

Chitosan-based Schiff base-metal complexes (Mn, Cu, Co) as heterogeneous, new catalysts for the β -isophorone oxidation

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Abstract. A new chitosan-based Schiff base was prepared and complexed with manganese, cobalt and copper. These Schiff base metal complexes were used as heterogeneous catalysts for the air oxidation of β -isophorone to ketoisophorone. The obtained complexes were characterized by means of FT-IR, ¹HNMR spectroscopy, elemental analysis, powder X-ray diffraction, field emission gun scanning electron microscopy, electron spin resonance spectroscopy, ICP-AES and solubility tests. Thermal properties were also investigated using thermal gravimetric analysis. Data obtained by thermal analysis revealed that these complexes showed good thermal stability. The conversion and selectivity of β -isophorone to ketoisophorone for each prepared catalyst was studied using a batch reactor and gas chromatography for product identification and quantification. The results were compared against the homogeneous *bis*-salicylaldehyde ethylenedi-imine-Mn catalyst. The use of methanol, acetone, methyl isobutyl ketone and *n*-hexane as solvent and its effect on conversion and selectivity was also investigated. Acetone was found to be a promising solvent for the β -isophorone oxidation. The role of triethyl amine and acetyl acetone in the oxidation reaction has also been investigated.

Keywords. Acetone; β -isophorone; chitosan-triazene-ethylenediamine-salen-Mn; ketoisophorone.

1. Introduction

The development of heterogeneous catalysts for fine chemical synthesis has gathered paramount interest in the research field due to their recovery and reusability and their major impact on the environmental performance of a given synthesis.^{1,2} The majority of these catalysts are based on silica, since silica displays much advantageous properties *viz.*, stability, high surface area, porosity and affinity to organic groups, which provide catalytic centres and can be easily affixed to the silica surface. 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.³ The flexibility of the material, its insolubility in the vast majority of common solvents along with its inherent chirality makes chitosan as 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^{4–7} and for phenol and nitroaromatics using Ni, Cu, Cr, Zn.^{8–11} Functionalization of the chitosan support has also been studied for

the cyclopropanation of olefins (Cu-Schiff base),¹² oxidation of alkylbenzenes (Mn or Ni-Schiff base)¹³ and the oxidation of DOPA (3, 4-dihydroxyphenylalanine) with (Co-Salen).¹⁴ A patent to UOP¹⁵ 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,¹⁶ ester synthesis in non-aqueous media,¹⁷ breakage of glycosidic linkages,¹⁸ hydrolysis of casein (important reaction in cheese industry),¹⁹ synthesis of a monoglycerides from palm oil triglycerides.²⁰

Oxidation of organic molecules using molecular oxygen to oxygenated compounds is an important industrial reaction. There are numerous commercial applications of catalytic liquid phase oxidation reactions of aliphatic, aromatic and cyclic organic compounds to give corresponding oxygenated derivatives. Schiff base transition metal complexes are widely reported as effective catalyst systems for the selective oxidation of cyclic olefins under milder conditions. The oxidation of β -isophorone to ketoisophorone is one example of such chemistry, which is an industrially important reaction. Ketoisophorone is an important intermediate in the industrial synthesis of vitamin E. Ketoisophorone

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is used as a building block for the synthesis in terpene chemistry and for producing compounds of vitamin A, E series and carotenoids. Oxidation of β -isophorone has been reported using homogeneous catalyst such as Mn-Salen, Co salen,^{21,22} or using heterogeneous catalysts such as silica immobilized metal catalysts,²³ or zeolite encapsulated Co (II) saloph,²⁴ complexes. The conversion efficiency of these catalyst systems is low with conversion of β -isophorone of only 17% and 25.8% reported for the silica and zeolite systems, respectively. This represents a significant area of improvement especially for an industrially important synthesis. We have presented here a systematic study involving the use of chitosan-based chemically modified chitosan Schiff base-metal complex as a heterogeneous catalyst for the oxidation of β -isophorone with excellent activity. The role of acetyl acetone and triethyl amine, which are used as additives in the reaction system, has also been established in this paper.

2. Experimental

2.1 Materials

Chitosan from prawn (degree of deacetylation 80%) was procured from Indian Sea Foods (Cochin). Reagents and solvents used for the preparation of catalysts were procured from E Merck and SD fine Chemicals. Pure β -isophorone was procured from SI-Group (I) Ltd. Zero air (Iolar) was used as the oxygen source for the oxidation reaction.

2.2 Techniques

Reaction samples were analysed with Agilent 6890 Gas chromatograph using FID detector in a Varian CP 8934 capillary column with dimensions of 10 m length x 100 μ m diameter x 0.40 μ m film thickness with GC parameters as specified.¹ Ketoisophorone was characterized by GC-MS,² IR and ¹H NMR studies. Using the GC parameters conversion and selectivity for each run were determined. XRD analysis of the catalysts was performed using X'pert Pro from P analytical using wavelength 260–850 nm. Elemental analyses (C, N, H) were performed using Flash EA-1112 Series instrument. Infrared spectra of the Schiff base and the complex were recorded in the Model Magna-550 and Shimadzu 8400S series machines. The ¹H NMR spectrum of the Schiff base in DMSO-d₆ was obtained

using a Bruker Avance-300 MHz NMR spectrometer. Manganese content was determined by ICP-AES on ICAP - 6200 duo, Electron spin resonance spectra were determined using E-112 ESR spectrometer USA, while BET surface area analyses were determined using Tristar 3000V6.05A using nitrogen adsorption. The morphology of the catalysts was observed using field emission gun scanning electron microscope (FEG-SEM) using JSM-7600F; Thermogravimetric analyses (TGA) were recorded in a Dupont-2000 USA thermogravimetric modulus machine. The samples were heated under nitrogen flow at 5°C/min until 400°C while recording weight changed.

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

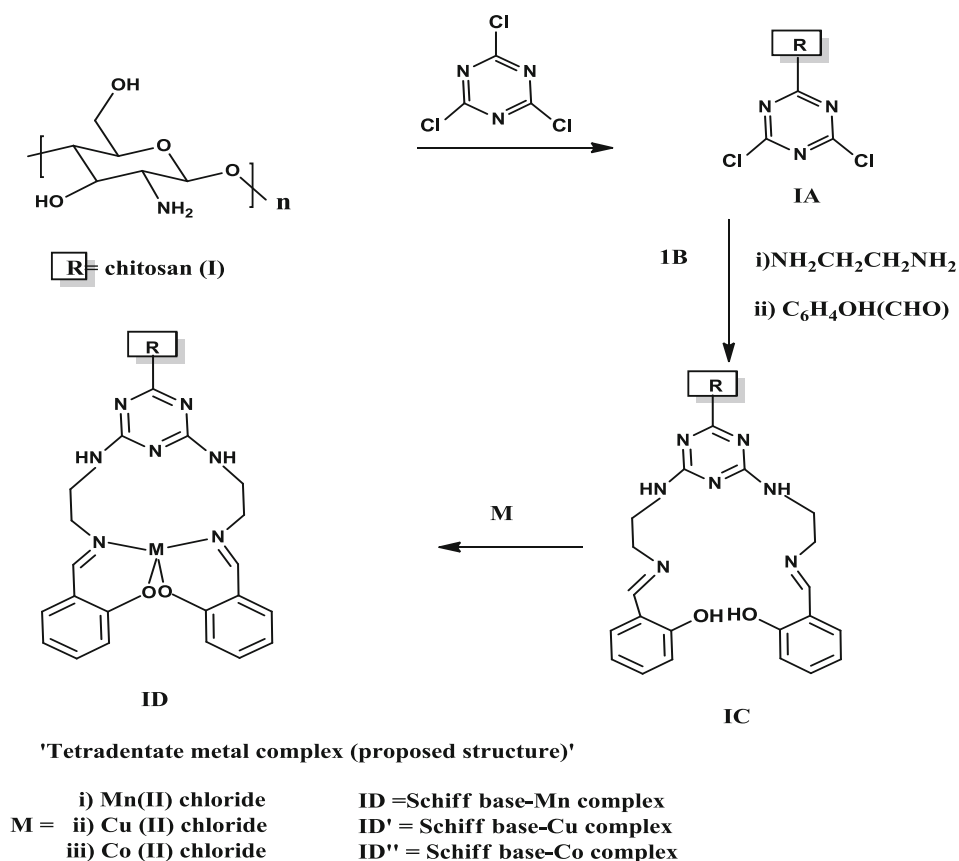
2.3 Synthesis of catalysts

2.3a Synthesis of Schiff base IC (scheme 1): The precursor IB required for the preparation of IC was prepared by following the literature methods using dioxan as a solvent.²⁵ Schiff base IC was prepared by mixing IB (20 g) with 32 ml of glacial acetic acid and 100 ml of methanol followed by the slow addition of salicylaldehyde (11.96 g, 0.098 mol) over 30 min. The mixture was refluxed for 24 h with efficient stirring. The resulting Schiff base IC was cooled, filtered and washed with ethanol (200 ml) and acetone (200 ml). The solid residue after filtering and washing was dried in an oven at 80°C for 3 h (yield = 21 g, 66%).

2.3b Synthesis of chitosan Schiff base - manganese based tetradentate metal complex ID: A literature method²⁶ was modified and used for the synthesis of Schiff base-metal complex. In a round bottom flask IC (4 g) was mixed with 40 ml of DMSO, further a solution of KOH (0.84 g, 0.015 mol) in methanol was added. The mixture was heated to 80°C. A solution of anhydrous manganese chloride (2.77 g, 0.022 mol) in methanol was added further. The mixture was refluxed for the period of 6 h. The contents were cooled, and quenched with 190 ml of acetone and 50 ml of *n*-hexane to precipitate the heterogeneous catalyst. The resulting catalyst was filtered and washed with water till free from any occluded manganese chloride, then washed with 200 ml of acetone. The final solid was dried in oven at 80°C for 3 h (yield = 3.8 g, 86.95%). A similar method was adopted for the preparation of copper and cobalt based catalysts **ID-ID'**.

¹Oven, 100°C–45°C/min–280°C – 2min hold., Inlet, 250°C, Detector, 300°, split ratio, 1:500, sample injection, 0.2 μ l.

²Gas chromatograph combined with mass spectrometry.



Scheme 1. Preparation of catalyst ID-ID''.

3. Results and discussion

3.1 Characterization of catalysts

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

3.1a XRD analysis of chitosan (I), Schiff base (IC) and its manganese, copper and cobalt based metal complexes (ID – ID''): The XRD patterns of chitosan, Schiff base and corresponding metal complexes (I – ID'') are shown in figure 1.

There are no reference diffraction data available for powders of new catalysts ID-ID'' 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.²⁷ This suggested the formation of inter and intra-molecular hydrogen bond in chitosan. In case of Schiff base IC, the reflection at 2θ of 9.93° disappears completely and new reflection appears at $2\theta = 6.38^\circ$ and 6.97° , where as the reflection at 2θ of 19.97° was found to shift at 20.77° . This demonstrated the formation of imine and deformation

of hydrogen bonds in chitosan backbone. The substitution resulted in increased crystallinity of Schiff base IC compared with chitosan. The increase in crystallinity of Schiff base can be explained. The change of crystallinity is mainly dependent on the formation of a Schiff base and to some extent on other factors, such as spacial hindrance, hydrophobic force and $\pi-\pi$ stacking.²⁸ In the present case, this chitosan-based Schiff base compound has different aromatic substituent groups and long hydrophobic chain. Thus, it

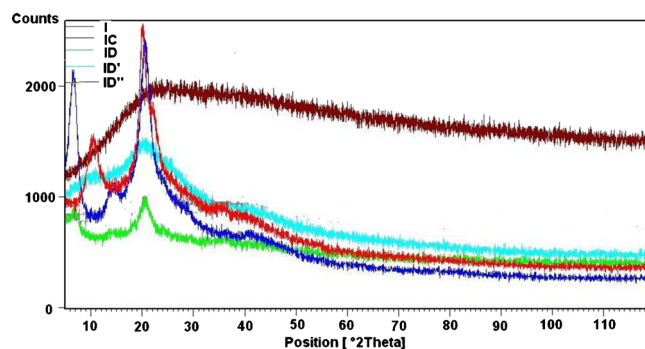


Figure 1. XRD analysis of chitosan (I), Schiff base (IC), and chitosan Schiff base-Mn (ID), chitosan Schiff base-Cu complex (ID') and chitosan Schiff base-Co (ID'').

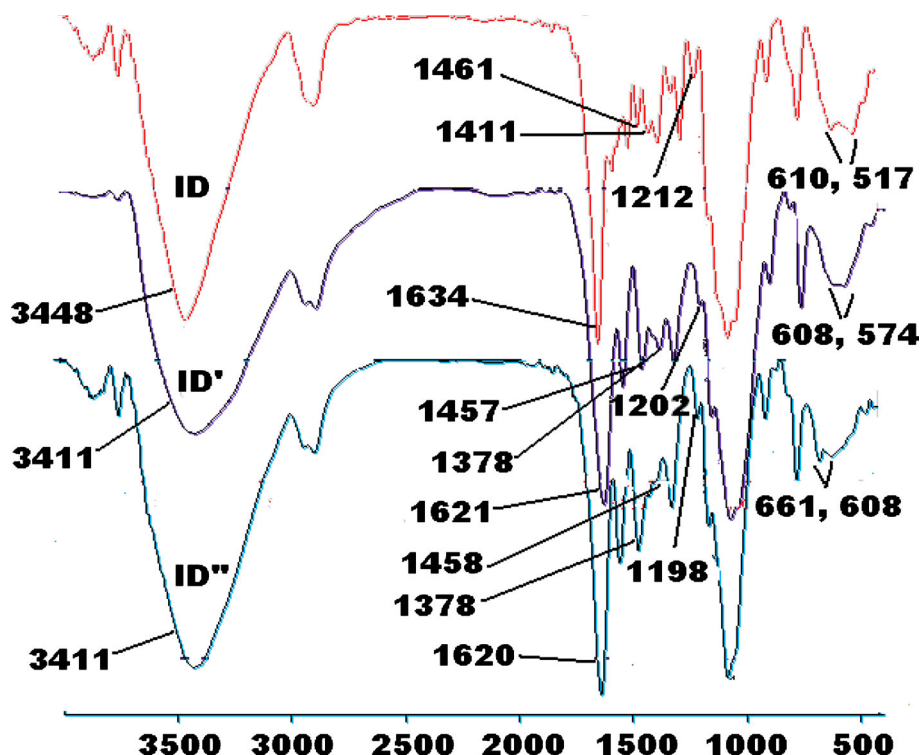


Figure 2. Chitosan Schiff base-Mn(ID), chitosan Schiff base-Cu complex (ID') and chitosan Schiff base-Co (ID'').

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 ID-ID'' showed decrease in crystalline character. This observation was similar to that reported by Ti Feng *et al.*²⁹ where chitosan-salicylaldehyde Schiff base was complexed with copper.

3.1b FT-IR characterization of Schiff base(IC) and their metal complexes (ID-ID''): The metal complexes (ID-ID'') were characterized by FT-IR spectra as shown in figure 2. The characteristic bands of FT-IR spectrum of Schiff base IC are given in table 1. IC is characterized by OH and NH band at 3455 cm⁻¹, an intense imine C=N band^{30,31} at 1635 cm⁻¹. The band at 1214 cm⁻¹ corresponds to C-O phenolic. Bands at

1462 cm⁻¹ and 1412 cm⁻¹ assigned to the characteristic CH₂-CH₂ bands. Some obvious shifts were seen in the FT-IR spectra of metal complexes as shown in figure 2. The vibrations of O-H and N-H groups of chitosan-Schiff base compound IC appeared at 3455 cm⁻¹ which was shifted to lower wavelength for the corresponding metal complexes, 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 metal complexes. The C-O vibrations of Schiff base IC at 1214 cm⁻¹ was weakened in the case of catalysts, indicating that hydroxyl hydrogen is replaced by metal to form Schiff base-metal complex.^{30,32,33} The characteristic CH₂-CH₂ bands of the corresponding metal complex ID showed shift at 1461 cm⁻¹, 1411 cm⁻¹. All the IR data suggest that the metal was bonded to

Table 1. IR characterization of Schiff base IC and catalysts ID-ID''.

Schiff base IC/ catalyst	ν OH,NH cm ⁻¹	ν C= N cm ⁻¹	ν CH ₂ -CH ₂ cm ⁻¹	Phenolic C-O cm ⁻¹	ν M-O cm ⁻¹
Schiff base (IC)	3455	1635	1462, 1412	1214	-
ID	3448	1634	1461, 1411	1212	Medium, 610
ID'	3411	1621	1457, 1378	1202	Medium, 608
ID''	3411	1620	1458, 1378	1198	Medium, 661

Table 2. Elemental analysis and BET surface area of catalysts.

	% C	% H	% N	% metal content	BET surface area m ² /g
Chitosan (I)	39.495	7.407	7.638	–	–
Schiff base (IC)	47.020	5.439	10.002	–	–
Schiff base-Mn (ID)	43.724	4.950	9.205	7.24	6.45
Schiff base-Cu (ID')	44.073	5.012	9.298	6.45	0.65
Schiff base-Co (ID'')	43.146	4.841	9.044	8.55	17.47

the Schiff bases through the phenolic oxygen and the imino nitrogen.^{34,35} Medium bands were observed at 610 cm⁻¹, 608 cm⁻¹, 661 cm⁻¹ in the spectra of **ID**, **ID'**, **ID''**. These were assigned to the metal-oxygen stretching vibration in each of these chelates.³⁶

3.1c ¹H - NMR characterization: The ¹H – NMR of Schiff base **IC** was determined in DMSO-d₆ (refer to Supplementary information).

It can be observed from the δ (ppm) values that a broad singlet peak in down field region at 12.78 δ was assigned as substituted aromatic OH group. This assignment was confirmed by D₂O exchange. The broad peak at 4.5 δ was assigned as an imine proton which was also confirmed by D₂O exchange. 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 in 3.33 δ .³⁷ The methyl group in the acetyl group of chitosan, which was present due to degree of acetylation in chitosan, was assigned at 1.77 δ .³⁷ All these data evidently proved the formation of **IC**.

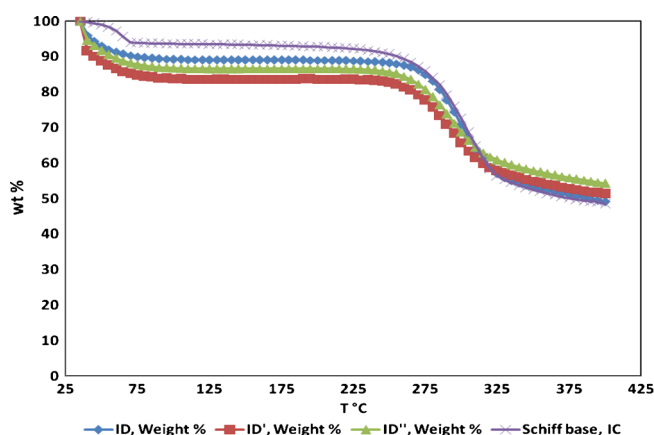
3.1d Elemental analysis and BET surface area of the catalysts: The prepared catalysts were analysed for carbon, nitrogen and hydrogen (table 2). It can be observed that Schiff base **IC** was substituted with triazene, ethylene diamine and salicylaldehyde (scheme 1) and hence returned a high N content than chitosan. The metal content of each catalyst was determined by ICP-AES and showed metal loadings considerably high.

3.1e TGA analysis of catalysts: The thermal properties of Schiff base **IC** and 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 figure 3. Schiff base and catalysts exhibited good resistance to thermal decomposition up to 240°C in nitrogen

and began to decompose gradually above the temperature. At 400°C, Schiff base **IC** and catalysts **ID**, **ID'** and **ID''** showed 51.6%, 50.89, 48.74, 45.74 % decomposition, respectively, indicating that the catalysts are more stable than chitosan-Schiff base.

3.1f Morphological studies of catalysts (ID-ID''): The scanning electron micrographs of chitosan, chitosan-Schiff base and chitosan-Schiff base-metal complexes **ID**, **ID'**, **ID''** are shown in figure 4a–e and, respectively at a magnification of 100000 X. The distinct morphology of chitosan, chitosan-Schiff base and chitosan Schiff base-metal complexes can be observed. Figure 4a showed the flaky nature of chitosan, which is modified into porous polymer in case of Schiff base **IC**, (figure 4b). Also figure 4c showed that the manganese-based complex reformed into a more porous form than the Schiff base **IC**. Copper-based complex (figure 4d) showed less porosity when compared with the manganese form, whereas cobalt-based complex (figure 4e) showed porosity of almost similar magnitude to that of manganese-based complex.

3.1g Heterogeneity of catalysts (ID-ID''): It is well-known that the dissolution of polymers depends not only on their physical properties, but also on their

**Figure 3.** TGA of Schiff base **IC** and catalysts **ID-ID''**.

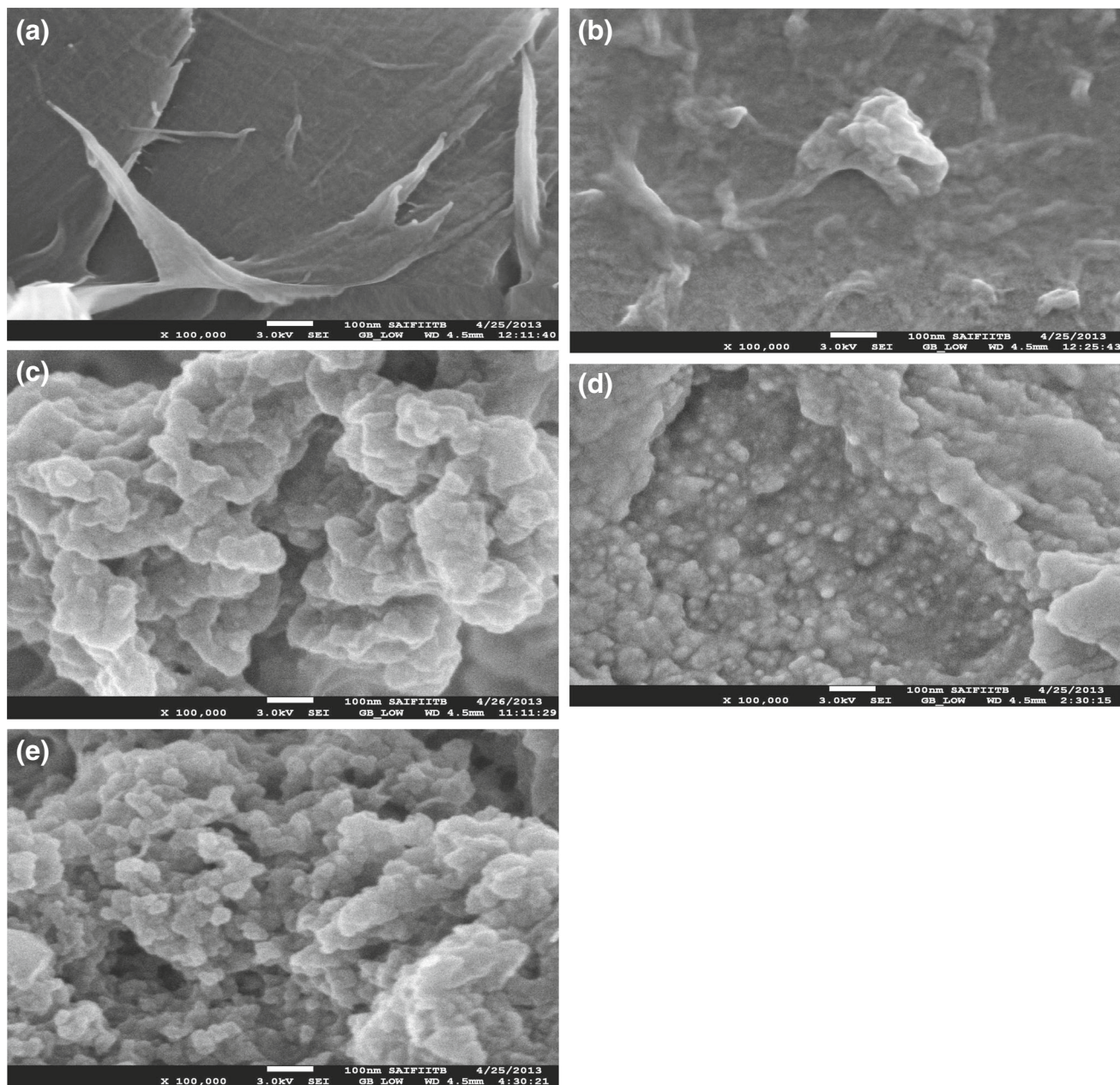


Figure 4. (a) FEG-SEM image of I chitosan. (b) FEG-SEM image of IC chitosan-Schiff base. (c) FEG-SEM image of ID chitosan-Schiff base-Mn complex. (d) FEG-SEM image of ID' chitosan-Schiff base-Cu complex. (e) FEG-SEM image of ID'' chitosan-Schiff base-Co complex.

chemical structure. One of the main objectives of this study was to produce efficient 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 in 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 (**IB**, scheme 1) was soluble in water, but not soluble in *n*-hexane, acetone, dichloromethane,

ethanol and methanol. Further, introduction of salicylaldehyde moiety with the formation of a Schiff base (**IC**) 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 (**IC**) was only soluble at 80°C in DMSO with 7% concentration. The catalysts (**ID-ID''**) were found to be insoluble in *n*-hexane, acetone, chloroform, ethanol, methanol, water and even in DMSO at room temperature.

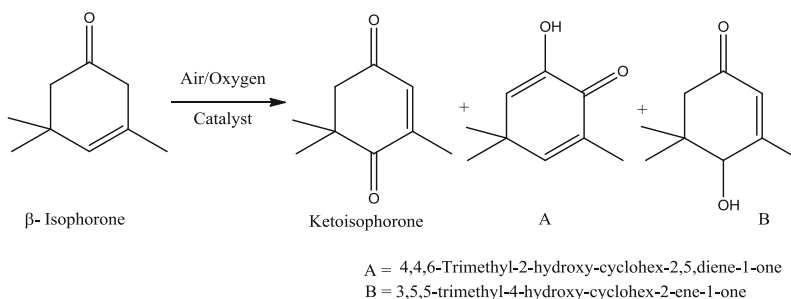


Figure 5. Schiff base-Mn complex catalysed oxidation of β -isophorone.

4. Catalyst activity testing

The catalytic activity of three different chitosan-based Schiff base-metal complexes (**ID-ID''**) were tested in the oxidation reaction of β -isophorone as represented in figure 5. A and B represent the side products formed in this reaction as per the literature.²² In a typical β -isophorone oxidation, the optimized concentration of additives along with solvent concentration, temperature and air flow is mentioned in table 3. The reaction was found to reach equilibrium conveniently before 18 h and hence the reaction time was maintained at 18 h for all the catalysts.

Catalyst **ID** was recycled five times without significant loss in catalytic activity. Each time the catalyst was washed with acetone, dried at 80°C and then reused. This has been represented graphically in terms of **TON** and **TOF** in figure 6. After the period of five cycles, we found that the catalyst was less active. The typical turn over number (**TON**) and frequency (**TOF**) observed during the first run are 277.18 mol/mol of catalyst and 15.4 mol/mol/h, respectively.

The oxidation reaction displayed a strong dependence on temperature and choice of solvent. Hence the effect of temperature, solvent and catalyst loading was further studied using manganese-based catalyst **ID**.

4.1 Influence of solvent

The solvent effect on this oxidation reaction was studied by performing the reaction in a variety of solvents with differing polarity (table 4). The solvents employed

were methanol, methyl isobutyl ketone (MIBK) and *n*-hexane using catalyst **ID**. During the comparison, reaction conditions, catalyst loading, quantities of reactant, additives and solvent were kept unaltered. The polarity of solvent had a profound influence on conversion and selectivity which can be clearly observed from table 4. In a non-polar solvent-like *n*-hexane, conversion and selectivity values were (18 h, 52.5, 55.2) (entry 1). The selectivity was highest when acetone was used as a solvent (18 h, 83.7) (entry 2). In the presence of MIBK the conversion and selectivity values were (18 h, 70.5, and 71.2) (entry 3), whereas in the presence of methanol, the conversion and selectivity values were (10 h, 99.9, 7.1) (entry 4). It was concluded that solvent–catalyst–solute interactions are predominant in the case of polar non-protic solvent. The absence of such interactions can lead to lower TON as in the case of non-polar solvent *n*-hexane. The polarity index values differed marginally between acetone and MIBK at 5.1 and 4.2, respectively. However, the interactions were more significant when acetone was used as a solvent. In case of methanol, the conversion was rapid, but the selectivity values were lowest. A significant amount of α -isophorone was formed instead of ketoisophorone, when methanol was used as a solvent. These observations were in consonance with the observations made by Costantini *et al.*²¹ while studying this reaction using homogeneous salen-manganese catalyst.

4.2 Influence of temperature

Effect of temperature on the oxidation of β -isophorone was studied at four different temperatures (10°C, 21°C,

Table 3. Quantities of reactant, additives and reaction conditions for oxidation of β -isophorone.

β -Isophorone mol	Acetyl acetone, g	TEA, g	Water, g	Cat. amount, g/mol	Acetone, g.	T°C	Air flow, ml/min
0.062	0.10	3.15	1.7	1.6	36	21	200

TEA: Triethyl amine

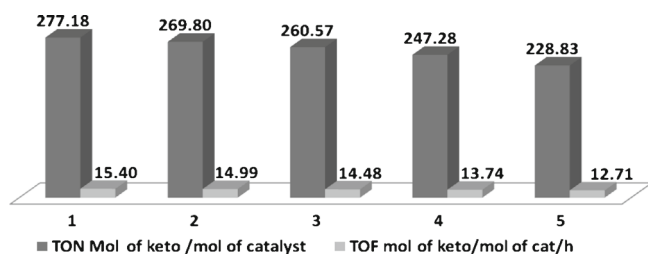


Figure 6. Catalyst reuse TON and TOF for catalyst ID. Conditions: β -isophorone – 0.062 mol, Acetyl acetone – 0.10 g, Triethyl amine – 3.15 g, Water – 1.7 g, Air flow – 200 ml/min, Temperature = 21+/-1°C.

35°C and 45°C) using acetone as a solvent and rest of the conditions were kept unaltered. The results are shown in table 4. The results showed that the equilibrium conversion at lower temperatures (15°C, 21°C) was 75% and 94.09%, whereas the selectivity values were 84.2% and 83.73%, respectively, indicating that lower temperature leads to less conversion but better selectivity. This was also observed²² when homogeneous Salen-Mn catalyst was used. At higher temperatures (35°C, 45°C) the conversions tend to decrease with decrease in the values of selectivity (entries 5 and 7). Higher temperature leads to side reactions, which can be observed from the selectivity values, while the apparent reason for drop in conversion at higher temperatures could be the deposition of side reaction products on the surface of the catalyst thus suppressing active sites.

4.3 Influence of catalyst loading

The effect of catalyst loading for catalyst **ID** on the conversion of β -isophorone and product selectivity was studied at two different catalyst loadings of 1.6 g/mol and 3.2 g/mol. The other reaction parameters like temperature, quantity of reactant and additives were kept constant. At 1.6 g/mol catalyst loading, the conversion and selectivity values were (18 h, 94.0, 83.7).

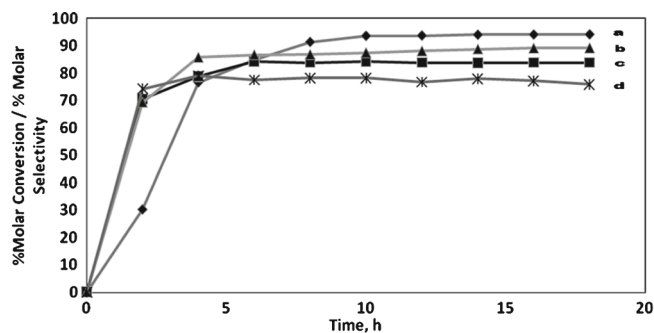


Figure 7. Influence of catalyst loading on conversion and selectivity, catalyst ID. a = Molar% conversion, catalyst load = 3.2 g/mol, b = Molar% conversion, catalyst load = 1.6 g/mol, c = Molar% selectivity, catalyst load = 1.6 g/mol, d = Molar% selectivity, catalyst load = 3.2 g/mol. Reaction Conditions: β -isophorone = 0.062 mol, Acetyl acetone = 0.105 g, triethyl amine = 3.15 g, water = 1.7 g, air flow = 200 ml/min., Temperature = 21+/-1°C.

It was observed that high conversion and low selectivity (18 h, 96.5, 78.0) were obtained when the catalyst loading was doubled to 3.2 g/mol, as given figure 7. The pronounced variation in product distribution values can be attributed to the advanced oxidation of the β -isophorone, which led to the formation of side products. The study indicates that there was an enrichment of oxygenated Schiff base-metal complex, involved in catalysing the reaction at a higher rate.

4.4 Study of molar conversion and molar selectivity for catalysts (ID-ID'')

All three (**ID-ID''**) catalysts were used for β -isophorone oxidation, and the conversion and selectivity for all of them were studied under the optimized conditions as mentioned earlier. As a means to eliminate the possibility of Mn-salen catalyst leaching into solution and homogeneously catalysing the oxidation reaction, experiments with homogeneous Mn-salen catalyst at different loadings were also performed (table 5). The

Table 4. Influence of solvent and temperature on β -isophorone oxidation.

Entry	Solvent used	Additives	Time, h	T °C	Molar % conversion	Molar % selectivity
1	<i>n</i> -hexane	TEA/AA	18	21	52.55	55.25
2	Acetone	TEA/AA	18	21	94.09	83.73
3	MIBK	TEA/AA	18	21	70.56	71.24
4	Methanol	TEA/AA	10	21	9.9	7.1
5	Acetone	TEA/AA	18	35	89.12	75.92
6	Acetone	TEA/AA	18	15	75	84.2
7	Acetone	TEA/AA	18	45	86.20	60.40

Reactant and additives and reaction conditions : β -isophorone, 0.062 mol, AA = acetyl acetone = 0.10 g, TEA = triethyl amine = 3.15 g, water = 1.7 g, air flow = 200 ml/min, catalyst load = 1.6 g/mol of β -isophorone, T = Temperature °C.

Table 5. β -Isophorone oxidation in presence of chitosan based heterogeneous and homogeneous Mn-salen catalyst.

Entry	Catalyst conc. g/mol of β -iph	Catalyst used	Additives	Time, h	Molar % conversion	Molar % selectivity/yield
1	–	No catalyst	TEA/AA	18	No reaction	–
2	1.6	ID	TEA	18	No reaction	–
3	1.6	ID	AA	18	No reaction	–
4	1.6	ID	TEA/AA	18	94.1	83.7/65.4
5	1.6	ID'	TEA/AA	18	10.6	68.22
6	1.6	ID''	TEA/AA	18	30.2	76.85
7	0.1	H-Salen	TEA/AA	2	5	55.8
8	0.2	H-Salen	TEA/AA	2	21	61.38
9	0.4	H-Salen	TEA/AA	2	51	65.85
10	0.8	H-Salen	TEA/AA	2	72	69.20
11	1.6	H-Salen	TEA/AA	2	98	75.9/57.2
12	3.2	H-Salen	TEA/AA	2	99.5	74.2

Reactant and additives and reaction conditions : β -isophorone = 0.062 mol, AA = Acetyl acetone = 0.10 g, TEA = triethyl amine = 3.15 g, water = 1.7 g, H-salen = homogeneous Mn-salen catalyst, air flow, 200 ml/min, Temperature = 21+/-1°C. Abbreviations : β -iph = β -isophorone.

study concluded that the reaction was extremely slow in the presence of extremely small amount of homogeneous salen catalyst (entry 7). As catalyst loading was increased, (1.6 g/mol) the conversion and selectivity also increased (entry 11), but at 3.2 g/mol of catalyst loading, the selectivity was tend to decrease (entry 12). The same reaction, when carried out in the presence of copper and cobalt-based catalyst, the effect of a β -isophorone conversion was only of 10.6 % and 30.2 %, (entries 5 and 6).

4.5 Kinetics of oxidation of β -isophorone by catalyst ID

The reaction displays first order kinetics with β -isophorone under the optimized reaction conditions mentioned in table 3. The kinetic plot of experimental data was made and the first order rate constant – k was calculated as shown in figure 8. The first-order rate constant for the oxidation of β -isophorone with catalyst ID was measured as 0.29 mol L⁻¹ h⁻¹.

4.6 Mechanism of oxidation and activated chitosan-salen-metal-oxo complex formation

As per literature information reference,²¹ the mechanism for oxidation is shown in scheme 2. The role of additives has been investigated here. The additives, acetyl acetone and triethyl amine react to form a conjugate base and acid as shown in scheme 2. This conjugate base extracts the active methylene proton from β -isophorone. It also imparts stability²⁴ to the manganese-based complex thereby facilitating the oxygen attack more rapidly. The next step is a formation of Schiff base-metal-oxygen complex. The Schiff base forms a

complex with molecular oxygen. The axially coordinating Schiff base facilitates the formation of the actual oxidizing species, which in the case of manganese complexes is a metal-oxo complex, and in the case of cobalt complexes usually a metal superoxo complex. Metal-peroxo complexes also exist when the metal is cobalt. The metal-oxo complexes having a salen type Schiff base and manganese as a metal have not been crystallographically characterized, but mass spectral studies have demonstrated the existence of these structures.^{38–40} Also, X ray structures for Mn⁵⁺oxo complexes bearing N⁴coordinating tetraamido type Schiff bases have been obtained.^{41,42} Several Co³⁺superoxo complexes having salen type Schiff bases have been structurally characterized.^{43–45}

In the next step, an addition of the oxo complex to the carbon occurs,²¹ followed by the formation of

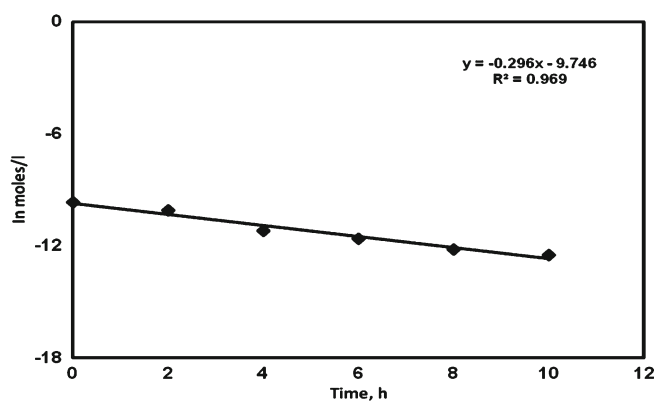
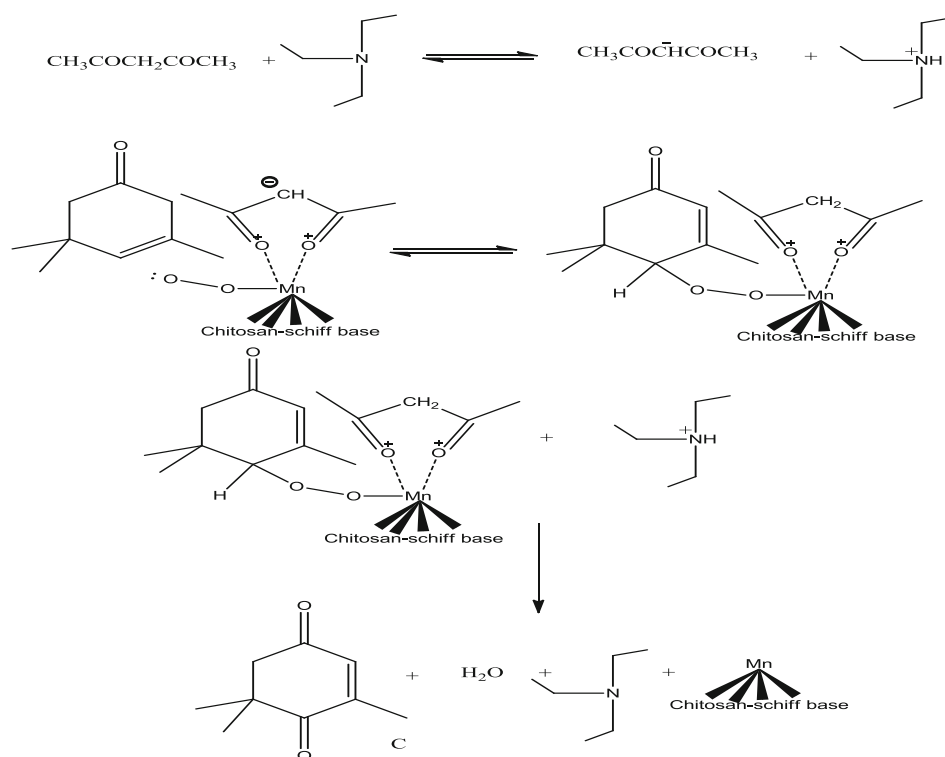


Figure 8. First order kinetic plot for the oxidation of β -isophorone oxidation using catalyst ID. Reaction conditions: β -isophorone = 0.062 mol, Acetyl acetone = 0.105 g, triethyl amine = 3.15 g, water = 1.7 g, air flow = 200 ml/min, catalyst load = 1.6 g/mol, Temperature = 21+/-1°C.



Scheme 2. Mechanism of β -isophorone oxidation, C = ketoisophorone.

ketoisophorone(C). The reaction was known to proceed via electron transfer than by radical coupling.⁴⁶ The Overall reaction yields ketoisophorone and water. The roles of acetyl acetone, triethyl amine and catalyst have been accounted for in the mechanism proposed by this investigation. The presence of all three is necessary for the reaction to proceed and the absence of any one ingredient hampers the reaction.

5. Conclusions

We have demonstrated a method to prepare three new chitosan-based Schiff base-metal complexes substituted with triazene, ethylene diamine and salicylaldehyde (**ID**, **ID'**, **ID''**) characterized by IR, NMR, elemental and ICP-AES analysis methods. ESR spectra of the catalysts reveal that the metals are in +2 oxidation state. Manganese loaded catalysts were efficient and showed significant catalytic activity for the oxidation of β -isophorone. Significantly high conversion (94.1%) and high selectivity (83%) was obtained. The TON and TOF were 277.18 mol/mol and 15.4 mol/mol/h, respectively. The catalyst was recycled five times. The oxidation reaction was dependent on catalyst loading, temperature and type of solvent. The β -isophorone conversion was high in the presence of acetone as a solvent. The XRD study reveals loss in crystalline character of the Schiff base-metal complexes. The TGA

curves indicate that all catalysts are more stable than chitosan-Schiff base. Role of acetyl acetone and triethyl amine in the oxidation of β -isophorone has also been investigated and explained in this paper. The present results illustrate that chitosan can be chemically modified into a stable Schiff base, which can form a complex with metal ion, 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.

Supplementary information

Spectroscopic characterization data are available as supporting information (figures S1–S11) in the Journal of Chemical Sciences website (www.ias.ac.in/chemsci).

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