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Synthesis, characterization and application of Chitosan based Schiff base-transition metal complexes (Mn,Cu,Co,Ni)

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ABSTRACT*

Chitosan-triazene-eda-salen based Schiff base was prepared and complexed with manganese, copper, cobalt, nickel to form four new Schiff base metal complexes. These were used as heterogeneous catalysts for the mukaiyama epoxidation. Characterization of these catalysts was based on XRD, FT-IR, ^{1}HNMR elemental analysis and TGA. The metal loading on four catalysts was determined by ICP-AES. The catalytic activity of each prepared catalyst was studied on L-Carvone in the Mukaiyama epoxidation involving isobutyraldehyde as co-reagent. Substrates like ά-terpineol, trans/cis-stilbene, α-methyl styrene, Limonene were also used for the epoxidation. Conversion and Selectivity for L-Carvone using each prepared catalyst were studied using gas chromatography. The effect of catalyst loading, solvent, temperature and co-reagent concentration was also investigated.

Keywords: Aerobic oxidation, L-Carvone, Chitosan-triazene-ethylenediamine-salen-Co, Isobutyraldehyde.

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INTRODUCTION

The aerobic epoxidation of alkenes with an aldehyde as a co-reagent is an efficient and useful method for the production of fine chemicals. Mukaiyama *et al.*, [1-3] has investigated a method in which transition metal is used as a catalyst, with isobutyraldehyde as a co-reagent for the epoxidation of alkene. The simplicity of the method makes it useful for industrial applications despite the fact that more than stoichiometric amounts of the co-reacting aldehyde are needed. Homogeneous catalysts such as Iron(III),[4, 5]copper(II),[6] and manganese,[7, 8] complexes are also active in the Mukaiyama epoxidation of alkenes. Anchoring homogeneous catalysts on a support to obtain selective and reusable heterogeneous catalyst is a popular research topic. Such types of catalysts also have been used for aerobic epoxidation such as zeolite encapsulated cobalt salen, [9] phthalocyanine and salophen complexes[10]. In all cases, allylic oxidation was observed.

Chitosan is produced by the deacetylation of biopolymer chitin. It has many applications in medicine such as wound dressings, artificial skin, in drug delivery and contact lenses and other areas such as adsorption of metals[11]. The flexibility of the material, its insolubility in the vast majority of common solvents along with its inherent chirality makes chitosan an excellent candidate for use as a support for catalysts. Several studies have demonstrated the catalytic activity of salts physically adsorbed onto chitosan and reduced to the corresponding metal for the reduction of chromate and phenol using Pd[12-15] and for phenol and nitroaromatics using Ni, Cu, Cr, Zn [16-19]. Functionalization of the chitosan support has also been studied for cyclopropanation of olefins (Cu-Schiff base) [20], oxidation of alkylbenzenes (Mn or Ni-Schiff base)[21] and the oxidation of DOPA (3, 4 - dihydroxyphenylalanine) with (Co-Salen) [22] . A patent to UOP [23] describes the deposition of palladium and platinum onto chitosan using basic solutions of glucose as the reductant. Further in a enzyme immobilization study several workers have immobilized enzymes on chitosan to explore enzyme immobilized chitosan as a catalyst for reduction of cyclohexanone [24], ester synthesis in nonaqeous media [25]**,** breakage of glycosidic linkages [26], hydrolysis of casein (important reaction in cheese industry) [27] synthesis of a monoglycerides from palm oil triglycerides [28].

In view of these importances of chitosan and derivatized chitosan as a catalyst, the present research has been undertaken to explore chemically modified form of chitosan as a novel heterogeneous organometallic catalyst for the epoxidation of L-Carvone, cis-stilbene, trans-stilbene, α- terpineol, α-methyl styrene.

MATERIALS AND METHODS

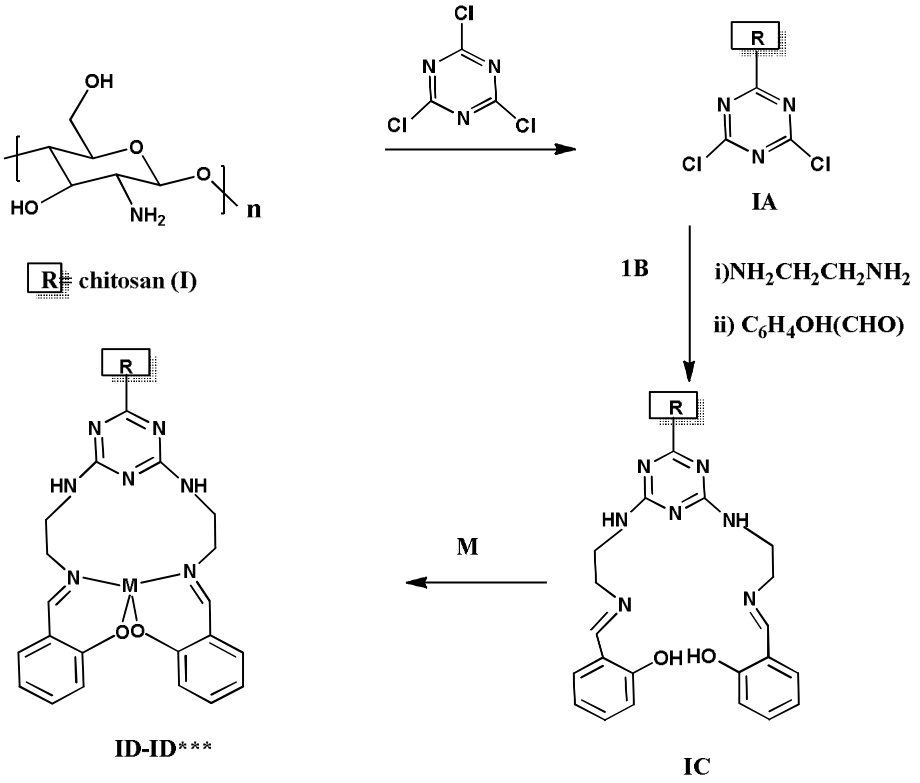
General Considerations: Chitosan from prawn (degree of deacetylation 80%) was procured from Indian Sea Foods (Cochin). All reagents used for the preparation of catalysts and for activity testing were pure and procured from E Merck., Aldrich, Fluka and S.D fine chemicals. Zero air (Iolar) was used as the oxygen source for the oxidation reaction. Reaction samples were analyzed with Agilent 6890 Gas chromatograph using FID detector in a Varian CP 8934 capillary column with dimensions of 10 m length x 100µm diameter x 0.40µm film thickness with G.C. parameters as specified (Oven, 100°C - 45°C- 1min- 280°C – 2min hold). Epoxide was identified by GC-MS and further characterized by FT-IR and ^{1}HNMR analysis. Based on the G.C. analysis conversions and selectivities for mono and diepoxides were determined. Elemental analyses (C, N, H) were performed in Flash EA-1112 Series instrument. Infrared spectra of the free ligand and the complex were recorded in the Model Magna-550 and Shimadzu 8400S series machines. The ^{1}H NMR spectra of the free ligand in DMSO-d6 was obtained using a Bruker Avance-300 MHz. Manganese content was determined by ICP-AES on ICAP - 6200 duo, while BET surface area was determined using Tristar 3000V6.05A using nitrogen adsorption.Thermogravimetric analyses (TGA) were recorded in a Dupoint-2000 USA thermogravimetric modulus machine. The samples were heated under nitrogen flow at 5^0C/min until 400^0C while recording weight changes.

The catalyst activity testing was done in a glass, stirred batch reactor attached with overhead agitator, reflux condenser, air sparger and spare nozzle for adding removing samples. The reactor was immersed in a water bath and the temperature of the water bath was controlled by a Julabo Circulator and Temperature Controller.

Synthesis of Catalysts

Synthesis of Schiff base 1C: Fig.1 was followed for the synthesis of catalysts. The precursor IB required for the preparation of 1C was prepared by modified literature methods using dioxan as a solvent [29]. Schiff base IC was prepared by mixing IB (20g) with 32ml of glacial acetic acid, and 100 ml of methanol followed by the slow addition of salicylaldehyde (0.098mole) over a period of 30 minutes. The mixture was refluxed for 24 h with efficient stirring. The resulting Schiff base IC was cooled, filtered and washed with ethanol (200ml) and acetone (200ml). The solid residue after filtering and washing was dried in an oven at 80°C for 3 h. (Yield = 21g).

General method for the Synthesis of Chitosan Schiff base – metal (Mn, Cu, Co, Ni) tetra dentate metal complexes (ID-ID*) :** A method from [30] was modified and used for the synthesis of Schiff base-metal complex. In a round bottom flask IC (**4**g) was dissolved in 40ml of DMSO, further a solution of KOH (0.015mol) in methanol was added. The mixture was heated to 80°C. A solution of anhydrous manganese chloride (0.022mol) in methanol was added further. The mixture was refluxed for the period of 6h. The contents were cooled, and quenched with 190ml of acetone and 50ml of n-hexane to precipitate the heterogeneous catalyst. The resulting catalyst was filtered and washed with water till free from any occluded manganese chloride, further washed with 200ml of acetone. The final solid was dried in oven at 80°C for 3 h. (Yield = 3.8g). Similar method was adopted for the preparation of all the catalysts.



Tetradentate metal complex

M = i) Mn(II) chloride
ii) Cu (II) chloride
iii Co (II) chloride
iv) Ni (II) chloride.

1D= Ch-Schiff base-Mn, 1D*=Ch-Schiff base-Cu, 1D**= Ch-Schiff base-Co, 1D***= Ch-Schiff base-Ni

Fig. 1 Synthesis of Schiff base-metal complexes

RESULTS AND DISCUSSION

The catalysts were characterized by XRD, FT-IR, ^{1}H - NMR, elemental analysis and ICP-AES.

XRD Analysis of chitosan (1), Schiff bases (1C) and their manganese, copper,cobalt and Nickel based metal complexes (1D – 1D***). The XRD patterns of chitosan, Schiff base and corresponding metal complex (1 – 1D*******) are shown in fig. 2**.**

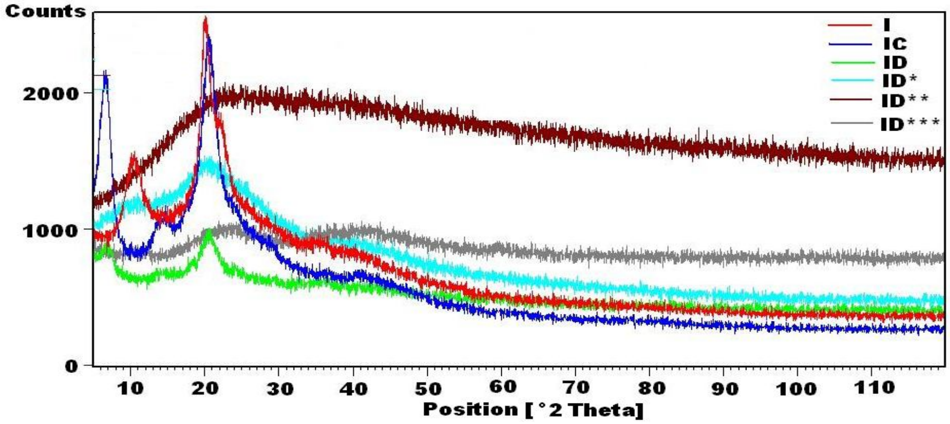


Fig. 2: XRD analysis of chitosan (1), Schiff base (1C), and Chitosan Schiff base-Mn(ID), Chitosan Schiff base-Cu (1D*), chitosan Schiff base-Co (1D**), chitosan Schiff base-Ni (1D***)

There are no reference diffraction data available for powders of new catalyst **1D** or similar compounds with other transition metals in the available ICDD database. Two prominent reflections were seen in chitosan at 2θ of 9.93° and 19.97°. The former indicated the presence of crystal form I and the later one corresponds to crystal form II [31]. This suggested the formation of inter and intra- molecular hydrogen bond in chitosan. In case of Schiff base **1C,** the reflection at 2θ of 9.93° disappears completely and new reflection appears at $2\theta =$ 6.38° and 6.97°, where as the reflection at 2θ of 19.97° was found to shift at 20.77° . This demonstrated a formation of imine and deformation of hydrogen bonds in chitosan backbone. Moreover, it should be noted that the relative intensities of diffraction peaks of chitosan and that of Schiff base IC at 2θ=19.96 and 20.77 were at 100% and 88% respectively. The substitution resulted in increased crystallinity of Schiff base **1C** compared with chitosan. The increase in crystallinity of Schiff base can be explained. The change of crystallinity is mainly dependent on the formation of Schiff base and to some extent on other factors, such as special hindrance, hydrophobic force and π-π stacking [32].In the present case, this chitosan-based Schiff base compound has different aromatic substituent groups and long hydrophobic alkyl chain. Thus, it seems that the crystallinity and designed structures can be regulated by the modification of substituent groups in chitosan molecule. The XRD pattern of their corresponding metal complexes 1D-1D*** showed decrease in crystalline character. This observation was similar to that reported by Ti Feng et al [33] where chitosan-salicylaldehyde Schiff base was complexed with copper.

FT-IR Characterization of Chitosan (I), Schiff base(IC) and their metal complexes(ID-ID***, Fig.3,Fig.4)

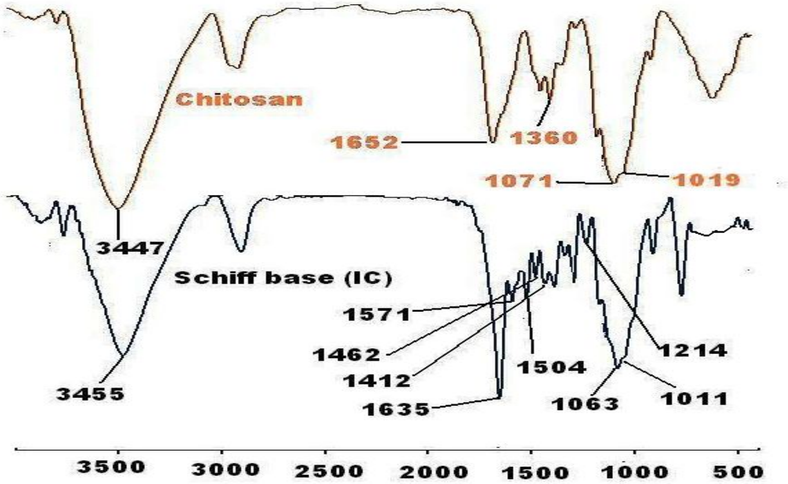
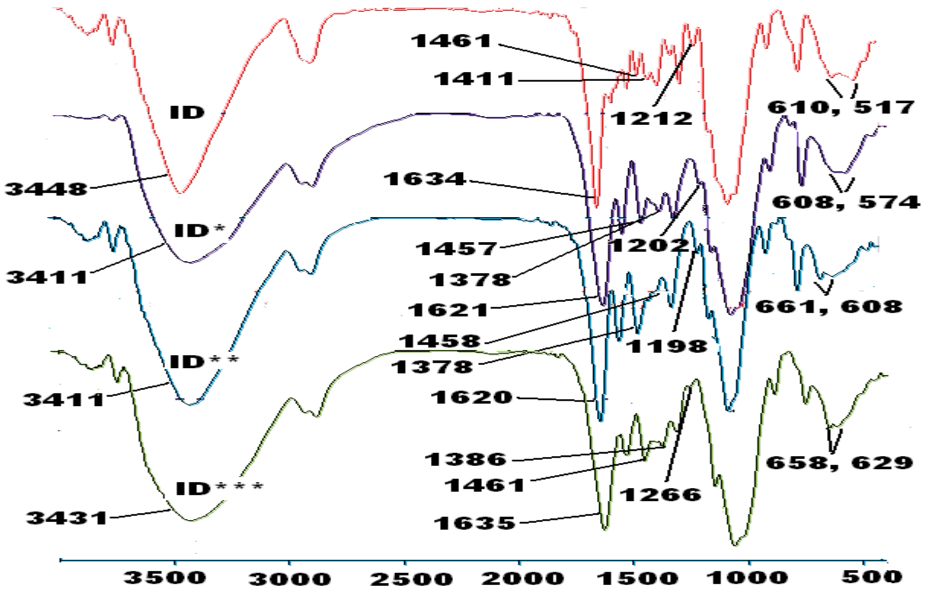


Fig. 3 FT-IR spectrum of Chitosan, and Chitosan Schiff base (1C)

Table 1. IR characterization of Schiff base IC and Catalysts 1D-1D***

Schiff base 1C/ catalyst	ν OH,NH cm^{-1}	ν C= N cm^{-1}	ν CH$_2$-CH$_2$ cm^{-1}	N Phenolic C-O cm^{-1}	ν M-N cm^{-1}
Schiff base (1C)	3455	1635	1462, 1412	1214	-
1D	3448	1634	1461, 1411	1212	medium,610
1D*	3411	1621	1457, 1378	1202	medium, 608
1D**	3411	1620	1458, 1378	1198	medium, 661
1D***	3431	1635	1461, 1386	1266	medium, 658

1C = chitosan- Schiff base, 1D=Chitosan- Schiff base – Mn, 1D*=Chitosan-Schiff base-Cu, (1D**) = Chitosan Schiff base-Co. 1D*** = Chitosan- Schiff base-Ni



1C = chitosan- Schiff base, 1D=Chitosan- Schiff base – Mn, 1D*=Chitosan-Schiff base-Cu, (1D**) = Chitosan Schiff base-Co. 1D*** = Chitosan- Schiff base-Ni

Fig. 4 IR spectra of Schiff base 1C and Catalysts 1D-1D***

The FT-IR spectrum of Chitosan (I) as shown in Fig.3 is characterized by broad OH group peak at 3447cm^{-1}, an amide peak at 1652 cm^{-1} and primary and secondary hydroxyl groups at 1019 cm^{-1} and 1071 cm^{-1}, respectively. The Schiff base 1C, Fig.3 showed OH and NH peak at 3455cm^{-1}, an imine C=N peak [34,35] at 1635cm^{-1}. Peaks at 1571cm^{-1} and 1504cm^{-1} corresponding to the aromatic ring, where as the band at 1214cm^{-1} corresponds to C=O phenolic. Peaks at 1462cm^{-1} and 1412cm^{-1} assigned to the characteristic CH$_2$-CH$_2$ bands. Some obvious shifts were seen in the FT– IR spectra of Schiff base compound and its corresponding complexes as shown in Fig.4**, (**Table1**).** The vibrations of O-H and N-H groups of Chitosan-Schiff base compound - 1C appeared at 3455 cm^{-1} which was shifted to lower wavelength for the corresponding catalysts, indicating the involvement of oxygen in the formation of metal complex. A red shift was observed for a strong band C=N, which was shifted to lower frequency in case of catalysts. The C-O vibrations of Schiff base 1C was weakened in the case of catalysts, indicating that hydroxyl hydrogen is replaced by metal to form ligand -metal complex [34, 36, 37]. The characteristic CH$_2$-CH$_2$ bands in case of 1C appeared as intense bands at 1462 cm^{-1}, 1412 cm^{-1}, while the corresponding metal complex 1D showed shift at 1461cm^{-1}, 1411cm^{-1}. This suggested possible involvement of the methylene group as a donor ligand. All the IR data suggest that the metal was bonded to the Schiff bases through the phenolic oxygen and the imino nitrogen[38, 39] .Medium peaks were observed at 610 cm^{-1}**,** 612cm^{-1}, 609 cm^{-1} and 629 cm^{-1} in the spectra of 1D, 1D*, 1D**and 1D*****. These were assigned to the metal-oxygen stretching vibration in each of these chelates [40].

^{1}H - NMR characterization: The ^{1}H – NMR of Schiff base 1C was determined in DMSO-d_6 as shown in Fig.5**.**

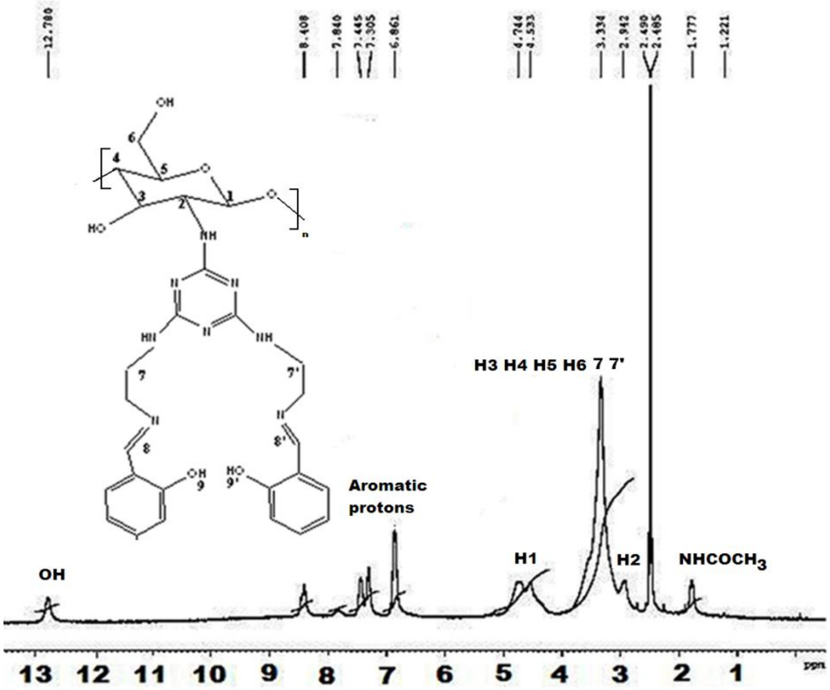


Fig. 5: ^{1}H NMR spectrum of Schiff base IC in DMSO-d_6

It can be observed from the δ (ppm) values in Fig.5 that a broad singlet peak in down field region at 12.78δ can be assigned as substituted aromatic OH group. This assignment was confirmed by D_2O exchange. The broad singlet at 7.84δ was assigned as an imine proton. Appearance of peaks in the aromatic region 6-8 δ indicated the introduction of the aromatic nucleus into the chitosan molecule. The chitosan protons and the methylene protons from ethylene diamine branching are equivalent hence they merged together at 2.94-3.33δ [41]. The methyl group in the acetyl group of chitosan, which was present due to degree of acetylation in chitosan, was assigned at 1.77δ. All these data evidently proved the formation of 1C**.**

Elemental Analysis of Catalysts 1D-1D***

Table 2. Elemental Analysis and BET surface area of catalysts

	% C	% H	% N	% metal content	BET surface area m^2 g^{-1}
Chitosan **(1)**	39.958	7.057	7.174	-	-
Schiff base **(1C)**	47.020	5.439	10.002	-	-
Schiff base- Mn **(1D)**	43.724	4.950	9.205	7.24	6.45
Schiff base- Cu **(1D*)**	44.073	5.012	9.298	6.45	0.65
Schiff base- cobalt **(1D**)**	43.146	4.841	9.044	8.55	17.47
Schiff base- Nickel **(1D***)**	43.346	5.041	8.943	8.14	0.19

A perusal of table 2 reveals that the metals loaded on the catalysts are reasonably high. This shows that the metals are not adsorbed but bonded to the biphenolic structure as shown in Fig.1. It can be also observed from the analysis that the catalysts show increased nitrogen content, which also indicates that chitosan polymer, has undergone the substitution reactions.

TGA analysis of catalysts : The thermal properties of three catalysts ID, ID', ID'' were examined by TGA in a nitrogen atmosphere at a heating rate of 5°C min^{-1} up to 400°C. The thermal behaviour of catalysts can be observed from Fig.6 .All catalysts exhibited good resistance to thermal decomposition, up to 240°C in nitrogen, and began to decompose gradually above the temperature. At 400°C ID, ID* and ID**, and ID*** showed 51%, 49% and 46% decomposition respectively. Literature reports of TGA of Chitosan showed 50% decomposition at 360°C [42], indicating that the catalysts are more stable than chitosan.

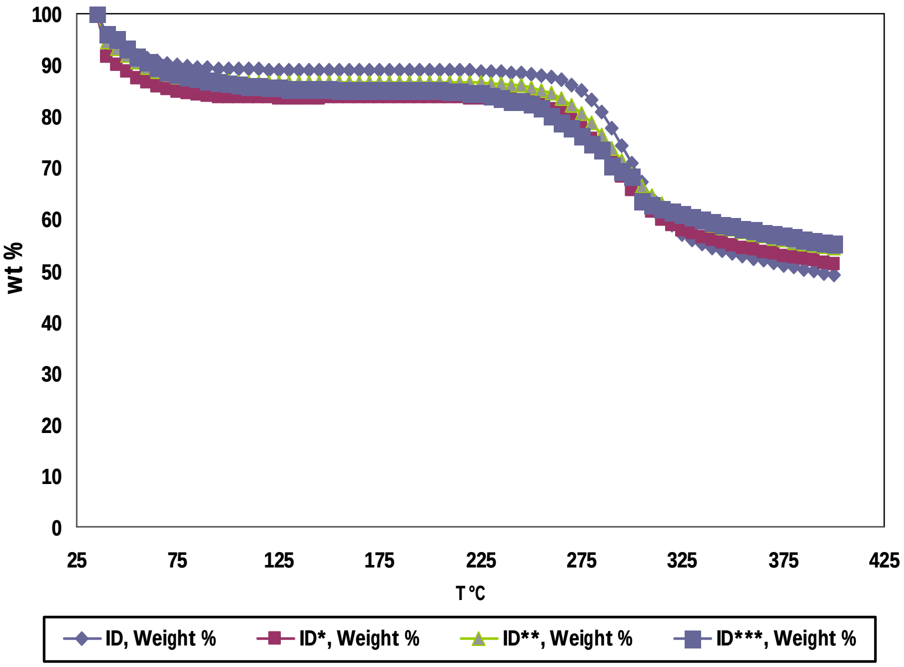


Fig.6: TGA of Catalysts 1D-1D***

Heterogeneity of Catalysts (1D-1D''): It is well-known that the dissolution of polymers depends not only on their physical properties, but also on their chemical structure. One of the main objectives of this study was to produce efficient organometallic catalysts which do not possess solubility in most of the solvents, thus to obtain heterogeneous catalysts. Therefore the introduction of flexible linkages and polar functional groups into the main chain of aliphatic polymer like chitosan was expected to be soluble after the introduction of triazene and ethylene diamine into the chitosan. We found the intermediate (1B, Fig.1) was soluble in Water, but not soluble in n-hexane, acetone, dichloromethane, ethanol and methanol. Further introduction of salicylaldehyde moiety with formation of Schiff base (1C) tend to reduce the solubility. Thus the Schiff base was insoluble in solvents like water, methanol, ethanol, acetonitrile, chloroform, acetone, dichloromethane and n-hexane. The Schiff base (**1C**) was only hot soluble in DMSO with 10 % concentration at R.T. The organometallic catalysts (1D-1D***) were found to be insoluble in n-hexane, acetone, chloroform, ethanol, methanol, water and even in DMSO at room temperature.

Catalytic activity testing: The catalytic activity of four different chitosan based Schiff base metal complexes 1D-1D*** were compared in the oxidation reaction of L-Carvone Fig.7**.** The most active catalyst among the four was 1D**, i.e cobalt based catalyst**.** Using this catalyst, cis-stilbene, trans-stilbene, α-methyl styrene, α-terpineol and Limonene were subjected to the aerobic epoxidation reaction with the conditions mentioned under table 3. The conversion[1] and selectivities[2] were determined by the G.C.analysis of corresponding substrates are shown in Table 3. Stereoselectivity for epoxidation was not determined, but the overall product selectivity for monoepoxide and diepoxide was studied. The main product of limonene epoxidation was in all cases the mono 1, 2-epoxide, *i.e.* the endocyclic epoxide fig.5. As per literature the isopropenyl ring was found to be much less reactive toward epoxidation under the ambient temperature conditions [43], whereas in case of Carvone, literature supports preferable formation of 4, 5-monoepoxide [44]. The epoxy compound formation was established by GC/MS of epoxides as well as FT-IR and ^{1}H NMR studies of pure isolated epoxides. Catalyst 1D****** was recycled six times using limonene as a substrate without any loss in catalytic activity. This has been represented graphically in terms of TON and TOF in Fig.8. The catalyst was found to be active even after six recycles. It can be observed from the graph that after each use the TON for diepoxy compound turns to be higher than monoepoxy, which can be attributed to the enrichment of the catalytic sites by oxygen to form metal superoxo complex [45, 46, 47] which catalyse the reaction more efficiently.

The polyaniline supported cobalt catalyst [48] reported good oxidation efficiency for limonene at 60°C, similar to the chitosan-Schiff base-cobalt catalyst, however the methodologies adopted for the preparation are more complex. The chitosan based catalysts are simple to prepare and show oxidation efficiency for limonene at ambient temperature (25°C).

Compared with the polymer bound catalysts [43], the chitosan based Schiff base-cobalt catalyst did not show decrease in the conversion values during successive recycles.

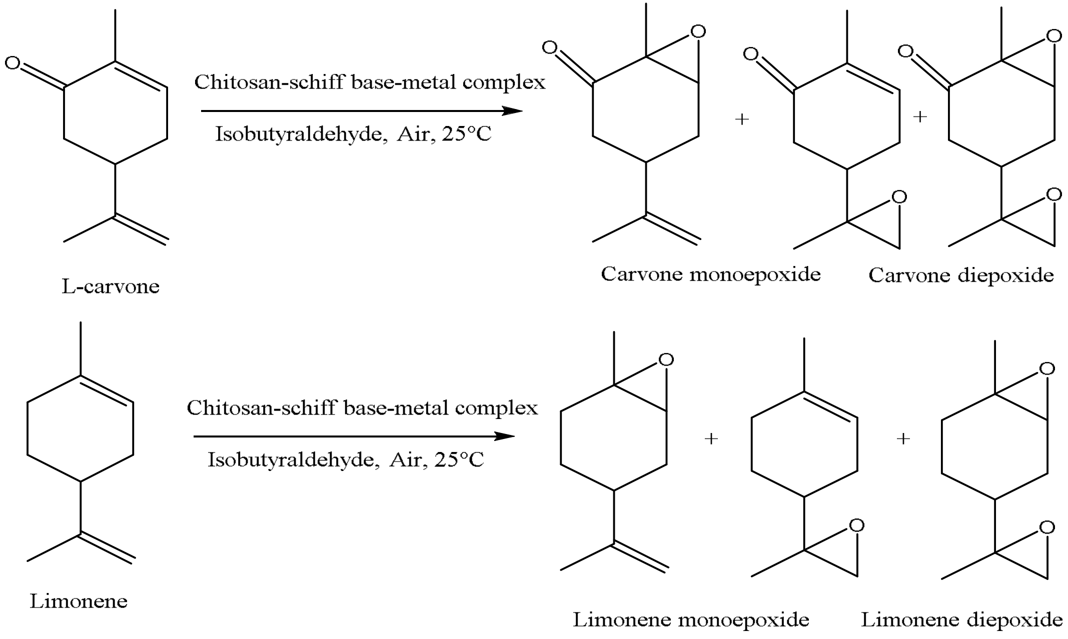


Fig 7. Catalytic aerobic epoxidation of L-Carvone and Limonene

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[1] % conversion = 100- (% of substrate unreacted)

[2] % selectivity = (% of product) /(100) – (% of reactant + % of co-reagent)

Table 3. Epoxidation of different alkenes using chitosan based catalysts

Entry No.	Substrate	Cat used	Time /h	Alkene conv./%	monopoxide /diepoxide Selectivity/yield**
1	L-carvone*	No catalyst	10	3	20.6/67.34
2	L-carvone	ID	10	45.48	16.38/48.83
3	L-carvone	ID*	10	6.5	56.6/14.54
4	L-carvone	ID**	10	77.23	11.64/36
5	L-carvone	ID***	10	12	29.95/35.68
6	Limonene	ID**	10	96	64.23/19.15
7	Limonene	ID	10	86.6	67.03/11.9
8	Cis-stilbene	ID**	10	63.22	90.36
9♦	Trans-stilbene	ID**	10	92.49	87.7 / 60**
10	α-terpineol	ID**	7	100	82 / 55**
11	α-methyl styrene	ID**	5	100	80

Reaction Conditions: Substrate concentration – 0.064 mol, Isobutyraldehyde – 0.19mol, Acetonitrile -35g, catalyst loading – 0.66g mol^{-1}, air flow - 250ml min^{-1}, Temperature = 25°C, * = reaction conducted with co-reagent, solvent and no catalyst, under the same conditions mentioned. ** = isolated yield, g mol^{-1} of catalyst load signifies g of catalyst per sum of mole of co-reagent and substrate together.
♦ = Solvent used chloroform.

Mass spectrum of trans-stilbene epoxide showed m/z (EI) 196 with peaks and relative intensities, %) as 178(20.2), 167 (100), 152(15), 105(18), 90(75), 77(20), 63(14), 51(14.4)
FT-IR (KBr, cm^{-1}) of trans-stilbene epoxide showed peaks 3038 (C-H stretching vibrations), 853, 1282(C-O-C stretch)
^{1}**H-NMR** (300 MHz, $CDCl_3$, ppm) of trans-stilbene epoxide showed 3.865(s, 2H, CH-O-CH), 7.24-7.415 (m, 10H, aromatic).
Mass spectrum of α-terpineol epoxide showed m/z (EI) 170, with peaks and relative intensities, %) as 152(1.91), 137.3(6.54), 108(12.92), 93.15(12.49), 71.15(50.22), 55.15(22.21), 43.1(100).
FT-IR (KBr, cm^{-1}): of α-terpineol epoxide showed peaks 1653 (C=O stretching vibrations), 839, 753, (C-O-C asymmetric stretch), 1295(C-O-C symmetric stretch)
^{1}**H-NMR** (300 MHz, $CDCl_3$, ppm) of α-terpineol epoxide: 1.126(s, 3H, CH_3), 1.144(s, 3H, CH_3), 1.160(s, 3H, CH_3), 3.002-3.08(t, 1H, CH), 1.317-2.20(m, 7H, cyclohexane), 5.38 (s, 1H, OH)
Mass spectrum of L-carvone epoxide showed m/z (EI) 166, with peaks and relative intensities, %) as 138.1(1.64), 123(20.91), 95(23.73), 67.1(48.23), 43.05(100).
Mass spectrum of L-carvone diepoxide showed m/z (EI) 182, with peaks and relative intensities, %) as 166.6(0.36), 151(3.24), 123(13.62), 109(100), 82.1(56.64), 65.1(17.88), 51.1(18.18), 41.05(49.16).
FT-IR (KBr, cm^{-1}): of L-Carvone epoxide showed peaks 896, 803, (C-O-C asymmetric stretch), 1248 (C-O-C symmetric stretch)
Mass spectrum of Limonene monoepoxide showed m/z (EI) 152, with peaks and relative intensities, %) as 137(14), 123(5), 108(79), 94(100), 81(64), 67(90), 51(4.16).
FT-IR (KBr, cm^{-1}): of Limonene epoxide showed peaks 835, 878, 791 (C-O-C asymmetric stretch)
Mass spectrum of Limonene diepoxide showed m/z (EI) 168, with peaks and relative intensities, %) as 152(29.16), 137(29), 108(35.4), 93(33.33), 82(22.91), 71(100), 51(8.33).

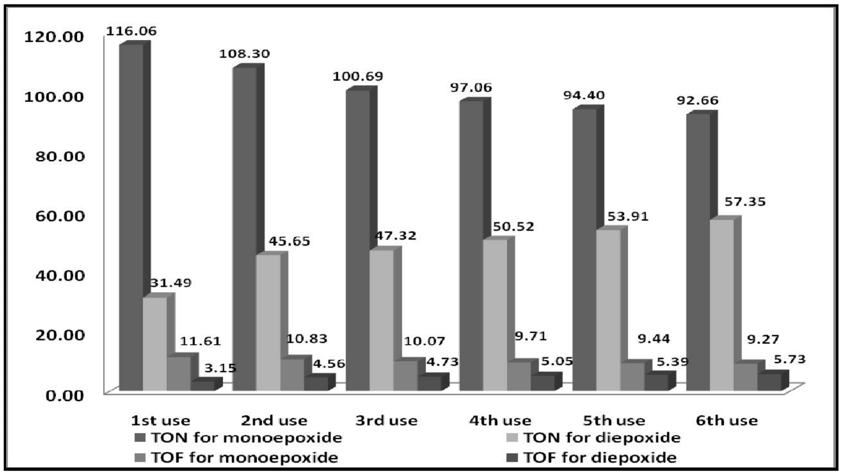

Fig. 8: Catalyst reuse, TON and TOF for catalyst 1D**

Reaction Conditions: Limonene concentration –0.064 mol, Isobutyraldehyde – 0.19mol, Acetonitrile -35g, catalyst loading – 0.66g mole^{-1}, air flow - 250ml min^{-1}, Temperature = 25°C, g mol^{-1} of catalyst load signifies g of catalyst per sum of mole of co-reagent and substrate together.

The oxidation reaction displayed a strong dependence on choice of solvent, effect of catalyst loading, effect of temperature and effect of co-reagent concentration and catalyst loading. Hence effect of solvent, effect of solvent and catalyst loading, co-reagent concentration were further studied for L-carvone, using catalyst 1D**.**

Influence of solvent

Table 4. Influence of solvent on L-carvone epoxidation

Entry No.	Substrate	Solvent used	Time /h	Alkene conv./%	monoepoxide /diepoxide selectivity
1	L-carvone	n-hexane	10	35.75	15.85/51.38
2	L-carvone	Acetone	10	60.84	16.38/28.05
3	L-carvone	Isopropyl alcohol	10	62.69	15.46/19.72
4	L-carvone	Acetonitrile	10	77.23	11.64/36.0

Reaction Conditions: Substrate concentration – 0.064 mol, Isobutyraldehyde – 0.19mol, solvent-35g, catalyst ID** loading – 0.66g mol^{-1}, air flow - 250ml min^{-1}, Temperature = 25°C, g/moles of catalyst load signifies g of catalyst per sum of mole of co-reagent and substrate together.

The solvent effect on this oxidation reaction was studied by performing the reaction in a variety of solvents with differing polarity. The solvents employed were acetonitrile, acetone, isopropyl alcohol and n-hexane using catalyst 1D**. During the comparison, the reaction conditions, catalyst loading, quantity of the reactant and co-reagent, quantity of solvent were kept unaltered. The polarity of solvent had a profound influence on conversion and selectivity can be clearly observed in Table 4. In the presence of n-hexane, the % conversion and % selectivity values were (10h, 35.75, 15.85/51.38), where as in the presence of acetone the conversion and selectivity were (10h, 60.84, 16.38/28.05). The selectivity was highest when n-hexane was used as a solvent. Presence of Isopropyl alcohol leads to formation of side reaction products, which can be observed by the values of mono and diepoxy selectivities. Presence of acetonitrile resulted in good conversion and moderate selectivity of the epoxides. It was concluded that the radical reactions are rather sluggish in non polar solvent but the product selectivities are higher. Solvent-catalyst-solute interactions are predominant in case of polar nonprotic solvent. The reduction of such interactions can lead to lower

TON as in case of non polar solvent n-hexane, however the reaction path appears to proceed in a selective direction in case of non-polar solvent.

Influence of Catalyst loading

Table 5. Influence of Catalyst loading on Conversion and Selectivity, catalyst 1D**

Entry	Catalyst loading	Time, h	% Conversion	% Selectivity for monoepoxide /diepoxide
1	0.66g/mole	10	68.8	12.73/33.75
2	1.32g/mole	10	77.23	11.64 / 36

Reaction Conditions: Reactant concentration – 0.064 mol, Isobutyraldehyde – 0.19mol, solvent acetonitrile-35g, catalyst 1D** air flow - 250ml/min, Temperature = 25°C, g/mole of catalyst load signifies g of catalyst per sum of mole of co-reagent and reactant.

The effect of catalyst loading for catalyst 1D*** on the conversion of L-carvone and product selectivity for monoepoxide as well as for diepoxide was studied at two different catalyst loadings of 0.66g/mole and 1.32g/mole. The other reaction parameters like temperature, quantity of reactant and co-reagent were kept constant. At 0.66 g mol^{-1} catalyst loading, the conversion and selectivity values were (10h, 77.23, 11.64/36). It was observed that high conversion and low selectivity values (10h, 79.42, 14.17/23.37) were obtained when the catalyst loading was doubled to 1.32 g mol^{-1}, can be observed in table 5**.** The pronounced variation in product distribution values can be attributed to the advanced oxidation of the L-carvone, which led to the formation of side products. The study indicates that there was an enrichment of oxygenated- Schiff base-metal complex, involved in catalyzing the reaction at a higher rate.

Influence of Temperature: Effect of temperature on the oxidation of L-carvone was studied at two different temperatures (25°C and 40°C) with the reaction conditions mentioned under fig.9. The results showed that the kinetic profile at both higher and lower reaction temperature is similar, the major difference being the equilibrium values of selectivity. The equilibrium conversion at 25°C and 40°C at 76.12% and 84.58% respectively was higher at higher temperature while the selectivity for monoepoxide at 12.39% and 14.2% respectively was also higher at higher temperatures. The selectivity values for diepoxide at 25°C and 40°C were 38.32 and 19.25 respectively. Higher temperature leads to side reactions, which can be observed from the diepoxide selectivity values. The monoepoxide selectivity was found to be higher at higher temperature. It can be concluded from the results that 25°C is the most suitable temperature for Mukaiyama oxidation of L-carvone using catalyst 1D**.

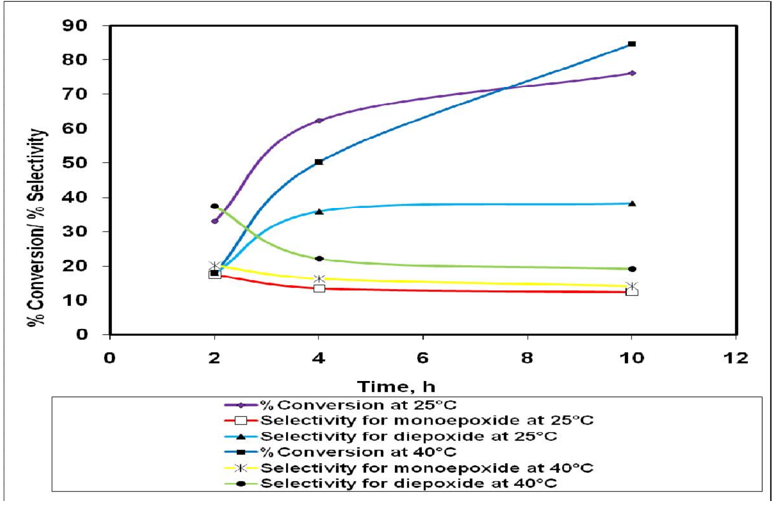

Fig. 9: Influence of Temperature on Conversion and Selectivity, catalyst ID***

Influence of Co-reagent concentration

Table 6. Influence of Co-reagent concentration

Entry	Co-reagent Concentration, moles /mole of reactant	% Conversion	% Selectivity for monoepoxide /diepoxide
1	1.58	47.11	18.05 / 53.2
2	3.16	77.23	11.64 /36

Reaction Conditions: Reactant concentration-0.064 mole, Isobutyraldehyde as co-reagent-1.48 mole of co-reagent/mole of reactant (mole of co-reagent -0.095), co-reagent - 2.968 mole of co-reagent/mole of reactant (mole of co-reagent- 0.19), solvent acetonitrile-35g, catalyst ID**, 0.66gmol^{-1}, air flow-250ml min^{-1}

Isobutyraldehyde was used as a co-reagent in the reaction; hence the influence of variation in co-reagent concentration was investigated at two different co-reagent loadings such as 1.48mole/mole of reactant (mole of co-reagent, 0.095) and 2.968mol (mole of reactant 0.19mol) under the reaction conditions mentioned below Table 6**.** It can be observed from the conversion and selectivity values, that the % conversion was higher (10h, 77.23), when the co-reagent concentration was higher, whereas selectivity values were (11.64/36) for mono and diepoxide. At lower co-reagent concentration the conversion and selectivity values were (10h, 47.11, 18.05/53.2). It can be observed that, at lower co-reagent concentration the selectivity for mono and diepoxide was high. It can be concluded that lower co-reagent concentration does not promote side reactions; hence the selectivity values are higher.

Kinetics of oxidation of Limonene by catalyst 1D:** The reaction displays first order kinetics with Limonene under the optimized reaction conditions mentioned under Fig.10. The kinetic plot of experimental data was made and the first order rate constant – k was calculated as shown in Fig. 10. The first – order rate constant for the oxidation of Limonene with catalyst 1D****** was measured as -0.927 mol L^{-1} h^{-1}.

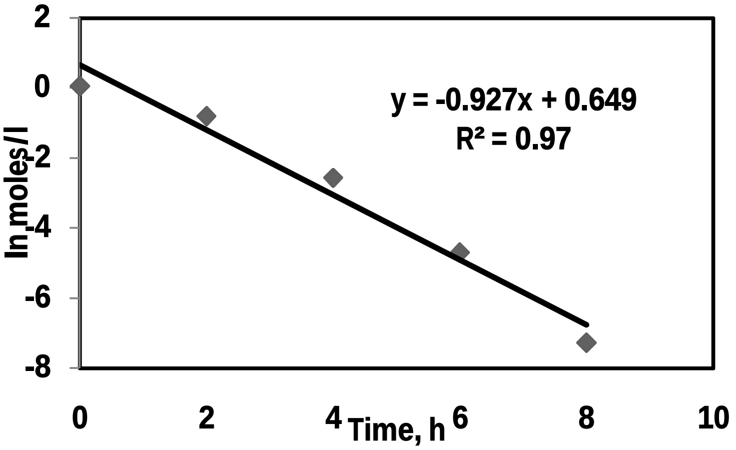

Fig. 10: Kinetics of epoxidation of Limonene by catalyst ID**

Reaction Conditions: Limonene concentration – 0.064 mol, Isobutyraldehyde – 0.19, Acetonitrile -35g, catalyst loading – 0.66g mol^{-1}, air flow - 250ml min^{-1}, Temperature = 25°C, g mol^{-1} of catalyst load signifies g of catalyst per sum of mol of co-reagent and reactant.

Mechanism of Mukaiyama Oxidation: The transition-metal catalyzed epoxidation of alkenes using molecular oxygen and *i*-butyraldehyde as a co-reagent (the Mukaiyama epoxidation) was studied in detail by Nam *et al* [49]. It was proposed that autoxidation of aldehyde plays an important role in this metal catalyzed reaction, just as it does in the uncatalyzed oxidation of alkene and aldehyde with molecular oxygen. It was concluded that the oxidizing species is an acylperoxy radical, and not a peroxy acid. Acylperoxy radicals are known to preferentially react with the double bonds of alkenes yielding epoxides. It was also concluded that the only role of the metal complex was the stabilization the acylperoxy radical as shown in fig.11. This acyl peroxy radical, which is stabilized by the complex formation with the catalyst, further reacts with the alkene to transfer oxygen as shown in step 4**.** The generated acid can undergo further oxidation to give out carbon dioxide.

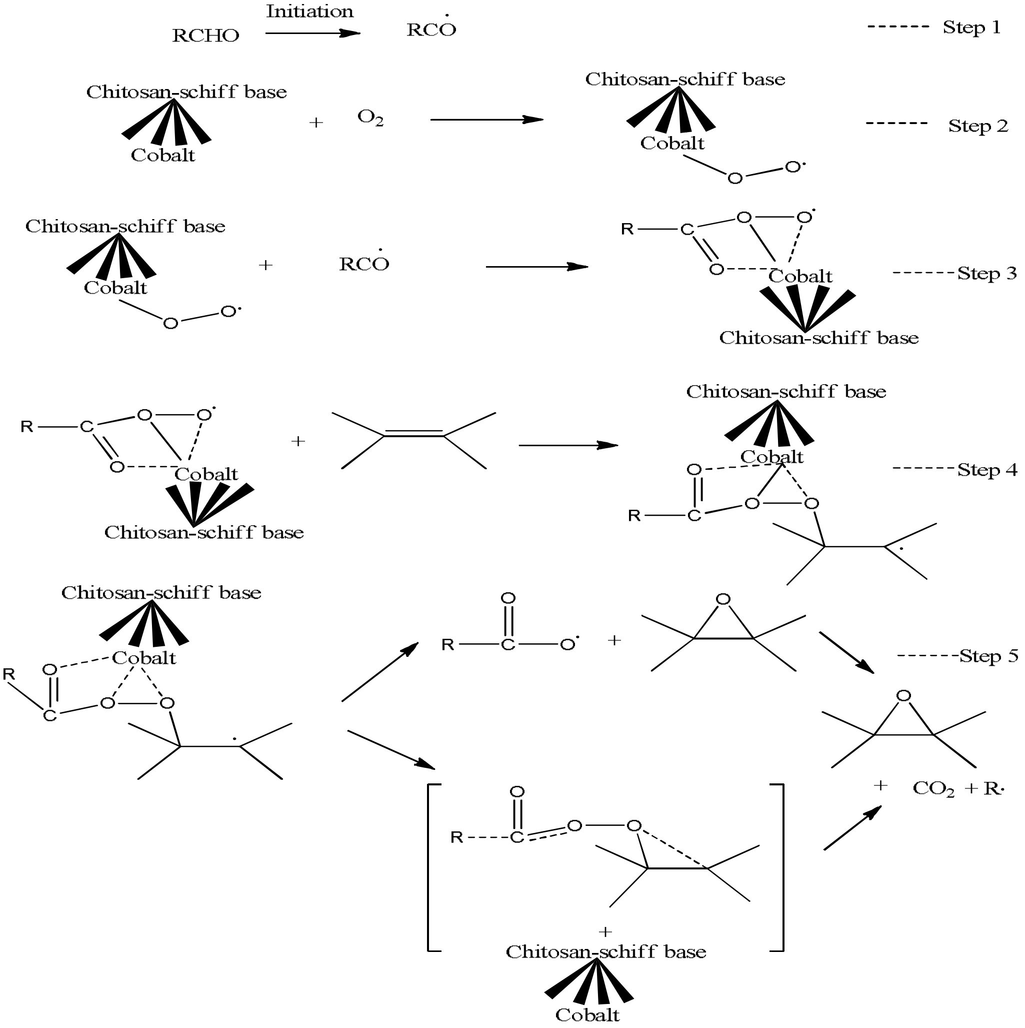

Fig. 11 Mechanism of Mukaiyama oxidation.

APPLICATIONS

The Chitosan-Schiff base-metal complexes have been used as efficient heterogeneous catalysts for the Mukaiyama oxidation at room temperature**.**

CONCLUSIONS

We have demonstrated a new method to prepare four novel, heterogeneous, chitosan-based Schiff base substituted with triazene, ethylene diamine and salicylaldehyde and its manganese, copper, cobalt and nickel complexes (**1D-1D*****), characterized by IR, NMR, elemental and ICP-AES analysis methods.

Efficiency of these catalysts was tested with L-carvone, Limonene, cis-stilbene, trans-stilbene, α-terpeneol, α-methyl styrene. During the study we found that Cobalt loaded catalyst (ID**) was found to be the most efficient catalyst. n-Hexane was found to be promising solvent for selectivity, where as acetonitrile was found to be good solvent for conversion and moderate for epoxide selectivity. Doubling the catalyst loading leads to increase in conversion but reduces the selectivities of epoxides. Higher temperature (40°C) improves the conversion but hampers the selectivities for mono and diepoxides. Lowering the co-reagent concentration lowers the conversion but enhance the selectivities for mono and diepoxides. The catalyst 1D** was used six times for limonene epoxidation without loss in its catalytic activity. During the first use TON are 116.06 and 31.49 for monoepoxide and diepoxide respectively, and the TOF are 11.61, 3.15 for mono and diepoxide respectively. The oxidation reaction was dependent on catalyst loading, temperature, type of solvent and co-reagent concentration. Present results illustrate that chitosan can be chemically modified into a stable ligand, which can form a complex with metal, resulting in a promising catalyst. The natural abundance and biodegradability of chitosan makes it easily obtainable and an environmentally benign catalyst for the current application in industry.

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