

Zeolite encapsulated ruthenium and cobalt schiff base complexes catalyzed allylic oxidation of α -pinene

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Abstract

The allylic oxidation of α -pinene to its oxygenated products has been investigated using bis-salicylaldehyde-*o*-phenylene-diimine (Saloph) and substituted (Cl, Br and NO₂) Salophs of ruthenium and cobalt in zeolite-Y. The oxidation of α -pinene resulted in various products like camphene, 2,7,7-trimethyl SS pinene (3-oxatricyclo-4,1,1,02,4-octane), 2,3-epoxy (epoxy), campholene aldehyde and D-verbenone. Ru(III)Saloph-Y showed higher catalytic activity than Co(II)Saloph-Y with a turn over frequency >18 000 (mole of α -pinene oxidized per mole of Ru per hour) at 100 °C and 30 atm air. The selectivity for epoxy and D-verbenone was found to be higher in α -pinene oxidation with both Ru and Co catalyst systems. The catalytic performance of the encapsulated complexes was better than the neat complexes. Air was a more convenient oxidant than H₂O₂ and TBHP. No leaching of the metal complex in encapsulated systems were observed in the oxidation reaction. X-ray diffraction (XRD), thermogravimetric and X-ray photoelectron spectroscopy (XPS) studies supported the fact that the metal complexes were entrapped inside zeolite cages and not on its surface. Electronic spectra of the reaction mixture indicated that the oxidation of α -pinene proceeds through a free radical mechanism involving peroxoruthenium species as an active intermediate. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Epoxidation; α -Pinene; Allylic; Peroxoruthenium; D-Verbenone

1. Introduction

Even though lot of knowledge has been acquired regarding heterogeneous catalysis, the fine and specialty chemical industry is still based on stoichiometry rather than on catalysis. There is a need to find efficient and ecofriendly catalyst systems, which would operate under milder reaction conditions for many industrially important processes. Various attempts for the development of new catalyst system led to the emergence of a new class of catalyst called “zeolite encapsulated metal complexes” (ZEMC). A number

of encapsulated metal complexes have been reported in [1,2] and these catalysts under ideal conditions can mimic certain enzymes [3–7]. Jacobsen’s Mn(Salen) complex has emerged as an important catalyst for the oxidation of olefins in pharmaceutical industry [8,9].

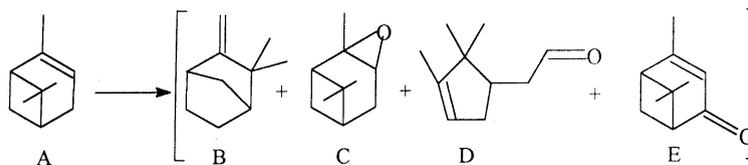
Oxidation of terpenes to oxygenated products is of interest since these products find their use in the preparation of natural product [10]. The allylic oxidation of α -pinene gives various products (Scheme 1) out of which D-verbenone is important because it is used in the preparation of taxol, which has been recently introduced as a therapeutic agent [11,12].

Cobalt and palladium catalyst systems have been reported in the literature for the oxidation of α -pinene [13,14]. Pd/C promoted with Co, Mn, Bi, Cd and Zn have also been used for the oxidation of

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Scheme 1. Products of catalytic oxidation of α -pinene (A: α -pinene; B: camphene; C: epoxy; D: campholene aldehyde; E: D-verbenone).

α -pinene with molecular oxygen to give verbenol and D-verbenone [15]. Cobalt salts such as cobalt dibromide containing bipyridyl($\text{Co}(\text{C}_2\text{H}_5\text{N})_2\text{Br}_2$) and $\text{Co}(4\text{-Me}(\text{C}_5\text{H}_4\text{N})_2\text{Br}_2)$ or fatty acids and chromium salts of fatty acids have been reported as catalysts for the selective oxidation of α -pinene to D-verbenone [16,17] and these catalysts have been now rejected because of the stoichiometric amounts required and toxicity of waste products, which are not preferred from environmental view point. There is still a scope to develop efficient catalysts for the oxidation of α -pinene to achieve commercially viable and environmentally acceptable reaction conditions.

The aim of the present paper is to encapsulate the metal complexes in the zeolite and investigate the catalytic and mechanistic studies of α -pinene oxidation using $\text{Co}(\text{II})\text{Saloph-Y}$ and $\text{Ru}(\text{III})\text{Saloph-Y}$ and to optimize the condition to get higher yields of epoxy and D-verbenone.

2. Experimental

2.1. Materials

Salicylaldehyde, *o*-phenylenediamine, chlorosalicylaldehyde, bromosalicylaldehyde, nitrosalicylaldehyde, α -pinene and Na-Y were procured from M/s Aldrich Chemicals (USA). Cobalt acetate, ethanol, acetonitrile, *t*-butanol, concentrated HCl and KCl were procured from M/s Loba Chemicals (Mumbai) and M/s Arora Mathey Ltd., Calcutta, supplied $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$.

2.2. Preparation of catalysts

2.2.1. Preparation of bis-salicylaldehyde-*o*-phenylenediimine (Saloph)

Stoichiometric amount of salicylaldehyde (2.44 g) dissolved in ethanol (25 ml) was added drop by drop to

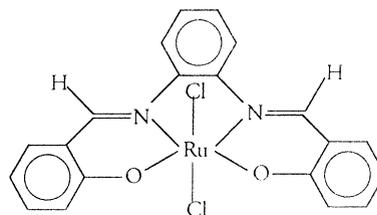
o-phenylenediamine solution (1.08 g in 25 ml ethanol). The contents were refluxed for 3 h and a bright yellow precipitate of Saloph was obtained. The yellow precipitate was separated by filtration, washed and dried in vacuum. It was then recrystallized from ethanol to yield Saloph (3.0 g).

2.2.2. Preparation of $\text{K}_2[\text{RuCl}_5(\text{H}_2\text{O})]$

$\text{K}_2[\text{RuCl}_5(\text{H}_2\text{O})]$ was prepared by following the procedure described elsewhere [21]. A known amount of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (0.25 g) was dissolved in 12 M HCl and refluxed for 30 h and to it stoichiometric amount of KCl was added and the solution was stirred with mercury until the solution became green, indicating the formation of some Ru(II). Mercurous chloride formed was removed by filtration. This solution was evaporated to small volume and cooled. The resulting red crystals were separated by filtration, washed with ethanol and recrystallized from 6 M HCl to give $\text{K}_2[\text{RuCl}_5(\text{H}_2\text{O})]$.

2.2.3. Preparation of $[\text{Ru}(\text{III})(\text{Saloph})\text{Cl}_2]$ neat complex

Stoichiometric amounts of schiff base ligand (Saloph) was dissolved in ethanol to which $\text{K}_2[\text{RuCl}_5(\text{H}_2\text{O})]$ was added in an appropriate mole ratio. This mixture was refluxed for 15 h and after the completion, the reaction mixture was filtered and the filtrate concentrated to a small volume by heating. To this solution ether was added to precipitate the complex $[\text{Ru}(\text{III})(\text{Saloph})\text{Cl}_2]$.



2.2.4. Preparation of Ru(III)-Y

Ru(III)-Y was prepared by dissolving 0.2 g of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ in 50 ml demineralized water. To it, 1.0 g of Na-Y was added and the same was refluxed for 16 h. After cooling, the solid product was filtered and washed thoroughly with warm water till all the Cl ions were removed (by testing the filtrate for Cl content with AgNO_3 solution). The solid product thus separated was dried at 150°C and used in the experiment.

2.2.5. Preparation of Ru(III)Saloph-Y

Ru(III)Saloph-Y was prepared by dissolving Saloph in *t*-butanol and Ru-Y was added to it and this was refluxed for 8 h. After cooling the solid was separated by filtration, dried and then was Soxhlet extracted with *t*-butanol for 48 h. It was then treated with 1 M NaCl and refluxed for 8 h, filtered and washed with warm water to remove Cl ions. This solid Ru(III)Saloph-Y was then dried and used in oxidation experiments.

2.2.6. Preparation of Co(II)-Y, Co(II)Saloph neat, Co(II)Saloph-Y, Co(II)ClSaloph-Y, Co(II)BrSaloph-Y and Co(II)NO₂Saloph-Y

Co(II)Saloph neat, Co(II)-Y, Co(II)Saloph-Y, and substituted Salophs (Co(II)ClSaloph-Y, Co(II)BrSaloph-Y and Co(II)NO₂Saloph-Y) were prepared by following the earlier described method [18].

2.3. Characterization of catalysts

The C, H, N analysis of the neat complexes was obtained from Carlo ERBA (Italy) Model EA 1108 analyzer. The electronic spectra of the neat complexes were taken on a Shimadzu UV-VIS scanning spectrophotometer (Model 2101 PC). FT-IR spectra of the solid samples were recorded on a Shimadzu FT-IR instrument (Model 8201PC). Powder X-ray diffraction of the zeolite encapsulated metal complex catalysts were carried out using a Rigaku (Model D/MAXIII VC, Japan), setup with Cu K α radiation and a graphite monochromatic with scan 16°min^{-1} and scanning in the 2θ range from 5 to 50° . Silicon was used to calibrate the instrument. The cobalt content of the samples were measured by atomic absorption spectrometer (AAS-Hitachi Model Z-8000) and the ruthenium content of the sample were estimated by Inductively Coupled Plasma-Optical Emission Spectroscopy

(ICP-OES) Model Perkin-Elmer PE-1000. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of the neat and zeolite encapsulated metal complexes were recorded on Rheometric Scientific (STA 1500) Analyzer. Surface area and pore volume of the zeolite encapsulated catalysts were determined by Omnisorb 100 CX (Coulter, USA). XPS spectra are recorded on a VG Microtech Multilab-ESCA 3000 spectrometer equipped with a twin anode of Al and Mg. All measurements are made on as received powder samples using Mg K α X-ray at room temperature. Base pressure in the analysis chamber was 4×10^{-10} Torr. Multichannel detection system with nine channels is employed to collect the data. The overall energy resolution of the instrument is better than 0.7 eV, determined from the full width at half maximum of the $4f_{7/2}$ core level of gold surface. The errors in all the BE values were within ± 0.1 eV. Neat metal complex spectrum was normalized to the encapsulated one in the figure presented.

2.4. Catalytic study

The α -pinene oxidation experiments were carried out in a 300 ml Parr autoclave under (O_2) air pressure. In a typical experiment, reaction mixture containing known amounts of α -pinene, catalyst, acetonitrile solvent (excess) and small amounts of azobis-isobutyronitrile (a radical initiator) were placed into the autoclave. The autoclave was then pressurized with air and was then heated to the desired temperature and kept at that temperature under constant stirring. The reaction mixtures were withdrawn at fixed time intervals and analyzed by gas chromatography (Shimadzu 14B) using FID detector and a capillary column. From the gas chromatographic analysis, the conversions of α -pinene and the yields (selectivities) of the oxidation products were estimated. The identities of these products were confirmed by GC-MS (Shimadzu GCMS QP 5400).

3. Results and discussion

3.1. Chemical analysis

The C, H, N analysis results of the neat cobalt and ruthenium complexes showed close similarity

Table 1
IR spectra (cm^{-1}) of the neat and zeolite encapsulated complexes^a

Catalyst	$\nu\text{C}=\text{C}$	$\nu\text{C}-\text{H}$	$\nu\text{C}=\text{N}$	$\nu\text{C}-\text{N}$	$\nu\text{C}-\text{O}$	Ring vibrations
Ru(III)L	1600(m)	2923(vs), 2854(s)	1578(w)	1180(m)	1033(m)	1458(s), 110(w), 761(s)
Ru(III)L-Y	1600(s)	2923(vs), 2854(s)	1575(m)	1180(m)	1012(s)	1456(s), 110(w), 792(s)
Co(II)L	1610(s)	2923(vs), 2854(s)	1581(m)	1184(s)	1028(s)	1410(s), 109(w), 746(s)
Co(II)L-Y	1602(m)	2910(m), 2849(m)	1572(w)	1181(m)	1035(m)	1400(s), 1082(w), 754(w)
Co(II)CIL	1602(s)	2854(vs), 2322(m)	1570(s)	1178(s)	1049(s)	1406(s), 1082(s), 756(s)
Co(II)CIL-Y	1608(m)	2879(m), 2898(m)	1572(s)	1179(m)	1080(w)	1456(s), 1110(m), 765(w)
Co(II)BrL	1600(s)	2890(s), 2900(m)	1558(s)	1165(s)	1049(m)	1400(s), 1070(s), 754(s)
Co(II)BrL-Y	1600(m)	2898(m), 2880(m)	1571(m)	1141(m)	1041(w)	1456(s), 1060(m), 808(w)
Co(II)NO ₂ L	1598(s)	2880(vs), 2941(m)	1562(s)	1151(s)	1049(m)	1457(s), 1080(s), 760(s)
Co(II)NO ₂ L-Y	1600(s)	2882(m), 2936(m)	1560(w)	1155(m)	1065(w)	1460(s), 1071(s), 775(m)

^a L: Saloph; w: weak; s: strong; vs: very strong; m: medium.

to the theoretical values. The cobalt and ruthenium contents of the ZEMC catalysts were estimated by dissolving known amounts of the catalyst in conc. HCl and from these solutions, the cobalt and ruthenium contents were estimated using atomic absorption spectrometer (AAS) and inductively coupled plasma (ICP) spectrometer, respectively. The Co contents of the ZEMC systems was almost the same and was equal to 1.1 wt.%, while that of ruthenium was 2.11 wt.%.

3.2. IR spectroscopy

IR spectra of neat as well as encapsulated complexes presented in Table 1 gave information on the stretching vibration of the functional groups, the environment of the complex and the crystallinity of the zeolite. The IR bands of all encapsulated complexes are weak in comparison with the neat complexes due to their low concentrations in zeolite cages.

3.3. Surface area and pore volume of the catalysts

The surface area and micropore volume of the catalysts used in the oxidation reaction are presented in Table 2. The encapsulation of metal ions and metal Saloph complexes reduced the surface area and adsorption capacity of zeolite. The lowering of the pore volume and surface area supported the fact that Co(II)Saloph and Ru(III)Saloph complexes are present within the zeolite cages and not on the external surface.

3.4. X-ray diffraction

X-ray diffractograms of the Na-Y and Ru(III)Saloph-Y are shown in Fig. 1(A) and (B), respectively. The XRD of Co(II)Saloph complexes were studied earlier and have been already reported [18]. All samples exhibit patterns which can be indexed to Na-Y and not to the complex. This indicates that the crystallinity and morphology of zeolite was preserved during encapsulation.

3.5. Thermal analysis

DTA and TGA have been used to characterize metal complexes encapsulated in zeolite. TGA, DTA and differential thermogravimetry (DTG) data with respect to the catalysts studied are presented in Fig. 2(A)–(D). The neat complexes of Co and Ru showed weight loss at 327 °C. However, for the corresponding

Table 2
Surface area and pore volume of catalysts

Catalyst	Surface area ($\text{m}^2 \text{g}^{-1}$)	Macropore volume (ml g^{-1})
Na-Y	836.3	0.4234
Ru-Y	546.0	0.2415
Ru(III)Saloph-Y	458.3	0.2345
Co(II)-Y	554.0	0.2323
Co(II)Saloph-Y	442.9	0.2147
Co(II)ClSaloph-Y	484.9	0.2027
Co(II)BrSaloph-Y	475.7	0.2050
Co(II)NO ₂ Saloph-Y	369.2	0.1710

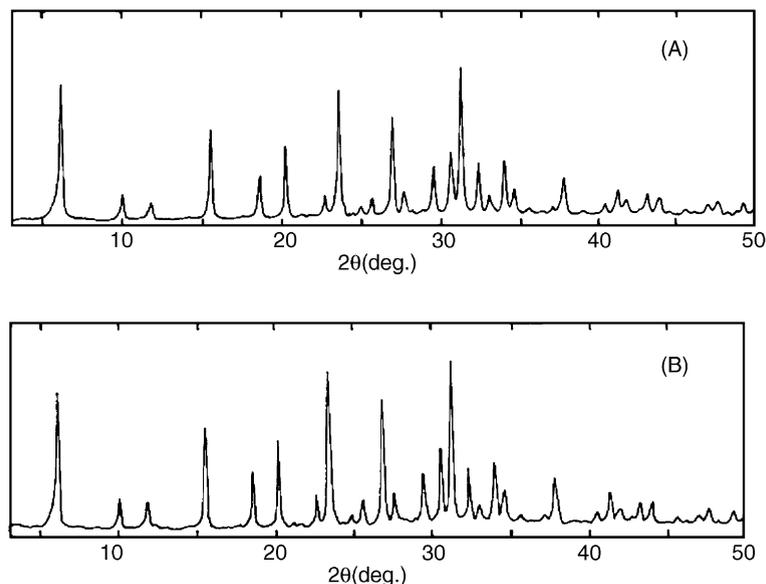


Fig. 1. XRD of (A) Na-Y and (B) Ru(III)Saloph-Y.

encapsulated complexes (Fig. 2(B) and (D)), there is a continuous weight loss, which extends upto 527 °C. The TGA and DTG of neat and encapsulated Co(II)ClSaloph under the same conditions showed weight loss at 400 °C, which indicated that the presence of Cl increased the thermal stability of the metal complex in the neat and encapsulated forms.

3.6. X-ray photoelectron spectroscopy (XPS) of neat and encapsulated complexes

Encapsulated complexes are referenced to the binding energy of 102.7 eV for the Si 2p core level due to its extensive use of this binding energy in Na-Y system [19–22]. However, neat complexes are referenced to the binding energy of 292.7 eV for the K 2p_{3/2} core level. Due to the strong overlap between Ru 3d and C 1s core levels, the above reference was chosen.

Fig. 3(A) shows the Ru 3p core levels of neat and encapsulated complexes. The binding energy of Ru 3p levels are very close to the BE of Ru³⁺ reported [22]. However, upon encapsulation a clear shift towards higher BE is seen compared to the neat complex. It is attributed to the complexation of Ru with Saloph ligand inside the zeolite cages. Additionally a

clear satellite is seen at 473 eV for encapsulated complex and this is due to charge transfer from ligand to metal as observed in transition metal compounds.

Fig. 3(B) shows the Co 2p core levels of neat and encapsulated complexes. In Co-complexes also similar experimental trend has been observed, as in Ru cases. Cobalt remains in the 2+ oxidation state in both the neat and encapsulated complexes and it matches well with the reported values for similar systems [22]. There is a strong increase in satellite intensity for Co 2p levels and a large energy gap (16.3 eV) between them is observed from encapsulated complex, which results in higher catalytic activity than neat complex. Table 3 lists the relevant parameters for Ru and Co complexes.

Table 3
XPS data of Ru and Co complexes

Complex	BE, Ru 3p _{3/2} or Co 2p _{3/2} (eV)	p _{3/2} and p _{1/2} separation (eV)
Ru(III)Cl ₂ Saloph neat	461.4	22.4
Ru(III)Saloph-Y encapsulated	462.2	22.3
Co(II)Saloph neat	781.0	15.5
Co(II)Saloph-Y encapsulated	781.9	16.3

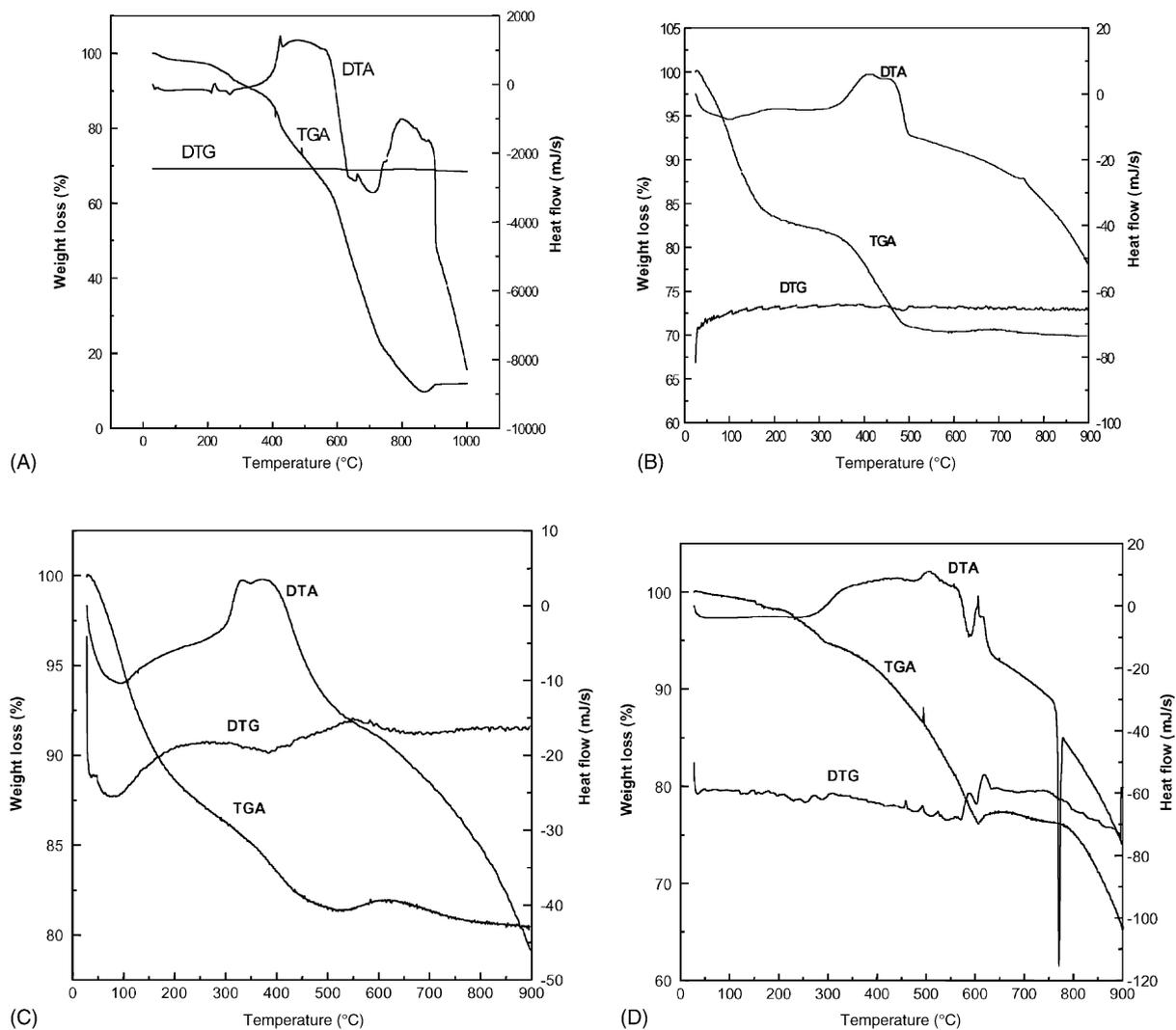


Fig. 2. TGA, DTA and DTG of (A) Co(II)ClSaloph neat, (B) Co(II)ClSaloph-Y, (C) Ru(III)Cl₂Saloph neat and (D) Ru(III)Saloph-Y.

3.7. Catalytic activities

The neat and zeolite encapsulated Co(II)Saloph and Ru(III)Saloph catalysts were used for the aerial oxidation of α -pinene and the experimental conditions and the results are presented in Table 4. The encapsulated catalysts systems were more active than the corresponding neat complexes. Among the Co(II) complexes, Co(II)NO₂Saloph was more active than Br and Cl substituted complexes. Substitution of electron withdrawing groups on the ligand decreases

the electron density over the metal center and thus increasing the catalytic activity. Similarly, the encapsulated systems of Ru(III)Saloph-Y and Co(II)Saloph-Y showed the above trend.

Ru(III)Saloph-Y and Co(II)Saloph-Y were tested in the oxidation of α -pinene under similar reaction conditions at 100 °C and the reaction was monitored as a function of time. The conversion of α -pinene as a function of time is shown in Fig. 4. It is seen from the figure that Ru(III)Saloph-Y was found to be more active than Co(II)Saloph-Y throughout. A highest conversion

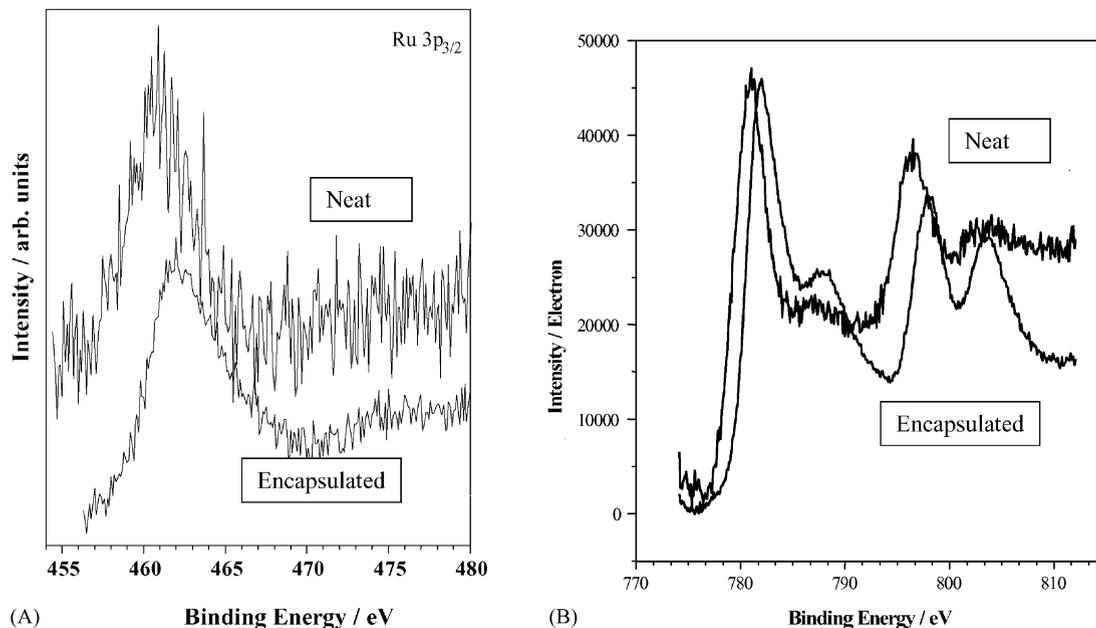


Fig. 3. XPS of (A) Ru and (B) Co in neat and encapsulated complex.

(75%) of α -pinene is obtained with Ru(III)Saloph-Y in a contact time of 3 h. The effect of temperature on conversion of α -pinene monitored as a function of time with Ru(III)Saloph-Y catalyst is shown in Fig. 5. At 70 °C, the conversions of α -pinene were low and at 100 °C and above, conversions of α -pinene were enhanced considerably with time.

The effect of solvent on the α -pinene oxidation reaction was carried out with Ru(III)Saloph-Y. Under the reaction conditions studied, the catalyst showed higher activity with acetonitrile solvent compared to

acetone and benzene. The higher catalytic activity in acetonitrile is attributed to higher solubility of O₂ and polarity of solvent. Hence, the solvent effect in the oxidation of α -pinene decreased in the order: acetonitrile > acetone > benzene.

The product selectivities of α -pinene oxidation catalyzed by Ru(III)Saloph-Y monitored as a function of time is shown in Fig. 6. It is seen from the figure that the selectivities for epoxy were higher throughout the reaction and the maximum selectivity for epoxy was 35% at 3 h. The selectivity for D-verbenone increases

Table 4

Catalytic activities of neat and zeolite encapsulated complexes in α -pinene oxidation^a

Neat complex (0.004 g)	Conversion of α -pinene (wt.%)	TOF ^b	Encapsulated complex (0.04 g)	Conversion of α -pinene (wt.%)	TOF ^b
Co(II)Saloph	13.2	3524	Co(II)Saloph-Y	30.4	7826
Co(II)BrSaloph	18.7	6864	Co(II)BrSaloph-Y	31.8	11153
Co(II)ClSaloph	20.3	6394	Co(II)ClSaloph-Y	33.8	11868
Co(II)NO ₂ Saloph	23.0	7402	Co(II)NO ₂ Saloph-Y	39.7	15341
Ru(III)Cl ₂ Saloph	29.4	9044	Ru(III)Saloph-Y (0.02 g)	49.5	18210

^a Conditions: α -pinene: 2 g (0.0146 mol); acetonitrile: 30 g; azobis: 0.05 g; temperature: 100 °C; air: 30 atm; time: 1 h.

^b Mole of α -pinene oxidized per mole of metal per hour and are calculated using 1.1 wt.% cobalt and 2.11 wt.% ruthenium metal contents in encapsulated catalysts. The metal contents in neat complexes were calculated from the respective formula weights.

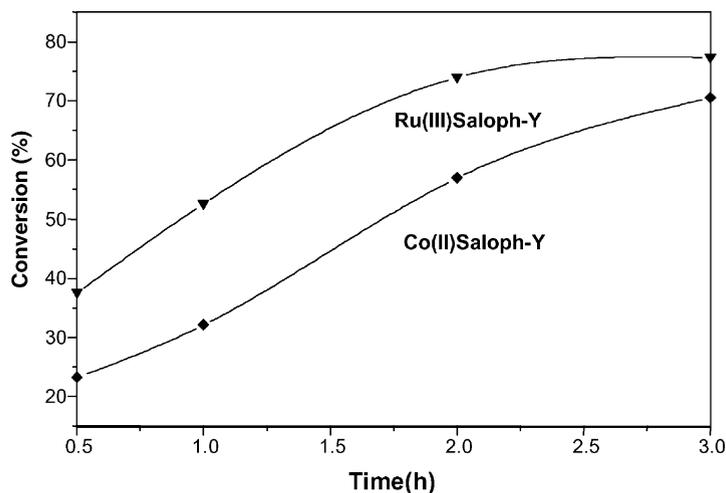


Fig. 4. Conversion as a function of time. Conditions: α -pinene: 2 g (0.0146 mol); acetonitrile: 30 g; Ru(III)Saloph-Y: 0.02 g; Co(II)Saloph-Y: 0.050 g; air: 30 atm; azobis: 0.05 g; temperature: 100 °C.

marginally with time. Similarly, the graph of selectivity of products (%) versus time for Co(II)Saloph-Y is shown in Fig. 7.

3.7.1. Mechanistic studies

Ru(III)Cl₂Saloph neat complex was used to study the mechanism of oxidation of α -pinene to epoxy derivatives. The reaction mixture was monitored by UV–VIS spectrophotometer and the absorption

spectra are shown in Fig. 8. Neat complex in acetonitrile showed absorption maximum at 391 nm, which is a characteristic LMCT absorption band corresponding to Ru^{III} species. The absorption at 391 nm shifted to 400 nm when the above solution was interacted with O₂ (air). This shift could be due to the formation of peroxoruthenium species Ru^{IV}O₂⁻ via one electron transfer oxidation. When α -pinene was added to the above solution the absorption at 400 nm shifted to

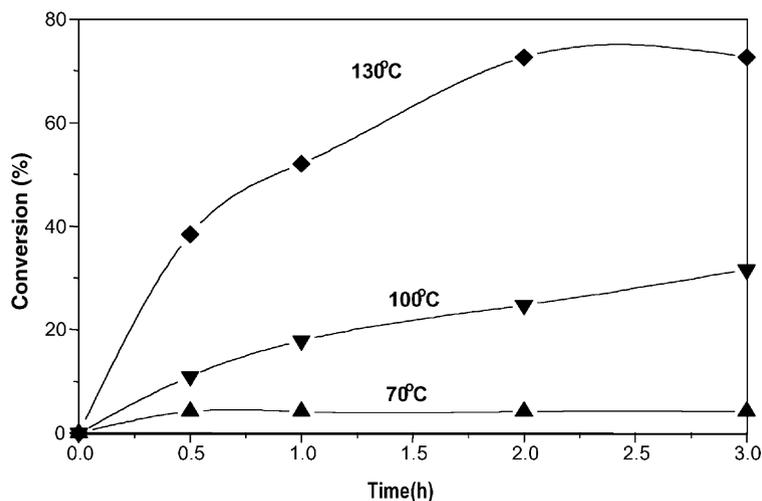


Fig. 5. Effect of temperature on the performance of Ru(III)Saloph-Y. Conditions: α -pinene: 2 g (0.0146 mol); acetonitrile: 30 g; Ru(III)Saloph-Y: 0.02 g; air: 30 atm; azobis: 0.05 g.

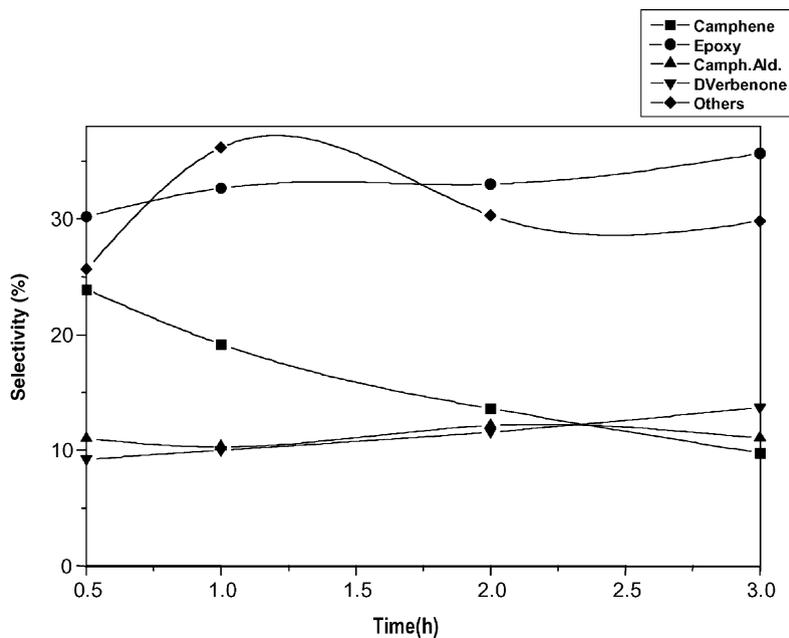


Fig. 6. Selectivity of products as a function of time with Ru(III)Saloph-Y. Conditions: α -pinene: 2 g (0.0146 mol); acetonitrile: 30 g; azobis: 0.05 g; Ru(III)Saloph-Y: 0.02 g; air: 30 atm; temperature: 100 °C.

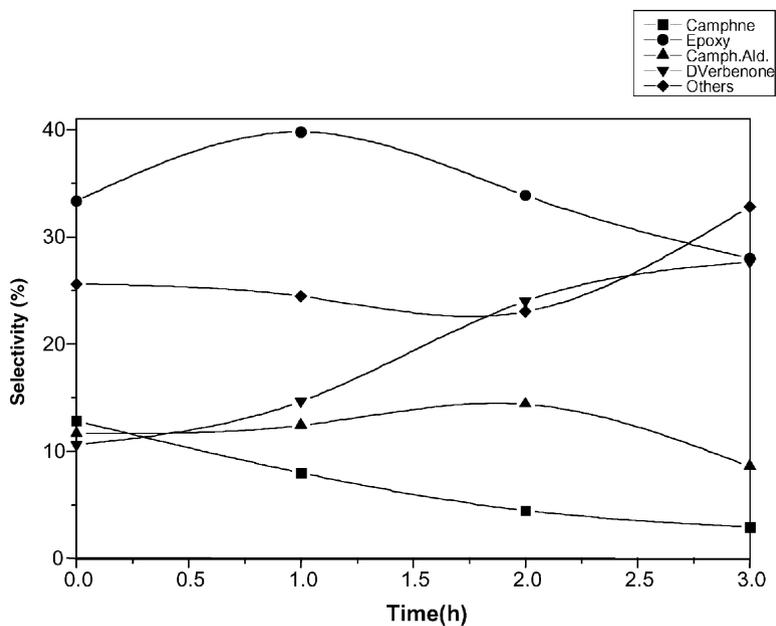


Fig. 7. Selectivity of products as a function of time with Co(II)Saloph-Y. Conditions: α -pinene: 2 g (0.0146 mol); acetonitrile: 30 g; azobis: 0.05 g; Co(II)Saloph-Y: 0.05 g; air: 30 atm; temperature: 100 °C.

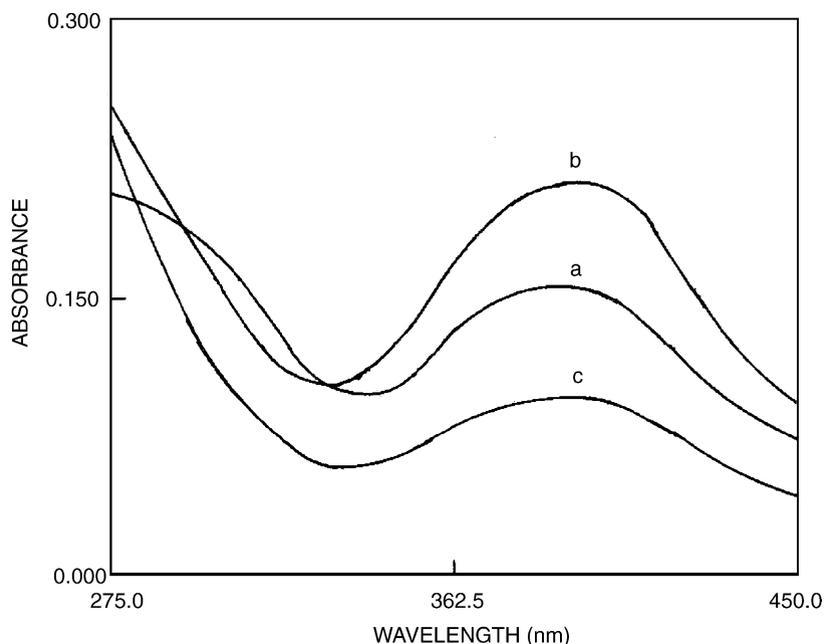
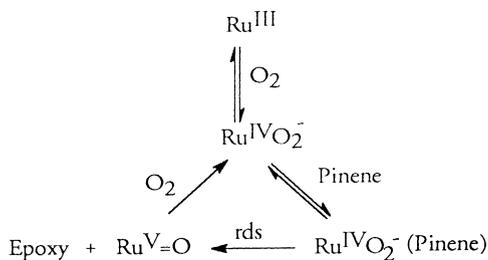


Fig. 8. UV–VIS spectrophotometric study: (a) Ru(III)Cl₂Saloph neat in acetonitrile; (b) Ru(III)Cl₂Saloph neat in acetonitrile + air; (c) Ru(III)Cl₂Saloph neat in acetonitrile + air + α -pinene.

402 nm with a reduction in the intensity. This has been attributed to the transfer of oxygen to olefin bond of α -pinene to give epoxy in rate determining step, while Ru^V=O species in presence of O₂ active peroxy species is regenerated in a catalytic cycle. Based on the above study, the mechanism proposed for [Ru(III)Cl₂Saloph] neat catalyzed oxidation of α -pinene is as shown below.



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