Introduction
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The velocity of chemical reactions may be increased or decreased by the presence of small amounts of substances which do not enter into the resulting compound. Thus, a catalyst is defined as a substance which, by its presence in a medium where a chemical reaction takes place increases the reaction velocity without being changed itself or appearing in the compound resulting from the reaction. Consequently, a catalyst may enter into the reaction over and over again. This definition includes the effect of solvents or gaseous reaction media which may act as catalytic substances. In the majority of positive catalytic reactions, the catalyst causes chemical reactions to take place at an energy level lower than that at which they would occur without the catalyst. Sometimes, catalysis is due to the transfer of energy of activation from energy-rich molecules. A chemical reaction, the velocity of which is influenced by a catalyst, is called a catalyzed or catalytic reaction, and the phenomena involved in all such reactions are called catalysis.

In the study of catalysis, besides the physical factors influencing chemical reactivity, the presence of substances, other than those accounted for in the empirical formulae for pure compounds, must be considered. As such substances may influence the mechanism of the reactions by either accelerating or retarding or concurrently retarding and accelerating, the reaction velocity.
Catalysis may be homogeneous or heterogeneous. Heterogeneous catalysis was the business of heavy industries and homogeneous catalysis was a laboratory novelty. Catalytic reactions may take place in homogeneous or heterogeneous systems. The conditions in the two cases are so different that they may well be used as a basis for classification. Catalysis is an extremely widespread phenomena, and only a few examples are given here.

**Homogeneous reactions in liquid phase**

In liquid phase reactions, we have to consider ionization in aqueous solvents, associations between solute and solvent, and other solvent effects, and as in gas reactions, wall reactions. Bimolecular reactions in solvents are much slower than in the gaseous state due to the deactivating influence of the solvent\(^1\) molecules and the effectiveness of bimolecular collisions, between molecules with appropriate energies, appears to be several powers of ten smaller in the presence of a solvent\(^2\). Catalysis in solutions is very widespread, and there is reason to believe that the majority of reactions in liquids are catalytically affected.

**Heterogeneous catalytic reactions**

Heterogeneous catalysis takes place at the surface of a catalyst which is in a different phase from the reactants. The basic steps involved in heterogeneous catalysis are:
i) diffusion of the reactant(s) towards the catalyst,

ii) adsorption of the reactant(s) onto the catalyst,

iii) reaction of the adsorption complex(es) to yield the product

iv) desorption of the product(s) from the catalyst, and

v) diffusion of the product(s) away from the catalyst.

1. Transition metals

Many examples of heterogeneous catalysis involve transition metals. Their empty ‘d’ orbitals allow them to bond with many substances to form reactive intermediates. In the Haber process for the manufacture of ammonia, the catalyst is a mixture of iron and vanadium:

\[
\begin{align*}
\text{Fe/V} \\
\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \xrightarrow{\text{Fe/V}} 2\text{NH}_3(\text{g})
\end{align*}
\]

In the hydrogenation of alkenes, a process which is used in the conversion of liquid oils into solid fats, nickel is used. It is finely divided to increase the area of surface over which the reactants can come into contact:

\[
\begin{align*}
\text{R}_2\text{C} = \text{CR}_2(\text{g}) + \text{H}_2(\text{g}) \xrightarrow{\text{Ni}} \text{R}_2\text{CH-CHR}_2(\text{g})
\end{align*}
\]

2. Cracking

Catalysis is important in the petroleum industry. The ‘cracking’ of hydrocarbons in the petroleum industry is catalysed by a mixture of silica and alumina:

\[
\begin{align*}
\text{C}_8\text{H}_{18(\text{g})} \xrightarrow{\text{Al}_2\text{O}_3/\text{SiO}_2} \text{C}_4\text{H}_{10(\text{g})} + \text{C}_4\text{H}_{8(\text{g})}
\end{align*}
\]

Octane

Butane

Butene
3. **Autocatalysis**

Autocatalysis is a special case in which one of the products of a chemical reaction acts as a catalyst for the same reaction. A good example is the oxidation of hydrogen peroxide by acidified manganate (VII):

\[
2\text{MnO}_4\text{(aq)}^- + 6\text{H}^+\text{(aq)} + 5\text{H}_2\text{O}_2\text{(aq)} \rightarrow 2\text{Mn}^{2+}\text{(aq)} + 5\text{O}_2\text{(g)} + 8\text{H}_2\text{O}\text{(l)}
\]

The Mn\(^{2+}\) ions produced catalyse the reaction. The reaction starts slowly, and then speeds up after a small amount of catalyst (Mn\(^{2+}\)) has been formed.

**Phase transfer catalysis**

The organic chemist is frequently faced with the necessity of conducting a reaction between two molecules which have widely differing solubility products. The reaction between an ionic species and a neutral molecule is a typical example where the former, commonly a water-soluble alkali metal salt, is usually only marginally soluble in non-polar aprotic solvents, whereas a neutral organic molecule has a much greater solubility in these solvents. Reactions between substances located partly in an organic phase and partly in an aqueous phase, are usually very slow.Employing non-polar organic solvents alone frequently leads to heterogeneous reaction mixtures and the use of polar, aprotic solvents³ (DMSO; DMF etc.) to achieve homogeneous solutions, increases both the cost and the difficulties encountered in the work-up procedures.
In the late sixties, the phase transfer technique otherwise called ‘Phase Transfer Catalysis’ (PTC) as coined by Starks, appeared as a new method for overcoming the problem of mutual solubility as well as offering the potential for activation of anions\textsuperscript{4,5}. The catalytic nature of this technique also presented the promise of substantial cost savings over more traditional approaches. It is probably well understood by a specific example, viz., simple cyanide displacement on alkyl chloride:

\[
\begin{align*}
\text{R-Cl} & \quad + \quad \text{NaCN} & \quad \longrightarrow & \quad \text{R-CN} & \quad + \quad \text{NaCl} \\
\text{(Org)} & \quad \quad \text{(aq)} & \quad \quad & \quad \text{(org)} & \quad \quad \text{(aq)}
\end{align*}
\]

Upon heating and stirring a two-phase mixture of 1-chlorooctane with aqueous sodium cyanide, resulted in zero yield of 1-cyanoctane even after several days of reaction time. However, if a small amount of appropriate quaternary ammonium salt is added, then rapid formation of 1-cyanoctane is observed in essentially 100% yield after 1 or 2 hours.

**Applications of Phase Transfer Catalysis**

Phase transfer catalysis has been extensively applied to the reactions by Starks, reported in two important papers\textsuperscript{4,6}, which laid the basic foundation for most of the mechanistic understanding of PTC known today. Starks pioneered oxidation in the presence of PTC. In fact, he was the first to show that oxidations with hydrogen peroxide worked best with phosphoric acid and tungstate. Starks classic patent\textsuperscript{7} reports the effect of 15 metals on hydrogen peroxide oxidation of olefin and further describes the extensive
application of PTC, not only for oxidation, but also for nucleophilic aliphatic substitution involving cyanide, iodide, acetate, cyanate, thiocyanate and strong base reactions such as dichlorocarbene addition to olefins, C-alkylation, hydrolysis of esters and finally reduction.

Makosza and his co-workers published\textsuperscript{8-10} enormous amount of work on the use of quaternary ammonium salts in ‘Catalytic Two-phase Alkylation’ reactions particularly with phenyl acetonitrile derivatives. Makosza’s early work was partially based on work by Jarrouse\textsuperscript{11} and Brandstrom, also working on alkylation problems, discovered the technique he first called "Extractive Ion-pair Alkylation"\textsuperscript{12,13}. Hennis and co-workers\textsuperscript{14}, after making a detailed mechanistic examination of the trialkylamine catalysed two-phase synthesis of benzyl esters:

\[
\text{C}_6\text{H}_5\text{CH}_2\text{Cl} + \text{RCO}_2\text{Na} \quad \longrightarrow \quad \text{C}_6\text{H}_5\text{CH}_2\text{COOR}
\]

concluded that the quaternary ammonium salt was formed \textit{in situ}, and that this organic cation coupled with the carboxylate ion was sufficiently soluble in the organic phase to be transferred into the benzyl chloride layer, and then to form esters. With the recognition of phase transfer catalysis as a general technique, there appeared the extremely important and elegant work of Montanari\textsuperscript{15-17}, Herriott and Picker\textsuperscript{18} of Freedman\textsuperscript{19}, Regan\textsuperscript{20,21}, Dehmlow\textsuperscript{22,23} and their many co-workers. These chemists provided an enormous wealth of information and discovery. Several workers particularly Liotta\textsuperscript{24}, Gokel\textsuperscript{25,26}, Weber\textsuperscript{27}, Montanari\textsuperscript{28,29} and their co-workers developed the use of crown ethers, cryptands, and open-chain polyethers as new types of PTCs with properties which complimented the use of quaternary salts.
Dehmlow's\textsuperscript{30} group has contributed to a greater extent in the field of PTC and has synthesized a variety of quarts in which the nitrogen was usually alpha or beta to an optically active center. Alper\textsuperscript{31}, made an extensive and significant contributions to the use of transition metal co-catalysis in synthetic PTC.

Balakrishnan and Ford\textsuperscript{32} made comprehensive study for the first time on the butylation of phenylacetonitrile using polymer-bound PTC. Balakrishnan\textsuperscript{33-38} along with his co-workers made valuable contributions on the kinetics and mechanistic aspects of PTC aided reactions, polymerisation kinetics using PTC, polymer-supported PTC and 'Multi-site' PTC.

Improved yields of products were observed using the new "multi-site" phase transfer catalysts as compared to those catalysed by a "single site" PTC under identical conditions for the addition of dichlorocarbene to styrene\textsuperscript{36}.

The possibilities include the preparation of compounds from an unreactive or unstable starting materials and more generally the increase of yields or selectively in a large number of syntheses. Quaternary onium salts, are most commonly used for phase transfer catalysis. Applying phase-transfer conditions, the esterification was made without solvent if one of the reactants is a liquid\textsuperscript{38-42}. This process was developed for the synthesis of acetals and aromatic carboxylic esters\textsuperscript{40}. 
Phase Transfer Catalysis - Classification

Phase transfer catalytic processes can be conveniently classified as Liquid-Liquid, Solid-Liquid, Gas-Solid and Gas-Liquid systems.

Liquid-Liquid Phase Transfer Catalysis (LL-PTC)

Liquid - Liquid phase transfer catalysis corresponds to a system made of two phases, an organic phase containing a liquid reagent with (or without) an organic solvent immiscible with water and an aqueous phase in most cases, a nucleophilic reagent, $M^+Y^-$, in the presence of a quaternary ammonium or phosphonium salt acting as catalyst partitioned between the two phases.

Solid-Liquid Phase Transfer Catalysis (SL-PTC)

Solid-Liquid PTC corresponds experimentally to reactions occurring with an organic reagent soluble in a solvent and solid substrate insoluble in that solvent. When a complexant such as crown ether, cryptand and chelatant is added to the reaction mixture, the solid substrate is solubilized in the solvent and reacts under mild conditions. For instance, when potassium permanganate was added to a solution of benzene containing an olefin, the crystals of potassium permanganate stand at the bottom of the flask, the solvent remained colorless and absolutely no reaction occurred. If a small amount of 18-crown-6 is added, the solvent immediately turns purple (the permanganate dissolves) and the olefin is smoothly oxidised.
Gas-Solid Phase Transfer Catalysis (GS-PTC)

A report on Gas-Solid phase transfer catalysis\textsuperscript{46} indicated that by passing a gaseous alkyl halide over a catalytic column composed of a salt, a solid support and a phase transfer catalyst, a substitution product was obtained. The phase transfer catalyst was either free or immobilised on a silica matrix and thus the synthesis of alkyl iodides and esters were possible:

\[
\text{RX} + \text{(gas)} \quad \text{M}^+\text{Y}^- \quad \text{(solid)} \quad \text{Catalyst} \quad \rightarrow \quad \text{RY} + \text{M}^+\text{X}^- \quad \text{(gas)} \quad \text{(solid)}
\]

Gas-Liquid Phase Transfer Catalysis (GL-PTC)

GL-PTC, one of the interesting variant of the two-phase catalytic method with great potential was reported and developed by Tundo and Co-workers\textsuperscript{47-49}. Crown ethers, cryptands, phosphonium salts and polyethylene glycols were used as PT catalysts because they promote the transfer of anions into the organic phase and then activates. Number of reactions had been carried out following GL-PTC technique, for instance, the synthesis of ethers and thioethers\textsuperscript{50,51}, interconversion of alkyl halides\textsuperscript{52,53}, esterification\textsuperscript{54} and transesterification\textsuperscript{55} are very important reactions.

Role of Inverse PTC

Several studies were reported\textsuperscript{56-60} for two phase reactions in which an organic soluble reagent was converted to a reactive ionic intermediate and
transported into the aqueous phase where the reaction takes place. The process of these nature was conveniently termed as ‘Inverse Phase Transfer Catalysis’\textsuperscript{61}. The reaction of benzoyl chloride and sodium benzoate in the presence of a catalytic quantity of pyridine-1-oxide in methylene chloride-water two-phase system to form benzoic anhydride has been reported\textsuperscript{62,63}. From the experiments using different carboxylates, it was concluded that anhydride formation takes place in both the aqueous phase and at the interfacial region of the reaction system\textsuperscript{61}. Mathias and Vaidya had reported\textsuperscript{61} that 4-dimethylaminopyridine is a kind of highly active acylation catalyst undergoing an inverse phase transfer catalysis. Fife et al.\textsuperscript{64}, Zeldin et al.\textsuperscript{65}, and Rabinsztajn et al.\textsuperscript{66}, also demonstrated that silanes and siloxanes functionalized with 4-(dialkylamino) pyridine moieties are the other kinds of oxidation catalyst undergoing an inverse phase transfer catalysis. Mathias and Vaidya\textsuperscript{61} carried out the reaction of DL-alanine with decanoyl chloride or p-chlorobenzoyl chloride using 4-dimethylaminopyridine as an inverse phase transfer catalyst and demonstrated a scheme of inverse phase transfer catalysis. From a qualitative experiment, they had concluded that the interfacial mass transfer of reaction species was the rate-limiting step.

Recently, Asai et al.\textsuperscript{67} successfully synthesized hippuric acid from benzoyl chloride and glycine in the presence of 4-dimethylamino pyridine as an inverse phase transfer catalyst in heterogeneous liquid-liquid reaction system using an agitated vessel with a flat interface. They had also proposed a theoretical model for the inverse phase transfer catalysis
considering the mass transfer resistance of relevant reaction species to reasonably explain the overall reaction rates.

Soluble Phase Transfer Catalysis - Disadvantages

The use of soluble phase-transfer catalysts in biphasic catalytic reaction always encounters some problems. Eventhough the inexpensive soluble quaternary phosphonium and arsonium salts are very attractive to synthesize speciality chemicals, they also disturb the reaction system by forming stable emulsion which makes isolation of the product from the organic phase very difficult. The foremost important difficulties of soluble PTC is the separation of the catalyst from the product in the purification process. The reason is that the chemical equilibrium separation processes which are used in the purification of the product usually consume a lot of energy to get a product of high purity.

Triphase Catalysis - Development

The triphase catalysis technique developed by Regen\textsuperscript{21,68-71} is an extension of both LL-PTC and SL-PTC. It makes use of biphasic organic-aqueous system and a catalyst (quaternary salt, crown ether or glyme) supported on a polymeric backbone and termed it as "Triphase Catalysis". So, the replacement of soluble phase-transfer catalysts in aqueous organic two phase reactions with insoluble analogues affords unique three-phase catalytic systems is the concept of triphase catalysis (TPC). The basic characteristic features and mechanistic principles are thoroughly studied
and are reasonably well understood. The insoluble PSPTC utilized by Montanari et al.\textsuperscript{72-74}, Brown et al.\textsuperscript{75}, Ohtani et al.\textsuperscript{76}, Chaudhari et al.\textsuperscript{77}, Marconi et al.\textsuperscript{78}, Ford et al.\textsuperscript{79,80} and Balakrishnan et al.\textsuperscript{32,81-83} had created a remarkable record in the synthesis organic compounds.

Synthesis of new methods using solid-phase catalyst like polymer-supported insolubilized crown ethers\textsuperscript{43} and cryptands\textsuperscript{44}, immobilized poly(ethylene glycol)\textsuperscript{84} and poly(ethylene glycol monoether)\textsuperscript{85} had progressed rapidly in the last few years. The major feature of TPC is that the catalyst and each of a pair of reactants are located in separate phases, like, organic, aqueous and solid phase (catalyst phase).

There are many types of heterogeneous catalysis possible, but recently developed ones are (i) insoluble polymer-supported phase transfer catalysts (triphase), (ii) insoluble surface-enriched polymer-supported phase transfer catalysts, and (iii) insoluble polymer-supported metal complex catalysts. The immobilized onium catalysts are ordinarily synthesised by the reaction between pendent chloromethyl groups in the supports with tertiaryamines or phosphines. The catalyst and each one of a pair of reactants are located in separate phases. This principle has been successfully applied to certain aqueous phase-organic phase reactions employing a solid phase catalyst.

Applications of Triphase Catalysts

Many authors reported the catalyst synthesis, properties, mechanism and uses of Triphase catalysts\textsuperscript{86-91}. In most of the systems, they had used cross-linked insoluble macromolecular networks as the support. Because of
its wide industrial applicability, spherical particulate materials are preferred since it has characteristics such as mechanical stability, narrow size distribution and dynamic behaviour.

Regan reported relevant results for displacement reaction of cyanide ion with 1-bromo and 1-chlorooctane in water-benzene system using polymer-supported quaternary ammonium groups as the catalyst\textsuperscript{20}. Control experiments proved that in the absence of polymeric catalyst, no reaction occurred and the catalyst has not dissolved in the medium or decompose to yield a soluble catalyst. Triphase catalysts could effectively catalyze nucleophilic substitutions in alkyl halides, dichlorocarbene addition to alkenes, Williamson's ether synthesis, oxidation of alcohols and other reactions under Liquid-Solid-Liquid polymer-supported phase transfer catalyst conditions\textsuperscript{58,92,93}.

A similar study has been carried out by Cinquini \textit{et al.}\textsuperscript{72} examined resins bearing polymer-supported quaternary ammonium salts and phosphonium salts in converting 1-bromoocctane into 1-iodooctane and octane carbonitrile in toluene/resin/water system. Phosphonium salts are more reactive than its ammonium salt in the displacement of alkyl halides with cyanide or another halide. Moreover, it was shown that all triphase reactions proceeded slower than the comparable transformations carried out using soluble phase transfer catalyst.

Dou \textit{et al.}\textsuperscript{54} reported the C-alkylation of phenylacetonitrile under triphase conditions. The observed results that triphase catalysis was possible with these catalysts and reproducibility of the reaction has not yielded good results.
Polymer-supported benzyltributyl phosphonium and benzyltriethyl ammonium chloride were employed in the displacement reactions of benzyl bromide, benzyl chloride, 1-bromoocatane and 1-bromohexadecane with excess of sodium cyanide under triphase conditions by Ford et al.\textsuperscript{95,96}. The observed reaction rates depended upon stirring speed, catalyst particle size, percentage of crosslinking and chemical structure of the substrate. The rate of reactions were discussed in terms of mass transfer, intraparticle diffusion and intrinsic reactivity limitations on reaction rates.

Balakrishnan et al.\textsuperscript{32,34} reported the C-alkylation of phenylacetonitrile with 1-bromobutane catalysed by polystyrene bound benzyltriethyl ammonium chloride. In this reaction, they established a term called "reverse addition method" wherein the substrate to be alkylated (phenylacetonitrile) was added first to the reaction flask. It was found that the order of addition of the substrate to the catalyst drastically increased the reaction rate\textsuperscript{34,83}. Commercial macroporous anion exchange resin had activities comparable to that of 2\% cross-linked microporous catalysts. The observed kinetic results were discussed in terms of mass-transfer effect and intraparticle diffusional limitations.

The effect of liquid phase ratio on the kinetics of the displacement reaction between 1-bromoocatane and potassium cyanide catalysed by polystyrene bound benzyltributyl phosphonium ion under triphase conditions was reported by Chau et al.\textsuperscript{97}. The drastic kinetic reaction rate improvement
was achieved with proper adjustment of phase ratios and the quantity of the
catalyst for a given volume of organic phase.

Tomoi et al.\textsuperscript{98} reported the effects of solvent on intrinsic activity of the
prepared polymer-supported crown ethers from chloromethylated
polystyrene resins and hydroxy methylbenzo-18-crown-6 and 15 or 8
membered monoazacrown ethers. Effects of the cavity size of crown ethers,
the degree of crosslinking, the percent ring substitution, particle size, spacer
chains and solvents on the cavity of the polymer-supported crown ethers in
the reaction of 1-chloro or 1-bromoocotane with aqueous NaI and KI were
investigated. It was concluded that polymer-anchored crown ethers showed
a cation dependence of rates. The optimum activity was not obtained
because the size of cations of the inorganic reagents was not suited to the
size of the crown ethers.

Balakrishnan et al.\textsuperscript{99} carried out triphase reactions with surface
enriched polymer-supported phase transfer catalysts and studied the
kinetics of dichlorocarbene addition to cyclohexene using 50% NaOH and
alkylation of phenylacetonitrile and the kinetic results were discussed.

**Mechanism of Polymer - supported phase transfer catalysis**

The mechanism of phase transfer catalysis using a polymer-supported
catalyst has been described \textsuperscript{96,100-102} in which, not all the differences between
soluble and insoluble catalysis were considered. For example, migration of
ion pairs between both phases is free when a soluble catalyst is used; in the
case of the insoluble catalyst, the free migration is excluded, the cation is part of the solid polymer. Most of the authors do not assume any difference between the reaction mechanism using low-molecular weight catalysts and polymer ones. In fact, it cannot be neglected that the phase boundary, through which the complete ion pairs $Q^+Y^-$ (Quaternary ammonium salts), or the anions $Y^-$ only are transported, is an area in the two phase system. In the case of three-phase system, this suggestion fails. Because, the original flat boundary changes to a very small volume and thereby it is located closely to the bound cation of the polymer chain (eqn.). Taking all these facts, a few different approaches to explain of the role of the polymer-supported phase transfer catalysts was proposed by Telford et al.,$^{103}$.

![Chemical Structure](image)

The process of transporting anions back and forth across the boundary can then occur via local backbone and side-chain motion of the catalyst support. This model would predict the efficiency of catalysis to be improved by increasing the length and hence the flexibility of the linkage between the catalyst and the polymer backbone by introducing 'spacer arm' and this seems to be so in practice$^{104,106}$. 

This technique has the advantage of soluble phase transfer catalysts, to the insoluble polymer-supported phase transfer catalysts because the overall reaction rates are limited by four fundamental processes, viz., (i) mass transfer of the reactants from bulk liquid phase to the surface of the solid catalyst, (ii) diffusion of the reactants from the catalyst surface to the active site\textsuperscript{106,107}, (iii) the intrinsic reaction at the active site and (iv) diffusion of products from the active site to the particle surface and mass transfer of products to the bulk solution. Each of these process depends on several experimental parameters since the insoluble phase transfer catalyst is easily filtered off and recovered after the reaction. However the rates were of ten less than most of analogous soluble phase transfer catalysts because of diffusional limitations\textsuperscript{108}.

**Supported metal complexes**

In recent years the study of soluble catalysts offer certain advantages over conventional heterogeneous catalysts in that the steric and electronic environment about the catalytic centre can be more precisely controlled in such a manner that higher activities and product selectivities can be obtained. However, the use of homogeneous catalysts in commercial processes can result in operational problems such as catalyst recovery and corrosion of equipment, the former being of particular importance when expensive metals are employed.

Several groups of workers, have developed a new class of heterogeneous catalysts which combines the high activities and selectivities
associated with homogeneous systems while maintaining the practical advantages associated with the handling of a solid material\textsuperscript{109}. Essentially the method involves the linking of a transition metal complex to the solid material via ligand groups chemically bonded to the solid surface; most workers have used organic polymers as the support, the most common being polystyrene.

A special situation arises where the active homogeneous catalyst readily dimerises, because once the monomeric units have been bound to support, dimerisation is prevented. Thus titanocene is a reactive intermediate in the reduction of olefins by mixtures of titanocene complexes\textsuperscript{110}, but it is rapidly converted into an inactive dimeric compound\textsuperscript{111}. Crosslinked polymeric ligand bound to titanocene catalyst is more reactive than the soluble titanocene catalyst. The zirconium and hafnium analogues of these catalysts have been prepared and they have little activity as hydrogenation catalysts\textsuperscript{112-114}.

Insoluble polymer-bound metal complexes have been used as catalysts for a wide range of reactions, principally for olefinic substrates, including hydrosilylation, carbynylation, acetoxylation, hydroformylation, polymerization\textsuperscript{116}, and hydrogenation.

Transition metal complexes which act as homogeneous catalysts can be anchored to styrene-divinylbenzene resins and still function as "immobilized homogeneous catalysts". They can be conveniently recycled. These dual catalyst systems can be employed sequentially in one "pot" to
carry out multistep catalytic organic synthesis. Thus, intermediate purification steps are avoided. Where diffusion is rate-limiting, reactions promoted by anchored catalyst are slower but in some cases rates are known to increase using anchored catalysts\textsuperscript{116}. This could be due to a higher concentration of coordinately unsaturated metal complex within the polymers relative to that which would be achieved in solution.

Types of polymer-supported metal complexes

Two broad classes of supported metal complex catalysts had been developed. In the first class, the metal complex is linked to the support through one of its ligands. In the second class, reaction of a metal complex with the support results in the displacement of ligands attached to the metal and their substitution by groups that form an essential part of the support. In both classes two broad types of supports are used, organic polymers and inorganic oxides. Both have advantages as well as disadvantages. A significant difference between them is the degree to which they can be functionalised. Inorganic matrices have an upper limit of monofunctional groups of 1-2 meq/g of matrix whereas organic matrices can carry up to 10 meq/g of matrix\textsuperscript{117}.

Inorganic supports that have been employed include silica, alumina, glasses and zeolites. These supports had rendered disadvantages such as lack of chemical stability (many inorganic oxides actually dissolve in high alkaline or acidic solutions) and flexibility. Inflexibility can also introduce
complication in that the distance between the surface and the functional group may sometimes be critical to catalytic performance\textsuperscript{118}.

Organic polymers that have been used as supports include polystyrene, polypropylene, polyacrylates and polyvinyl chloride. Polymers offer several advantages over other supports\textsuperscript{119}, viz., (i) They are easily functionalised; this is particularly true of polymers containing aromatic groups, (ii) most hydrocarbon polymers are chemically inert. As a result, the support does not interfere with the catalytic group and (iii) Polymers, particularly, poly(styrene-divinylbenzene) can be prepared with a wide range of physical properties. As a result their porosity, surface area and solution characteristics can be altered by varying the degree of cross-linking\textsuperscript{120-122}. Thus with polystyrene, which is by far the most widely studied polymer, variation in the degree of cross-linking allows an almost continual change from virtually a soluble material (2\% cross-linking polystyrene) to a completely insoluble material at 20\% cross-linking polystyrene.

**General considerations for organic polymers**

For the present purpose, organic polymers can be divided into two groups, linear and cross-linked.

Linear organic polymers are prepared by one of the two methods: a polycondensation or addition polymerisation. Polycondensation usually requires reaction between two difunctional reagents with chain growth at both ends of forming polymers. Examples of this type of reaction include a diacid reacting with either a diol or a diamine to gives a polyester or a
polyamide, respectively. It is often advantageous to use the diacid chloride or a diisocyanate in place of the diacid. These reactions are capable of forming materials with very high average molecular weights and are produced commercially in many forms, for instance, the range of nylons (polyamides). As supports for catalysts, their major drawback is the difficulty in modifying them to give donor sites to support transition metal complexes particularly for the polyesters. Polyamides can be modified using the amide N-H as the reactive site. Addition polymerisation is the reaction of alkene monomers undergoing self-polymerisation catalysed by either Ziegler-Natta, cationic or free radical catalysts. It is relatively easy to control chain length and this factor will be important in determining the behaviour of linear polymers in contrast with organic solvents.

Suspension polymerisation is probably the most important method of achieving addition polymerisation as this produces approximately spherical solid particles called ‘beads’. This process employs a solvent in which the monomer is insoluble and in a suitable stirred reactor the liquid monomer will form spherical droplets, the size of which can be controlled by experience. The catalyst precursor is dissolved in the monomer and is activated once the stirring and droplet formation are established. The usual catalyst is the free radical formed by thermal cleavage or ultraviolet irradiation of azobis (iso-butyronitrile). Problems may arise in suspension polymerisation when this method is used to form a copolymer.
Copolymerisation is an addition polymerisation in which two or more different monomer types are to be incorporated into the polymer.

Cross-linked polymers consist of linear polymer chains joined together either in random manner or in a highly symmetrical pattern, thus forming an infinite three-dimensional network. Condensation crosslinked polymers may be formed by the addition of a trifunctional species to the difunctional reagents which would be employed to form a linear polymer. These types of crosslinked polymers have yet to be studied as supports for metal complex catalysts.

The use of crosslinked polymers in chemical application\textsuperscript{124-127} is associated with some advantages, such as, they are insoluble in all solvents, they offer the greatest ease of processing, they can be prepared in the form of spherical beads which do not coalesce when placed in a suspending solvent and can be separated from low molecular weight contaminants by simple filtration and washing with various solvents. Polymer beads with low degrees of crosslinking swell extensively, exposing their inner reactive groups to the soluble reagents. More highly crosslinked resins may be prepared with varying porous structures which allow solvents and reagents to penetrate inside the beads to contact the reactive groups and the copolymers which are highly crosslinked only swell a little in good solvents.
Properties of functionalized polymers

Synthetic macromolecules have also been increasingly recognized as organic species, capable of behaving as organic reactants and susceptible under appropriate conditions to all the chemical transformations of smaller organic species. Ion-exchange resins had previously been widely examined as acid and base catalyst\textsuperscript{128}, though no technological application appears to have been developed at that time. The rediscovery of polymers as organic molecules and their use in organic synthesis was made by Merrifield in 1963\textsuperscript{129}. When he introduced his "solid-phase technique" for the synthesis of peptides, in which an insoluble cross-linked macromolecule was used as a protecting group, simultaneously providing a facile method for isolating and purifying the product of each condensation step. Since that announcement, functionalized polymers had found widespread application in organic synthesis and related fields. They have been employed as stoichiometric reagents, as catalysts, as protecting groups, as substrate carriers in analytical chemistry, in ion-exchange, in the detection of reaction intermediates, in chromatography, in biologically and pharmacologically active systems, in the immobilization of enzymes and cells, in the application of dyes and colorants, and in the field of agricultural chemicals. Properties of functionalized polymers will prove a novel and valuable addition to the review articles which precede it\textsuperscript{130-144}.

A functionalized polymer in the present context is a synthetic macromolecule to which are chemically bound functional groups which can
be utilized as reagents, catalysts, protecting groups, etc. The macromolecules can be a linear species capable of forming a molecular solution in a suitable solvent, or alternatively a cross-linked species, or so called resin, which though readily being solvated by a suitable solvent remains macroscopically insoluble. Of the two approaches, the use of resins has been more widespread because of the practical advantages accruing from their insolvability. Active functional groups may be incorporated into polymer chains, (i) by direct polymerization and copolymerization of monomers containing the desired functional groups, (ii) by chemical modification of a preformed polymer and (iii) by a combination of (i) and (ii). A difficulty with the first method is that considerable manipulation of the copolymerization procedure may be necessary to ensure a good yield of the required copolymer and, in the case of resins, to ensure also a satisfactory physical form. In the second method commercially available resins of high quality are normally employed and the desired functional groups introduced using standard organic synthetic procedures.

The ease of chemical modification of a resin, and indeed the level of success in its subsequent application as a reagent or a catalyst, can depend substantially on the physical properties of the resin itself. Functionalized polymeric supports must possess a structure which permits adequate diffusion of reagents into the reactive sites, a phenomenon which depends on the extent of swelling or solvation, the effective pore size and pore volume, and the chemical and mechanical stability of the resins under the conditions of a particular chemical reaction or reaction sequence. These in
tern depend on the degree of cross-linking of the resin and the conditions employed during preparation of the resin. Three main types of resin can be identified: (a) macroporous or gel type resins; (b) macroporous resins, and (c) macroreticular resins. These have been described in detail elsewhere\textsuperscript{143}, but the essential differences can be summarized as follows:

Macroporous species are prepared from a vinyl monomer and a difunctional vinyl comonomers in the absence of any additional solvating media. In the dry state, they are microporous, with polymer chains being separated by typical solid-state intermolecular distances. On contact with a good solvent, a soft gel network is formed with the generation of considerable porosity depending on the degree of cross-linking. In contrast, commercially available microporous resins with $> 8\%$ cross-linking are mechanically very stable but unfortunately give rise to acute diffusional limitations resulting in slow and incomplete reactions. In practice, resins of $\sim 2\%$ cross-link ratio provide a satisfactory compromise generally allowing adequate penetration by most reagents and yet retaining sufficient mechanical stability to provide ease of handling. Copolymer beads made by suspension polymerization of 98\% styrene and 2\% divinylbenzene isomers (in practice $\sim 4\%$ commercial divinylbenzene) have found very wide application as a result of these factors.

Very similar properties can arise with macroporous resins. These are prepared as before but with the inclusion of an inert solvent. Where the solvent solvates both monomer and polymer, a fully expanded network is
formed with a considerable degree of porosity\textsuperscript{146}. Removal of the solvent causes a reversible collapse of the matrix, and in the dry state such materials are similar to microporous resins. In order to achieve mechanical stability in the solvent swollen state, it is usual to employ larger quantities of difunctional comonomer in the preparation, upto \( \sim 20\% \). Materials of this type are not readily available from commercial sources.

Where the solvent employed during polymerization is a good solvent for the monomers but a precipitant for the polymer, the term macroreticular is generally employed to describe the product\textsuperscript{146}. The latter is a highly porous rigid material which retains its overall shape and volume when the precipitant is removed. They have a large and permanent pore volume, and reaction sites may be regarded as being located on a permanent interior surface of the resin. Such materials are available from a number of commercial sources. Macroporous species were also prepared in the presence of large inert molecules which subsequently can be washed away to create permanent voids\textsuperscript{157}.

The choice of using a microporous or macroreticular resin in preparing a functionalized polymer can be a difficult one and depends very much on the application in question. In a swelling solvent, microporous species can often be loaded or functionalized to higher levels than macroreticular ones. However, the latter are generally much less sensitive to the choice of solvent\textsuperscript{147,148}, which is not always a readily variable parameter in some chemical reactions. Swollen microporous resins are less
sensitive to sudden shock but cannot be subjected to steady and high pressures. Conversely rigid macroreticular species are brittle and fracture under sudden stress, but can withstand considerable steady pressures.

The role of solvent in the application of a functionalized resin is complex. Ideally it should interact with the polymer matrix to optimize the diffusional mobility of reagent molecules. It should have the correct solvating characteristics to aid any chemical transformations being carried out. It should not limit the reaction conditions which are to be applied (e.g., the temperature), and in the case of bound photosensitizers, for example, it should encourage translucence and not opacity. Naturally it is difficult to satisfy all of these criteria simultaneously, and the selection of a solvent is often a compromise. There have been a number of attempts to quantify the interaction of solvents with a polymer-support matrix and have achieved this with respect to the local motions of the polymer backbone and the associated side-chain substituents\textsuperscript{149,150}.

**Advantages in using functionalized polymers**

Probably the most important advantage in using a functionalized polymer as a reagent or catalyst is the simplification of products work-up, separation, and isolation. In the case of cross-linked polymer resins, simple filtration procedures can be used for isolation and washing and the need for complex chromatographic techniques can be eliminated. With linear polymers, techniques such as precipitation, sedimentation, and ultrafiltration can be employed, although these are by no means as
convenient and readily available in all laboratories. Resins, in addition, provide the possibility of automation in the case of repetitive stepwise syntheses and the facility of carrying out reactions in flow reactors on a commercial scale.

Supported reagents may also be used more conveniently in excess to drive reactions to completion, without incurring a penalty in the work-up procedure. Scarce and/or expensive materials can be efficiently retained when attached to a polymer and, if appropriate chemistry is available, they can in principle be recycled many times. The reactivity of an unstable reagent or catalyst may be attenuated when supported on a resin, and the corrosive action of, for example, protonic acids can also be minimized by this effective encapsulation. Finally, toxic and malodorous materials can be rendered environmentally more acceptable.

In addition to these factors, a number of potentially important reactivity changes may be induced by the use of a functionalized polymer\textsuperscript{143}. When the latter is cross-linked, restricted interaction of functional groups may be achieved. A high degree of cross-linking, a low level of functionalization, low reaction temperatures, and the development of electronic charges near the polymer backbone tend to encourage this situation, which may be regarded as mimicking the solution condition of "infinite dilution".
In these circumstances intermolecular reaction of bound molecules is prevented and such attached residues can be made either to react intramolecularly or to react selectively with an added soluble reagent.

Polymer-supported metal complexes with vacant coordination sites can be regarded as fulfilling this description, with the resin inhibiting the normal solution oligomerization processes of such species. Under certain circumstances, it is also possible to achieve the complementary state of "high concentration" by nearly loading a flexible polymer matrix with one particular moiety in an attempt to force its reaction with a second polymer-bound species\textsuperscript{139}.

Finally in the use of functionalized polymers, there always exists the additional chemical option of a side reaction with the polymer itself. A number of classic cross-linking side reactions have been identified\textsuperscript{151,152}, but many other low yields may well be associated with intrapolymeric reactions, which have never been recognized, let alone characterized.

\textbf{Polymeric Reagents}

A polymeric reagent is a reactive organic group bound to a macromolecular support and used in stoichiometric quantities to achieve the chemical modification of an added substrate. Such groups may be attached to polymeric carriers by physical adsorption or by chemical binding:

\begin{align*}
\text{P - X + Substrate} & \longrightarrow \text{P - Y + Product} \\
\text{Polymeric reagent} & \quad \text{Polymeric byproduct}
\end{align*}
Physically adsorbed species are generally unsatisfactory since in use, the components tend to dissociate and they are, therefore, unsuitable for column or cyclical application.

Those chemical reagents covalently attached to polymeric carriers and successfully used in organic synthesis are described below. The byproducts remain attached to the insoluble polymer after the reaction and can be removed by simple filtration. Some of these can be regenerated for repeated use.

A. Polymeric phosphine reagents

Though many useful procedures for olefin synthesis have been reported by Wittig, a principal disadvantage of this reaction is the difficulty of separating the main product from the byproduct, triphenylphosphine oxide. In addition, the phosphine itself is a costly reagent. However, by the use of the insoluble polymeric phosphine reagent, the byproduct remains attached to the polymer after the reaction and is readily separated from the desired product. Moreover, the polymeric phosphine oxide byproduct can be readily recycled and reused in further Wittig reactions$^{153-155}$.

The presence of lithium ions in conventional Wittig reactions, arising during the generation of the ylide lead to the formation of transolefin. Polymeric phosphonium reagents can give high yields of olefins since inorganic lithium salts may be filtered off before the addition of the carbonyl compound$^{153}$. 
Polymeric condensing reagents

Several functional polymers have been reported in the literature for use in the synthesis of peptides\textsuperscript{156,157}. For example, the insoluble polymer containing carbodiimide derivatives (1) was used for conversion of carboxylic acids to their anhydrides\textsuperscript{158}, particularly in the oxidation of highly sensitive alcohols\textsuperscript{159}. Polymeric carbodiimides have the advantage that the byproduct 5 remains attached to the polymer and can be readily converted back into the polymeric carbodiimide 2\textsuperscript{158},

\[
\text{PS - NH - CO - NH - R} \xrightarrow{\text{TsCl, Et}_3\text{N}} \text{PS - N = C = N - R}
\]

Another polymeric condensing reagent incorporates sulfonyl chloride groups and has been used in oligonucleotide synthesis\textsuperscript{160}. The use of a supported reagent has some advantages over the non-supported system, such as the reduction in the contamination of nucleotide product.

c. Polymeric sulfonium salts

Thiols and thioethers are very useful synthetic reagents because of their low cost and high reactivity, which often allows the use of mild reaction conditions. Unfortunately the noxious odour of sulfide or thiol derivatives and the difficulty of removing sulfide byproduct from reaction mixtures detract from their usefulness. A polymeric sulfide reagent may be used to overcome these disadvantages and in addition in some applications, it can be reused after washing since the original reagent is automatically
reformed\textsuperscript{161}. Insoluble polymeric thiol-disulfide systems have been successfully used in a number of oxidation - reduction processes\textsuperscript{162,163}.

\[
R - S - S - R + 2H^+ + 2e \rightleftharpoons 2R - SH
\]

If the reactive sites on the polymer maintain separation during reaction, polymeric sulfonium salts may be used for selective monoxidation of diol compounds\textsuperscript{161}. In addition, other polymeric reagents have been used in the epoxidation of aldehydes\textsuperscript{164,165} and homologation of alkyl iodides and diiodides\textsuperscript{166}.

**Polymeric redox reagents**

Although many useful procedures for oxidation processes had been reported, the main disadvantages of these were the relative difficulty in the preparation of the reagents and in the working-up of the reaction mixture. Polymeric redox systems were one of the earliest examples of polymeric reagents to alleviate these difficulties. The most important classes of polymeric redox systems are the hydroquinone-quinone, thiol-di-sulfide, pyridine-dihydropyridine, polymeric dyes, and polymeric metal complex systems\textsuperscript{162,163}.

Aliphatic peroxy acids explode very readily on impact, and analogous polymeric reagents based on polyacrylic acids behave similarly\textsuperscript{167-169}. Aromatic peroxy acids in contrast are more stable, and the polymer-supported analogues of these had proved very useful indeed\textsuperscript{147,170,171}. 
Insoluble polymeric organotin dihydride\textsuperscript{172} was prepared and used as a selective reducing agent for carbonyl compounds and alkyl halides. This polymeric reagent combines the advantages of both the monomeric dihydride reagent, i.e., its high stability.

E. Polymeric oxidizing reagents

In a polymer-supported heterogeneous organic reaction, the reactive group or catalytic moiety is attached to a cross-linked insoluble polymeric backbone and it comes out during the reaction and effects the required functional conversion. Polymer-supported solid phase organic reagents have several inherent advantages such as the ease of separation and purification\textsuperscript{142,143,173-175} for which simple filtration is usually sufficient. Another advantage is their recyclability\textsuperscript{176,177}. The field of polymer-supported catalysts has received wide attention during the past decades\textsuperscript{129,178,179}. Many workers have studied different polymeric backbones\textsuperscript{180}.

Frechet et al., used chlorochromate supported on polyvinylpyridine as an oxidizing agent for alcohols\textsuperscript{181}. Crosby et al. used polymer-supported thioanisoles for the oxidation of alcohols\textsuperscript{161}. Similar chromate-supported oxidizing agents on different polymeric supports were reported by various workers\textsuperscript{182,183}. The major problems encountered in all these oxidations were long reaction time of more than 24h and/or low yield. They can be used only for easily oxidizable alcohol oxidation a reactions using peroxycacid and peracid supported on polymeric backbone were also studied\textsuperscript{170}. John and Pillai used beads of permanganate supported on poly(vinylpyridine) and
polyvinyl pyridine-co-styrene\textsuperscript{184} for the oxidation of alcohols to the corresponding aldehydes or ketones with varying yields. In these studies, reactions were limited to easily oxidizable alcohols like benzyl alcohol, benzhydrol, cinnamyl alcohol, o-cresol etc. and a much longer reaction time was required for the conversion.

Permanganate functionalized polyvinylamine with permanganate content 3.3 meq/g has been synthesized by Prabhakaran et al.\textsuperscript{185}. Its effectiveness as an oxidizing agent for primary and secondary alcohols has been demonstrated. The extent of oxidation was found to be strongly dependent on the degree of crosslinking. The reagent is more efficient than previously reported for PVPMnO\textsubscript{4}. The effect of crosslinking the backbone polymer on the reaction was also studied and 5\% crosslinking was found to be optimum. The spent polymeric reagents could be regenerated in a single step, many times without the loss of its capacity. The catalytic resin was insoluble in the medium during oxidation and therefore, filtration and purification of the products were easy.

F. Polymer-supported halogenating reagents

The success of these functionalized insoluble polymers is attributed to a combination of several advantages, including changes in the specificity and reactivity of the functional group, the ease of removal of excess reagent and product separation, and the facile ability to regenerate the reagents. Interesting but different polymeric halogenating reagents\textsuperscript{186-189} have been successfully used for the specific addition of halogen to olefins and for allylic
halogenation. For example halogenation of alkyl aromatic compounds with N-chlorosuccinimide in the absence of solvents and free radical initiators leads to the formation of a mixture consisting of side-chain and arylchlorinated compounds. However, with poly(n-chloromaleimide) under the same conditions, arylchloro-substituted derivatives are the only product(s) obtained$^{190}$.

G. Polymer-supported acylation and alkylation reagents

Several functional polymers have been reported in the literature for use in the alkylation and acylation of different substrates. For example, the insoluble polymer containing the anhydride functional group 3 was used for the conversion of an amine or alcohol to amide or ester$^{191,192}$,

$$\text{PS} - \text{CO} - \text{O} - \text{CO} - \text{R} \xrightarrow{\text{R'NH}_2} \text{RCO} - \text{NHR'} \text{ (or) } \text{RCO} - \text{OR'} \text{ or R' OH}$$

The insolubility of a resin-bound reagent in all common solvents can have the effect of isolating the reactive groups on the polymer from each other. Patchornik and his coworkers$^{193,194}$ had used this property in the crossed alkylation of ester derivatives. The reactive carbanion derivative of a bound ester is first generated and self condensation with unreacted ester inhibited by the rigid matrix. The production of these stable monoanions then allows the reaction with acyl or alkyl halides to give selectively monoacylated or monoalkylated products.
H. Polymer-bound nucleophiles

Anion-exchange resins in which the bound negative ion is exchanged for a reactive nucleophile prior to use in a reaction have been employed as polymeric reagents. There exists a close relationship between these systems and polymer-supported onium salts as phase-transfer catalysts, where the anion exchange may be regarded as taking place in situ during reaction. Where the ion exchange is carried out as a separate process, the reagent can be isolated and dried before use under essentially anhydrous conditions. Most applications have employed halide ions as the nucleophile, but recently a bound benzenesulfinate anion, has been used in the synthesis of sulfones\textsuperscript{195},

\[ \text{PS} - \text{CH}_2\text{N}^+\text{Me}_2 - \text{O}_2\text{SPh} + \text{RX} \longrightarrow \text{RSO}_2\text{Ph} + \text{PS} - \text{CH}_2\text{N}^+\text{Me}_2\text{X} \]

I. Polymeric protecting groups

There is no group capable of reacting selectively with only one functionality of a completely symmetrical bifunctional compound. However, functionalized insoluble polymers have been used with some success in this role. The selectivity of functional polymer resins for monoblocking utilizes the approximation to "infinite dilution" which can be achieved with a polymer-bound group. In this type of reaction, a large excess of a symmetrical bifunctional substrate is employed to ensure that only one of the functional groups reacts with the polymer-bound protecting group. For
example, Leznoff and his coworkers\textsuperscript{196,197} had used a polymer containing a diol functional group as a monoblocking agent for symmetrical dialdehydes.

Insoluble resin techniques offer several advantages in preparative procedures. Resins can be used as diluents to hold reagents during a reaction\textsuperscript{198}, polymers can be used to hold catalysts during chemical transformations\textsuperscript{199}, and polymers can be used as centers upon which large molecules can be grown\textsuperscript{129,192,200} and the surrounding polymer protect the active site from reagents which destroy the catalytic activity of a similar species in solution.

**Polymer-supported catalysts**

Polymer-supported catalysts are generally used in catalytic quantities relative to reaction substrates. The absolute activity and selectivity of the catalyst was improved on attachment of the polymer\textsuperscript{142}. Diffusional limitations normally associated with supported catalysts’ reactivity. Normally, a wide variety of catalysts have been supported in this way ranging from strong acids and bases (ion-exchange resins), polymeric dyes and photosensitizer catalysts, polymeric hydrolysing catalysts and hydrogenation catalysts.

The functionalized polymers, which have been used as hydrolyzing system are an essential functional structure of enzymes, have been prepared and used to promote enzyme-type reactions\textsuperscript{201}. The imidazole moiety of histidine is present in the active sites of several hydrolyzing enzymes. The
polymer-supported catalysis is attributed to specific adsorption of the substrate and cooperative interaction of imidazole and other groups of the active center. After hydrolysis, the product is eliminated from the polymer active center which is then available for further catalysis.

Polymer-bound Rose Bengal\textsuperscript{202} have been prepared and employed to sensitize the generation of singlet molecular oxygen for photooxidations of olefins. The advantages of using a polymer-supported photosensitizer lie in the fact that the dye could be easily separated by filtration from the product and be reused many times.

Ion-exchange resins are required in various purification circuits of moderators and coolants. Besides the basic functions of removing impurities, it is also expected to remove the corrosion and fission products at trace levels. Helfferich\textsuperscript{203} had synthesized ion-exchange resins and the use of these materials in this way has been reviewed previously\textsuperscript{204}.

**Pyridine complexes and their applications**

When gold is present as chlorauric acid, its presence can be demonstrated by the addition of pyridine hydrobromide reagent, which causes the separation of the complex, \( \text{C}_6\text{H}_5\text{N.HBr.AuBr}_3 \). The latter appears in the form of characteristic crystals, and the test is specific for gold\textsuperscript{205}.

Pyridine forms \( \text{FeCl}_3.\text{Py} \), a neutral species that is consistent with low dielectric constant of pyridine. However, there is a sharp distinction between
the anionic species present. If no specific co-ordination of an anionic species is possible, a large anion can be solvated away from its cation more easily than a small one of the same charge; thus FeCl$_4^-$ is the stable anion in MeCN, MeNO$_2$, acetone, DMA, and pyridine$^{206}$.

Two complexes of chromium (VI) oxide with pyridine are useful as selective oxidants for primary alcohols and other alcohols containing acid-sensitive groups: Pyridinium dichromate (PDC)$^{207}$, and pyridinium chlorochromate (PCC)$^{208}$.

Chromium(VI) oxidising reagents have been developed, including the Collins reagents$^{209}$ [(C$_5$H$_5$N)$_2$CrO$_3$], pyridinium chlorochromate [PCC],[(C$_5$H$_5$NH$^+$) Cl$^{\ominus}$.CrO$_3$]$^{206}$ and PDC,[(C$_5$N$_5$NH)$^+$ .Cr$_2$O$_7^{2-}$]$^{210}$. The use of PCC is illustrated in the preparation of heptanal from heptan-1-ol.

The most common example of ligand addition reaction is SnCl$_4$ + 2pyridine → SnCl$_4$.2Py; the (4d$^{10}$) Sn(IV) atom increasing its coordination number from 4 to 6. Reactions of this type are expected to be very fast except where considerable reorganisation of energy is required during the change. Reactions involving metal atoms which are initially coordinatively unsaturated are often important in catalysis. Lewis acids such as the halides of B, Al, Ga, Fe, Zr, Ti, Sn, Zn, Nb and Tn accept halide ions from alkyl halides or acid chlorides$^{211}$.

Zr(benzyl)$_4$ reacts reversibly with compounds such as pyridine, quinoline, and tri-n-butyl phosphine oxide, giving compounds such as
Zr(phenyl)_4L and Zr(phenyl)_4 L₂. They are readily detected by observation of methylene protons of the benzyl groups or the relevant ligand protons in the 220-MHz NMR\textsuperscript{212}. For example, pyridine reacts as shown in equation:

\[
\begin{align*}
\text{CH}_2\text{C}_6\text{H}_5 & \quad \text{CH}_2\text{C}_6\text{H}_5 \\
\text{Zr(CH}_2\text{C}_6\text{H}_5)_4 + \text{C}_5\text{H}_5\text{N} & \rightleftharpoons \text{Zr} \\
\text{H}_5\text{C}_6\text{CH}_2 & \quad \text{CH}_2\text{C}_6\text{H}_5 \\
\text{NC}_5\text{H}_5
\end{align*}
\]

The spectroscopic studies show that the co-ordination complex is in equilibrium with free Zr(phenyl)_4 and pyridine but this equilibrium is predominantly to right hand side. In fact, both the pyridine complexes were isolated.

Monomeric pyridine-borane in refluxing benzene reduces aldehydes and ketones in moderate yield\textsuperscript{213,214}.

The organic derivatives of ammonia form addition compounds with zirconium tetrachloride similar to those formed by ammonia itself. The pyridine complexes ZrCl₄.2C₅H₅N and ZrCl₄.4C₅H₅N have been reported, and measurements of the heat of reaction of pyridine and ZrCl₄ have indicated no compound to exist between these two in composition\textsuperscript{215}. 
The active centers on the cobalt phthalocyanine surface had been studied by EPR and reflection spectroscopy prior to and after coordination of pyridine. An increase in catalytic activity was observed after coordination of pyridine. This effect was ascribed to the influence of the trans-coordinated (with respect to the hydrogen peroxide) ligands on the electron transfer between the cobaltous ion and the peroxyde molecule$^{216}$.

It is possible to titrate the base pyridine against the compound boron trichloride, $\text{BCl}_3$. The solvent has to be nonaqueous such as chlorobenzene ($\text{C}_8\text{H}_8\text{Cl}$). An indicator which works well for this titration is thymol blue (yellow to blue in the pH range 8.0 to 9.6)$^{217}$.

The heterocyclic amines, although they contain tertiary nitrogen, coordinate readily, and a large number of pyridine complexes were described. In general, these resemble the corresponding ammonia compounds. Davis and his students$^{218}$ had found the stability of certain nickel and zinc pyridine compounds to decrease as the temperature is lowered. For example, $\text{Ni Py}_4(\text{SCN})_2$ was stable at room temperature, but decomposes at -3$^\circ$.

**Polymer-supported(vinylpyridine)-metal complex catalysts and their applications**

An extensive literature search revealed that the utility of polymer-supported (vinylpyridine) - metal complexes in various organic reactions and synthesis are at infant stages as given briefly:
Saltykov et al.,\textsuperscript{219} reported that the Pd (II) complexes supported on poly (vinylpyridine) [PVP] was suitable catalyst for the hydrogenation of unsaturated aldehydes and alcohols in water and ethanol. The catalytic activity has been shown to depend on the composition of the complexes and the valency state of the palladium contained therein. The rate is also determined by the ability of the complexes to swell in organic solvents and by the diffusion of reactants to active centres within the bulk of the polymer-metal complexes.

A very high catalytic activity was observed for the esterification, acetalization and ketalization catalyzed by PVP-SnCl\textsubscript{4} complex catalyst\textsuperscript{220}. The kinetic study of catalytic esterification of acrylic acid with n-butanol using PVP-TiCl\textsubscript{4} has been reported by Balakrishnan et al.,\textsuperscript{221} The rate of formation of product depended on many experimental parameters and thermodynamic parameters were also reported. Ivanova et al.,\textsuperscript{222} used PVP-FeCl\textsubscript{3} complex as catalyst for the kinetics of the esterification of methacrylic acid (MA) with ethylene oxide (EA). As a result, a kinetic model of the reaction was proposed. The optimum conditions for the progress of the reaction allowing maximum yield of the desired product are: Temperature 80°C, catalyst content 1-3 wt % and initial mole ratio of methacrylic acid to ethylene oxide, 1:1.

A rhodium hydrogenation catalyst ligated by diphenylphosphininated ethylene oligomers was used as a homogeneous catalyst to effect alkene reduction of a substrate which is at the same time being oxidized by an
insoluble poly (vinylpyridine) - bound Cr (VI) oxidant. Zoran Zdravkovski et al., had studied the oxidation phenylethanol and various alcohols in the presence of PVP-Cr (VI) reagent. Rajasekharan Pillai et al., used poly (4-vinylpyridine)(PVP) which was crosslinked with divinylbenze, PVP-MnO₄ and used them in the oxidation of benzylalcohol, cinnamyl alcohol, Benzhydrol, Benzoin, and o-Cresol. The influence of solvent, duration of reaction, and molar excess of the reagent in these oxidation reactions were investigated to find out the optimum conditions for effective oxidation reactions. The reactions were found to be more facilitated in nonpolar solvents and large excess of the polymeric reagent did not bring out any significant effect on the extent of reactions.

The reduction of ketones such as substituted cyclohexanone and aliphatic and aromatic groups substituted aldehydes in benzene at room temperature by solid PVP-BH₃ complex was reported by Menger et al.,. Reduction of various carbonyl compounds in high yield were performed using PVP-Zr(BH₄)₄ and representative results are listed by Tamami et al.,.

Cu(II) supported on poly(4-vinylpyridine) and polystyrene bound 2,2'-bipyridine catalyse the oxidation of thiosuphate, trithionate and tetrathionate to sulphate:

\[ \text{S}_2\text{O}_8^{2-} + 2\text{O}_2 + \text{H}_2\text{O} \rightarrow 2\text{SO}_4^{2-} + 2\text{H}^+ \]
The effectiveness of the catalyst depends on particle size, increasing with decreasing particle size. Although the initial rates of the polymer-supported catalysis are less than that of homogeneous analogues, the rate of the homogeneous catalyses quickly fall, so that the overall rate is greater when the supported catalysis are used. This is due to the reduced stability of the supported complexes, which allows the nitrogen ligands to be displaced by the thiosalt. The studies on Cu(II) complex catalyst with polymeric ligand, such as poly (4-vinylpyridine) have been performed. The studies had indicated that the high catalytic activity of polymeric catalyst is primarily caused by an increase in the local concentration of active site and substrate by means of hydrophobic or electrostatic interaction between substrate and polymer chains.

In order to combine the two advantageous properties i.e. the easy adsorption of sulfonated porphyrins onto ion-exchange resins and proximal effect of pyridine, Labet et al., used poly(4-vinylpyridine) (PVP) which was crosslinked with divinylbenzene, MnTMPS-PVP and used them in the oxidation of Liginin dimer molecule. The recycling experiments were also conducted using these PVP catalysts. The MnTMPS-PVP is also a suitable catalyst to perform the oxidative chlorination of dimedone. This reaction was catalysed by chloroperoxidase and was difficult to mimic using simple metalloporphyrins. Recently, Campestrini and Meunier reported that the robust sulfonated manganese porphyrine supported on PVP showed higher oxygenase activity. They efficiently catalyzed the peroxidation of cyclooctene and hydroxylation of cyclooctane by PhIO.
Relatively few hydroformylations using supported cobalt complexes have been reported. Moffat showed that poly-2-vinylpyridine reversibly reacted with both [CO$_2$(CO)$_6$] and [HCO(CO)$_4$], the cobalt carbonyl being displaced by excess carbon monoxide$^{236,237}$. This enabled the polymer to pick up the cobalt carbonyl at the end of the reaction, so enabling it to be separated from the products by filtration. When CoCl$_2$ or [Co(acac)$_2$] was supported on polyethylene to which 4-vinylpyridine has been grafted, the resulting catalyst gave higher yields of polybutadiene and polyisoprene than their homogeneous counterparts$^{238}$. This is believed to be due to the inhibition of cobalt (II) reduction.

The palladium (II) catalysed acetoxylation of aromatic compounds is of particular interest because it gives an anomalously high meta-selectivity. This is retained when Pd (II) acetate is supported on poly(4-vinylpyridine). The polymer-supported catalyst can be reused several times with little loss of activity between runs$^{239}$. Stable polymeric complexes of poly(4-vinylpyridine) with [RuCl$_2$(CO)$_3$)$_2$ or [RhCl(CO)$_2$]$_2$ have been synthesized and used to catalyse the isomerization and hydrogenation of alkenes$^{240}$.

Neckers et al.$^{241}$ published a detailed report that expanded on preliminary reports with enhanced catalyst performance of Co(OAc)$_2$ and related transition metal compounds, such as Zn (II), Ni (II) and Mn (II) which serve as catalysts for aldol condensation when complexed with bipyridine, triphenyl phosphine, and crown ether as well as those immobilized to polystyrene by triphenylphosphine and poly (4-vinylpyridine)
were also reported. The reaction studied in the present investigation is the crossed condensation of benzaldehyde with acetophenone catalyzed not with aqueous base, but with the Co(II) complexes. The results show that Co(II) is the best catalyst for the process, followed by Zn (II), Ni (II) and Mn (II), with the latter two metals having about the same catalytic activity. The best counter ion, in all cases, is the acetate.

Oxidative cleavage of olefines has been achieved by the simultaneous use of polymer-supported (4-vinylpyridine) osmium tetraoxide and sodium periodate. Good yields of carbonyl compounds, fast reaction rate and easy workup are the main features of the proposed procedure. PVP-OsO₄ has been used in the presence of secondary oxidants, such as hydrogen peroxide, tert-butyl hydroperoxide and trimethylamine N-oxide to accomplish the catalytic hydroxylation of olefines. The polymeric reagent offers the advantages of easy and safe handling and simple separation from the reaction medium. Generally good yields of vicinal diols have been obtained.

Other catalysts used in esterification of acetic acid with cyclohexanol and phenethyl alcohol

The equimolar reactions of acetic acid with phenethyl alcohol was undertaken by the use of 2-chloro-1-methylpyridinium iodide to determine the influence on the yield. The consideration that both the counter ion and halogen atom attached to 2-position of the pyridinium salt would influence the yield of carboxylic ester urged to look for more effective pyridinium salt. Sekine reported a practical and useful method for the acylation of alcohols by the use of dialkyl acylphosphonates. It was found that the use of 1,5-
diazabicyclo (5,4,0) undec-5-ene (DBU) increased the rate of the acylation dramatically. When one equivalent of DBU was used in CH$_2$Cl$_2$, the acylation was completed within 10 min and ester was obtained in 99% yield.

Graphite bisulfate$^{246,247}$ was an efficient catalyst for the formation of acetates from acetic acid with phenethyl alcohol and cyclohexanol. Kinetic studies show that the yield of ester reaches 90-100% in less than 1 hr for primary alcohols and 80-90% for secondary alcohols. The esterifying capacity of graphite bisulfate can be estimated to be $5.5 \times 10^{-2}$ mol of acid and alcohol per gram.

Esterification was catalyzed by synthetic Zeolites$^{248}$. Primary, secondary, and tertiary alkyl esters were prepared over synthetic zeolite. Yields in the case were 75-85%. Secondary and tertiary alcohols were lower, but still higher than those catalyzed by mineral acids. Also, allyl alcohol which is sensitive to mineral acids, was esterified satisfactorily with carboxylic acid (acetic acid) in the presence of zeolite.

Esterification reactions were catalyzed by hydrated sulfate salts$^{249}$. Kinetic measurements were carried out in the esterification reaction of phenethyl alcohol with acetic acid in the presence of hydrated sulfate salts. The system can be described in the Taft equation and linear free energy equation was presented.

Cyclohexylacetate, dodecyl and octyl acetates and octyl pelargonate were prepared by reacting a monobasic organic acid with a secondary alkyl halide in the presence of Fe, Sn or Zinc chloride or bromides$^{250}$. Thus, 2-octyl
chloride was heated for 16 hr at 115°C in the presence of metal chlorides to give (metal chloride, % conversion of octenes, and % conversion to octyl acetate given): FeCl₃, 39.0, 53.9; FeBr₃, 46.0, 51.0; and SnCl₄, 37.3, 54.5; ZnCl₂, 45.0, 49.0; HgCl₂, 20.0, 15.0; and MoCl₅, 12.0, 10.0.

Olah et al.,²⁵¹ interested in the catalytic ability of the Nafion-H, the results of the convenient esterification reaction of acetic acid with cyclohexanol (3:1 molar ratio) and 1-hexanol by Nafion-H, the moderate yields of the corresponding ester were obtained. It has been noticed that no reactivation of the catalyst is needed since the catalytic activity of the Nafion remains unchanged for prolonged periods of operation.

Trimethyl chlorosilane²⁵² was a convenient reagent for the esterification of acetic and with cyclohexanol and 1-hexanol. The results obtained showed that the esterification with secondary alcohol is slower than that with primary alcohol, the yields of all the esters are very high. Therefore, Me₂SiOCl can be said to be a very efficient and convenient reagent for the esterification of carboxylic acid with primary and secondary alcohol at room temperature.

Yadav et al.,²⁵³ reported the kinetic study of esterification of acetic acid with cyclohexanol and phenethyl alcohol using solid acidic catalysts, such as Amberlyst-15, Filtrol-24, Sulfated zirconia, DTPA/Silica and DTPA/Carbon. The application of solid acidic and superacidic catalysts can prove to be very effective from the viewpoint of activity, selectivity, reusability and economy in the manufacture of perfumary ester of cyclohexylacetate, phenethylacetate with a variety of solid acids including
a complete theoretical and experimental analyses. Yi-Qun Li\textsuperscript{254} used sodium bisulfate monohydrate catalyst for the esterification of acetic acid with cyclohexanol and various primary and secondary alcohols. The experimental results show that the esters can be synthesized in large quantities, the reaction condition is mild, the reaction time is short, the yields are excellent and the operation is simple.

Uses of Zirconium Tetrachloride in chemical industry

The major uses of zirconium tetrachloride have been in the preparation of zirconium metal and of zirconium compounds. ZrCl\textsubscript{4} has found some industrial applications in catalysis. Literature on these processes is summarized.

Since ZrBr\textsubscript{4} and ZrCl\textsubscript{4} are very similar chemically but the former considerably more expensive, the tetrabromide has not been used to any extent. ZrI\textsubscript{4} has found use only in the preparation of zirconium metal of high purity, and in current procedures, it is usually generated and used immediately in the same equipment.

Zirconium tetrachloride is a catalyst for the synthesis of ketones according to Friedel-Crafts reaction. Krishnamoorthy has previously reported\textsuperscript{255} zirconium tetrachloride to be effective in the preparation of the ketones, acetophenone and benzophenone.

Heine \textit{et al.},\textsuperscript{256} had conducted a preliminary comparison of ZrCl\textsubscript{4} and AlCl\textsubscript{3} by measuring the yield of p-methyl acetophenone from acetyl chloride
and toluene. The procedure and analytical method used in this investigation were essentially those developed by Dermer and Co-workers\textsuperscript{257,258}. The yields of ketone obtained with ZrCl\textsubscript{4} and AlCl\textsubscript{3} are given. The results with ZrCl\textsubscript{4} are at once better but less consistent than those obtained with AlCl\textsubscript{3}. No explanation is offered for the erratic behaviour of ZrCl\textsubscript{4}.

Aristid Grosse \textit{et al.},\textsuperscript{259} described how different classes of hydrocarbons, such as paraffins, napthenes, aromatics, etc., originally considered very unreactive, react among themselves. TaCl\textsubscript{5} seems nearly as efficient as AlCl\textsubscript{3}, whereas ZrCl\textsubscript{4} appears equal or superior to the latter. TiCl\textsubscript{4} is the poorest catalyst of those investigated.

Among the Lewis acids available in literature, zirconium tetrachloride is one of the most widely used inorganic reagent for various reactions and synthesis such as alkylation\textsuperscript{260}, chlorination\textsuperscript{261}, isomerization of hydrocarbons,\textsuperscript{262} etc.

Polycyclic hydrocarbons can be carried out, often in good yields, by treating a diarylmethane or a diaryl ether or a dichloromethylether with stannic chloride in CH\textsubscript{2}Cl\textsubscript{2} at low temperatures\textsuperscript{263}. Bartlett and Johnson\textsuperscript{264} effected cyclization of olefines with this Lewis acid. The conditions were carefully chosen and the desired isomer was formed predominantly.

Spanish chemists\textsuperscript{265} synthesized dl-taondiol methyl ether by the cyclization of the epoxide with a catalytic amount stannic chloride in benzene\textsuperscript{266} and also is the most effective catalyst for cyclization of dienic
acetals. Thus the trans-dienic acetal is converted in high yield into a mixture of trans-octalol ethers. In fact, trans-octalol ethers can be obtained in about 80% yield in nitromethane as solvent. Cyclization of the cis-dienic acetal with stannic chloride gave a similar mixture of cis-fused tricyclic products.

Treatment of the epoxide of the sesquiterpene cyperene\textsuperscript{267} with stannic chloride in benzene at room temperature gives the cyclopentanone (70% yield) and the methyl ketone (10% yield). The cleavage involves six rearrangements.

Lewis acid like aluminum chloride catalyses Diels-Alder reactions and also influences the course of the reaction\textsuperscript{268}. Thus the reaction of 2-methylene cyclopentanone with isoprene in the presence of SnCl\textsubscript{4} gives the product in the ratio 24:1. In the absence of SnCl\textsubscript{4}, the ratio is 2:1. This reaction was used in the synthesis of α-alaskene and δ-acoradiene from 3-methyl-2-methylene cyclopentanone\textsuperscript{269}.

Stannic chloride was used for a one-step synthesis of 1,4-dimethylcyclohex-3-enyl methyl ketone from isoprene and isopropenyl methyl ketone\textsuperscript{270}. If the reaction is carried out at 140° (autoclave) without this catalyst, product is obtained in about 30% yield together with an isomer, probably 1,3-dimethylcyclohexenyl methylketone.

Anderson and Uh\textsuperscript{271} had developed a method for the preparation of acetals of aldehydes that tend to undergo cyclization in the presence of
Lewis acids. The aldehyde is added to a solution of SnCl$_4$ and Dicyclocarbodiimide (DCC) in benzene. Yields of acetals are about 95%.

Chloromethylation of polystyrene can be effected by the Friedel-Crafts reaction of chloromethylmethylether in the presence of tin (IV)$^{272,273}$. 

β-hydroxyethylation of azulenes can be carried out with ethyleneoxide, using either AlCl$_3$ or SnCl$_4$ as the Lewis acid and methylene chloride as solvent$^{274}$. The reaction was carried out with azulene itself and several 6-substituted azulenes. A disubstitution product was obtained in minor amounts (5-10% yield). The method is a modification of a procedure of Searles$^{275}$ for β-hydroxyethylation of benzene and anisole.

Epoxides and aldehydes yielded ketones in the presence of SnCl$_4$ from acetals or ketals readily$^{276,277}$. It is common to use dry CCl$_4$ as a solvent and to hold the temperature of the exothermic reaction down to 20-30°C. Yields from a variety of aliphatic and aromatic ketones vary from 45 to 83%.

Although zirconium tetrachloride and stannic chloride have many advantages in homogeneous conditions; they have predominant drawbacks such as, corrosive nature, difficulties in separation, recovery and reuse and the large volumes of environmentally hazardous waste associated with their use. Hence, in recent times, heterogenization of zirconium tetrachloride and stannic chloride has become prime target.
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