CHAPTER VII

CATALYTIC STUDIES ON

ZEOLITE ENCAPSULATED COMPLEXES

Abstract

The catalytic activity of zeolite encapsulated complexes for hydrogen peroxide decomposition and the oxidation of benzyl alcohol or ethylbenzene with hydrogen peroxide has been investigated. The activity for the aerobic oxidation of organic substrates has also been studied. Zeolite complexes are suitable for the partial oxidation of organic compounds. Cu(II) complexes, especially that with 3-formyl salicylic acid have exhibited maximum activity. The recycling ability of this zeolite complex has also been tested. The poison resistance of the zeolite complexes has also been investigated. The encapsulated complexes of substituted salen ligands were evaluated for activity and poison resistance in comparison with that of salen. The bulkier salen like ligands reduce activity, but exhibit good poison resistance.
7.1 **INTRODUCTION**

Zeolite encapsulated complexes are known to exhibit catalytic behaviour similar to the corresponding homogeneous complex catalysts. The reactivity of such systems is considered to be bio-mimetic due to their structural similarity with natural enzymes. The special interest on these catalytic materials is due to their ability to possess the advantages of both homogeneous and heterogeneous catalysis. Of late, intensive research efforts have been initiated to investigate the utility of zeolite complexes as catalysts for oxidation reactions\(^1\)\(^-\)\(^4\). The efficiency of such systems depends, to a large extent, on the structural and electronic properties of encapsulated complexes. Therefore, the design and synthesis of novel zeolite complexes with improved characteristics and evaluation their catalytic activity are the main tasks in this area of investigation.

In this study, the following reactions were carried out on zeolite encapsulated complexes:

a) Decomposition of hydrogen peroxide
b) Oxidation of benzyl alcohol
c) Oxidation of ethylbenzene
d) Oxidation of 4-methoxybenzaldehyde

a) **Decomposition of hydrogen peroxide**

The catalytic decomposition of hydrogen peroxide has found wide application in the oxidation of organic substrates\(^5\). This process has attracted considerable attention in the development of an oxygen electrode for electrochemical fuel cells\(^6\). This reaction is also a convenient alternative to the electrolysis of water for the production of oxygen\(^7\). Furthermore, this reaction has been employed as a convenient and reliable test for the determination of catalytic activity\(^8\).

The decomposition of hydrogen peroxide has been studied homogeneously using transition metal ions and their complexes as catalysts\(^9\). Transition metal oxide or noble metal catalysts have been used for carrying out this reaction heterogeneously\(^10\).
Supported transition metal complexes have also received wide attention as catalysts for this application. Zeolite encapsulated metal complexes are expected to be active for the decomposition of hydrogen peroxide.

b) Oxidation of benzyl alcohol/ethyl benzene

The complete oxidation of organic substrates over various catalysts has been studied at length, especially with respect to pollution control. However, studies on catalytic partial oxidation of hydrocarbons and oxygenated compounds are relatively scanty. But, the partial oxidation is an attractive method for the production of aldehydes and ketones from primary and secondary alcohols respectively. The production benzaldehyde from benzyl alcohol over perovskite catalysts is an excellent example for such partial oxidation. Catalytic oxidative dehydrogenation of ethylbenzene to acetophenone is also important in fine chemical industry. This reaction could be taken as a model for the oxyfunctionalisation of hydrocarbons in catalytic studies.

c) Oxidation of 4-methoxybenzaldehyde

The Baeyer-Villiger oxidation or Dakin reaction for the synthesis of phenols from aldehydes using peracids or hydrogen peroxide is an important reaction in organic chemistry. Methyltrioxorhenium (MTOR) has been reported to be an effective homogeneous catalyst for this oxidation with hydrogen peroxide. A variety of phenols have been synthesized using this catalyst. However, the operational difficulty of this homogeneous catalyst was the major problem encountered in MTOR based process. Zeolite encapsulated transition metal complexes are generally considered to avoid operational inconvenience associated with homogeneous catalysis. It was therefore thought interesting to study the catalytic activity of zeolite complexes for the Baeyer-Villiger oxidation of 4-methoxybenzaldehyde.

In this study, zeolite encapsulated Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) complexes of dmg, fsal, Mesalen and Benzosalen were screened with respect to the
efficiency for $\text{H}_2\text{O}_2$ decomposition and oxidation of benzyl alcohol or ethylbenzene. $\text{H}_2\text{O}_2$ and molecular oxygen are the oxidants used in this study. These oxidants are expected to be very effective due to their high mobility in zeolite cavities. The effect of oxidant/substrate mole ratio and reaction temperature on activity was studied. The recycling ability and the poison resistance properties of the catalysts were evaluated. The effect of using substituted ligands instead of salen in zeolite systems was investigated. The suitability of zeolite complex as catalyst for the oxidation of 4-methoxybenzaldehyde was studied using the most promising catalyst. The details of these studies are presented in this chapter.

7.2 EXPERIMENTAL

7.2.1 Materials

Zeolite encapsulated complexes of dmg, fsal, Mesalen and Benzosalen were used for catalytic studies. The various reagents used for the experiments are mentioned in Chapter II.

7.2.2 Determination of Catalytic activity

a) Decomposition of hydrogen peroxide

The experimental set up used for the decomposition of hydrogen peroxide is shown in Figure VII. 1. The decomposition efficiency was evaluated by monitoring the volume of oxygen evolved using a gas burette attached to the reaction flask. The procedure of this test is as follows:

Hydrogen peroxide solution (30 ml, 10 % $\text{H}_2\text{O}_2$ (wt/v) ) was taken in a reaction flask of 100 ml capacity containing a magnetic paddle for stirring. A plastic float containing catalyst sample (50 mg) was placed over the solution in the reaction flask.
Gas burette was filled with ~ 20 % NaCl solution acidified with dil. HCl and coloured using methyl orange. The solution levels in both arms of gas burette were equalized at 'zero' before connecting to reaction flask. The three-way valve connecting reaction flask and gas burette can be adjusted to maintain atmospheric pressure in the system before starting the reaction. The catalyst was dispersed in the H$_2$O$_2$ solution by magnetic stirring. As the reaction proceeds, oxygen liberated was collected in the right arm of gas burette. The volume of oxygen liberated was noted after equalizing the solution levels in both arms at intervals of 5 minutes. The experiment was continued until 10 ml (total capacity of gas burette) of oxygen was liberated or for 90 minutes.

b) Oxidation of benzyl alcohol/ethylbenzene

The experimental set up used for performing oxidation reactions is shown in Figure VII. 2. An oil bath with a temperature controller was used for maintaining the reaction temperature with an accuracy of ± 2 °C.
The procedure of the experiment is as follows: The catalyst sample (50 mg) was taken in the reaction flask containing a magnetic paddle. It was immersed in the oil bath whose temperature was previously adjusted to that specified for the test. The required amount of the substrate, benzyl alcohol or ethylbenzene and benzene (10 ml) was taken in the reaction flask. Hydrogen peroxide required for keeping the specified oxidant/substrate mole ratio was also added. The reaction mixture was stirred magnetically for 8 hours. After the experiment, the flask was cooled and the organic layer was separated. The aqueous layer was extracted several times with diethyl ether to collect the traces of substrate and product, dissolved in the aqueous solution. After evaporating ether, this extract was mixed with the organic layer collected previously. The product and unreacted substrate were analysed using gas chromatograph.

Molecular oxygen was also used as oxidant. A flow of dry air at 10 ml/minute was scrubbed in the substrate-solvent mixture in the reaction flask under atmospheric
pressure. Tertiary butyl hydrogen peroxide (0.25 ml) was added as an initiator for the reaction.

The reaction conditions specific to each test are given along with the results in section 7.3. The oxidation activity of the catalyst was represented as the percentage conversion of the substrate.

c) Oxidation of 4-methoxybenzaldehyde

The experimental set up shown in Figure VII. 2 was used for the oxidation of 4-methoxybenzaldehyde. The procedure of the experiment is as follows: 4-methoxybenzaldehyde (1.57 g, 11.5 mmol) was mixed with hydrogen peroxide (30% H₂O₂ (wt/v); 3.3 ml) and 10 ml methanol in the reaction flask. The oxidant/substrate mole ratio in this mixture was ~ 2.5. 50 mg of the catalyst was added and the mixture was then stirred at 50 °C for 24 hours. Then, the reaction mixture was extracted with diethyl ether and the unreacted substrate was separated by silica gel column chromatography using a mixture of hexane and dichloromethane (7:3) as eluent.

7.2.3 Recycling test

After the initial activity measurement for the oxidation of benzyl alcohol, the catalyst in the aqueous layer of the reaction mixture was filtered, washed with acetone and again tested for activity at identical conditions. After the test, the catalyst was filtered and analysed for IR spectrum.

7.2.4 Poison resistance test

The poison resistance of encapsulated complexes was studied by determining the activity using a substrate containing traces of pyridine. The percentage loss in activity indicates the extent of deactivation by poisoning.
7.2.5 Catalytic studies on salen type complexes

The activity and poison resistance properties of the encapsulated Cu(II) complexes of substituted salens, Mesalen and Benzosalen were studied in comparison with those of zeolite Cu(II)salen complex. Zeolite encapsulated Cu(II)salen was synthesized for this purpose as per the method given in the literature\(^\text{16}\).

7.3 RESULTS

(a) Decomposition of hydrogen peroxide

The \(\text{H}_2\text{O}_2\) decomposition data are given in Table VII. 1. The catalysts can be graded with respect to the decomposition activity on the basis of volume of oxygen evolved and time taken for this evolution. Figure VII. 3, a plot of volume of oxygen liberated against time, provides a comparison of the rate of decomposition of hydrogen peroxide over encapsulated complexes of each ligand.

Table VII. 1

<table>
<thead>
<tr>
<th></th>
<th>dmg</th>
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</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Duration (min.)</td>
<td>(V_{O_2}) (ml)</td>
<td>Duration (min.)</td>
<td>(V_{O_2}) (ml)</td>
<td>Duration (min.)</td>
<td>(V_{O_2}) (ml)</td>
<td>Duration (min.)</td>
<td>(V_{O_2}) (ml)</td>
</tr>
<tr>
<td>YMn(II)</td>
<td>90</td>
<td>1.92</td>
<td>90</td>
<td>2.78</td>
<td>90</td>
<td>3.75</td>
<td>90</td>
<td>3.88</td>
</tr>
<tr>
<td>YFe(III)</td>
<td>90</td>
<td>5.45</td>
<td>90</td>
<td>3.20</td>
<td>90</td>
<td>3.70</td>
<td>90</td>
<td>3.42</td>
</tr>
<tr>
<td>YCo(II)</td>
<td>90</td>
<td>7.18</td>
<td>65</td>
<td>9.47</td>
<td>90</td>
<td>8.31</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>YNi(II)</td>
<td>90</td>
<td>6.44</td>
<td>90</td>
<td>4.56</td>
<td>90</td>
<td>2.44</td>
<td>90</td>
<td>2.40</td>
</tr>
<tr>
<td>YCu(II)</td>
<td>35</td>
<td>9.59</td>
<td>15</td>
<td>8.9</td>
<td>55</td>
<td>9.56</td>
<td>45</td>
<td>9.45</td>
</tr>
</tbody>
</table>

* Co-Benzosalen could not be encapsulated ( vide page 145 )

Reaction conditions

| Catalyst weight | 50 mg | Temperature | 30 \(^\circ\)C | \(\text{H}_2\text{O}_2\) (10 %) | 30 ml | Duration | 90 min. |
Figure VII. 3

H₂O₂ decomposition - Volume of oxygen liberated versus time

Since hydrogen peroxide itself decomposes in alkaline medium, a solution of pH ~ 6 was used for determining the activity of the catalyst. A blank experiment was carried out at identical test conditions using NaY zeolite. Only a negligible decomposition, which might be due to impurities, was observed over NaY zeolite. The decomposition data reveal that the catalytic activity of Cu(II) complexes is higher than that of complexes of
other metal ions. Co(II) complexes are found to be moderately active as compared to others. The complexes of Mn(II), Fe(III) and Ni(II) ions are weakly active. In general, the decomposition efficiency of zeolite encapsulated complexes of each ligand varies in the order of metal ions as Cu(II) > Co(II) > Ni(II) ~ Mn(II) ~ Fe(III).

The decomposition data of Cu(II) complexes are represented in Figure VII. 4. Among them, fsal complex shows distinctly better activity than others. The activity of Cu(II) complexes varies in the order YCu-fsal > YCu-dmg > YCu-Mesalen ~ YCu-Benzosalen. There is only a minor difference in activity between YCu-Mesalen and YCu-Benzosalen.

![Graph](image.png)

**Figure VII. 4**

H$_2$O$_2$ decomposition data of encapsulated Cu(II) complexes

**b) Oxidation of benzyl alcohol/ethyl benzene**

The oxidation of benzyl alcohol or ethylbenzene was performed over the zeolite complexes using H$_2$O$_2$ or molecular oxygen as the oxidant. The extent of oxidation of organic substrates usually depends on the relative concentration of oxidant in the reaction mixture. Therefore, oxidant/substrate mole ratio was optimized for the
oxidation of benzyl alcohol with hydrogen peroxide. YCu-fsal, the most active catalyst for H2O2 decomposition was used for this optimization study. The oxidant/substrate mole ratio was varied in the range 0.5-2.5. The effect of mole ratio on activity is represented as a plot of % conversion of benzyl alcohol against the oxidant/substrate mole ratio in Figure VII. 5. The oxidation efficiency was found to be enhanced on increasing the mole ratio upto 2 and then almost stabilised in the range 2.0-2.5. Therefore, the optimum mole ratio can be fixed as 2.0-2.5. In this study, the oxidant/substrate mole ratio was kept at 2.5 for carrying out the oxidation reactions.

Figure VII. 5
% Conversion of benzyl alcohol versus oxidant/substrate mole ratio

Reaction conditions

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst weight</td>
<td>50 mg</td>
<td>Temperature</td>
</tr>
<tr>
<td>Benzyl alcohol</td>
<td>5 ml</td>
<td>Duration</td>
</tr>
<tr>
<td>Solvent ( benzene )</td>
<td>10 ml</td>
<td></td>
</tr>
</tbody>
</table>
Table VII. 2
Activity for benzyl alcohol oxidation

<table>
<thead>
<tr>
<th></th>
<th>dmg</th>
<th>fsal</th>
<th>Mesalen</th>
<th>Benzosalen</th>
</tr>
</thead>
<tbody>
<tr>
<td>YMn(II)</td>
<td>11.6</td>
<td>7.4</td>
<td>6.9</td>
<td>9.3</td>
</tr>
<tr>
<td>YFe(III)</td>
<td>13.5</td>
<td>6.9</td>
<td>8.3</td>
<td>8.9</td>
</tr>
<tr>
<td>YCo(II)</td>
<td>18.7</td>
<td>23.5</td>
<td>12.1</td>
<td></td>
</tr>
<tr>
<td>YNi(II)</td>
<td>12.9</td>
<td>7.1</td>
<td>8.1</td>
<td>12.1</td>
</tr>
<tr>
<td>YCu(II)</td>
<td>30.0</td>
<td>44.7</td>
<td>28.3</td>
<td>32.7</td>
</tr>
</tbody>
</table>

Reaction conditions

<p>| | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst weight</td>
<td>50 mg</td>
<td>Temperature</td>
<td>50 °C</td>
<td></td>
</tr>
<tr>
<td>Benzyl alcohol</td>
<td>5 ml</td>
<td>Duration</td>
<td>8 hours</td>
<td></td>
</tr>
<tr>
<td>Oxidant/substrate</td>
<td>2.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solvent (benzene)</td>
<td>10 ml</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

% Conversion of benzyl alcohol over zeolite complexes

Figure VII. 6

The oxidation efficiency of zeolite Cu(II) complexes is much greater than that of corresponding complexes of other metal ions. The Co(II) complexes of dmg and fsal are also active, but not to the extent of respective Cu(II) complex. However, the activity of YCo-Mesalen is not promising. Among Cu(II) complexes, YCu-fsal is distinctly better as compared to others. However, the activity of other Cu(II) complexes, YCu-dmg.
YCu-Mesalen and YCu-Benzosalen are comparable to each other and about 30% lower than that of YCu-fsal. From the above results, it was understood that zeolite encapsulated Cu(II) complexes exhibit maximum activity and, therefore, further catalytic studies were confined to only Cu(II) complexes.

Table VII. 3
Effect of reaction temperature on benzyl alcohol oxidation

<table>
<thead>
<tr>
<th>Reaction temp. (°C)</th>
<th>YCu-dmg</th>
<th>YCu-fsal</th>
<th>YCu-Mesalen</th>
<th>YCu-Benzosalen</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>30.0</td>
<td>44.7</td>
<td>28.3</td>
<td>32.7</td>
</tr>
<tr>
<td>60</td>
<td>40.8</td>
<td>61.6</td>
<td>36.8</td>
<td>44.2</td>
</tr>
<tr>
<td>70</td>
<td>52.6</td>
<td>76.7</td>
<td>47.7</td>
<td>56.1</td>
</tr>
</tbody>
</table>

Reaction conditions
Catalyst weight 50 mg
Benzyl alcohol 5 ml
Oxidant/substrate 2.5
Solvent (benzene) 10 ml

Figure VII. 7
% Conversion of benzyl alcohol versus reaction temperature
The oxidation of benzyl alcohol was carried out at temperatures 50 °C, 60 °C and 70 °C with a view to evaluate the influence of reaction temperature on oxidation activity. These activity results are given in Table VII. 3. The variation of activity on increasing the temperature is shown in Figure VII. 7. Generally, the activity is found to increase on increasing the reaction temperature. From the plot, it is clear that the extent of elevation of activity with temperature is higher for YCu-fsal.

Table VII. 4
Effect of reaction temperature on ethylbenzene oxidation

<table>
<thead>
<tr>
<th>Reaction temp. (°C)</th>
<th>YCu-dmg</th>
<th>YCu-fsal</th>
<th>YCu-Mesalen</th>
<th>YCu-Benzosalen</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>24.0</td>
<td>37.8</td>
<td>23.1</td>
<td>25.9</td>
</tr>
<tr>
<td>60</td>
<td>33.6</td>
<td>51.2</td>
<td>29.4</td>
<td>33.7</td>
</tr>
<tr>
<td>70</td>
<td>46.3</td>
<td>65.6</td>
<td>39.2</td>
<td>43.8</td>
</tr>
</tbody>
</table>

Reaction conditions

- Catalyst weight: 50 mg
- Ethylbenzene: 5 ml
- Oxidant/substrate: 2.5
- Solvent (benzene): 10 ml
- Temperature: 50/60/70 °C
- Duration: 8 hours

Figure VII. 8

% Conversion of ethylbenzene versus reaction temperature
The results of ethylbenzene oxidation are given in Table VII. 4. The % conversion of ethylbenzene is higher for YCu-fsal as in the case of benzyl alcohol oxidation. Figure VII. 8 indicates that the activity for ethylbenzene oxidation also increases on increasing the reaction temperature. However, the activity values are lesser in this case as compared to those for benzyl alcohol oxidation. YCu-fsal showed 90 % conversion for the oxidation of 4-methoxybenzaldehyde.

The oxidation reactions were also carried out using molecular oxygen. The efficiency of encapsulated Cu(II) complexes for the aerobic oxidation is lower than that obtained when hydrogen peroxide is used as the oxidant. However, YCu-fsal is much better than others for aerobic oxidation as well. During benzyl alcohol oxidation, the formation of traces of benzoic acid is quite possible by the oxidation of benzaldehyde on contacting with air. However, it would not affect the comparative evaluation of zeolite complexes.

Table VII. 5
Activity results of benzyl alcohol / ethylbenzene oxidation with oxygen

<table>
<thead>
<tr>
<th></th>
<th>YCu-dmg</th>
<th>YCu-fsal</th>
<th>YCu-Mesalen</th>
<th>YCu-Benzosalen</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Benzyl alcohol oxidation</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>% Conversion</td>
<td>18.6</td>
<td>28.1</td>
<td>16.8</td>
<td>19.8</td>
</tr>
<tr>
<td><strong>Ethylbenzene oxidation</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>% Conversion</td>
<td>16.8</td>
<td>24.1</td>
<td>11.1</td>
<td>12.9</td>
</tr>
</tbody>
</table>

**Reaction conditions**
- Catalyst weight: 50 mg
- Substrate: 5 ml
- TBHP: 0.25 ml
- Solvent (benzene): 10 ml
- Temperature: 50 °C
- Duration: 12 hours
- Air flow: 10ml/min.
- Pressure: atmospheric

The ability of YCu-fsal to recycle for the oxidation of benzyl alcohol was evaluated. The initial conversion of 44.7% is reduced to 42.3% indicating a marginal loss in activity.
on recycling the catalyst. The IR spectrum of the reused sample is quite similar to that of fresh sample.

Table VII. 6
Poison resistance of Cu(II) complexes

<table>
<thead>
<tr>
<th>%Conversion</th>
<th>YCu-dmg</th>
<th>YCu-fsal</th>
<th>YCu-Mesalen</th>
<th>YCu-Benzosalen</th>
</tr>
</thead>
<tbody>
<tr>
<td>without poisoning</td>
<td>30.0</td>
<td>44.7</td>
<td>28.3</td>
<td>32.7</td>
</tr>
<tr>
<td>with poisoning</td>
<td>14.2</td>
<td>27.1</td>
<td>20.5</td>
<td>20.9</td>
</tr>
<tr>
<td>% Loss in conversion</td>
<td>52.7</td>
<td>39.4</td>
<td>27.6</td>
<td>36.1</td>
</tr>
</tbody>
</table>

Reaction conditions

<p>| | | | | |</p>
<table>
<thead>
<tr>
<th></th>
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<tr>
<td>Catalyst weight</td>
<td>50 mg</td>
<td>Temperature</td>
<td>50 °C</td>
<td></td>
</tr>
<tr>
<td>Benzyl alcohol with</td>
<td>5 ml</td>
<td>Duration</td>
<td>8 hours</td>
<td></td>
</tr>
<tr>
<td>traces of pyridine</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solvent (benzene)</td>
<td>10 ml</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure VII. 9
Poison resistance of encapsulated Cu(II) complexes

The poison resistance of Cu(II) complexes was evaluated using benzyl alcohol poisoned with pyridine as substrate. The activity results of this test along with those of
corresponding fresh catalysts are presented in Table VII. 6. Figure VII. 9 provides an idea about the rate deactivation of different Cu(II) complexes on poisoning. The encapsulated Cu(II) complexes can be graded with respect to poison resistance as YCu-Mesalen > YCu-Benzosalen > YCu-fsal > YCu-dmg.

Table VII. 7
Activity of Cu(II) complexes of salen and substituted salens

<table>
<thead>
<tr>
<th>% Conversion</th>
<th>YCu-salen</th>
<th>YCu-Mesalen</th>
<th>YCu-Benzosalen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without poisoning</td>
<td>37.8</td>
<td>28.3</td>
<td>32.7</td>
</tr>
<tr>
<td>With poisoning</td>
<td>20.3</td>
<td>20.5</td>
<td>20.9</td>
</tr>
<tr>
<td>% Loss in conversion</td>
<td>46.3</td>
<td>27.6</td>
<td>36.1</td>
</tr>
</tbody>
</table>

Reaction conditions

- Catalyst weight: 50 mg
- Benzyl alcohol with traces of pyridine: 5 ml
- Solvent (benzene): 10 ml
- Temperature: 50 °C
- Duration: 8 hours

Figure VII. 10
Poison resistance of salen and substituted salen complexes
The oxidation activity and poison resistance of zeolite encapsulated Cu(II) complexes of salen and substituted salens are presented in Table VII. 7. The poison resistance of these catalysts is represented in Figure VII. 10. From these results, the effect of using bulkier salen like ligands on catalytic activity can be assessed in comparison with salen ligand. The oxidation activity of YCu-salen is better than that of encapsulated complex of Mesalen or Benzosalen. However, YCu-salen was undergone severe deactivation on poisoning, whereas YCu-Mesalen and YCu-Benzosalen are more resistant to poisoning. The poison resistance of these complexes varies in the order YCu-Mesalen > YCu-Benzosalen > YCu-salen.

7. 4 DISCUSSION

The decomposition of hydrogen peroxide is usually catalysed by transition metal ions or their complexes. In order to explain this reaction, a radical chain mechanism has been proposed in which the catalyst increases the rate of initiation reaction for the formation of HOO radical \(^{16}\). In the case of zeolite encapsulated complexes, this mechanism can be represented as follows:

\[
2 \text{H}_2\text{O}_2 \rightarrow 2 \text{HOO}^- + 2\text{H}^+ \\
2 \text{Z(LM)}^{n^+} + 2 \text{HOO}^- \rightarrow 2 \text{Z(LM)}^{(n-1)^+} + 2 \text{HOO} \\
2 \text{HOO} \rightarrow \text{O}_2 + \text{H}_2\text{O}_2 \\
2 \text{Z(LM)}^{(n-1)^+} + \text{H}_2\text{O}_2 \rightarrow 2 (\text{LM})^{n^+} + 2 \text{OH}^- 
\]

As per this reaction scheme, the redox potential of active metal ion plays a vital role in the decomposition of hydrogen peroxide. The coordination of metal ion with ligand may slightly alter the redox potential and as a result of this, a modified catalytic activity might have obtained

In another mechanism proposed, the decomposition reaction occurs in the coordination sphere of the metal ion with the formation of intermediate peroxo species, \((\text{LM}^{n^+})(\text{OOH}^-)^9,11\).
The following reaction scheme may be suggested for this mechanism:

\[
Z(LM)^{n+} + H_2O_2 \rightarrow Z(LM)^{n+} (H_2O_2)
\]

\[
Z(LM)^{n+} (H_2O_2) \rightarrow Z(LM)^{n+} (OOH^-) + H^+
\]

This peroxy intermediate can also be formed by the action of OOH\(^-\) generated from free H\(_2\)O\(_2\) molecules in solution.

\[
H_2O_2 \rightarrow H^+ + OOH^-
\]

\[
Z(LM)^{n+} + OOH^- \rightarrow Z(LM)^{n+}(OOH^-)
\]

The accessibility of the coordination sphere for H\(_2\)O\(_2\) or OOH\(^-\) and the availability of vacant coordination sites at the metal ion are the main requirements for the decomposition to proceed via this mechanism. Sigel has found that the vacant coordination site in copper polyammine chelate leads to high decomposition rate whereas fully coordinated Cu(II) complexes are inactive\(^1^7\). Mn(II) and Fe(III) chelates of diethyltriammine have also been found to be active as two metal sites are available for coordination with peroxy anions\(^1^8\).

In the case of zeolite encapsulated complexes, the mechanism involving peroxy intermediates is more probable at the available coordination sites of metal ion. A colour change was observed for the complexes on contacting with H\(_2\)O\(_2\) which is an indicative of the formation of intermediate peroxy species. Similar colour change has been found in the case of supported Cu(II) complex by previous workers\(^1^1\).

The decomposition data show that zeolite encapsulated Cu(II) complexes are more active than other metal complexes. The characterization data of these complexes indicate the possibility of a tetrahedrally distorted square planar geometry for Cu(II) complexes. This geometry may facilitate the formation of peroxy intermediates in the coordination sphere leading to enhanced decomposition activity. The distinctly better activity of YCu-fsal among encapsulated Cu(II) complexes may be due to the formation of an intermediate in which two peroxy groups are coordinated in the binuclear structure.
as shown below. The formation of such active peroxo intermediates in binuclear complexes has been proposed in earlier studies\textsuperscript{19}.

$$\text{Cu}^{2+} \rightarrow \text{Cu}^{2+}$$

Although Co(II) complexes possess octahedral or tetrahedral symmetry with no vacant sites, they are moderately active indicating the formation of peroxo intermediates on them. The peroxo species can be formed in octahedral Co(II) complexes only by the replacement of coordinated water molecules or oxide ions of zeolite framework, whereas in tetrahedral symmetry, a rearrangement of coordination sphere is essential for the reaction to proceed. The process of ligand replacement or rearrangement of coordination sphere restrict the rate of formation of peroxo intermediate which leads to a lower activity for Co(II) complex as compared to Cu(II) complex. YNi-dmg is also moderately active, may be because of the slightly distorted square planar symmetry observed for it. The other Ni(II) complexes are comparatively inactive as they possess an octahedral symmetry. All the Mn(II) and Fe(III) complexes are weak for $\text{H}_2\text{O}_2$ decomposition. The fine-tuning of redox potentials of metal ions by ligation also might have played a major role in the decomposition of $\text{H}_2\text{O}_2$.

Zeolite encapsulated complexes can be screened with respect to the catalytic activity for the oxidation of benzyl alcohol. The oxidation of benzyl alcohol is negligible over NaY zeolite under the same experimental conditions employed for screening zeolite complexes. This indicates that zeolite support is inactive for the oxidation reaction. Furthermore, hydrogen peroxide only slightly oxidises these substrates in the absence of a catalyst. Therefore, the catalysis by encapsulated complex is the sole reason for the oxidation reaction. The percentage conversion of benzyl alcohol varies depending on the nature of encapsulated complex. This observation also suggests that the reaction is
catalytic in nature i.e. it proceeds by the catalysis of metal complexes encapsulated in zeolite.

The optimum oxidant/substrate mole ratio was found to be 2.5 for the oxidation of benzyl alcohol over YCu-fsal. An excess of hydrogen peroxide is required because of its parallel decomposition which is independent of the oxidation of organic substrate. The oxygen gas liberated may partially involve in the oxidation reaction by interacting with the active sites of the catalyst \(^{20}\). The catalytic oxidation of benzyl alcohol to benzaldehyde can be represented as given below:

\[
\begin{align*}
\text{H}_2\text{O}_2 + Z(\text{ML}) & \xrightarrow{\text{oxygen transfer}} \text{Catalyst precursor} \\
& \xrightarrow{\text{decomposition}} \text{O}_2
\end{align*}
\]

The above mechanism involves the interaction of the encapsulated complex with hydrogen peroxide. The oxidant donates an oxygen atom to coordinate at the vacant metal site in the complex forming the catalyst precursor. This oxygen atom is transferred to benzyl alcohol molecule approaching the metal complex to form benzaldehyde. The interaction of the substrate with the catalyst precursor is considered to be weak as per this mechanism. The ability of transition metal complexes to oxidise non-interacting type compounds like saturated hydrocarbons may hint the lack of interactions between the metallic site and substrate \(^{21}\). The oxidation of ethylbenzene is also expected to follow a similar mechanism.

Zeolite encapsulated Cu(II) complexes are found to be more active than others for the oxidation of benzyl alcohol. The tetrahedrally distorted square planar structure of these complexes may account for their higher activity. High activity is also expected for Co(II) complexes as they are usually very efficient for the reversible adsorption of
oxygen. But, YCo-dmg and YCo-fsal are only moderately active as compared to Cu(II) complexes, whereas YCo-Mesalen is weakly active. The octahedral symmetry of YCo-dmg and YCo-Mesalen and tetrahedral symmetry of YCo-fsal may restrict them to effectively catalyse oxidation reactions. The structure necessitates the replacement of coordinated water molecules in octahedral case and the rearrangement of coordination sphere in tetrahedral case for the catalysis to occur. In spite of having distorted square planar geometry, YNi-dmg is weakly active, may be because of the poor affinity of Ni sites for oxygen atoms to form the intermediate complex. The poor activity of other Ni(II) complexes can be attributed to their octahedral geometries in zeolite pores. The encapsulated Fe(III) and Ni(II) complexes are generally inactive. However, the oxidation activity of all zeolite complexes increases on increasing the reaction temperature.

The structure of encapsulated Mn(II) and Fe(III) complexes could not be recognized from their magnetic moment and electronic spectral data. However, the lower catalytic activity of these complexes hints the absence of vacant coordination sites. Therefore, an octahedral symmetry can be assumed for encapsulated Mn(II) and Fe(III) complexes.

YCu-fsal is superior to other Cu(II) complexes with respect to oxidation activity. The binuclear structure of Cu-fsal is expected to have facilitated the reaction by forming an intermediate precursor complex, which is entirely different from that formed on mononuclear complexes. However, further studies are necessary to confirm the effect of binuclear structure. The oxidation activity of other Cu(II) complexes is comparable to each other and less than that of YCu-fsal by around 30 %. Similar trend could be observed in the efficiency of Cu(II) catalysts for the oxidation of ethylbenzene also. However, these values are slightly lower than corresponding values for benzyl alcohol oxidation showing the difficulty in oxidising hydrocarbons YCu-fsal is also active for the oxidation 4-methoxybenzaldehyde.

Zeolite encapsulated complexes have been found to be active for the aerobic oxidation of organic substrates⁴. The ability of zeolite complexes for the oxidation of
benzyl alcohol and ethylbenzene with molecular oxygen was evaluated. The activity observed in these cases is lower than that obtained on using hydrogen peroxide as oxidant. The ability of H₂O₂ to donate active oxygen atoms to metallic site might be the reason for the higher reactivity.

The oxidation of benzyl alcohol with hydrogen peroxide over zeolite complexes gives benzaldehyde as the exclusive product. In contrast to conventional metal oxides, the formation of benzoic acid by the further oxidation of benzaldehyde or other side products is not observed in the present cases. This shows that zeolite encapsulated complexes can act as catalysts for partial oxidation. Similar behaviour of zeolite encapsulated iron phthalocyanine complex for the partial oxidation of hydrocarbons has been reported²².

One of the attractive features of zeolite encapsulated complexes is the ability to be recycled without much deterioration. The recycling test was performed on YCu-fsal. The retention of catalytic activity indicates the ability of this system to be used for longer periods and to be recycled in oxidation reactions. The IR spectrum recorded for the catalyst collected after recycling test is quite comparable to that of fresh sample showing little changes in the coordination of the ligand. The zeolite framework is expected to prevent the deactivation of encapsulated complexes by processes like dimerisation. Furthermore, there is no scope for the leaching of metal complexes as observed in polymer supported systems due to their exclusive immobilization in zeolite cavities.

Poison resistance properties of encapsulated Cu(II) complexes were studied by using a substrate poisoned with traces of pyridine. The extent of poison resistance was found to vary as YCu-Mesalen > YCu-Benzosalen ~ YCu-fsal > YCu-dmg. In the case of YCu-Mesalen, the steric effects of methyl group may prevent the approach of pyridine molecules to the vacant coordination sites. Relatively, a high degree of tetrahedral distortion was observed for YCu-Mesalen by EPR studies ( vide page 136 ). This distortion may also induce poison resistance for this complex. YCu-fsal and YCu-
Benzosalen exhibit relatively moderate poison resistance whereas YCu-dmg is severely affected.

The activity and poison resistance of encapsulated Cu(II) complexes of substituted salen ligands are compared with those of zeolite salen complex. Zeolite Cu(II)salen is more active than substituted salen complexes. The lower activity of substituted salen complexes could be explained in terms of the lower mobility of reactant molecules in zeolite cavities. A high degree of distortion, which is likely in the case of zeolite encapsulated complexes of bulkier substituted salens is expected to lower the mobility of reactant molecules in the cage. The steric effects of methyl groups in YCu-Mesalen may further reduce the mobility of reactants and therefore exhibit lower activity. These aspects may also account for the enhanced poison resistance properties of substituted salen complexes in comparison to salen complex. However, molecular modeling studies with a simulation for these oxidation reactions are necessary to confirm the steric effects on activity and poison resistance.

7.5 Summary and Conclusion

Zeolite encapsulated complexes can act as catalysts for hydrogen peroxide decomposition and the partial oxidation of organic substrates like benzyl alcohol and ethylbenzene with hydrogen peroxide. The oxidant/substrate mole ratio has been optimised as 2.0-2.5. These systems are also suitable for aerobic oxidation of organic compounds. Generally, encapsulated Cu(II) complexes are more active than complexes of other metal ions. Co(II) complexes are moderately active as compared to Cu(II) complexes. YCu-fsal is the most promising catalyst with respect to activity among various complexes studied. The geometries of the encapsulated complexes may account for their catalytic behaviour. The activity of YCu-fsal is almost sustained on recycling indicating little deactivation for the encapsulated complex. However, poison resistance of this complex is slightly lower than that of complexes of substituted salens. The use of bulkier substituted salens as ligand reduces the catalytic activity as compared to salen complex, but imparts poison resistance. The lower activity and enhanced poison resistance of these bulkier complexes could be attributed to the reduced mobility of molecules in the cage.
REFERENCES

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