Oxidation of \( p \)-cresol catalyzed by neat and zeolite encapsulated cobalt salen complexes

Trissa Joseph, C S Sajanikumari, S S Deshpande & Sarada Gopinathan

Inorganic & Catalysis Division, National Chemical Laboratory, Pune 411 008, India

Received 22 March 1999; revised 24 May 1999

Salen and substituted salen Schiff base complexes of cobalt(II) have been synthesized. These complexes have been encapsulated in the supercages of Na-Y zeolite employing flexible ligand method. The neat as well as the zeolite encapsulated complexes have been characterized by XRD, FTIR and UV-vis spectroscopy. Aerial oxidation of \( p \)-cresol using these catalysts in presence of a base affords \( p \)-hydroxybenzaldehyde (PHBA) in good yield. Among the catalysts studied, cobalt-chlorosalen-Y gives almost 100\% conversion of \( p \)-cresol with 97\% selectivity towards PHBA with a turnover frequency of 1049/h. The spent encapsulated catalysts retain their identity after the oxidation reactions as seen from their IR spectra.

\( p \)-Hydroxybenzaldehyde (PHBA) is obtained as a by-product from the Reimer-Tiemann reaction of salicylaldehyde with phenol. PHBA is an important intermediate in agriculture and pharmaceutical industry. It is also used as an additive for metal plating brighteners and in perfumes. Cobalt salts are frequently used as catalysts in oxidation reactions\(^1\). The liquid phase aerial oxidation of \( p \)-cresol was reported by Sharma et al\(^7\), using cobaltous chloride as catalyst in presence of excess sodium hydroxide to give an overall \( p \)-cresol conversion of 90\% with 60\% selectivity to PHBA. Other by-products included \( p \)-hydroxybenzyl alcohol, \( p \)-hydroxybenzoic acid, \( p \)-hydroxybenzyl methyl ether and minor quantities of tarry materials. An increased yield of PHBA has been achieved using heterogeneous catalysts such as CoAPO-5 and CoAPO-11\(^1\). Recently, compounds like hydrotalcite also have been used as catalysts to get a high \( p \)-cresol conversion\(^5\).

In this paper we report aerial oxidation of \( p \)-cresol under alkaline conditions using catalysts consisting of neat salen complexes of cobalt(II) as well as these complexes heterogenized by encapsulation in the voids of Y-type zeolites for the first time with a view to obtaining an increased selectivity towards PHBA.

Materials and Methods

\( p \)-Cresol, cobalt chloride hexahydrate and cobalt acetate tetrahydrate and the ligands such as salicylaldehyde, 5-chlorosalicylaldehyde, 5-bromosalicylaldehyde, 5-nitrosalicylaldehyde and ethylenediamine were of Aldrich make.

**Synthesis of salen Schiff base**

Salicylaldehyde (12.2 g, 0.1 mol) was diluted with ethyl alcohol (100 ml) and mixed with a solution of ethylenediamine (3 g, 0.05 mol) dissolved in ethyl alcohol (50 ml) dropwise to get salen ligand as yellow flakes. The slurry was then refluxed for 1 h to complete the reaction. The solid product was filtered, washed with cold ethyl alcohol and dried *in vacuo*; yield 13.2 g. The substituted salens were likewise prepared.

**Synthesis of cobalt(II)-salen**

The cobalt(II)-salen was freshly prepared by following the procedure described in the literature\(^6\). The Schiff base salen (7.34 g, 0.03 mol) was dissolved in ethyl alcohol (200 ml) by warming in nitrogen atmosphere. An ethanolic solution of Co(OAc)\(_2\).4H\(_2\)O (6.46 g, 0.03 mol in 100 ml ethanol) was boiled until all the crystalline solid had gone into solution. Both the solutions were mixed and refluxed for 4 h under nitrogen, cooled to obtain a wine red precipitate which was filtered and dried *in vacuo*; yield 11 g. Cobalt-chlorosalen, cobalt-bromosalen and cobalt-nitrosalen were prepared in a similar manner.

**Synthesis of Co-Y by ion-exchange**

Co(OAc)\(_2\).4H\(_2\)O (3.5 g) was dissolved in warm distilled water (700 ml) to which Na-Y (7.5 g) was
added and the contents were refluxed for 8 h. A pink solid obtained was collected by filtration, and washed several times with water. This solid was again treated with a solution of Co(OAc)$_2$ (3.5 g) for a second loading. Similarly, a third loading was also carried out. The cobalt exchanged zeolite thus obtained was filtered, washed with water and dried in air overnight at 110°C. The product was characterised by XRD, UV and IR spectra.

**Synthesis of cobalt-salen-Y by flexible ligand method**

The salen ligand (3 g) was melted in a round-bottom flask kept in an oil-bath at 160°C. To the molten salen was added, Co-Y (1 g) and the contents were kept at the same temperature for 24 h. The molten mass was then cooled to get a brown solid which was powdered and soxhlet-extracted with methylene chloride. The product was then refluxed with 0.1 N NaCl solution for 4 h to remove the uncomplexed Co$^{2+}$ ions adhering to the zeolite. The solid was then washed with hot water till free from chloride ions. Similarly, cobalt-chlorosalen, cobalt-bromosalen and cobalt-nitrosalen were encapsulated using the above procedure. The cobalt content in the encapsulated complexes, estimated by atomic absorption spectroscopy after destroying the zeolite structure by HF treatment, was found to be in the range of 2.8-3 % by wt.

**Catalytic oxidation reaction**

$p$-Cresol (6 g, 0.06 mol) was added to a warm methanolic solution (25 ml) of sodium hydroxide (6.2 g, 0.16 mol) in a Parr autoclave of 300 ml capacity and to that was added neat cobalt(II) salen catalyst (0.7 mg/g of $p$-cresol). The reactor was then pressurised with air up to 600 psi and heated to 100°C with stirring. A drop in pressure suggested commencement of reaction which was continued over a period of 3 h. After the reaction, the autoclave was cooled, gases were released and the product was obtained as a brown solid slurry. It was homogenised by dissolving in water and analysed by HPLC using external standard method.

Similarly, kinetic runs using neat and encapsulated complexes were carried out and samples were analysed after every 30 min. The results show that $p$-cresol conversion was only 40-50% after 1 h and was almost complete at the end of 3 h.

**Characterization**

The electronic spectra of the neat and encapsulated complexes were taken on a Shimadzu UV-VIS scanning spectrophotometer (Model 2101PC). IR spectra were scanned on a Shimadzu FTIR instrument (Model 8201PC). X-ray diffraction analysis was carried out using a Rigaku DMAX-IIIB set-up with CuKα radiation and a graphite monochromator, scan speed 16°/min and scanning from 5 to 50°. The reaction product was analysed by HPLC using a Shimadzu liquid chromatograph (Model LC-9A) equipped with Chrompak C18 15 cm column.

**Results and Discussion**

The XRD pattern of the cobalt-salen encapsulated zeolite catalysts was comparable with that of neat Na-Y suggesting retention of zeolite crystallinity.

The UV-vis electronic spectra of the salen ligands show the typical absorptions at ~253 and ~326 nm attributable to ligand $n$-$\pi^*$ and $\pi$-$\pi^*$ charge transfer bands. In the cobalt complexes, these bands are red-shifted by 10 to 20 nm suggesting complex formation. Further, an additional peak in the higher wavelength between 470 and 540 nm present in all the complexes (as shown in Fig. 1) is suggested to be due to O→Co ligand-to-metal charge transfer band.

IR spectra display characteristic difference between the spectra of cobalt-salens and the corresponding free schiff base ligands. The ligands show absorption due to $\nu$(C=N) at 1635 cm$^{-1}$. In the spectra of all the complexes in nujol this band is shifted to lower frequencies and is observed in the region 1600-1614 cm$^{-1}$. This shift is characteristic of coordination of azomethine nitrogen to cobalt as a result of complex formation. The phenolic $\nu$(C-O) of the free ligand shifts to higher wave numbers in the complexes due to
increased C-O bond order compared to the hydrogen-bonded structure in the Schiff base.

IR spectra of zeolite encapsulated complexes in DRS mode exhibit characteristic absorption bands of coordinated ligand along with a broad peak between 1100 and 1000 cm\(^{-1}\) due to Si-O-Si of the zeolite framework. IR spectra of the spent catalysts also exhibit a broad band between 1100 and 1000 cm\(^{-1}\) similar to the fresh catalyst, which indicates that the zeolite framework is intact and has not undergone any distortion. Absorption due to \(\nu(C=N)\) at 1637 cm\(^{-1}\) is also observed showing that the ligand has not been leached out from the zeolite during the reaction.

Aerial oxidation of \(p\)-cresol was carried out using neat as well as zeolite encapsulated cobalt-salens as catalysts. Table 1 gives \(p\)-cresol conversion values and product selectivities. The results of control reactions using CoCl\(_2\)·6H\(_2\)O and Co(OAc)\(_2\)·4H\(_2\)O as catalysts have also been included in the table. Among the neat catalysts studied, the chlorosalen derivative gives maximum substrate conversion and PHBA selectivity. The bromo- and nitro-salen complexes also show marginally better performance compared to the unsubstituted cobalt-salen. This increased activity shown by the catalysts containing electron withdrawing substituents on salen ligand could be attributed to the stabilization of cobalt peroxy radical.

![Fig. 2](image-url)

**Fig. 2**—Effect of reaction temperature using neat catalyst on the rate of \(p\)-cresol conversion and product selectivity. Reaction conditions: \(p\)-cresol = 6 g, NaOH = 6.2 g, catalyst (cobalt-chlorosalen) = 0.6 mg of cobalt/g of \(p\)-cresol, reaction time = 3 h.

[Co\(^{III}\)-O-O\(^{-}\)] formed during the chain radical oxidation reaction of the substrate.

The zeolite encapsulated cobalt salens as catalysts are found to be far superior to the corresponding neat
complexes as seen from the increased p-cresol conversion and PHBA selectivity even at lower concentrations of cobalt per gram of substrate. The turnover frequency (TOF) for these catalysts is also increased by a factor of -4. This increased selectivity for PHBA could be attributed to an optimum residence time for the substrate near site isolated active catalyst intermediate in the supercage of the zeolite. A considerable reduction in tar formation also has been noticed with these catalysts.

Effect of temperature

The reactions have been conducted using neat and encapsulated chlorosalen catalysts in the temperature range 40-80°C to study the effect of temperature on the rate of reaction and aldehyde selectivity. The results are furnished in Tables - 2 (Fig 2) for neat complex and in Table - 3 (Fig 3) for encapsulated complex. The reaction is found to be incomplete at lower temperatures (say, 40°C) even after increasing the reaction time up to 5 h. The selectivity towards PHBA is also decreased considerably due to unwanted benzyl methyl ether formation. An

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Conv. of p-cresol (%)</th>
<th>PHBA</th>
<th>Ether</th>
<th>PHB aldehyde</th>
<th>PHB acid</th>
<th>Others</th>
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<td>2</td>
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<td>97</td>
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<td>1</td>
<td>0.5</td>
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</table>

Table 3—Effect of temperature on encapsulated cobalt-chlorosalen-Y [p-cresol=6 g; NaOH=6.2 g; catalyst=cobalt-chlorosalen-Y=0.175 mg of cobalt/g of cresol; time=3 h]

<table>
<thead>
<tr>
<th>Ammt. of Co(mg) /6g of cresol</th>
<th>Conv. of p-cresol (%)</th>
<th>PHBA</th>
<th>Ether</th>
<th>PHB aldehyde</th>
<th>Alcohol</th>
<th>Acid</th>
<th>Others</th>
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<td>4</td>
<td>2</td>
<td>3</td>
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<td>57.6</td>
<td>83</td>
<td>79</td>
<td>8</td>
<td>4</td>
<td>5</td>
<td>4</td>
<td></td>
</tr>
</tbody>
</table>

Table 4—Effect of cobalt content on neat cobalt-chlorosalen [p-cresol=6 g; NaOH=6.2 g; catalyst=neat cobalt-chlorosalen; temp=80°C; time=3 h]
enhancement of reaction rate has been observed with an incremental increase in reaction temperature between 60 and 70°C. A further increase in temperature gives products having less PHBA yield due to tar formation.

**Effect of cobalt content**

Reactions have been carried out at different p-cresol to catalyst ratios at 80°C. The results (Fig 4, Table 4) show that on increasing the amount of catalyst, the percentage conversion of p-cresol increases to an optimum value and then decreases with further increase in the amount of catalyst which may be attributed to a catalytically inactive dimer formation in case of neat complexes. Thus, in order to get maximum conversion and product selectivity, the cobalt content for the reaction is found to be in the narrow range of 4-5 mg of cobalt /6g of p-cresol in case of neat complexes. Similar conversion and selectivity can be achieved using one-fourth amount of cobalt in the case of encapsulated complexes which may be suggested to be due to site isolation of the complex in the zeolite super cage.

Catalytic behaviour of neat and encapsulated cobalt complexes in the reaction of p-cresol oxidation was studied. Results show that encapsulated complexes have higher TOF than neat complexes. The cobalt content and NaOH to p-cresol ratio have an obvious effect on the catalytic activity. Choice of a suitable reaction temperature and reaction time improves the rate of reaction. Cobalt-chlorosalen gives the best selectivity towards PHBA. Encapsulated cobalt schiff base complexes are expected to be novel and efficient catalysts for selective oxidation of p-cresol to p-hydroxybenzaldehyde.

**References**