x}M^{3+}_{x}(OH)_2]A^{n-}_{x/n}$. mH_2O, where M^{2+} and M^{3+} are divalent and trivalent cations respectively and A^{n-} the interlayer anion. Structural studies showed that these solids have a laminar structure consisting of positively charged brucite-type metal hydroxide layers with balancing exchangeable interlayer anions and water molecules in the interlayer space[5-7]. These interlayer anions can be easily exchanged with other anions with desired properties and following this route several hydrotalcite-like materials intercalated with different sorts of anions (organic or inorganic) have been prepared[8-11]. In this way, new materials can be tailored in order to fulfill specific requirements. Moreover, convenient synthetic method and low cost of the materials have made them attractive candidates for industrial applications.

On the other hand, polyoxometalates (POMs), the polyoxoanions of the early transition metals, are a fascinating class of compounds which have a wide range of molecular structural diversity, existing in a variety of shapes, sizes and compositions. The versatility and accessibility of POMs have led to various applications in the fields of medicine, material science and catalysis[12-14]. Especially, the catalytic function of POMs has attracted much attention because their chemical properties such as redox and acidic properties can be controlled at atomic or molecular levels[15-18]. However, they also show disadvantages consisting of low thermal stability and poor specific surface area development. In order to increase POMs' thermal stability and specific surface area for improving their catalytic performance, they may be fixed on suitable supports. Currently, there is a great deal of interest in the intercalation of POMs between the interlayer spaces of hydrotalcite compounds. When POMs are intercalated in the interlayer space of hydrotalcite compounds, their thermal stability increases, and, in addition, acid and redox sites develop in their basic structure, making them suitable catalysts in oxidation reactions. Therefore, the development of catalytic oxidation process using different LDHs intercalated with POMs as heterogeneous catalysts for selective oxidation of alkenes remains an important research objective[19-21]. Furthermore, developing systems using environmentally benign oxidizing agents under mild conditions has received significant attention from an environmental standpoint. Catalytic epoxidation reaction in presence of hydrogen peroxide (H_2O_2) as terminal oxidant has some advantages compared with other conventional epoxidation reagents, because (i) H_2O_2 generates only water as a side product, (ii) It contains the largest amount of active oxygen species among the known oxidants and (iii) It is inexpensive and safer to use than organic peroxides or peracids. This makes H_2O_2 the ideal oxidant from the viewpoint of green chemistry.

This paper reports on the intercalation of $M_7O_{24}^{6-}$ (M= Mo, W) anions into an Mg/Al-LDH following the ion exchange method, starting from the corresponding terephthalate-intercalated precursor (LDH-TA). The starting LDH-TA and the resulting POM-intercalated LDHs have been characterized by using various instrumental techniques. The synthesized LDHs have been examined as catalysts in the selective oxidation of alkenes using mild H_2O_2 at room temperature. The effect of different reaction parameters on the catalytic activity of intercalated LDHs has also been studied in this work.

Materials and Methods

Materials

All chemicals used for the synthesis were reagent grade and obtained from S. D. Fine Chemicals Ltd. Alkene substrates, reaction products and pentafluoroiodobenzene (internal standard) were procured from Sigma Aldrich and were used as received. The solvents were distilled under argon and stored over molecular sieves (4 Å). The active oxygen content of the oxidant H_2O_2 (as ~30% solution in water) was determined iodometrically prior to use.

Physical measurements

All samples prepared have been characterized using different techniques. The chemical compositions of synthesized samples were determined by EDXRF (PANalytical Epsilon 5). Powder X-ray diffraction (XRD) patterns were recorded with Philips 1710 diffractometer (40 kV, 20 mA) with Cu-Kα radiation (λ = 1.5406 Å). FT-IR spectra in the range 400-4000 cm^{-1} were recorded with a Shimadzu model FTIR-8300 spectrometer using the KBr pellets technique. The morphologies and sizes of the specimen were examined by scanning electron microscopy (SEM) (JSM-6360, JEOL) and transmission electron microscopy (TEM) (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).

Preparation of LDHs

Preparation of LDH-TA

LDH-TA was prepared according to the method used by Drezdzon[22] and stored as a suspension in deionized water.

Polyoxometalate intercalated LDHs

The LDH-TA precursor was converted to the desired POM intercalated LDHs according to the procedure followed by Drezdzon[22]. To a 100 g portion of the preceding LDH-TA slurry was added a solution consisting of $Na_2MoO_4.2H_2O$ (10.0 g, 0.04 mol) or $Na_2WO_4.2H_2O$ (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 HNO_3. After 10 min of additional stirring, the product was filtered, washed several times by deionized water and dried at 125 ºC overnight.

Typical procedure for oxidation reaction

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 acetonitrile. 2 mM of H_2O_2 was then added and the contents were magnetically stirred at room temperature. After completion of the reaction, it was centrifuged and the product analysis was done by injecting an aliquot of (1 µL) from the reaction vial into a capillary column of a preheated GC using pentafluoroiodobenzene (PFIB) as internal standard. The identification and quantization of the products were done from the response factors of standard product samples as usual.

Results and Discussion

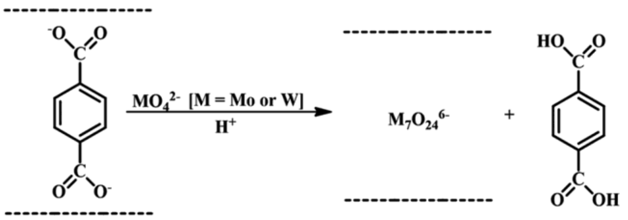
Mo- and W-containing POM-intercalated LDHs have been prepared by direct anion exchange, starting from the corresponding terephthalate precursor, LDH-TA[22]. The method involved intercalation of terephthalate ion into the interlayer space of hydrotalcite to facilitate the subsequent incorporation of POMs. Acidification of the organic-anion-pillared clay slurry (LDH-TA) in the presence of monometalate (MO_4^{2-}, M = Mo or W) resulted in the oligomerization of the metalate to form POM ($M_7O_{24}^{6-}$) which is the most stable species under the pH conditions used for synthesis. Acidification also weakened the electrostatic interaction between the organic species and the brucite layers by protonation of the terephthalate anion and hence allowed migration of the organic species out of the clay interlayer forming LDH-POM catalysts (Scheme 1). The solids were characterized by various instrumental techniques such as chemical analysis, XRD, FTIR spectroscopy, TG-DTA, SEM and TEM.

Chemical analysis

The results obtained from the element chemical analysis for the prepared catalysts are summarized in Table 1. The Mg/Al ratio in the LDH-TA precursor is close to 2 and it did not change significantly in the intercalated LDHs containing $Mo_7O_{24}^{6-}$ and $W_7O_{24}^{6-}$ as the intercalating anion with the values 2.0 and 1.92, respectively.

Powder X-ray diffraction

The PXRD pattern of LDH-TA precursor and the POM-intercalated LDHs are given in Fig. 1. The PXRD pattern exhibited the basal spacing of LDH-TA of 14.2 Å (2θ = 6.2°)[22], corresponding to the vertical arrangement of the terephthalate anion within the gallery[23]. On the other hand, the basal spacing of LDH-Mo_7O_{24} was recorded at 12.2 Å (2θ = 7.2°)[22] and that of LDH-W_7O_{24} at 12.1 Å (2θ = 7.3°), which are in agreement with those reported in literature[24].



Scheme 1 — Intercalation of POM in LDH-TA

Infrared spectroscopy

The IR spectra of the LDH-samples show a broad absorption band between 3400-3450 cm^{-1} (Supplementary Data, Fig. S1) associated with the stretching mode of the layer OH groups and of the interlayer H_2O molecules and other of medium intensity at 1630-1632 cm^{-1} due to the bending mode of the same species, characteristic of hydrotalcite-type solids[25].

Thermogravimetric (TG) analysis

The TG curves of the LDH-samples exhibited two important stages of weight loss (Supplementary Data, Fig. S2). The mass loss in the range from the room temperature to around 250 ºC can be attributed to the removal of interlayer and adsorbed water molecule[26-28]. The second one corresponds to dehydroxylation of the brucite-like layers in the range of 250-500 ºC[26-28]. For LDH-TA, the third loss, above 500 ºC corresponds to the elimination and combustion of the terephthalate anion[29,30].

Table 1 — Element chemical analyses of the precursor sample and of the catalysts studied[a]

Sample	Chemical composition (%)[b]						
	Mg	Al	C	M (Mo /W)	1-x	x	Mg/Al[c]
LDH-TA	7.41	4.11	13.8	-	0.67	0.33	2.03
LDH-Mo_7O_{24}	5.13	2.68	-	12.08	0.67	0.33	2.0
LDH-W_7O_{24}	5.53	3.44	-	23.9	0.66	0.34	1.92

[a]Assuming a formula $[M^{2+}_{1-x}M^{3+}_x(OH)_2]A^{n-}_{x/n}$, [b]Weight percentage, [c]Molar ratio

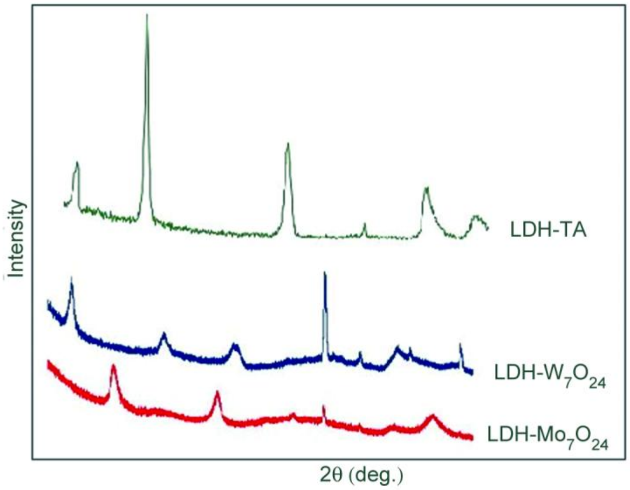


Fig. 1 — Powder X-ray diffraction patterns of synthesized LDHs

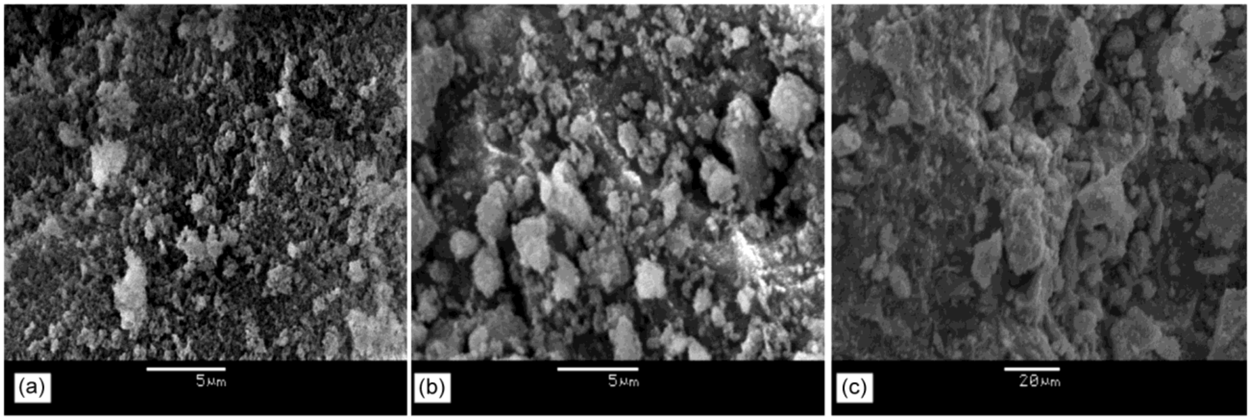


Fig. 2 — SEM micrographs of (a) LDH-TA, (b) LDH-Mo_7O_{24} and (c) LDH-W_7O_{24}

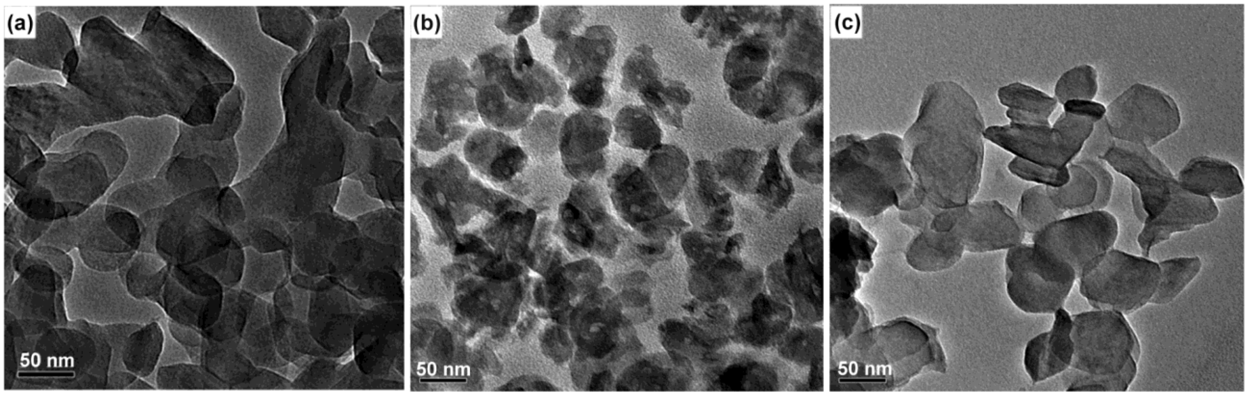


Fig. 3 — TEM micrographs of (a) LDH-TA, (b) LDH-Mo_7O_{24} and (c) LDH-W_7O_{24}

SEM and TEM micrographs

The scanning electron micrographs for both parent sample and the exchanged ones displayed slightly flattened bead like particles with a diameter ranging between 5-20 μm (Fig. 2). Examination of these samples by TEM at high magnification revealed the layered structure of these materials. TEM micrographs indicated the existence of lamellar particles with rounded hexagonal shape, typical of hydrotalcite-like materials[30]. The TEM micrographs of LDH-TA, LDH-Mo_7O_{24} and LDH-W_7O_{24} have been shown in Fig. 3.

Catalytic oxidation of alkenes with H_2O_2

The catalytic behaviour of Mo- and W-containing LDHs has been explored in the mild oxidation of various alkenes at room temperature with green H_2O_2 as oxidant. The effect of different reaction parameters such as nature of the solvent, nature of the intercalated POM, amount of catalyst and substrate-oxidant concentration ratio have been studied to optimize the reaction conditions in order to achieve maximum yield in the epoxidation reaction.

Table 2 — Oxidation of cyclooctene with H_2O_2 in various solvent system[a]

Solvent	Epoxide yield (%)[b]			
	LDH-TA	LDH-Mo_7O_{24}	LDH-W_7O_{24}	$(NH_4)_6Mo_7O_{24}$
CH_3CN	0	46	33	2
CH_3CN/CH_2Cl_2 (1:1, *v*/*v*)	2	58	42	4
CH_2Cl_2	5	70	55	7

[a] Reaction condition: cyclooctene (200 mM), catalyst (50 mg), H_2O_2 (2 mM) in 2 mL solvent, 24 h

[b] Yields are reported with respect to the concentration of the oxidant

Reaction conditions

Nature of the interlayer anion

The $M_7O_{24}^{6-}$-intercalated LDHs (M = Mo or W) have been tested in the epoxidation of cyclooctene, chosen as model substrate. The results obtained using LDH-Mo_7O_{24}, LDH-W_7O_{24} and LDH-TA along with non-intercalated $Mo_7O_{24}^{6-}$ in three different reaction media are summarized in Table 2. The results obtained in the presence of pure POM salt, $(NH_4)_6Mo_7O_{24}$ were also included in this table.

As it can be seen from table, low conversion (2-5%) was obtained in the presence of the LDH sample (LDH-TA) which does not contain POM-species. On the other hand, the epoxide yield has been substantially increased when POM-intercalated LDHs were used as catalyst showing that the intercalated $Mo_7O_{24}^{6-}$ and $W_7O_{24}^{6-}$ have significant contribution in the oxidation reaction. It has also been found that the catalytic activity strongly depends on the nature of the interlayer anion. For the same amount of catalyst and reaction time, the conversion is substantially higher when molybdenum containing LDH material was used as catalyst (LDH-Mo_7O_{24}) than LDH-W_7O_{24}. The epoxidation was also carried out in the presence of $Mo_7O_{24}^{6-}$ (without intercalation) and very low product yield (2-7%) was obtained under similar reaction conditions.

Nature of the solvent

Solvent plays an important role in catalytic oxidation reaction in the presence of LDH-materials. The epoxidation reaction was carried out using some common organic solvents, such as acetonitrile (CH_3CN), dichloromethane (CH_2Cl_2) and mixture of acetonitrile and dichloromethane (1:1, *v*/*v*) with H_2O_2 as oxidant (Table 2). As it can be observed from Table 2, CH_2Cl_2 proves to be a very effective solvent for the cyclooctene epoxidation and the efficiency follows the order: $CH_2Cl_2 > CH_3CN/CH_2Cl_2$ (1:1, *v*/*v*) $> CH_3CN$ (Fig. 4).

Optimization of catalyst amount

The optimization of catalyst amount on the oxidation of cyclooctene has been undertaken using LDH-Mo_7O_{24} as catalyst, where the concentration of substrate (200 mM) and oxidant (2 mM) was kept constant. Five different amounts of catalyst (0.02 g, 0.03 g, 0.04 g, 0.05 g and 0.06 g) have been used and an amount of 0.05 g has been found to be most effective in terms of epoxide yield for the fixed amount of oxidant and substrate in various solvent systems (Fig. 5).

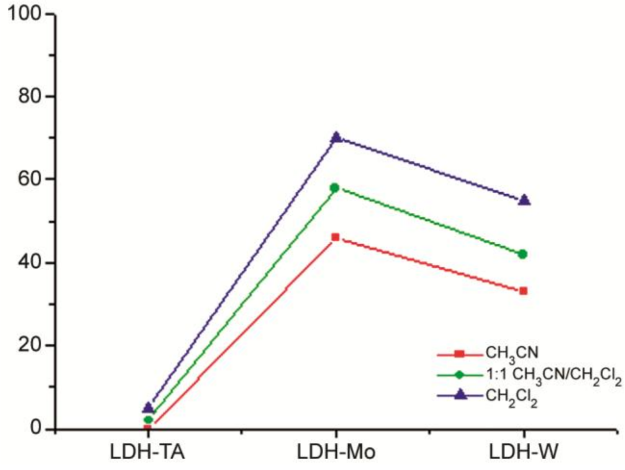


Fig. 4 — Effect of solvent on the epoxidation of cyclooctene with H_2O_2

Reaction time

The time course profiles of LDH-Mo_7O_{24} catalyzed epoxidation of cyclooctene with H_2O_2 in all the three solvents is given in Fig. 6. It has been found that the catalytic epoxidation was practically accomplished within 18 h in CH_2Cl_2 and within 24 h in both CH_3CN and 1:1 mixture of CH_3CN/CH_2Cl_2.

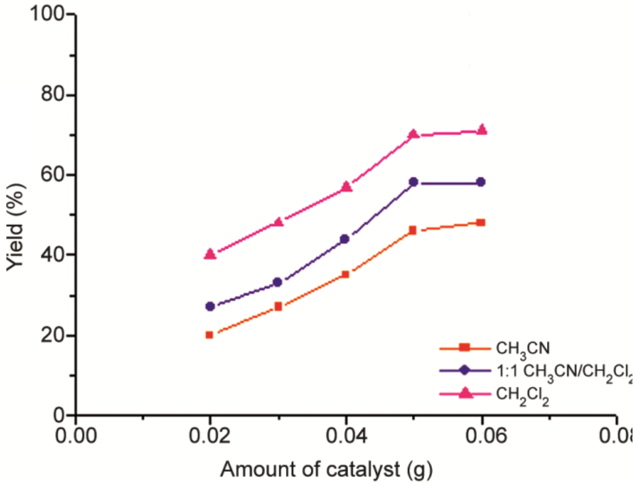


Fig. 5 — Optimization of catalyst amount

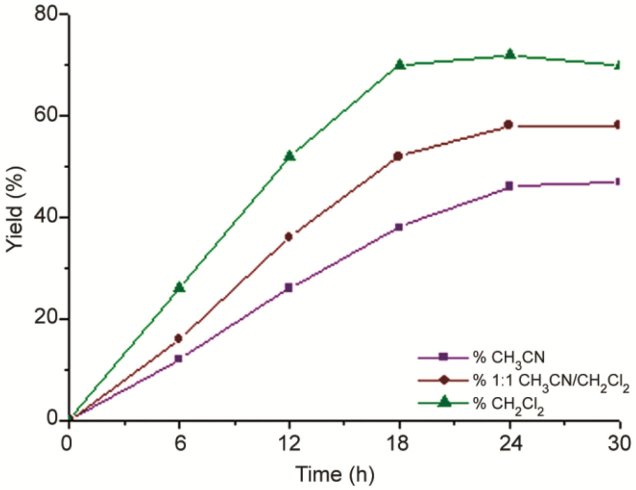


Fig. 6 — Optimization of reaction time

Optimization of substrate-oxidant ratio

To explore the optimum substrate-oxidant molar ratio, a first set of catalytic experiments was performed where the concentration of H_2O_2 was kept constant (2 mM) and the amount of substrate was varied, using the optimum amount of catalyst (0.05 g). Subsequently, a second set of catalytic experiments was run for varied amounts of H_2O_2, using the optimum amount of substrate found in the first screening. For this screening, epoxidation of cyclooctene was studied using LDH-Mo_7O_{24} as catalyst in a mixture of CH_3CN/CH_2Cl_2 (1:1, *v*/*v*). The results obtained are summarized in Fig. 7. Based on the data of Fig. 7, it has been revealed that 200 mM of cyclooctene is most effective in terms of epoxide yield with 2 mM of H_2O_2 concentration.

Oxidation of other alkenes

The catalytic performance of intercalated LDHs was further investigated for the oxidation of 1-octene, norbornene and dihydronaphthalene under argon atmosphere using the optimized reaction conditions. The results are summarized in Table 3.

The intercalated LDHs catalyze the epoxidation of non-activated terminal 1-octene at room temperature with H_2O_2 to afford 1,2-epoxy octane with the yield of 20-25%. The data summarized in Table 3 indicated no significant effect of the hydrotalcite composition or the solvent used in the epoxidation of 1-octene. For other alkenes, $Mo_7O_{24}^{6-}$ intercalated LDH exhibited better catalytic activity than $W_7O_{24}^{6-}$ intercalated LDH towards epoxidation. In case of epoxidation of dihydronaphthalene, overall yield of oxygenate reached to 37-65% by LDH-Mo_7O_{24} and 29-55% by LDH-W_7O_{24} with H_2O_2 in various solvent system used. The present catalytic system also catalyzes the oxidation of norbornene to its *exo*-epoxide with the product yield of 45-76% by LDH-Mo_7O_{24}; however, the conversion decreased to 35-63% when LDH-W_7O_{24} was used as catalyst. Like for cyclooctene, here also, CH_2Cl_2 as solvent led to the highest product yield. Thus, at room temperature, Mo-containing LDH exhibited better catalytic activity than W-containing LDH towards oxidation of alkenes at room temperature in presence of H_2O_2 as the terminal oxidant.

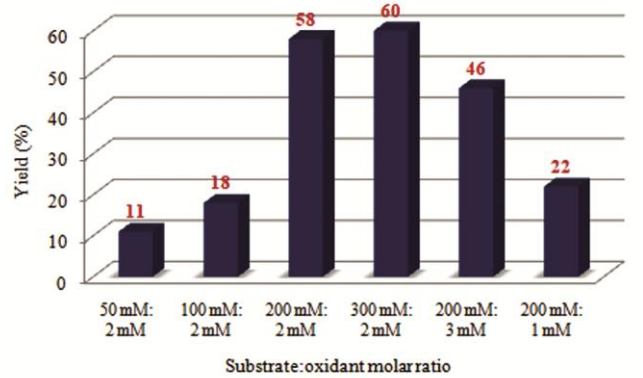


Fig. 7 — Optimization of substrate-oxidant ratio

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 4. It has been found that the use of the catalysts

Table 4 — Recycling of the catalyst in the epoxidation of cyclooctene with H_2O_2[a]

No. of catalytic cycle	Yield (%)[b]	
	LDH-Mo_7O_{24}	LDH-W_7O_{24}
1	70	55
2	68	55
3	67	53

[a]Reaction condition: cyclooctene (200 mM), catalyst (50 mg), H_2O_2 (2 mM) in 2 mL CH_2Cl_2,24 h

[b]Yields are reported with respect to the concentration of the oxidant

Table 3 — Oxidation of alkenes by H_2O_2 in different solvents[a]

Substrate	Epoxide yield (%)[b]					
	LDH-Mo_7O_{24}			LDH-W_7O_{24}		
	CH_3CN	CH_3CN/CH_2Cl_2 (1:1, *v*/*v*)	CH_2Cl_2	CH_3CN	CH_3CN/CH_2Cl_2 (1:1, *v*/*v*)	CH_2Cl_2
1-Octene	20	23	25	18	20	22
Dihydronaphthalene	37	53	65	29	43	55
Norbornene	45	64	76	35	47	63

[a]Reaction condition: Substrate (200 mM), catalyst (50 mg), H_2O_2 (2 mM) in 2 mL solvent, 24 h

[b]Yields are reported with respect to the concentration of the oxidant

in three consecutive reaction cycles did not lead to a significant loss of their activity. These results suggest that the $M_7O_{24}^{6-}$ containing LDH material is very stable under the catalytic reaction conditions.

Conclusions

LDHs with Mo- and W-containing polyoxometalate anions in the interlayer have been prepared by direct anion exchange of LDH-TA precursor. The structural and textural properties of solids and the nature of the metal species have been investigated by different physico-chemical studies. The intercalated LDHs exhibited good catalytic activity in the mild and selective oxidation of various alkenes with green oxidizing agent, H_2O_2 as oxidant under very mild conditions. However, the catalytic performances strongly depended on the nature of the anionic species in the interlayer gallery, the Mo-LDH sample being more active than the W-LDH sample. Remarkable improvement in product yield has been observed in dichloromethane as reaction medium. The catalysts were easily recovered and reused for three successive cycles without significant loss of catalytic activity.

Supplementary Data

Supplementary data associated with this article are available in the electronic form at http://nopr.niscair.res.in/jinfo/ijca/IJCA_60A(05)656-662_SupplData.pdf.

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