Catalase-like Activity of Polystyrene-, and N-vinyl-2-pyrrolidone-Acrylic Acid Copolymer-supported Metal Complexes
Catalysis may be defined as the art of manipulating chemical molecules in order to facilitate their transformation along the desired reaction pathway. This manipulation is achieved through the interaction of this molecule with a group of atoms called the active centre, and the formation of the appropriate intermediate complex. The chemistry and applications of the functionalised polymers depend largely on the characteristics of the specific active functional groups. The architectural characteristics of the macromolecule influence the behaviour of these functional groups. This interdependence of the polymer microstructure and reactivity of functional groups in functionalised polymers dictates the applications of such systems in a number of areas of functional and technological interest.

Catalysis by transition metal complexes has gained prominence in recent years. During the last 15 years chemists have been interested with the idea of anchoring transition metal catalysts to organic polymers. Such studies have sought to produce heterogenised catalyst systems that are as active and selective as their homogeneous counterparts while having the distinguishing characteristic of being easily separable from the reaction media. The advantages apart from recovery and reuse are: (a) isolation of catalytic sites and prevention of agglomeration leading to inactivation, and (b) coordinate unsaturation introduced by the polymeric matrix resulting in enhanced specificity.
The catalytic cycle of a polymer-metal complex catalysed reaction is illustrated by the following equations.

\[
ML_n + S \rightleftharpoons L_{n-1}M\cdot S
\]

\[
\uparrow \quad \downarrow
\]

\[
M'L + S^* \rightleftharpoons L_{n-1}M'S^*
\]

where M is the metal ion, L the ligand and S the substrate.

In the first step, substrate coordinates to a metal catalyst forming an intermediate mixed complex \((LMS)\). The substrate is then activated by metal ions and dissociates from the catalyst. The complex catalyst, having accomplished its purpose, is regenerated to the original complex. The catalytic action of a metal ion depends substantially on the nature of the ligands in the intermediate mixed complex.\(^{52}\)

Many biological systems are capable of selecting substrates for reaction from solution on the basis of bulk molecular properties. The effect of chemical anchoring of molecular complexes on functionalised resins was studied with various catalytic systems.\(^{279,280}\) The catalytic activity of a polymer-anchored metal complex, compared with those of analogues molecular complexes in a homogeneous systems, is dependent on the availability of inner sites of the polymer support.\(^{281}\) This availability may be determined by the swellability of the polymer support,\(^{282}\) distribution of the active complex on the polymer texture,\(^{283}\) and by the fit of pore sizes to the substrate molecules.\(^{284}\) The attachment of homogeneous catalysts to polystyrene-divinyl benzene copolymer produces a new class of catalysts with many of the best properties of both heterogeneous and homogeneous catalysts.\(^{285}\)

The catalytic effects of polymer-metal complexes prepared from synthetic or natural polymer and metal ion have been studied by several authors in recent
years. Polymer metal complexes are widely used as immobilised catalysts with high efficiency. Several attempts have been made to use fully synthetic polymeric catalysts that incorporate all the functional features like specificity and activity of the natural enzymes. The effective catalysts from such complexes are now being developed to imitate the enzymic reaction which proceed effectively under mild conditions, i.e., at ambient temperature and atmospheric pressure. Various polymer-metal complexes are found to be effective in mimicking catalase-like activity in the decomposition of hydrogen peroxide. Several authors have also described similar catalytic activity in polymeric chelates.

The enzyme ‘catalase’ catalyse the disproportionation of hydrogen peroxide. This enzyme is very widespread and protect against the build-up of dangerous concentration of hydrogen peroxide in living systems as a consequence of partial reduction of dioxygen. Polymer-supported complexes have found numerous applications recently as catalysts in organic synthesis as well as model reactions. Some polymer-supported chelating agents which utilise a Schiff base linkage containing the salicylideminine ligand have been reported. Drago et al. reported the synthesis and catalytic oxidising potential of polymer-supported chelating amine and Schiff base complexes. The metal ion decomposition of hydrogen peroxide has received the attention of research workers as well as industry. The decomposition of hydrogen peroxide in homogeneous medium has been studied using metal ions and their complexes as catalysts. It is known that a homogeneous catalyst when attached to a support or in other words if it is heterogenised, may undergo modifications due to preferred orientation and changed the stereochemistry about the metal atoms.
Further its motion is restricted and the reaction on such a catalyst may be more rapid than that of a free catalyst.

5.1 Polystyrene Systems

In order to investigate the catalase-like activity of polystyrene-supported glycine-metal complexes, the decomposition reaction of hydrogen peroxide was chosen as a model. The decomposition of hydrogen peroxide is effected by using various metal complexes as catalysts. This catalysis has its origin in the redox action of a metal complex. The catalytic decomposition of hydrogen peroxide can be schematically represented as:

\[ \text{H}_2\text{O}_2 \rightarrow \text{HO}_2^- + \text{H}^+ \]

\[ \text{HO}_2^- + \text{PMC} \rightarrow \text{PMC} (\text{HO}_2) \]

\[ \text{PMC} (\text{HO}_2) + \text{H}_2\text{O}_2 \rightarrow \text{PMC} + \text{H}_2\text{O} + \text{O}_2 + \text{OH}^- \]

\( \text{PMC} = \text{Polymer Metal Complex} \)

A transient intermediate is formed between the metal catalyst and the substrate, at least in the initial step of the reaction, proceeds through chain decomposition. This reaction has been employed as a convenient model, because the reaction take place even if the catalyst is insoluble in the reaction solvent, and because the experimental technique to follow the reaction is not difficult. The catalytic decomposition of hydrogen peroxide has found wide application in the oxidation of organic substrates. Catalase-like activity is a key factor in therapeutic usage also.301

The reactivity of a ligand function on a crosslinked polymer support is highly dependent on the variables of the polymeric network structure. The
catalytic activity of the \( \text{Cr(II)}, \text{Mn(II)}, \text{Fe(III)}, \text{Co(II)}, \text{Ni(II)}, \text{Cu(II)} \) and \( \text{Zn(II)} \) complexes of polystyrene-supported glycine with different crosslinking agents were investigated in the decomposition of hydrogen peroxide. In all polystyrene systems the catalytic activity decreased in the order: \( \text{Co(II)} > \text{Cu(II)} > \text{Ni(II)} > \text{Cr(III)} > \text{Fe(III)} > \text{Mn(II)} > \text{Zn(II)} \). The variation in reactivity with metal ions can be explained in terms of coordination geometry and nature of crosslinking agents. In the case of \( \text{Zn(II)} \) complexes no considerable change was observed in reactivity with time. But compared with other metal complexes high reactivity of the \( \text{Co(II)} \) complex was due to its vacant coordination site and its distorted octahedral geometry. The \( \text{Co(II)} \) and \( \text{Cu(II)} \) complexes also have similar unsaturation making them reactive by the easy accessibility of the peroxide ion for complexation. The catalytic activities of the different crosslinked systems of polystyrene-supported glycine showed variation in reactivity with the nature of crosslinking agent which are summarised here.

5.1.1 Catalytic activity of DVB-crosslinked polystyrene-supported glycine-metal complexes

The development of a catalyst formulation should take into account not only the chemical nature and dispersion of the active species but also the topology of the polymer support which involve the surface area, pore size, pore volume and mechanical strength. For DVB-crosslinked system, the molecular character is found to exert a striking influence on the reactivity. The amount of metal ion complexed is minimum for DVB-crosslinked system due to its comparatively higher hydrophobicity and rigidity of the DVB-crosslinked systems. The reactivity of the various metal complexes decreased in the order: \( \text{Co(II)} > \text{Cu(II)} > \text{Ni(II)} > \text{Cr(III)} > \text{Fe(II)} > \text{Mn(II)} > \text{Zn(II)} \). The variation in reactivity of
various metal complexes of DVB-crosslinked polystyrene-supported sodium salt of glycine is shown in Figure 5.1.

![Figure 5.1. Catalytic activity of the various metal complexes of 2 mol% DVB-crosslinked polystyrene-supported glycine](image)

**Figure 5.1.** Catalytic activity of the various metal complexes of 2 mol% DVB-crosslinked polystyrene-supported glycine

### 5.1.2 Catalytic activity of EGDMA-crosslinked polystyrene-supported glycine-metal complexes

In the case of EGDMA-crosslinked systems, the ligand capacity and catalytic activity were observed to be higher than that of DVB-crosslinked system due to its more flexible nature. Among the various metal complexes, the reactivity decreased in the order: Co(II) > Cu(II) > Ni(II) > Cr(III) > Fe(III) > Mn(II) > Zn(II). The catalytic activity of the 2 mol% crosslinked system is depicted in Figure 5.2.
5.1.3 Catalytic activity of HDODA-crosslinked polystyrene-supported glycine-metal complexes

The complexation characteristics of insoluble macromolecular systems are strongly influenced by the nature of crosslinking in the polymeric ligand. In the case of HDODA-crosslinked system, the ligand capacity and catalytic activity was observed to be higher than that of DVB- and EGDMA-crosslinked systems. This is due to the greater accessibility of the reactive sites originating from the flexible nature of crosslinks. For the HDODA-crosslinked system; the catalytic activity decreased in the order: Co(II) > Cu(II) > Ni(II) > Cr(III) > Fe(III) > Mn(II) > Zn(II). The catalytic activities of the various metal complexes are depicted in Figure 5.3.
5.1.4 **Kinetics of hydrogen peroxide decomposition by polystyrene-supported sodium salt of glycine-Cu(II) complexes**

Kinetic studies of hydrogen peroxide decomposition by Co(II) complexes of different crosslinked systems were followed. In all crosslinked systems, the catalytic activities of Co(II) and Cu(II) complexes were higher than other metal complexes. The decomposition of $\text{H}_2\text{O}_2$ was found to be first order (Figures 5.4 and 5.5). The activation energy calculated by these two methods gave consistent values. Since, Co(II) complexes are very active, they require less activation energy. The activation energy required for the decomposition of hydrogen peroxide by Co(II) complexes are given below (Table 5.1).
Figure 5.4. Kinetic curves for the decomposition of $\text{H}_2\text{O}_2$ catalysed by 2 mol% HDODA-crosslinked polystyrene-supported glycine-Co(II) complex.

Figure 5.5. Variation of rate constant with temperature in the decomposition of hydrogen peroxide catalysed by Co(II) complexes of HDODA-crosslinked polystyrene-supported glycine.
The less activation energy of Co(II) complex compared with other metal complexes could arise from the unsaturation in the coordination sphere making the easy accessibility of hydrogen peroxide molecule to get involved in the catalytic decomposition. Of the various crosslinked systems, HDODA-crosslinked system shows higher catalytic activity is due to the flexible and hydrophilic nature of the crosslinking agent. In HDODA-crosslinked system, catalytic sites are more accessible than in other crosslinked systems.

The activation energy of EGDMA-crosslinked system is less when compared to DVB-crosslinked system and high compared to HDODA-crosslinked system. DVB-crosslinked system requires high activation energy due to the hydrophobic and rigid nature of the crosslinking agent.

Thus depending upon the nature of crosslinking agent, catalytic activity of the metal complexes varied. So catalytic activity of a polymer catalyst depends upon the nature of the polymer support and chemical nature of the crosslinking incorporated.

5.1.5 Effect of the nature of crosslinking agent on the decomposition of hydrogen peroxide

In order to investigate the effect of the nature of crosslinking agent on the decomposition reaction of hydrogen peroxide, Co(II) complexes of 2 mol% DVB-, EGDMA- and HDODA-crosslinked systems were followed. The variation in
reactivity with different crosslinking agents is given in Figure 5.6. The reactivity of 2 mol % Co(II) complex varied in the order: HDODA- > EGDMA- > DVB-crosslinked system. In the case of flexible crosslinking agent the catalytic site is randomly arranged and therefore is more easily accessible to the reaction medium. Regarding this fact the nature of crosslinking has significant role in the catalytic decomposition of hydrogen peroxide (Figure 5.6).

Figure 5.6. **Effect of the nature of crosslinking agent on the catalytic decomposition of \( \text{H}_2\text{O}_2 \) by DVB-, EGDMA- and HDODA-crosslinked polystyrene-supported glycine-Co(II) complex**

5.2 *N*-Vinyl-2-Pyrrolidone-Acrylic Acid Copolymer Systems

The complexes of synthetic macromolecular ligands with transition metal ions have been widely investigated.\textsuperscript{302-304} In some recent publications\textsuperscript{305,306} the possibility is noted of modelling the complexation of metal ions with biological ligands through synthetic macromolecular systems. Among the synthetic polyelectrolytes, amphoteric copolymers most closely resemble structure and behaviour of biopolymers.\textsuperscript{307} However, the complexation reaction between polyampholytes and metal ions has been little studied.\textsuperscript{308,311}
The reactivities of the ligand groups attached to crosslinked NVP-AA copolymer supports have been studied with respect to the nature of the crosslinking agent and pH of the reaction medium. The high solvation and swelling characteristics of the NVP-AA copolymer systems exhibited high catalytic activity compared with hydrophobic polystyrene systems. Because in aqueous medium it can completely exposed the catalytic site to the reaction medium. The complexation of ligand function supported on polymer matrix with flexible and hydrophilic network have higher complexation than the corresponding system with rigid network. This results from the increased availability of ligand function in the polymer network by the flexible and hydrophilic nature of the polymer matrix.

5.2.1 Catalytic Activity of DVB-crosslinked NVP-AA Copolymer-metal Complexes

The catalase-like activity of 4 mol% NVP-AA copolymer-supported metal complexes were investigated. The catalytic activities were studied with various metal complexes like Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Co(II) and Zn(II). The reactivity of various metal complexes decreased in the order: Co(II) > Cu(II) > Ni(II) > Cr(III) > Fe(III) > Mn(II) > Zn(II) as shown in Figure 5.7.

Figure 5.7. Catalytic activity of various metal complexes of DVB-crosslinked NVP-AA copolymer system
5.2.2 Catalytic Activity of EGDMA-crosslinked NVP-AA Copolymer-metal Complexes

In the case of EGDMA-crosslinked system the ligand capacity and catalytic activity was observed to be higher than that of DVB-crosslinked system due to its more hydrophilic nature. The general trend is: Co(II) > Cu(II) > Ni(II) Cr(III) > Fe(III) > Mn(II) > Zn(II) which is shown in Figure 5.8.

![Graph showing catalytic activity of various metal complexes of EGDMA-crosslinked sodium salt of NVP-AA copolymer system](image)

Figure 5.8. Catalytic activity of various metal complexes of EGDMA-crosslinked sodium salt of NVP-AA copolymer system

5.2.3 Catalytic Activity of HDODA-crosslinked NVP-AA Copolymer-metal Complexes

The catalytic activity of the metal complexes of 4 mol% HDODA-crosslinked system was studied in the decomposition of hydrogen peroxide. Due to the introduction of flexible HDODA crosslinks, the system become more hydrophilic and is considered as an efficient catalytic system compared with DVB- and EGDMA-crosslinked systems. The catalytic activity of various complexes were studied and the reactivity decreased in the order: Co(II) > Cu(II) > Ni(II) > Cr(III) > Fe(III) > Mn(II) > Zn(II) as shown in Figure 5.9.
5.2.4 Catalytic Activity of Linear NVP-AA Copolymer-metal Complexes

Though the linear NVP-AA system is found to be more catalytically active, it cannot be recycled because of the irrecoverability of the polymer system. The general trend for catalytic activity is the same as above cases and is shown in Figure 5.10. The high reactivity of the linear system compared to crosslinked system is due to the increased availability of metal centres of the polymer chain.
5.2.5 Kinetics of Hydrogen Peroxide Decomposition by NVP-AA Copolymer-Co(II) Complexes

Kinetics of catalytic decomposition was followed by using DVB-, EGDMA-, and HDODA-crosslinked Co(II) complexes. The kinetics of hydrogen peroxide decomposition catalysed by these complexes was found to be first order reaction. The kinetic curve for the decomposition of hydrogen peroxide catalysed by Co(II) complexes of 4 mol% HDODA-crosslinked NVP-AA copolymer is shown in Figures 5.11 and 5.12. The activation energy calculated by the two methods was in good agreement.

**Figure 5.11.** Kinetic curves for the decomposition of $\text{H}_2\text{O}_2$ catalysed by HDODA-crosslinked NVP-AA copolymer Co(II) complex

**Figure 5.12.** Variation of rate constant with temperature in the decomposition of hydrogen peroxide catalysed by Co(II) complex of HDODA-crosslinked NVP-AA copolymer
In all crosslinked systems of DVB, EGDMA and HDODA; HDODA-crosslinked N-vinyl-2-pyrrolidone-acrylic acid copolymer-Co(II) complex showed higher catalytic activity. This is due to its high hydrophilic and flexible nature, making the easy accessibility of the catalytic site. The activation energy required for the decomposition of hydrogen peroxide by various Co(II) complexes are given in Table 5.2.

<table>
<thead>
<tr>
<th>Crosslinking agent</th>
<th>( E (\text{kJmol}^{-1}) )</th>
<th>( A (\text{s}^{-1}) )</th>
<th>( \Delta S (\text{J}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>DVB</td>
<td>15.82</td>
<td>( 1.90 \times 10^3 )</td>
<td>-287.054</td>
</tr>
<tr>
<td>EGDMA</td>
<td>11.041</td>
<td>( 2.143 \times 10^3 )</td>
<td>-291.948</td>
</tr>
<tr>
<td>HDODA</td>
<td>7.480</td>
<td>( 2.47 \times 10^3 )</td>
<td>-310.7</td>
</tr>
</tbody>
</table>

**5.2.6 Effect of Crosslinking Agent on the Decomposition of Hydrogen Peroxide**

In order to investigate the effect of the nature of crosslinking agent on the decomposition reaction of hydrogen peroxide, Co(II) complexes of linear, and 4 mol% DVB-, EGDMA- and HDODA-crosslinked systems were followed. The variation in reactivity with crosslinking agents is given in Figure 5.13. The reactivity of the various Co(II) complexes varied in the order: linear > HDODA- > EGDMA- > DVB-crosslinked system.
5.2.7 Effect of Various Parameters on the Catalytic Decomposition of Hydrogen Peroxide

The effect of various parameters like time, temperature, amount of catalyst, concentration of hydrogen peroxide and pH were found to have vital role in the decomposition of hydrogen peroxide (Figure 5.14a-d). Co(II) complex of 4% HDODA-crosslinked NVP-AA copolymer was used for these investigations. In the catalytic decomposition of hydrogen peroxide, the extent of decomposition increased with time, temperature and amount of the catalyst as represented in Figure 5.14a-b. When the concentration of hydrogen peroxide was increased, the decomposition increased till 0.15 N and decreased further for a definite amount of the catalyst (Figure 5.14c). The influence of pH on kinetic study of polymer-supported Co(II) complexes were studied by using phosphate buffer with pH values of 5.6, 6.5, 7.2, 7.9 and 8.6. It was observed that at room temperature (303 K), the catalytic activity decreased in the order: 7.2 > 7.9 = 8.5 > 6.5 > 5.6.
Figure 5.14. Effect of various parameters on the catalytic decomposition of hydrogen peroxide: (a) temperature, (b) amount of catalyst, (c) concentration of hydrogen peroxide, and (d) pH of the medium.
5.2.8 Recyclability

In order to investigate the recyclability of the metal complexes for their catalase-like activity the Co(II) complex of 4 mol% HDODA-crosslinked NVP-AA copolymer was selected. The Co(II) complex of HDODA-crosslinked NVP-AA could be used several times without loss of efficiency. Thus, we can say that this is an effective catalyst.

![Recyclability of NVP-AA Co(II) complex](image)

The investigation based on the catalase-like activity of polystyrene-supported glycine-metal complexes and NVP-AA metal complexes leads to these points:

- The polystyrene-supported glycine-metal complexes and NVP-AA metal complexes are efficient catalyst to portrait the enzyme-like activity.
• All the crosslinking agents DVB, EGDMA and HDODA have remarkable role in catalytic activity depending on its hydrophilic/hydrophobic and rigidity/flexibility nature.

• The decomposition kinetics was found to be first order.

• Effect of various parameters like time, temperature, amount of catalyst, concentration of hydrogen peroxide and pH were found to have vital role on the decomposition of hydrogen peroxide.

• Decomposition of hydrogen peroxide is considered as a simple and unique reaction to explain the catalytic activity of the enzyme catalase.