



Selective oxidation of limonene over sodium salt of cobalt containing sandwich-type polyoxotungstate

$$[\text{WCo}_3(\text{H}_2\text{O})_2\{\text{W}_9\text{CoO}_{34}\}_2]^{10-}$$

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Abstract

A sandwich-type polyoxotungstate, $\text{Na}_{10}[\text{Co}_5\text{W}_{19}\text{O}_{70}\text{H}_4]\cdot 44\text{H}_2\text{O}$, was synthesized as the sodium salt from an aqueous solution containing sodium tungstate and cobalt nitrate in acidic medium by known methods. This was characterized by atomic absorption spectroscopy, IR, UV-Vis spectroscopy and thermogravimetric analysis (TG) and single crystal X-ray analysis and used as a heterogeneous catalyst for the oxidation of limonene using air or aqueous hydrogen peroxide as oxidants to form the epoxide, carveol and carvone. With either oxidant, one of the olefinic bonds of limonene is selectively oxidized to give the epoxide as the primary product. With H_2O_2 , the efficiency was poor leading to lower conversion of limonene. The polyoxotungstate is able to activate molecular oxygen at 80–120 °C, under 1.5 MPa pressure and oxidize limonene selectively.

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1. Introduction

Liquid-phase oxidation reactions of hydrocarbons utilizing molecular oxygen is an important area of research. Since dioxygen has a triple ground state, direct oxidation of organic compounds is not possible [1]. In most of the cases, while one atom of oxygen from molecular oxygen oxidizes a substrate, the other oxygen atom gets reduced to water. The types of metal complexes that are found to show this type of dioxygenase activity include compounds such as metalloporphyrins, enzymes, sandwich-type

polyoxometalates, and others. In many cases, metalloporphyrins and other metal coordinated Schiff base complexes often show high initial activity and selectivity but undergo irreversible deactivation of the catalytic species by self-oxidation of the organic ligand [2].

It has been found that the incorporation of low-valent transition metals into lacunary polyoxometalates helps in the formation of complexes that are oxidatively stable. These are the so-called transition metal substituted polyoxometalates (TMSP), which have the ability to coordinate [3] and activate dioxygen [4–6]. They form high valent metal-oxo intermediates [7,8] and catalyze the oxidation of a wide variety of substrates with various oxidants. Here, the incorporated transition metal acts as an efficient

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oxygen transfer agent. They provide better selectivity and higher conversion than most of the other catalysts and also can be used with environmentally friendly oxidants such as air and hydrogen peroxide.

The terpenes containing oxygen are very important as they are used in the production of fragrances, perfumes and food additives [9,10]. The epoxidation of limonene with H_2O_2 over supported heteropoly acids and Ti- β zeolite has been reported by Herrero et al. [10]. The products, which they have reported, include the epoxide and cetones, along with some glycols and acid catalyzed products. Recently, it was reported by de Villa et al. [11] that phosphotungstic acid anchored on Amberlyst IRA-900 gave a good yield of limonene oxide on epoxidation with H_2O_2 . Aramendia et al. [12] have reported the epoxidation of limonene to limoneneoxide with H_2O_2 in the presence of a nitrile using Mg/Al double-layered hydroxide (LDH) as a catalyst. Silva et al. [13] have reported the oxidation of limonene by Wacker $\text{PdCl}_2\text{-CuCl}_2$ catalytic oxidation process in acetic acid medium. The major product was carveol with 33% selectivity along with carveone and other acetylated products of the substrate. Autoxidation of olefins including limonene and α - and β -pinenes was reported by Gomes et al. [14] using Co(OAc)_2 /bromide system using dioxygen as the oxidant to various products including carveone and carveol for limonene and other oxygenated products for the two pinenes.

Here, we report our observations in the oxidation of limonene over cobalt containing sandwich-type polyoxotungstate using air or hydrogen peroxide as the oxidant to epoxide, carveol and carveone as the main products. The poly transition metal substituted polyoxometalates of the sandwich type have much higher solvolytic stability and are also highly active and chemoselective catalysts in the oxidation of alkenes with various oxidants.

2. Experimental

2.1. Materials

Unless otherwise specified, all reagents were purchased from commercial suppliers and used without further purification. The starting compounds used include $\text{Na}_2\text{WO}_4\cdot 2\text{H}_2\text{O}$ and $\text{Co(NO}_3)_2\cdot 6\text{H}_2\text{O}$.

Limonene was procured from M/s Merck India Pvt. Ltd.

2.2. Preparation of cobalt polyoxometalate

The preparation of the polyoxometalate was carried out by known methods [15]. A solution of $\text{Na}_2\text{WO}_4\cdot 2\text{H}_2\text{O}$ (127 g, 0.38 mol) in 350 cm^3 water was heated to 80°C . This was vigorously stirred and treated with 25 cm^3 (0.35 mol) of 14 mol dm^{-3} nitric acid until the light yellow precipitate initially formed dissolved completely. To this a solution of cobalt nitrate hexahydrate (29.12 g, 0.10 mol) in water (100 cm^3) was added with continuous stirring and heating at 90°C . A pink precipitate readily soluble in the solution was formed under these conditions. The addition was carried out slowly so that no amorphous material was formed. On adding the salt solution, the color changed to deep green, which intensified on prolonged heating. After the complete addition of the salt solution, the contents were stirred for an hour, filtered hot to remove the amorphous precipitate that was formed and the filtrate was kept for cooling. On cooling, deep green, needle-like crystals appeared. The liquid was evaporated to half the volume and kept covered without disturbing. Needle-like crystals were allowed to grow for 3–4 days. The resulting cold filtrate was shaken with an equal volume of acetone and the dense lower layer was diluted and heated to 50°C , and kept at this temperature. After the recovery of the product, the process was repeated with the filtrate till no more product separated out. All the different fractions of the product were recrystallized together from water to form a homogeneously hydrated product. The total yield of the final product was about 55%.

2.3. Characterization

The elemental analysis of the polyoxometalate was determined by atomic absorption spectroscopy. The thermogravimetric analysis (TG) and DTA analysis of the polyoxometalate were recorded on Rhometric Scientific (1500) Analyzer. The IR spectrum of the cobalt containing polyoxometalate was recorded in a Shimadzu FTIR-8201PC. The UV-Vis spectral characterization was done in a Shimadzu UV-2101PC spectrophotometer. The single crystal X-ray data were

collected on Bruker SMART APEX CCD diffractometer using Mo K α radiation with fine focus tube.

2.4. Catalytic oxidation of limonene

The reaction with H₂O₂ as the oxidant was carried out in a stirred glass reactor. To the substrate (10 mmol) dissolved in 15 cm³ acetonitrile, the catalyst (6.6 μ mol) was added followed by 34% aqueous hydrogen peroxide (10 mmol). The temperature was maintained at 80 °C by a thermostatic oil bath, fitted with a water condenser on top. The reaction was carried out for 5 h. Aliquots of the samples were withdrawn every hour and analyzed by gas chromatography.

The experiments on the oxidation of limonene with air were carried out in a 50 ml Parr reactor under pressure. Typically, substrate (10 mmol), dissolved in 15 cm³ acetonitrile was taken in the autoclave and the catalyst (6.6 μ mol) was added. This was pressurized to 1.5 MPa air and heated to 100 °C and kept at that temperature for 5 h. After the reaction was stopped, the autoclave was quenched with ice. A fall in the pressure of about 0.5 MPa could be observed on cooling. A sample was withdrawn and was analyzed by

GC for the substrate and its oxidation products after centrifugation.

2.5. Analysis of reaction products

The products of oxidation of limonene were analyzed by a HP-5890 gas chromatograph fitted with a fused megabore column SE-52, HP-% (cross linked 5% PhMe silicone), 30 m in length, 0.53 mm i.d., 0.3 μ m film thickness and a FID. The identity of the products was confirmed by GC-MS (Shimadzu QP 5000) and also by comparing the retention time with standards.

3. Results and discussion

3.1. Characterization

The TG analysis of the sample shows a major weight loss (10.8%) at around 100 °C, due to the removal of water of hydration and also another up to 375 °C (~13% total) which may be due to the loss of constitutional water molecules from the polyoxotungstate. Fig. 1 further shows that the compound

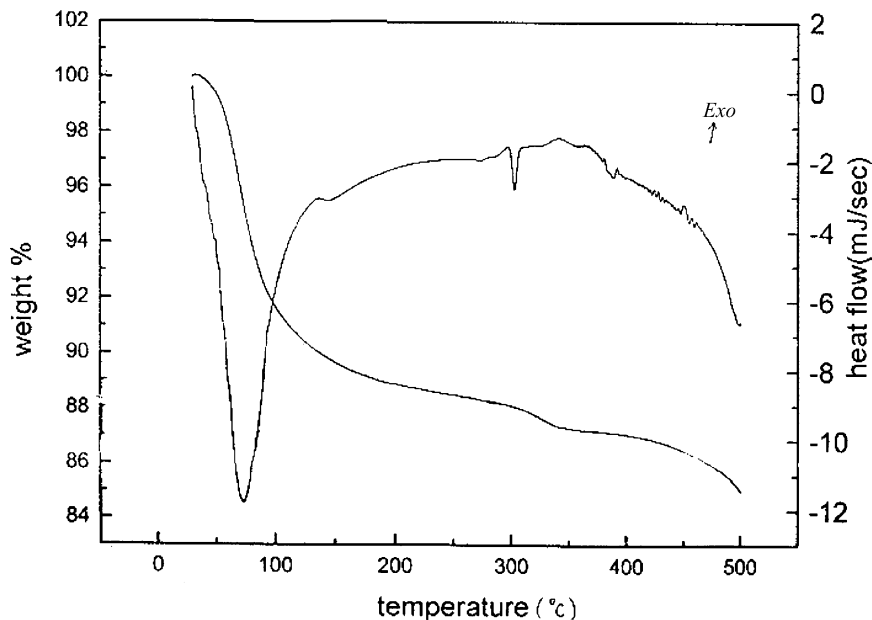


Fig. 1. TG/DTA profile of Na₁₀[Co₅W₁₉O₆₈].44H₂O.

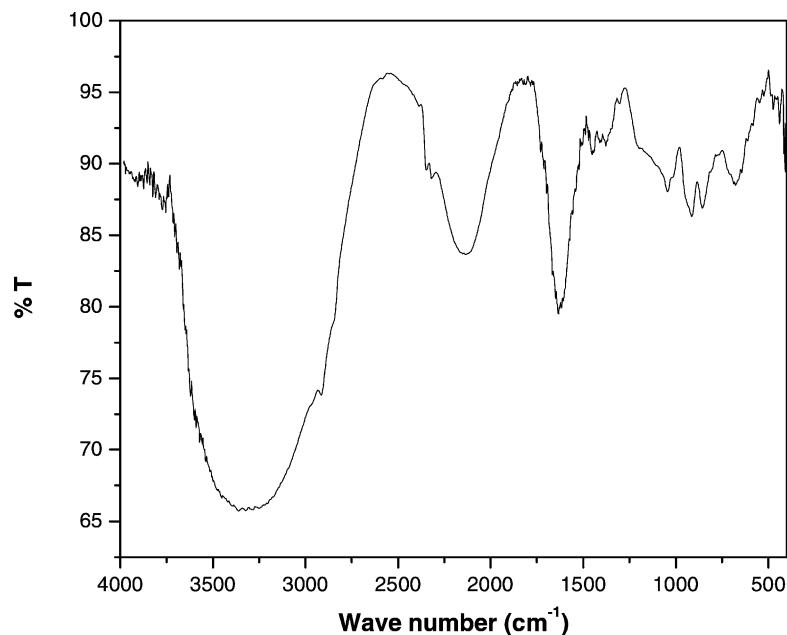


Fig. 2. FT-IR spectrum of $\text{Na}_{10}[\text{Co}_5\text{W}_{19}\text{O}_{68}]\cdot 44\text{H}_2\text{O}$.

undergoes total degradation at 500°C . The complete decomposition of the compound to its respective oxides takes place at 500°C . The origin of the endotherm at 295°C (with about 2.2 wt.% loss) is not clear.

The IR spectrum of the compound (Fig. 2) shows a band at 958 cm^{-1} , corresponding to the W=O (terminal) vibrations. The peaks at 850 and 804 cm^{-1} , are assigned, respectively, to W–O–W corner sharing of WO_6 octahedra and W–O–W edge sharing octahedral vibrations. The weak band at 585 cm^{-1} may be due to the stretching vibrations of the cobalt–oxygen bond. There is a sharp peak recorded between 2150 and 2300 cm^{-1} , which could not be assigned to specific bonds in the sample. The UV-Vis spectrum having the absorption bands of the free catalyst is shown in Fig. 3. The band due to $\text{O} \rightarrow \text{W}$ charge transfer of the polyoxotungstate at W=O is seen at 217 nm . Also present is the broad absorption spectrum $\text{O} \rightarrow \text{W}$ charge transfer at W–O–W bonds of the unit, normally seen at $255\text{--}256\text{ nm}$. There are three strong and broad bands coming at 558 , 610 , and 653 nm . Due to the presence of cobalt atoms in both tetrahedral and octahedral coordination sphere, there is a possibility of overlapping between the respective absorption bands. The fact that the incorporated transition metal

atoms occupy both tetrahedral and octahedral coordination sphere has been reported by the single crystal X-ray analysis carried out for sandwich polyoxometalates containing other transition metals like Zn, Cu, V, etc. [15]. Baker and Glick [16] have reported that the cobalt atom in the tetrahedral site takes part in oxidation reactions and not the one in the octahedral site.

Andres et al. [17] have reported the antiferromagnetic nature of the compound, $\text{Na}_{12}[\text{WCo}_3(\text{H}_2\text{O})_2\{\text{W}_9\text{CoO}_{34}\}_2]\cdot x\text{H}_2\text{O}$. They found that due to the presence of three octahedral and two tetrahedral oxo-coordinated Co(II) ions, two different types of interactions are present. As a result, there is a ferromagnetic interaction between the octahedral Co(II) ions and an antiferromagnetic interaction between the tetrahedral Co(II) ions. The results indicate that the compound is antiferromagnetic. We too expect that our compound may have antiferromagnetic property due to the presence of cobalt atoms in two different environments. Further study regarding this phenomenon is in progress.

In order to understand the composition and other structural details of the compound, its single crystal X-ray study was carried out. The deep green colored single crystals were obtained by the slow evaporation

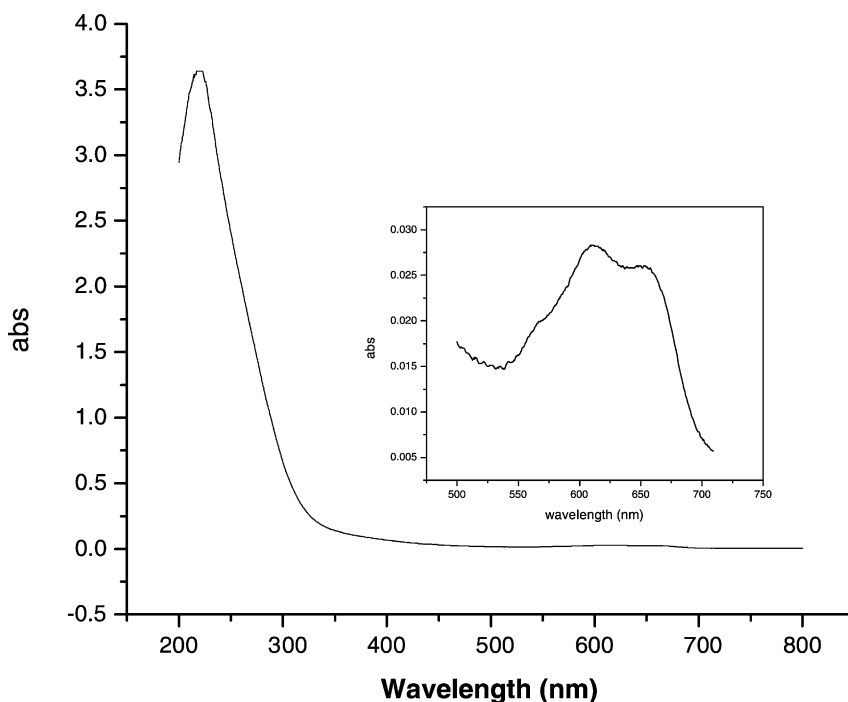


Fig. 3. UV-Vis spectrum of $\text{Na}_{10}[\text{Co}_5\text{W}_{19}\text{O}_{68}]\cdot 44\text{H}_2\text{O}$ in water.

of a dilute solution of the polyoxometalate in air at room temperature. The X-ray structure analysis of the compound, revealed a sandwich-type structure (Fig. 4). Crystals belong to monoclinic, space group $P2_1/n$, $a = 13.0408 \text{ \AA}$ (7), $b = 17.794 \text{ \AA}$ (1), $c = 21.058 \text{ \AA}$ (1), $\beta = 93.291^\circ$ (1), $V = 4878.5 \text{ \AA}^3$ (5), $Z = 2$, $D_c = 4.040 \text{ mg m}^{-3}$, μ (Mo $K\alpha$) = 23.301 mm^{-1} , $T = 293(2) \text{ K}$, 28,399 reflections measured, 10,978 unique [$I > 2\sigma(I)$], R -value 0.0562, $wR2 = 0.1337$. All the data were corrected for Lorentzian, polarization and absorption effects. SHELX-97 (ShelxTL) [18] was used for structure solution and full-matrix least-squares refinement on F^2 . The crystallographic data are given in Table 1. Here, we found that out of the five cobalt atoms, two are in tetrahedral and the other three are in octahedral coordination. The tetrahedral cobalt bond distance (Co–O) varies from 1.917 to 1.941 \AA and the octahedral from 2.074 to 2.168 \AA . Since only 10 sodium atoms are present as the counter ions, we assume that the two cobalt atoms in the tetrahedral environment are having a coordination number 3. It was found that the sodium atoms are surrounded mostly by six

neighboring oxygen atoms belonging mainly to water molecules.

3.2. Catalytic study

The catalytic application of the compound was studied by using the sodium salt for the selective oxidation of limonene using air or aqueous H_2O_2 as the oxidant. The reaction scheme (Scheme 1) is given below.

Blank reactions (Table 2) were carried out in order to ascertain that the reaction did not take place without the catalyst to an appreciable extent. We could observe some reaction in both cases even though there was an induction period of more than 5 h. The epoxidation in the absence of a catalyst was really slow and the products have been analyzed after 16 h. The reactions with aqueous H_2O_2 were carried out at the boiling point of acetonitrile for 5 h. In order to know the effect of solvents on the oxidation reaction, methanol and acetone were also used as solvents in a few experiments. The effect of oxidant, the catalyst concentration and temperature on the conversion of limonene was studied. The oxidation of limonene in presence of air was

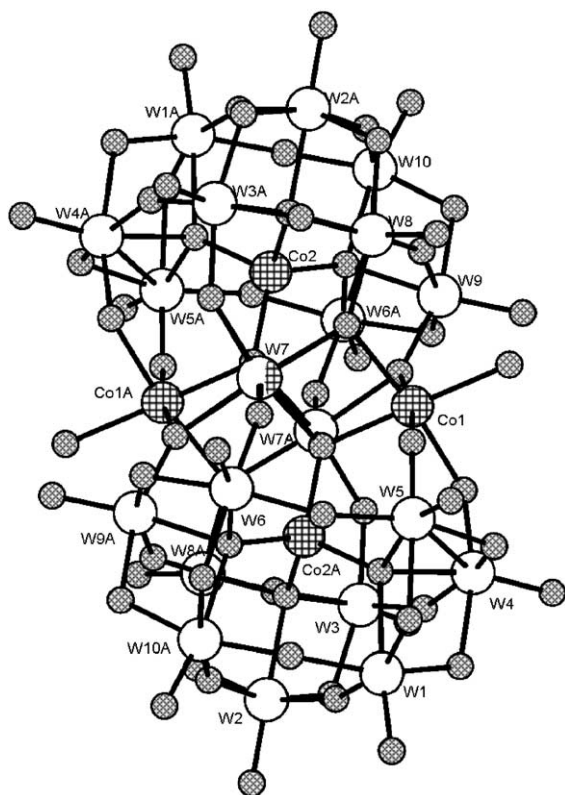
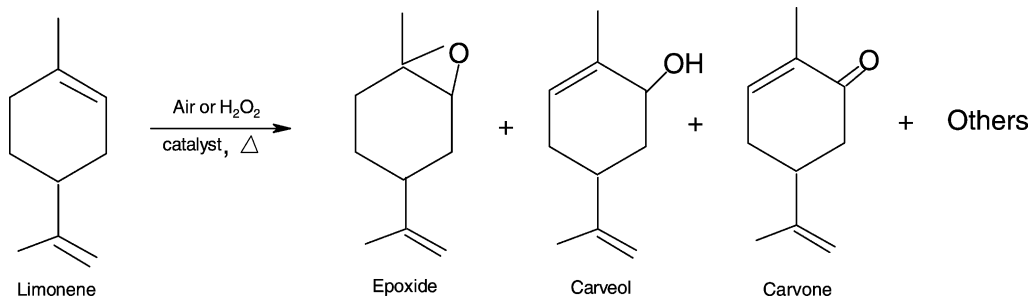


Fig. 4. PLUTO diagram of $[\text{Co}_5\text{W}_{19}\text{O}_{68}]^{10-}$ anion.

carried out at temperatures ranging from 80 to 120 °C for 5 h, in acetonitrile solvent.

3.2.1. Oxidation with aqueous H_2O_2

The conversion of limonene with aqueous hydrogen peroxide catalyzed by the cobalt containing sandwich-type polyoxometalate in different solvents and the



Scheme 1.

Table 1

Crystallographic data for $\text{Na}_{10}[\text{Co}_5\text{W}_{19}\text{O}_{68}] \cdot 44\text{H}_2\text{O}$

Formula	$\text{Na}_{10}[\text{Co}_5\text{W}_{19}\text{O}_{68}] \cdot 44\text{H}_2\text{O}$
M	5934.44
Crystal system, space group	$P2_1/n$
a (Å)	13.0408 (7)
b (Å)	17.7944 (10)
c (Å)	21.0579 (12)
β (°)	93.291 (1)
Volume (Å ³)	4878.5 (5)
Z, calculated density	2, 4.040
$F(000)$ (mg/m ³)	5310
Crystal size (mm)	0.28 × 0.09 × 0.04
Theta range for data collection (°)	1.50–28.25
Reflections collected/unique	28399/10978 [R (int) = 0.0742]
Completeness to theta (%)	28.25 90.9
Maximum and minimum transmission	0.4558 and 0.0585
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	10978/0/676
Goodness-of-fit on F^2	1.095
Final R indices [$1 > 2\sigma(1)$]	$R1 = 0.0562$, $wR2 = 0.1281$
R indices (all data)	$R1 = 0.0735$, $wR2 = 0.1337$
Largest diffraction peak and hole ($e \text{ \AA}^{-3}$)	3.363 and -3.934

product distribution are summarized in Table 3. Methanol, being more polar than acetonitrile and acetone, was found to be a better solvent for the oxidation of limonene with aqueous hydrogen peroxide. Acetone being less polar provided less conversion of limonene under the reaction conditions.

3.2.2. Oxidation with air

Although the results on the oxidation of limonene with aq. H_2O_2 (singlet oxygen) over cobalt containing sandwich-type polyoxotungstate as catalyst

Table 2
Blank reactions

No.	Oxidant	Conversion (%)	Product selectivity (%)			
			Epoxide	Carvone	Carveol	Others
1	Aq. H ₂ O ₂ (10 mmol)	11	15	40	2	20
2	Air (1.5 MPa)	24	25	45	22	8

Conditions: solvent = acetonitrile 15 cm³, temperature = 80 °C and time = 16 h.

Table 3
Conversion of limonene with aq. H₂O₂ in different solvents^a

No.	Temperature (°C)	Solvent	Conversion (wt.%)	Product distribution (%)			
				Epoxide	Carveol	Carvone	Others ^b
1	80	Acetonitrile	11	18	19	45	18
2	50	Methanol	20	15	30	40	15
3	40	Acetone	04	25	25	50	–

^a Conditions: aq. H₂O₂ = 10 mmol, limonene = 10 mmol, time = 5 h, solvent = 10 ml and catalyst = 4 wt.% of the substrate.

^b Mainly glycols and perillyl alcohol.

are interesting, we also carried out the oxidation of limonene with air as the oxidant. The sandwich-type polyoxometalate complexes are known to activate the triplet oxygen of dioxygen like metalloporphyrins and other metal complexes. Here, we could get better results on the oxidation reaction proving that the compound, Na₁₀[Co₅W₁₉O₆₈]-44H₂O, can indeed activate the triplet oxygen from dioxygen better than the singlet oxygen from aqueous hydrogen peroxide.

In the case of oxidation with air, the reactions were carried out by varying the pressure as well. A pressure drop of 0.3–0.6 MPa could be observed after 5 h, depending on the temperature of the system. Thus, it is confirmed that dioxygen is used in the reaction. The results obtained for the oxidation with air are summarized in Table 4.

It can be seen from Tables 3 and 4 that the major product formed during the oxidation of limonene using the cobalt containing sandwich complex, as catalyst is carvone. The maximum selectivity of 45% to carvone was found with aq. H₂O₂ in acetonitrile solvent. But a selectivity of 48% to carvone was found with air at 80 °C. At this temperature, only three products were formed. With increase in temperature, though the conversion of limonene increases, selectivity to the major product was found to decrease. Products like glycols, perillyl alcohol, etc. (included in the table as ‘others’) were also formed.

It may be noted that the major products that are formed in this reaction can be formed both by the autoxidation as well as the allylic oxidation of limonene under the reaction conditions. It was found

Table 4
Conversion of limonene with air at different temperatures^a

No.	Temperature (°C)	Conversion (wt.%)	Product distribution (%)			
			Epoxide	Carveol	Carvone	Others ^b
1	80	25	28	24	48	–
2	100	37	13	25	41	21
3	120	50	8	24	40	28

^a Conditions: pressure = 1.5 MPa, limonene = 10 mmol, time = 5 h, acetonitrile = 15 ml and catalyst = 4 wt.% of the substrate.

^b Mainly glycols and perillyl alcohol.

Table 5
Comparison of different catalysts in the oxidation of limonene using O₂

Catalyst	Solvent	Conversion (wt.%)	Product distribution (%)				Reference
			Epoxide	Carveol	Carvone	Others	
[WCo ₃ {W ₉ CoO ₃₄ } ₂] ¹⁰⁻	Acetonitrile	25	28	24	48	–	Present ^a work
PdCl ₂ -CuCl ₂ -O ₂	Acetic acid	17	–	33	6	61*	[13] ^b
Co(OAc) ₂ /bromide	Acetic acid	50	–	11.4	24.1	64.5*	[14] ^c

^a Time: 5 h; temperature: 80 °C.

^b Time: 24 h; temperature: 29 °C.

^c Time: 24 h; temperature: 50 °C.

* Includes mainly acetates, perillaldehyde and many other products.

that autoxidation of limonene does take place after a long period of time. Regarding allylic oxidation, it was found that in the initial stages of the reaction, the concentration of limonene epoxide is more. But its concentration was found to decrease with time and also with the increase in the conversion of the substrate. This means that carveol, carvone and other products are formed from the epoxide and not by the direct oxidation of limonene.

The lower conversion with aqueous hydrogen peroxide may be due to lower temperature of the reaction, and also due to the fact that the catalyst decomposes the H₂O₂ non-selectively. The H₂O₂ efficiency is rather low, even though the product spectrum is similar. When methanol was used as the solvent for the oxidation reaction with aq. H₂O₂, an increase in the conversion of limonene was observed. Also, there was a decrease in the selectivity towards carvone and an increase in carveol concentration. The conversion of limonene was very low when acetone was used as the solvent.

The epoxide formed during the reaction is not stable because it isomerizes to form carveol. It is also hydrolyzed by the water molecules present in the system and form glycols. Free water molecules are present in the catalyst as well and also it is produced during the oxidation reaction. It was also observed that, the catalyst provides a heterogeneous environment in the oxidation reaction and that after each experiment, the catalyst could be recovered by filtration and reused. Only in the case of methanol as solvent, we found that the catalyst is slightly soluble under reflux conditions.

The oxidation is selective to one of the two olefinic bonds in limonene, forming the epoxide as the primary oxidation product. This rearranges to form

carveol. Further oxidation of carveol leads to the formation of carvone. It was found that all the three products are formed within 1 h of the reaction. We have also observed during the course of the reaction that an increase in temperature, pressure and catalyst concentration markedly increases the conversion of limonene. As the conversion of the substrate increases with temperature (Table 4), the epoxide formed (primary product) decomposes non-selectively to other products such as glycols and so on, while the total selectivity to carveol and carvone remains fairly constant. A comparison of the activity of two catalysts reported earlier for this reaction along with that of the present catalyst is shown in Table 5. On the catalyst systems reported in references [13] and [14], the non-selective oxidation products constitute a major part of the product distribution. The epoxide, even if formed, probably decomposed faster to give a range of other by-products. The present catalyst, on the other hand showed good activity and more important, a high selectivity to epoxidation and products from epoxidation which are restricted to only to carveol and carvone.

4. Conclusions

A cobalt containing sandwich complex has been synthesized and characterized by several methods. The single crystal X-ray analysis of the compound was also carried out for proving its structure. This compound was then used as a catalyst for the oxidation of limonene. The said compound showed good catalytic activity in the oxidation of limonene with hydrogen peroxide as well as with air as oxidants and

high selectivity to epoxide, carveol and carvone at 80 °C. It was found that the complex could activate molecular oxygen and epoxidize selectively one of the olefinic double bonds. The complex as its sodium salt was found to be insoluble in solvents like acetonitrile, providing a heterogeneous environment for the reaction.

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