

Organotin-oxometalate coordination polymer catalyzed oxyfunctionalization of monoterpenes

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Abstract

The organotin-oxometalate coordination polymers $[(n\text{Bu}_3\text{Sn})_2\text{MO}_4] \cdot n\text{H}_2\text{O}$ (where, M = Mo or W) were prepared by the interaction of $n\text{Bu}_3\text{SnCl}$ with sodium salts of molybdate or tungstate and tested in oxyfunctionalization of monoterpenes with urea hydroperoxide (UHP) as an oxidizing agent. The oxyfunctionalization of monoterpenes gave commercially important products such as epoxides, ketones and hydroxyl derivatives. Among the two catalyst, organotin-oxomolybdate $[(n\text{Bu}_3\text{Sn})_2\text{MoO}_4]$ showed higher activities and epoxide selectivities under selected liquid phase oxyfunctionalization conditions with most of the monoterpenes such as limonene, α -pinene, β -pinene, carene, camphene, gerniol and linalool. The integrity of the organotin-oxometalates polymers were confirmed by X-ray diffraction BET surface area, FT-IR, FT-Raman, SEM, TG/DTA and MAS NMR (^{13}C , ^{119}Sn) analysis. The effects of reaction parameters on limonene conversions and product selectivities have been studied in detail using $[(n\text{Bu}_3\text{Sn})_2\text{MoO}_4]$ catalyst. There was no leaching of the active catalyst into the reaction medium and catalyst was recyclable without loss in its activity in the oxidation reaction.

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1. Introduction

Selective oxyfunctionalization of monoterpenes is an interesting route to utilize these inexpensive natural products for number of applications. Limonene, a monoterpene is the major component of citrus oil and is obtained easily from the citrus fruit peel waste. Limonene epoxide is a key raw material for a wide variety of applications, such as pharmaceutical, flavor and perfumery industry as well as useful synthetic intermediates, food additives and chiral building blocks. Limonene oxyfunctionalisation could be done either by epoxidation or by allylic oxidation reactions. Epoxidation is carried out with peracid (RCO_3H) route wherein stoichiometric amount of catalyst is consumed and this process is becoming unacceptable because of the non-selective formation of mono- and di-epoxides monoterpenes as well as cleaved products of these [1,2]. Allylic oxidation takes place usually via a free radical chain reaction pathway and occurs

when the intermediate metallic species are in a low oxidation states [3,4].

During the past few years, catalysts such as $\text{PdCl}_2/\text{CuCl}_2/\text{O}_2$ and $\text{Pd}(\text{OAc})_2/\text{H}_2\text{O}_2$ systems have been used for efficient and selective oxidation of limonene [5–10]. Drawbacks of the above homogeneous catalysts systems are the corrosive natures of copper and palladium chloride salts and the contamination of the reaction products with the catalyst and the formation of undesired organochlorine compounds [11]. Heteropoly acids [12] and transition metal substituted heteropoly acids [13] have been used with and without support for the oxidation of monoterpenes. Synthetic metalloporphyrins [14] and transition metal Schiff base complexes of various metals (Co, Mn, etc.) have also been used for the oxidation of monoterpenes. However, separation of the catalysts is usually troublesome and not economical for applications. Numerous attempts have been made to immobilize metal Schiff base complexes by anchoring onto polymeric matrix [15]. Encapsulation [16–18], entrapment [19] and anchoring of metal bases onto porous inorganic supports [20–23] have also been reported for the oxidation of monoterpenes. Ti incorporation inside the framework of the hexagonal

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mesoporous silica MCM-41 was successfully carried out by many researchers [24,25]. It was found that Ti ions leached out from the MCM-41 when the catalyst was used with hydrogen peroxide as an oxidant [26–28].

Recently, Abrantes et al. [29] reported that organotin-oxometalate coordination polymers formulated as $[(n\text{Bu}_3\text{Sn})_2\text{MO}_4]$ (M=Mo or W) exhibited good catalytic activities and product selectivities in the oxyfunctionalisation of olefins. Hence, these catalyst systems are interesting for the oxidation of monoterpenes. The purpose of our study is to investigate the performance of the organotin-oxometalate coordination polymer catalyst systems in the liquid phase oxidation of monoterpenes and to optimize reaction conditions for higher substrate conversions and desired epoxide selectivities. Therefore, we are presenting in this paper our results on the oxyfunctionalization of monoterpenes catalyzed by organotin-oxometalate coordination polymers using UHP as an oxidant.

2. Experimental

2.1. Materials

$\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, H_2O_2 (30%), $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ and $n\text{Bu}_3\text{SnCl}$ were procured from Merck India, Ltd., Mumbai. Limonene, α -pinene, β -pinene, 3-carene, camphene, geraniol and linalool were obtained from Aldrich. *tert*-Butyl hydrogen peroxide was purchased from Acros. Urea hydrogen peroxide (UHP) was freshly prepared in the laboratory following a standard procedure [30]. Solvents procured from Ranbaxy, were dried by standard methods, distilled under nitrogen and stored over molecular sieves prior to their use in the oxyfunctionalization reactions.

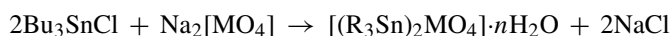
2.2. Catalyst preparation

2.2.1. $[(n\text{Bu}_3\text{Sn})_2\text{MoO}_4]$

$n\text{Bu}_3\text{SnCl}$ (3.25 g, 10 mmol) was dissolved in a mixture of water (6 ml) and acetone (27 ml). A saturated aqueous solution of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (1.21 g, 5 mmol in 8 ml H_2O) was added drop wise with magnetic stirring to $n\text{Bu}_3\text{SnCl}$ solution. A white precipitate was formed immediately and stirring was continued for 5 min. The precipitate was filtered, washed thoroughly with water, and dried in air at 100°C for 6 h to give 90% yield of $(n\text{Bu}_3\text{Sn})_2\text{MoO}_4$. Calculated for $\text{C}_{24}\text{H}_{54}\text{O}_4\text{Sn}_2\text{Mo}$ (740.1): C 38.9%, H 7.3%. Analytically found: C 38.7%, H 7.2% [29].

2.2.2. $[(n\text{Bu}_3\text{Sn})_2\text{WO}_4]$

This material was prepared as described above using $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ instead of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$. Calculated for $\text{C}_{24}\text{H}_{54}\text{O}_4\text{Sn}_2\text{W}$ (827.81): C 34.8%, H 6.6%. Analytically found: C 34.7%, H 6.5% The general reaction for the preparation of organotin-oxometalate coordination polymer is as shown below:



where M = Mo/or W, Bu = butyl group-organic moiety.

Elemental analysis of the above materials confirmed that these are as per the stoichiometric composition of the coordination polymers $[(n\text{Bu}_3\text{Sn})_2\text{MoO}_4]$ and $[(n\text{Bu}_3\text{Sn})_2\text{WO}_4]$, respectively.

2.3. Characterization

Elemental analysis has been done for Carbon and Hydrogen in Carlo Erba (Model EA1108) elemental analyzer. X-ray diffraction (XRD) measurements of the catalysts powders were recorded using a Rigaku Geigerflex diffractometer equipped with Ni filtered $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The specific surface areas of the catalysts were measured by N_2 sorption at liquid nitrogen temperature using a Quantachrome Nova-1200 surface area analyzer and standard multiunit BET analysis methods. Samples were degassed in N_2 flow for 12 h at 100°C before N_2 sorption measurements. The FTIR spectra of the samples were recorded on a Shimadzu (Model-820 PC) spectrophotometer under DRIFT (diffuse reflectance infrared Fourier transform) mode. Raman spectra of the catalyst were recorded on powder samples at room temperature with a Bruker IFS 66 spectrometer connected to a Raman module FRA 106. The $1.06 \mu\text{m}$ line of the NdYAG laser was used for excitation, and the spectral resolution was 3 cm^{-1} . The NMR spectra of ^1H , ^{119}Sn , and ^{13}C were recorded on a Bruker DSX-300 spectrometer operating at 111.82 MHz for ^{119}Sn , and 75.43 MHz for ^{13}C . The references are neat SnMe_4 (^{119}Sn) and TMS (^{13}C). ^{31}P and ^{119}Sn NMR spectra were recorded by using a single pulse with proton decoupling during acquisition, the ^{13}C spectra were obtained by using cross-polarization from protons (contact time 5 ms). The delay between two consecutive scans was typically 1–5 s for ^{13}C and ^{119}Sn . The spinning rate was ca. 10 kHz, the samples being placed in a 4 mm zirconia rotor. Differential thermal analysis (DTA) measurements were performed on a Pyris Diamond TG-DTA apparatus from room temperature to 1000°C in flowing dry oxygen (ca. 50 ml min^{-1}), using $\alpha\text{-Al}_2\text{O}_3$ as a reference. For each experiment, 5–8 mg of the sample was used, with a heating rate of $20^\circ\text{C min}^{-1}$. JEOL-JSM-5200 SEM determined the morphology of the catalytic material with a resolution of 5.5 nm. Thin layer chromatography (TLC) was carried out on silica gel plates (Merck silica gel 60 F254). Column chromatography was also performed on silica gel (Merck silica gel 60–120 mesh).

2.4. Catalytic activity measurements

The oxyfunctionalization of monoterpenes for example limonene was conducted in air atmosphere. In a typical experiment, reaction mixture containing a known amounts of limonene (0.68 g), urea hydrogen peroxide, UHP (0.98 g) and acetonitrile (10 ml) and 3 wt.% of catalyst (co-ordination polymers) is placed in the round bottom flask (batch reactor) fitted with reflux condenser, equipped with a magnetic stirrer and immersed in a thermostatic oil bath for maintaining the desired reaction temperature. The reactions was conducted at the desired temperature and the progress of the reaction was monitored by withdrawing reaction mixture samples periodically, cen-

trifuged and analyzed for their compositions by Shimadzu 14B gas chromatograph, equipped with a flame ionization detector using HP-5 capillary column (cross linked 5% ME silicone, 30 m × 0.53 μm × 1.5 μm film thickness). The identity of the products was confirmed by GC–MS (Shimadzu GCMS QP 5000) and ¹H NMR. Conversion is defined as the percentage of oxyfunctionalization of monoterpenes into products and the selectivity to individual product is accounted for total 100%.

3. Results and discussion

3.1. Characterization

3.1.1. XRD

Powder XRD patterns of [(nBu₃Sn)₂MoO₄], and [(nBu₃Sn)₂WO₄] are depicted in Fig. 1. The good crystallinity of [(nBu₃Sn)₂MoO₄], and [(nBu₃Sn)₂WO₄] can be seen by their XRD patterns. The XRD patterns of [(nBu₃Sn)₂MoO₄], and [(nBu₃Sn)₂WO₄] have shown characteristic peaks of MoO₄ and WO₄ of the materials at the range of 2θ, 22 and 28, which are similar to the one reported in literature [29]. The average crystallite size is estimated from the full width at half maximum of the diffraction peak by the following Scherrer equation:

$$D_{hkl} = \frac{k\lambda}{\beta(2\theta)\cos\theta}$$

where β(2θ) is the width of the pure diffraction profile in radians, k the constant, 0.89, λ the wavelength of the X-rays (0.154056 nm), θ the diffraction angle, and D_{hkl} is the crystallite diameter in the [h k l] direction. By fitting various peaks to the above formula and taking into account the instrumental broadening, the average crystallite size were found to be 200 nm.

3.1.2. N₂ sorption study

The textural characteristics such as BET surface area, pore size distribution and pore volume of the catalyst powders are

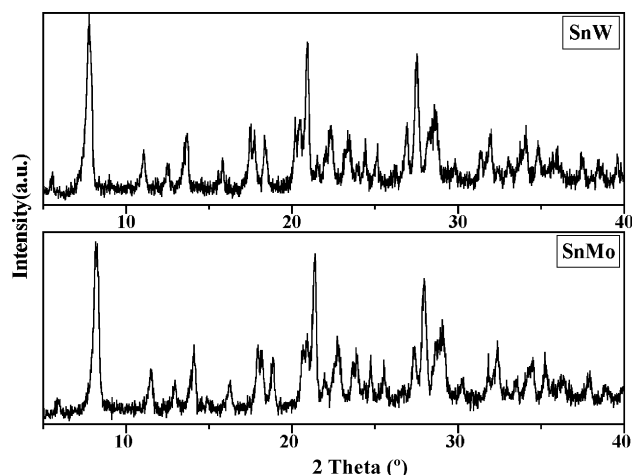


Fig. 1. Powder XRD patterns of (SnMo)=[(nBu₃Sn)₂MoO₄] and (SnW)=[(nBu₃Sn)₂WO₄].

Table 1
Physicochemical properties of different catalysts

Compound	Surface area (m ² /g)	Pore volume (cm ³ /g)	BJH average mesopore diameter (nm)
[(nBu ₃ Sn) ₂ MoO ₄]	20	0.013	2.57
[(nBu ₃ Sn) ₂ WO ₄]	19.4	0.012	2.46

summarized in Table 1. It is found that the surface area and pore volume of the materials are quite low.

3.1.3. FT-IR and FT-Raman

FT-IR spectra and FT-Raman spectra of [(nBu₃Sn)₂MoO₄], and [(nBu₃Sn)₂WO₄] are given in supplementary information. The [MoO₄]²⁻ and [WO₄]²⁻ units of catalyst [(nBu₃Sn)₂MoO₄] and [(nBu₃Sn)₂WO₄] give characteristic bands at 815 cm⁻¹. Broad bands observed in the range 2845–2975 cm⁻¹ are due to ν(CC) and ν(CH) stretching of the catalysts. The other characteristic bands observed for [(nBu₃Sn)₂MoO₄] and [(nBu₃Sn)₂WO₄] catalyst are 1459 cm⁻¹ (s), 1376 cm⁻¹ (s), 1151 cm⁻¹ (w), 1068 cm⁻¹ (w), 963 cm⁻¹ (w), 723 cm⁻¹ (w), 663 cm⁻¹ (w) and 1460 cm⁻¹ (s), 1337 cm⁻¹ (s), 1307, 1149 cm⁻¹ (w), 1083 cm⁻¹ (w), 968 cm⁻¹ (w), 720 cm⁻¹ (w), 670 cm⁻¹ (w), respectively, which are due to various organic and metal organic functionalities present in the coordinated polymers.

Since [MO₄]²⁻ unit [M = W or Mo] of the catalyst systems are in T_d symmetry, according to the mutual exclusion rule, the IR forbidden but Raman active vibrational bands of these two units of [MoO₄]²⁻ and [WO₄]²⁻ of the catalysts are observed at 309, 860, 924 and 312, 862 and 962 cm⁻¹, respectively. Raman shift observed at 513 cm⁻¹ in both the catalyst systems is due to the ν(SnC) stretching [31].

3.1.4. ¹¹⁹Sn and ¹³C MAS NMR

¹¹⁹Sn and ¹³C MAS NMR of [(nBu₃Sn)₂MoO₄], are given in supplementary information. ¹¹⁹Sn MAS NMR spectra of [(Bu₃Sn)₂MoO₄] shows a tetrameric structure in which each Sn atom has trigonal bipyramidal coordination geometry [32]. The material [(Bu₃Sn)₂MoO₄] gives rise a complicated ¹³C CP MAS NMR spectra at room temperature. Four main signals are observed for the four-methyl groups, two peaks each for the beta and gamma carbons, however, for alpha carbon; the signal is clearly the sum of two components. The two small broad signals at ca. 24 and 17 ppm are probably related to the coupling between ¹³C and ¹¹⁷Sn.

3.1.5. TG/DTA

Thermo gravimetric and differential thermal analysis of [(nBu₃Sn)₂MoO₄] and [(nBu₃Sn)₂WO₄] are given in supplementary information. The endothermic peaks around 240 and 269 °C, respectively, for [(nBu₃Sn)₂WO₄] and [(nBu₃Sn)₂MoO₄] in the DTA curve indicates the decomposition of the coordination polymers. The loss in weight (50% of the total weight) in the temperature range 269–309 °C for both the catalyst indicates the complete decomposition of the compounds (losing organic moiety).

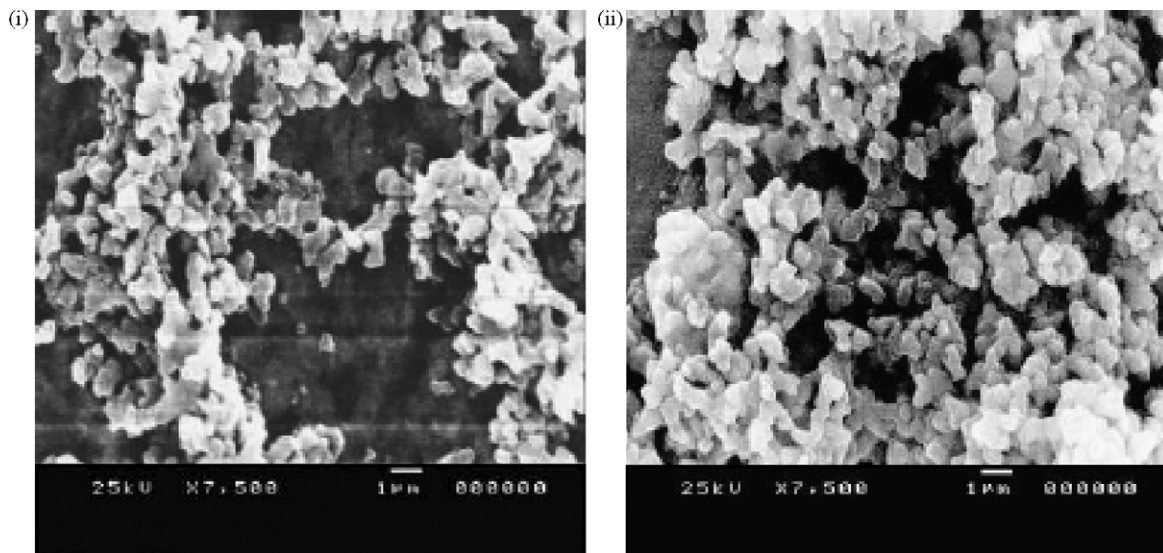


Fig. 2. SEM photographs of (i) $[(n\text{Bu}_3\text{Sn})_2\text{WO}_4]$ and (ii) $[(n\text{Bu}_3\text{Sn})_2\text{MoO}_4]$.

3.1.6. SEM

The SEM photographs of $[(n\text{Bu}_3\text{Sn})_2\text{MoO}_4]$ and $[(n\text{Bu}_3\text{Sn})_2\text{WO}_4]$ are shown in Fig. 2(i) and (ii). The typical average particle size estimated by SEM for the both the catalysts is around 500 nm.

3.2. Catalytic activity

Oxidation of limonene by UHP gave limoneneoxide (epoxide), carvone, carveol and carvacrol is shown in Scheme 1. The catalytic activities of $[(n\text{Bu}_3\text{Sn})_2\text{MoO}_4]$ and $[(n\text{Bu}_3\text{Sn})_2\text{WO}_4]$ are expressed in terms of limonene conversion (Fig. 7). It is found that under selected reaction conditions, the catalyst $[(n\text{Bu}_3\text{Sn})_2\text{MoO}_4]$ showed slightly higher activity (54% limonene conversion) than $[(n\text{Bu}_3\text{Sn})_2\text{WO}_4]$ (49% limonene conversion). This could be due to difference in acidity of the materials or the difference between decomposition rate of the oxidant. The reason for higher activity of $[(n\text{Bu}_3\text{Sn})_2\text{MoO}_4]$ is concomitant with the earlier reports [29,33].

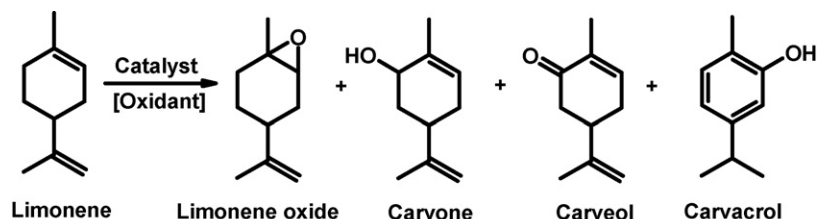
3.2.1. Spectral characteristics of the oxidation products of limonene

The products of oxidation of limonene by UHP are separated by column chromatography by following a standard procedure and analyzed by ^1H NMR. The details of the spectral characteristics of the limonene oxidation products are given below:

Limoneneoxide: 1.11 (3H, s), 1.24–1.59 (6H, m), 1.61 (3H, s), 2.11 (1H, m), 2.68 (1H, t), 4.57 (2H, s); *Carveol*: 1.51 (6H, s), 1.54–2.13 (5H, m), 3.59 (1H, m), 4.04 (1H, s), 4.53 (1H, s), 4.78 (1H, s), 5.27 (1H, m); *Carvone*: 1.51–1.7 (8, m), 1.49 (3H, s), 1.72 (3H, s), 1.9–3 (5H, m), 2.43 (1H, m), 4.49 (1H, s), (1H, s), 4.69 (1H, s), 6.15 (1H, m) and *Carvacrol*: 1.18 (6H, s), 2.15 (3H, s), 3.02 (1H, s), 6.39 (1H, s), 6.59 (2H, m), 9.53 (1H, s).

3.2.2. The performance of $[(n\text{Bu}_3\text{Sn})_2\text{MoO}_4]$ catalyst in the oxidation of monoterpenes

In order to delineate the scope and limitations of the catalyst system, based on their performances in limonene oxidation, the best catalyst is used for the oxidation of different monoterpenes to know its catalytic performance and products selectivities. Monoterpenes, like limonene, α -pinene, β -pinene, carene, camphene and germiol have been considered to evaluate the catalytic activity of $[(n\text{Bu}_3\text{Sn})_2\text{MoO}_4]$ under selected reaction conditions with UHP as an oxidant. UHP has been employed as an oxidant for limonene oxidation with an aim of controlled release of H_2O_2 into the solution, to get better activity and desired epoxide selectivity in the oxidation. Gradual increase in conversion with UHP is due to the slow release of H_2O_2 during the reaction in a controlled manner, which allows the formation of the epoxide more selectively. The data on the activities (conversion of substrates), product selectivities along with the reaction conditions used for the above study are presented in Table 2.



Scheme 1.

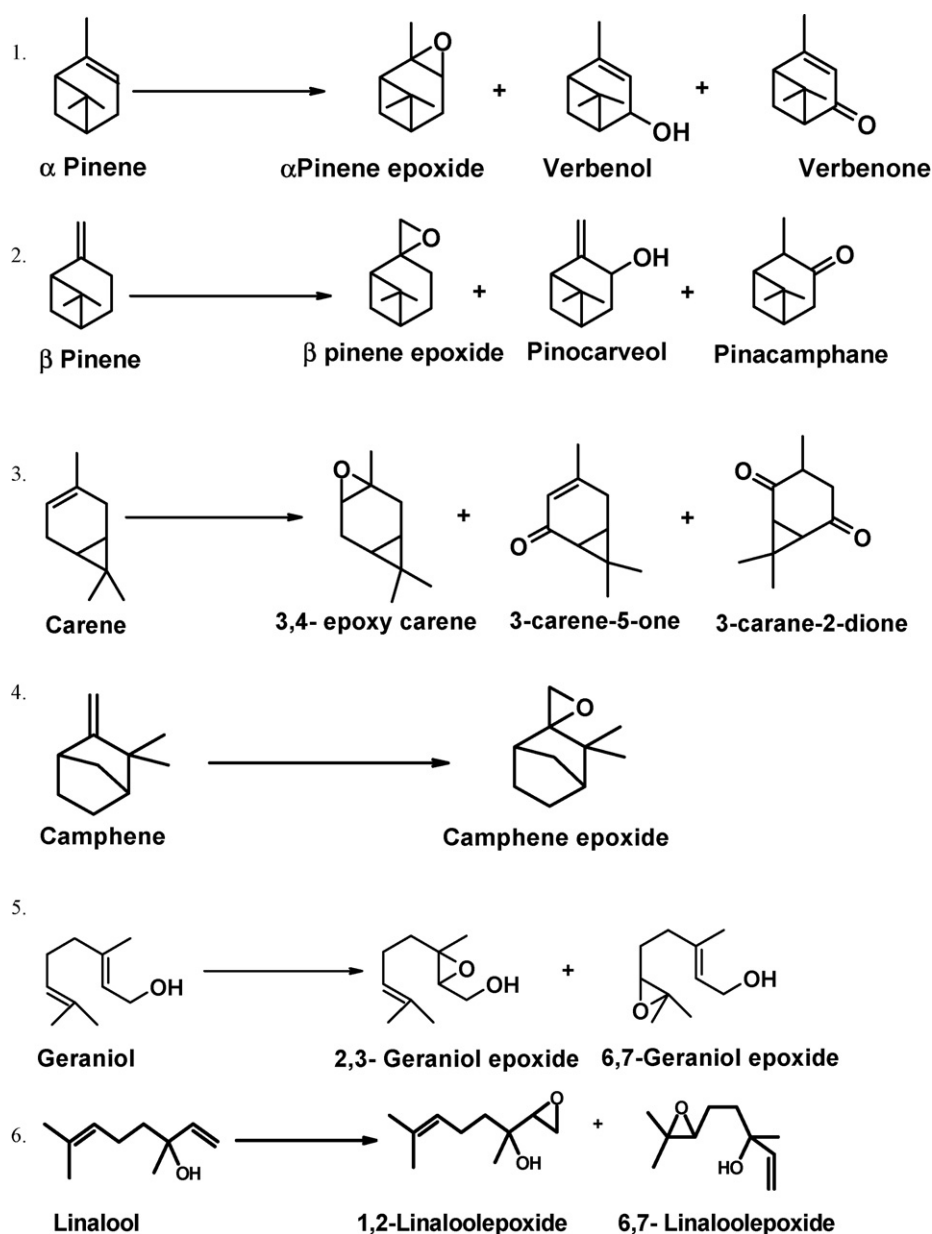
Table 2
Activity of $[(n\text{Bu}_3\text{Sn})_2\text{MoO}_4]$ in oxyfunctionalisation of monoterpenes

Mono-terpenes	Conversion (mol%)	Product selectivity (mol %)			
Limonene	54	Epoxide (76)	Carvone (7)	Carveol (3)	Carvacrol (3) and n.a. (2)
α -Pinene	66	Epoxide (60)	Verbenol (19)	Verbenol (13)	n.a. (8)
β -Pinene	40	Epoxide (70)	Pinacamphone (11)	Pinocarveol (9)	n.a. (10)
Carene	60	Epoxide (40)	3-carene-5-one (27)	3-carene-2-dione (22)	n.a. (11)
Camphene	20	Epoxide (70)	–	–	n.a. (30)
Gerniol	100	2,3-Epoxide (60)	6,7-Epoxide (24)	–	n.a. (16)
Linalool	70	1,2-Epoxide (67)	6,7-Epoxide (24)	–	n.a. (9)

Conditions: temperature, 50 °C; solvent acetonitrile, 10 ml; time, 10 h; substrate:UHP molar ratio, 1:2; catalyst weight, 0.030 g; n.a., not analysed.

The differences in the conversions of substrates has been considered as the measure of the efficiency of the catalyst $[(n\text{Bu}_3\text{Sn})_2\text{MoO}_4]$ under identical conditions. It is seen from the results (Table 2) that the activity (conversion of substrate) is

dependent on the nature of monoterpenes and the position of the olefinic bond and its ability to hold to metal centre in a metal-oxo mediated oxyfunctionalization of terpenes (Scheme 2, mechanism) and allowing oxygen transfer before reductive elimination



Scheme 2.

forming corresponding oxygenated products, while regenerating the active catalyst in a catalytic cycle.

The oxidation of α -pinene produces α -pinene epoxide, verbenol and verbenone (used as a building block of taxol) as shown in Scheme 2. At α -pinene conversion 66%, the selectivity towards α -pinene epoxide is 60% and the selectivity for other products verbenol (19%) and verbenone (13%), camphene, campholenic aldehyde and low molecular weight oligo/polymerization products are also formed in the reaction (8% not analyzed). Similarly, β -pinene gave β -pinene epoxide, pinocamphone and pinocarveol (Scheme 2) as its products. Some unidentified products were also obtained in the oxidation β -pinene, which are myrtemal, pinocarvone, etc. At β -pinene conversion, 40%, the highest selectivity is for its epoxide β -pinene epoxide (70%), pinocamphone (11%), pinocarveol (9%) and the remaining others.

The main product of oxidation of 3-carene is 3,4-epoxycarene and minor products are 3-carene-5-one and 3-carene-2,5-dione (Scheme 2). At 60% carene conversion, the product selectivities are 3,4-epoxycarene (40%), 3-carene-5-one (27%) and 3-carene-2,5-dione (22%) and the remaining others. Geranial shows an interesting properties, as it has two double bonds: one in allylic position with respect to the –OH group, while the other (6–7 double bond) is isolated. It is found that in oxidation of Geraniol, the catalyst is very active and gave 99% geraniol conversion. In principle, two different epoxidation products can be observed, but with the present catalyst system, only 2,3-epoxide is predominantly formed (Scheme 2). Oxyfunctionalisation of camphene is shown in Scheme 2 and it gives very low conversion (20%) and with a high selectivity for camphene epoxide (70%). Oxidation of linalool (Scheme 2) which contains two double bonds and hydroxy group gives rise to the predominant formation of the 1,2-epoxide (67%) whereas 6,7-isomer is formed in much lower concentration

Since, α -pinene molecule is rigid in structure in which the four-membered ring is puckered and five carbons of the six-membered ring are approximately in the same plane but β -pinene prefers a pseudo-chair conformation. Due to which a strong preference exhibited by α -pinene compared to β -pinene for oxidation. The carene conversion increases with the amount of UHP added but this was accompanied by a decrease in selectivity for the epoxide. The bicyclic monoterpene, camphene has an exocyclic disubstituted double bond, like β -pinene, but the only allylic hydrogen is at a bridgehead position and not easily abstractable. Therefore, we are unable to get the allylic derivatives. As for geraniol, the epoxidation is preferentially occurs at the 2,3 double bond, which has lower HOMO coefficients than 6,7 double bond, affording 6,7-epoxygeraniol as the major products. The result shows that no allylic assisted epoxidation of linalool occurs under our reaction conditions. This may be due to the steric situation around the hydroxyl group.

3.2.2.1. ^1H NMR of oxidation products. α -Pinene epoxide: ^1H NMR (CDCl_3), δ (ppm): 0.91 (6H, s), 1.19–1.58 (9H, m), 1.34–1.94 (6H, m), 2.61 (1H, m). Verbenol: ^1H NMR (CDCl_3), δ (ppm): 0.91 (6H, s), 1.59 (6H, s), 1.50 (3H, s), 1.61–2.47 (8H, m), 1.26 (1H, s), 3 (1H, m) 4.08 (1H, m), 4.62 (1H, m). Ver-

benone: ^1H NMR (CDCl_3), δ (ppm): 0.91 (6H, s), 1.61 (3H, s), 1.9–2.14 (2H, m), 2.61–2.69 (2H, m), 5.4 (1H, m).

β -Pinene epoxide: ^1H NMR (CDCl_3), δ (ppm): 0.91 (6H, s), 1.21–1.71 (8H, m), 2.24–2.49 (2H, m). Pinocarveol: ^1H NMR (CDCl_3), δ (ppm): 0.91 (6H, s), 1.31–2.67 (6H, m), 3.8 (1H, m), 4.02 (1H, m), 4.96 (2H, m). Pinocamphone: ^1H NMR (CDCl_3), δ (ppm): 0.91 (6H, s), 1.1 (3H, m), 1.61–2.29 (7H, m), 2.51–3.05 (3H, m).

3,4-Epoxycarene: 0.9 (6H, s), 1.21 (3H, s), 1.27–1.56 (8H, m), 2.68 (1H, m). 3-Carene-5-one: ^1H NMR (CDCl_3), δ (ppm): 0.9 (6H, s), 1.59 (3H, m), 0.4–0.8 (2H, m), 1.68–2.3 (2H, m), 5.85 (1H, s). 3-Carene-2-dione: ^1H NMR (CDCl_3), δ (ppm): 0.9 (6H, s), 1.1 (3H, s), 1.21 (2H, s), 2.37–2.75 (3H, m).

Camphene epoxide: ^1H NMR (CDCl_3), δ (ppm): ^1H NMR (CDCl_3), δ (ppm): 0.91 (6H, s), 1.19–1.69 (8H, m), 2.29–2.56 (2H, m).

2,3-Geranial epoxide: ^1H NMR (CDCl_3), δ (ppm): 0.81 (6H, s), 1.19–1.32 (9H, m), 1.73 (1H, m), 2.52 (1H, m), 3.2–3.69 (2H, m), 4.62 (1H, s). 6,7-Geraniol epoxide: ^1H NMR (CDCl_3), δ (ppm): 0.96 (3H, m), 1.13 (6H, m), 1.46–1.96 (9H, m), 2.41 (2H, s), 4.9 (1H, s).

1,2-Linalool epoxide: ^1H NMR (CDCl_3), δ (ppm): 1.01 (6H, s), 1.11 (3H, s), 1.21–1.83 (4H, m), 4.38–5.1 (2H, m). 6,7-Linalool epoxide: ^1H NMR (CDCl_3), δ (ppm): 1.26 (6H, s), 1.41–1.45 (7H, m), 2 (1H, s), 2.51 (1H, m), 5.23–5.89 (3H, m).

We further studied $[(n\text{Bu}_3\text{Sn})_2\text{MoO}_4]$ catalyzed oxyfunctionalization of limonene using UHP as an oxidant and acetonitrile solvent to know the effects of reaction parameters. The discussion is continued in further text.

3.2.3. Effect of reaction parameters

The effects of reaction parameters such as mole ratio of limonene:UHP, catalyst concentration, substrate and time on stream data concentration on the limonene conversions and epoxide selectivities were collected. The data along with the reaction conditions are listed in Table 3. It is generally found that the limonene conversion increased with increase in the concentrations of the parameters. The maximum limonene conversion of (39 mol%) was obtained at 50 °C, acetonitrile (10 ml), cat. wt. (0.030 g) and limonene:UHP mole ratio (1:2) to give highest epoxide selectivity (90 mol%) in 2 h (Table 3). However, in some cases epoxide selectivity is affected as seen from the results presented in Table 3. Conversion of limonene as a function of time is depicted in Fig. 3.

3.2.4. Catalyst recycling and leaching studies

In order to study the recyclability of the catalyst, the reaction was studied at 50 °C with 3 wt.% catalyst using UHP/limonene molar ratio 2. After 2 h, the limonene conversion is found to be 38%. Then catalyst is separated by filtration and is washed with dichloromethane and dried at 50 °C for 5 h and used again with fresh reaction mixture. The conversion of limonene after 2 h in a second cycle was almost the same as that of the first cycle. Few more cycles repeated and it was found that the conversions of limonene and product selectivities are not changed much and

Table 3
Effect of reaction parameters on limonene conversion and epoxide selectivity

Parameter	Conversion (mol%)	^a Products selectivities (mol%), oxide and (^d others)
(A) Effect of mole ratio of limonene:UHP ^b		
1:1	16	94 (6)
1:2	39	90 (10)
1:3	42	80 (20)
(B) Effect of catalyst weight (wt.% of total wt. of reaction mixture) ^c		
0.01	25	90 (10)
0.03	39	90 (10)
0.05	46	78 (22)
(C) Effect of substrate (limonene) concentration (M) ^d		
0.0025	22	90 (10)
0.0045	39	90 (10)
0.0100	42	80 (20)

^a Other products include carvone, carveol and carvacrol, which are identified by GC–MS and ¹H NMR and are present in the range 5–8% of the product mixture.

^b Conditions: temperature, 50 °C; time, 2 h; acetonitrile, 10 ml; Cat. Wt., 0.030 g.

^c Conditions: temperature, 50 °C; time, 2 h; acetonitrile, 10 ml; limonene,UHP mole ratio, 1:2.

^d Conditions: temperature, 50 °C; time, 2 h; acetonitrile, 10 ml; Cat. Wt., 0.030 g.

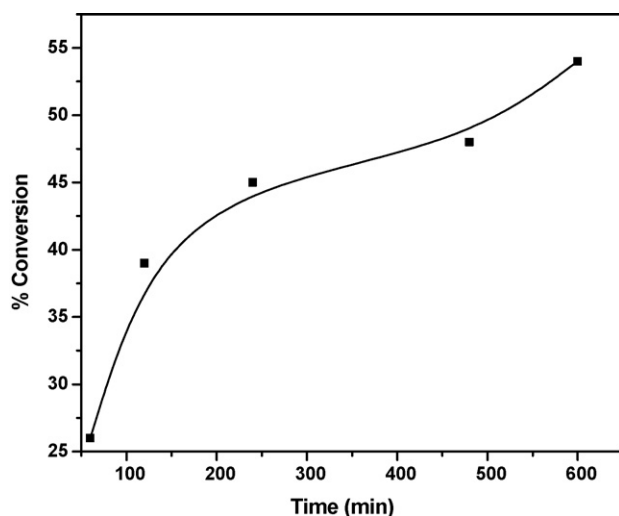


Fig. 3. Conversion of limonene as a function of time (conditions: temperature, 50 °C, acetonitrile, 10 ml; limonene:UHP mole ratio, 1:2; Cat. Wt., 0.03 g).

hence confirmed the recyclability of the catalyst in oxidation reaction. Catalyst leaching was studied by following the standard procedure, which did not show the presence of leached catalyst in the reaction mixture after several hours of its use and the catalyst system is truly heterogeneous.

4. Conclusions

Coordination polymers $[(n\text{Bu}_3\text{Sn})_2\text{MO}_4]$ ($M = \text{Mo}, \text{W}$) are used as a catalyst for the oxidation of monoterpenes. The interesting feature of these catalysts is their heterogeneity and selectivity. The molybdenum containing catalyst showed good

activity in terpene oxidation. $[(n\text{Bu}_3\text{Sn})_2\text{MoO}_4]$ is very active and chemo-selective catalyst system and could be used for further applications in oxidation reactions.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2007.02.004.

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