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Catalytic Activity of Polyacrylic Acid -Metal Complexes

Rakhi V. R.[1]

1(Lecturer in Chemistry, Carmel Polytechnic College, Alappuzha -Kerala.)

Abstract:

Recent discoveries using coordination metal complexes show that the economic potentialities and advantages are greater for the heterogeneous rather than homogeneous complexes. The metal atom immobilized to the polymeric backbone is found to exhibit characteristic catalytic behavior, which are distinctly different from their low molecular weight analogue. Polyacrylic acid shows complexing ability for metal ions. In order to investigate the catalytic activity of polymer-metal complexes, linear polyacrylic acid was complexed with Co (II), Ni (II), Cu (II) and Zn (II) ions. The polyacrylic acid- metal complexes were then used for the studying the catalytic decomposition of hydrogen peroxide. The present investigation of different type of polymer-metal complexes and their catalytic-like activity revealed the role of characteristics of the polymer support in controlling its catalytic activity.

Keywords — **Polymer-metal complexes, Polyacrylic acid- metal complex, Catalytic activity, Heterogeneous catalysis, Hydrogen peroxide, Decomposition.**

Catalysis may be defined as the art of transforming chemical molecules in desired reaction pathway. This 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 interdependence of the polymer microstructure and reactivity of functional groups in functionalised polymers dictates the application of such systems in a number of areas of functional and technological interest.

Catalytically active polymers having a metal complex bound to polymer would show a specific type of catalytic behaviour, reflecting the properties of the polymer chain. The development of a catalyst formulation should therefore take into account not only the chemical nature and distribution of the active species but also the design of the catalyst. Synthetic polymer-metal complexes exhibit high catalytic efficiency. In order. to throw light on the effect of the protein surrounding metal ion, intensive studies on the structure and catalytic activity of synthetic polymer-metal complexes were initiated.

Thus, catalyst may be defined as the art of transforming chemical molecules m order to facilitate their transformation along the desired reaction pathway. A polymer-metal complex 1s composed of synthetic polymer and metal ions, wherein the metal tons are bound to the polymer ligand by a coordinate bond. In a polymer-metal complex, a complex with a specific structure result since the metal ion is surrounded by a structured polymer chain.

Catalysis by transition metal complexes gained prominence in recent years[1,2]. During the last 15 years chemists have been interested with the idea of anchoring transition metal catalyst to organic polymers. 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[3].

The catalytic cycle of a polymer-metal complex catalysed reaction is illustrated by the following equations.

$$M L_n \ + \ S \ \rightleftharpoons \ L_{n-1} M - S$$

$$M'L \ + \ S^* \ \rightleftharpoons \ L_{n-1} M' - S^*$$
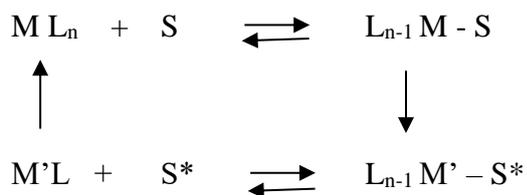
Where M is the metal ion, L the ligand and S the substrate. s

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[4].

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 resin was studied with various catalytic systems[5,6]. The catalytic activity of a polymer—anchored metal complex, compared with those of analogous molecular complexes in a homogeneous system, is dependent on the availability of inner sites of the polymer support[7]. This availability may be determined by the swelling of the polymer support[8], distribution of the active complex on the polymer texture[9] and by the fit of pore sizes to the substrate molecules. The attachment of homogeneous catalysts to polystyrene-divinyl benzene copolymer produces a new class of catalysts with many of the best properties of both homogeneous and heterogeneous catalysts[10].

Several authors have studied the catalytic effects of polymer-metal complexes prepared from synthetic or natural polymer and metal ion in recent years. Polymer metal complexes are widely used as immobilised catalysts with high efficiency[11]. Several attempts have been made to use fully synthetic polymeric catalysts that incorporate all the functional features like specificity and activity of natural enzymes[12]. The effective catalysts from such complexes are now being developed to imitate the enzymatic reaction which proceed effectively under mild conditions, i.e., at ambient temperature and atmospheric pressure[13,14] Various polymer metal complexes are found to be effective in mimicking catalase-like activity in the decomposition of hydrogen peroxide[15,16]

Recently the areas of polymer-supported organic reactions[17] and polymer-supported catalysts[18], have been reviewed from the point of the solid phase synthetic chemistry which can be carried out on resins and reactions that have been catalysed by polymer-supported metal complexes etc. In a polymeric catalyst or polymer-supported catalyst a conventional catalytic species is attached to a macromolecular backbone. The metal atoms attached to polymer backbone are found to exhibit characteristic catalytic behaviour, which are distinctly different from their low molecular weight analogue. Despite the fact that they usually show a much lower catalytic activity than a true enzyme. In these years polymer metal complex has been of interest to many chemists because it is not only an excellent model for metalloenzyme, but also lead to the development of highly efficient catalysts[17,18,19]

The catalytic activity of a polymer-metal complex is generally lower than the corresponding monomeric analogue due to steric effects. However, the activity can sometimes be higher than the monomer complexes due to the unsaturated coordination structure or by the strain in the formation of inactive dimeric complex due to steric effect[20].

2.1. Catalytic activity

A catalyst by definition increases the rate of a chemical reaction without being consumed in the reaction. The major thrust behind the Widespread use of polymer supports as catalyst is the simplification achieved in separation and purification of synthetic intermediate, side products, and decontamination from impurities, side products or toxins. The basis of all these applications and processes is the anchoring of the desired species to the insoluble polymer particles by ionic, covalent, coordination or other less specific interactions. The insolubilized species is then readily separated from

the working admixture by filtration, subsequent to separation, the polymer bound catalyst can be reused, thug the process is amenable to automation. In polymer metal complexes, the selectivity arises from the steric hindrance and/or chemical environment of the polymer matrix[21].

Organic reactions are catalysed by polymer-metal complexes[22]. A polymer-supported group often has catalytic properties analogous to that of the same group used in homogeneous catalysis. Polymer-metal complexes are markedly useful as immobilised catalyst for practical use because it 1s more reactive than the corresponding monomer analogous due to the specialities of their large ligand molecules. The catalytic activity of the polymeric metal complexes possesses the following features.

- Homogenous catalytic activity is retained by transition metal complexes on binding to the resin.

- Polymers can be used as insoluble carriers for catalyst. The domain in the solid phase or the boundary of its surface provides a specific catalytic site.

- The economy and convenience of the heterogeneous catalysis is attained.

- Selectivity of the reaction by polymer complexes are often different from the monomer complexes.

- The catalytic sites (single metal atom) can be separated by binding to the rigid region of the support. During the formation of ligand-bridged complexes greater catalytic activity is gained.

- The steric environment of the catalyst is altered and substrate Selectivity is increased.

- Polymer-bound Catalyst can be employed under conditions comparable to those of conventional homogeneous catalyst.

- Polymer can be used as an effective matrix for the formation of active metal centres.

Ion exchange resins have been widely used as polymeric catalysts and reagents in many commercial applications. This is especially true of the strongly acidic styrene sulfonic acid and flurosulfonic acid resins and membranes. Similarly, chelating resins also have many such applications. A thorough review[23] details the use of chelate forming polymers as redox catalysts and reagents in many applications.

Phase transfer catalysis using polymer-hooked functional group is another area of research where chelating polymers are used. This especially applies to the crown ether and cryptand polymers; a review[24] details the type of reaction mechanism found for such systems.

Metal complexes catalyse oxidation of compounds having mobile hydrogen, such as ascorbic acid, hydroquinone, phenols and amines, m the presence of molecular oxygen. In this reaction a substrate coordinates to the metal catalyst, and then the substrate is one-electron oxidised by the metal ion with higher valency.

$$2\,AH_2 + O_2 \longrightarrow 2A + 2\,H_2O$$

The first example of catalysis by a polymer-metal complex was reported by Lautsch *et al*[25], Metalloporphyrin was linked to a poly(phenylamine) chain by peptide bond. The catalytic properties of this polymeric Fe (III) porphyrin complex were compared with Fe (III) porphyrin in the oxidative reaction of phenylenediamine. The catalytic activity of the polymer complex was twice as large as that for the corresponding analogue.

Polymer complexes having more than two active sites are found to have high catalytic activity. In this example, metalloporphyrin which contains both an oxidation site (Co) and a proton acceptor site (amine) are effective catalysts for the oxidation of thiol to disulphides (1)[26]
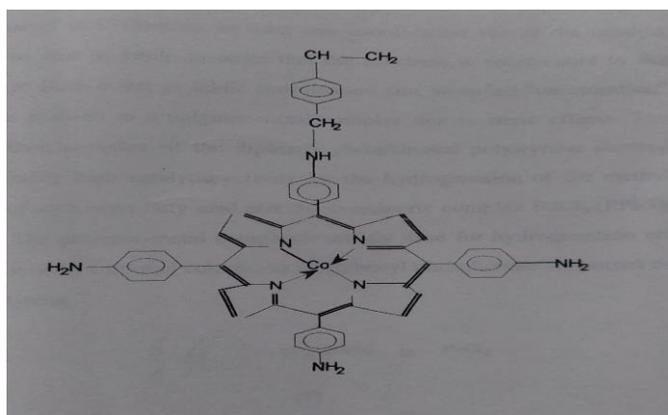
(1)

2.2. Polymer-metal complexes as heterogeneous catalysts

When a homogeneous catalyst such as a transition metal complex, transition metal or an enzyme is covalently bound or strongly absorbed on a polymer matrix we have a polymer-supported catalyst. The polymer can be organic or inorganic in nature and be soluble or insoluble in the reaction medium. Insoluble supports are preferred because the maw purpose of supporting a catalyst is to be able to recover and recycle it easily. 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.

There are three distinct stages in the preparation of a supported catalyst.

1. Choice of suitable support material

2. Introduction of suitable functional groups on the support which would interact with the catalytic species in the loading process

3. The incorporation of the catalyst on the support

It 1s usually carried out under mild conditions so as to retain the activity of the catalyst and finally, the extent of the loading achieved must be ascertained by chemical analysis.
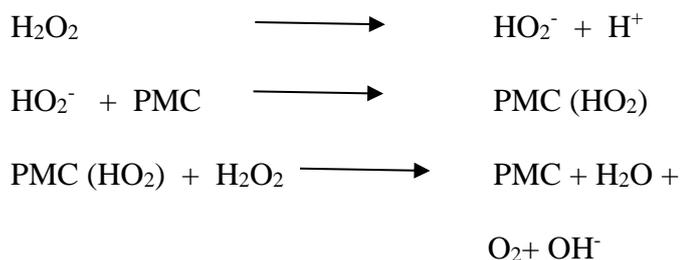
Metalloenzyme is a kind of polymer-metal complex present in nature, generally formed between a polypeptide and metal ion. A typical example of such a metalloenzyme whose structure has been determined is plastocyanin[27]. (A kind of blue-copper protein). In plastocyanin the copper ions show a distorted tetrahedral structure and are coordinated by methionine's sulphur atom, which is not normal in usual low molecular weight metal complexes. This abnormal coordination behaviour and the hydrophobic environment around the copper ion brought by giant protein molecule cause unusual redox behaviour of the copper ion. Generally, the protein in metalloenzyme not only decides the chemical structure but also causes an allosteric effect through conformational change of its polymer chain.

The presence of many kinds of biological substances having coordinating ability around the metal ion and the occurrence of reaction by metalloenzymes via the mixed complex with the substrates requires Study of mixed ligand complexes in order to elucidate the coordination behaviour of blood plasma, the complex formation of Mg (II), Cu (II), Mn (II), Fe (II), Co (II), Zn(I1) and Pb(I1) ions with amino acids and other organic acids are simulated[28]

The enzyme 'catalase' catalyses the disproportionation of hydrogen peroxide. This enzyme is very widespread and protects against the build-up of dangerous concentration of hydrogen peroxide in 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[29]. Drago *et al*.[30] reported the synthesis and catalytic oxidising potential of polymeric chelating amine and Schiff base complexes. The decomposition of hydrogen peroxide in homogeneous medium has been studied using metal ions and their complexes as catalysts[31-33]

In order to investigate the catalase-like activity of polyacrylic acid metal complexes, the decomposition reaction of hydrogen peroxide is affected 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:

$$H_2O_2 \longrightarrow HO_2^- + H^+$$

$$HO_2^- + PMC \longrightarrow PMC\,(HO_2)$$

$$PMC\,(HO_2) + H_2O_2 \longrightarrow PMC + H_2O + O_2 + OH^-$$

(PMC = 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 takes 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 wide spread application in the oxidation of organic substrates. Catalase-like activity is a key factor in therapeutic usage also[33].

2.3. Catalytic activity of polyacrylic acid-metal complexes

The catalase like activity of poly (acrylic acid) - metal complexes are investigated. A weighed quantity of the catalyst (10mg) was stirred with 5ml (0.2N) hydrogen peroxide in a reaction vessel at 32^0C. After a definite time, the insoluble polymers were collected by filtration and the concentration of hydrogen peroxide (filtrate) was estimated by titrating against standard potassium permanganate solution. The catalytic activities were studied with metal complexes like Co (II), Ni (I1), Cu (II) and Zn (II). The reactivity of various metal complexes decreased in the order: Co (II) > Cu (Il) > Ni (Il) > Zn (II) as shown in Figure 2.1
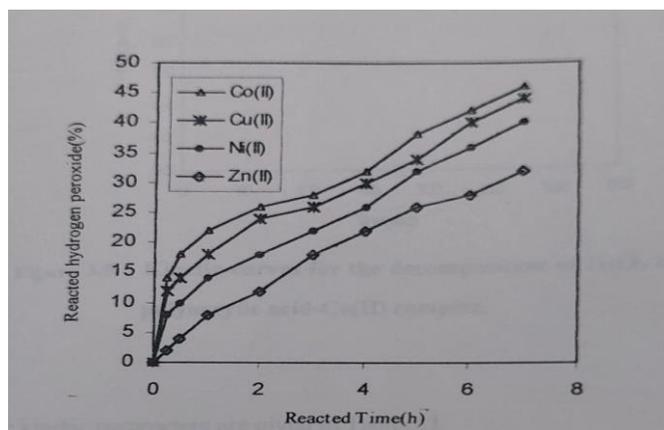

Figure 2.1. Catalytic activity of various metal complexes of polyacrylic-metal complexes

CONCLUSION:

- The catalytic activity of various metal complexes of polyacrylic acid was investigated. In these systems the catalytic activity decreased in the order: Co (II) > Cu (Il) > Ni (Il) > Zn (II) The variation in reactivity with metal ions can be explained in terms of their co-ordination geometry.

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