

Transition Metal Complexes and Catalysis

Balaji R Jagirdar

The applications of transition metal complexes in catalysis are described in this article.

Introduction

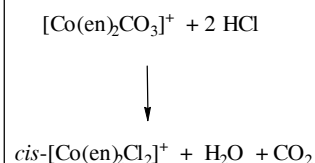
The study of coordination chemistry in the modern day context began with two notable scientists, Alfred Werner and Sophus Mads Jørgensen. Although there was considerable controversy between Werner and Jørgensen regarding the interpretation of their experimental results on the structures of coordination compounds, one can now conclude that Werner's interpretation of his results is 'correct.' The pioneering contribution of Werner to the study of coordination chemistry fetched him the Nobel Prize in Chemistry in 1913 and incidentally he is the first inorganic chemist to win the coveted distinction. Despite Jørgensen's interpretation being 'wrong' his contributions by no means are to be ignored. As chemists we owe a lot to these two people who contributed immensely to our understanding of the chemistry of coordination compounds. The details of the contributions of Werner and Jørgensen are out of scope of this review. Soon after the reports by Werner and Jørgensen, there have been different approaches towards the study of bonding in transition metal complexes.

Despite rigorous study, there still exist lacunae in the understanding of reaction mechanisms in the case of inorganic chemistry compared to organic chemistry. This lack of understanding of reaction mechanisms spills over into synthesis as well to a certain extent. Synthetic tricks are sometimes discovered that allow one to prepare a desired compound without the interference from an undesired product. Werner discovered that certain *cis* isomers could be prepared from a carbonato compound that would react with acid to generate carbon dioxide and insert two anions of the acid as ligands, *Box 1*. But now, from the knowledge of the fundamental reactions of coordination chemistry which will be



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Box 1.



discussed in the following paragraphs, one can predict the products of a certain reaction with a reasonable amount of success. The fundamental reactions of coordination chemistry, which appear in several combinations and sequences, constitute the major reaction pathways in catalysis.

The purpose of this review is to highlight some of the applications of transition metal compounds as catalysts. The subject matter of this review will consist of certain general principles outlining the features involved for a transition metal complex to act as a catalyst, some specific catalytic reactions that are being employed in industry currently, briefly some comments on industry-academia collaborations, current and future trends in catalysis, and finally conclusions.

General Principles

Transition metal atoms have one *s*, three *p*, and five *d* orbitals that possess geometrical and energetic features suitable for bonding with the ligands. In certain cases these nine orbitals permit the formation of bonds with nine ligands. An extreme example is the polyhydride complex $\text{ReH}_7(\text{PEt}_2\text{Ph})_2$, which contains seven covalent Re-H bonds and two coordinate $\text{P} \rightarrow \text{Re}$ bonds. The phosphine ligands donate electron pairs to vacant orbitals on rhenium atom resulting in the coordinate bonds. The seven valence electrons of rhenium present in seven orbitals pair up with the lone electrons provided by the seven hydrogen atoms forming the covalent bonds. In this compound, the metal is in its highest oxidation state, that is +7 and exemplifies that a metal ion can bind with the ligands in both covalent as well as coordinate fashion. This kind of versatility is the basis for the catalytic activity of certain transition metal complexes to a great extent. Upon coordination to a metal ion, changes take place in the electronic distribution in a ligand, which result in the modification of the reactivity of the ligand molecule, at times dramatically.

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metal because the added electrons will have to occupy orbitals at high energy. Therefore, ligand substitution reactions in such cases proceed by S_N1 type mechanisms, that is, one ligand dissociates from the complex resulting in a coordinatively unsaturated species, a species having 16 electrons in the valence orbitals of the metal. The coordinatively unsaturated complex would then bind with other potential ligands rather readily. This switching of electron count between 16 and 18 drives the catalytic cycle.¹

A catalyst is capable of accelerating a thermodynamically allowed reaction by lowering the energy barrier, it cannot however, favor a thermodynamically forbidden reaction. This is purely a kinetic effect. In certain cases, the species that is catalytically active is not the same compound that is added to the reaction mixture as a catalyst. Some transformations could occur to generate the active species that can bring about the catalysis. In addition, there could be an induction period before the catalytically active species starts to function as a catalyst. These are the essential characteristics of a cyclic process irrespective of whether the species acts as a homogeneous or a heterogeneous catalyst.

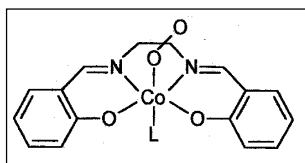
There has been an upsurge of research in the area of catalysis by transition metal complexes since the 1940s. The demand for cheaper and more efficient processes in the industry necessitated a major explosion of research in the area of synthetic chemistry to develop new systems that can act as catalysts. This also resulted in a rapid development of newer process technologies relevant to industrial scale reactions for the production of organic compounds using transition metal complexes as catalysts. The notable contributions of K Ziegler and G Natta and E O Fischer and G Wilkinson in this area of chemistry fetched them the Nobel prizes in 1963 and 1973 respectively. Their pioneering work is the stepping stone for the development of homogeneous catalysis. A great number of soluble metal complexes are now being employed in industry as catalysts for the generation of a variety of useful compounds. More are being developed in order to find processes

¹ The fundamental reactions that coordination and organometallic compounds (compounds that have a direct M-C bond) can undergo are (a) ligand replacement, (b) oxidation and reduction, (c) oxidative addition and reductive elimination, and (d) insertion and elimination reactions. These reactions can be observed in catalytic processes that are discussed below.



² The advantages and disadvantages of homogeneous and heterogeneous catalysis are as follows: in a heterogeneous catalytic process, the atoms or species that are catalytically active are only the surface ones, the reactions have to be carried out at relatively high temperatures and are often accompanied by low specificities. In addition, it is difficult to study the mechanistic aspects. However, the recovery of the catalyst is relatively easy in a heterogeneous process. On the other hand, a homogeneous catalyst can be tailor-made by ligand variation and is obtained reproducibly; the reactions can be carried out at low temperatures and are accompanied by high specificities depending upon the catalyst employed. The mechanism of a homogeneous catalytic process can be worked out much more easily; however the catalyst recovery is fraught with difficulties. A possible remedy to this problem is to attach a homogeneously active complex to a polymeric support and the process can be carried out. The catalyst can then be cleaved off easily from the support and thus recovered.

Figure 1. Cobalt salen complex showing the binding of O_2 ; $L=N$ -donor ligand.



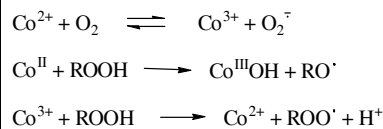
that would yield products in greater selectivity and purity and in high yields. With the advent of a variety of highly sophisticated and accurate spectroscopic techniques, the study of the mechanisms of catalytic reactions has been made possible compared to earlier days. These techniques have in fact enhanced our understanding of the difficult chemistry involved in the catalytic processes.²

Catalysis by Transition Metal Complexes

(i) **Hydrocarbon Oxidation by Molecular Oxygen:** Oxidation of hydrocarbon substrates by molecular oxygen is by far the largest industrial scale application of catalysis. For an understanding of the mechanisms of the catalytic processes, the reactions of metal complexes with molecular oxygen have been studied and it has then concluded that the complexes themselves do not get involved in the major oxidation pathways. A radical chain process takes place between the hydrocarbon and oxygen even in the absence of the catalyst. The result is an alkyl hydroperoxide, ROOH that is unstable under the reaction conditions and decomposes into alcohols, ketones, or carboxylic acids. Here the metal complex acts as a catalyst in the decomposition of the alkyl hydroperoxides thus enhancing the generation of the desired products by increasing the concentration of the free radicals that speed up the radical chain process. This in turn provides a higher yield and a greater rate for the overall reaction.

The metal ions that are catalytically active have two stable oxidation states related by one electron transfer reaction. The most important ones are cobalt, manganese, and copper among which the Co(II) salts are most widely used for hydrocarbon oxidations. However, they are usually used in combination with Mn, Cu or Cr salts. In order to understand the interaction of dioxygen with the transition metal ions, reactions of O_2 with certain Co(II) salts have been carried out. Among such studies, the noteworthy example is the Co-salen (Figure 1) complex that forms a stable complex with O_2 . Electron transfer takes place from the metal to the dioxygen ligand resulting in oxidation of Co(II) to Co(III). As pointed out earlier,

dioxygen complex formation is not a pre-requisite for catalysis. In the following step, the O-O bond weakens resulting in the breakdown of the complex and the formation of the energetic alkoxy radical. This rapid redox reaction of cobalt catalyzes the breakdown of ROOH into radicals that initiate the oxidation of hydrocarbon. These reactions are summarized in *Box 2*.



Box 2. Redox reactions of cobalt catalyzing the breakdown of ROOH.

The oxidation products of the hydrocarbons, namely, cyclohexane are cyclohexanol and cyclohexanone, butane is acetic acid, toluene is benzoic acid, *m*-xylene is isophthalic acid, and *p*-xylene are terephthalic acid and terephthalate esters respectively. These products have wide ranging applications in industry for the production of useful materials. Of these processes, only the acetic acid process will be dealt with here.

Acetic Acid Process

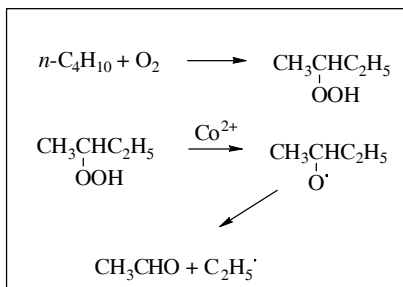
Acetic acid is a very important intermediate in the chemical industry. It is used as a solvent in xylene oxidation and as a starting material for the synthesis of certain esters. A large portion of the acetic acid produced in industry is utilized in making acetic anhydride that is used as an acetylating agent.

Acetic acid was earlier produced via the oxidation of butane in large-scale industrial processes using Co(II) salts as catalysts. This process was developed by BASF. Another process for the production of acetic acid is via the oxidation of acetaldehyde (produced by olefin oxidation) by the Wacker process. Yet another process, developed by Monsanto is the popularly known Monsanto Acetic Acid Process, which is the carbonylation of methanol using rhodium organometallic catalyst.³

The initiation step for the formation of radical species is the most important in the oxidation reaction. Free radical initiators, e.g., RO• and ROO• that are sufficiently energetic to abstract a hydrogen atom from secondary C-H bonds are usually added to the reaction mixtures at 150 °C. Butane is oxidized to 2-butyl hydroperoxide that ultimately provides acetic acid via different pathways. In

³ Alkane oxidation to acetic acid is quite a complex reaction because it involves C-C bond cleavage and C-H oxygenation. To an acetic acid solution of butane in the presence of a cobalt catalyst, air is passed at 160-200°C and 60-80 atm pressures. Separation of the reaction products, acetic, propionic, and butyric acids and some 2-butanone are continually carried out from the unreacted hydrocarbon. Usually a yield of 45% at 30% conversion is typical.



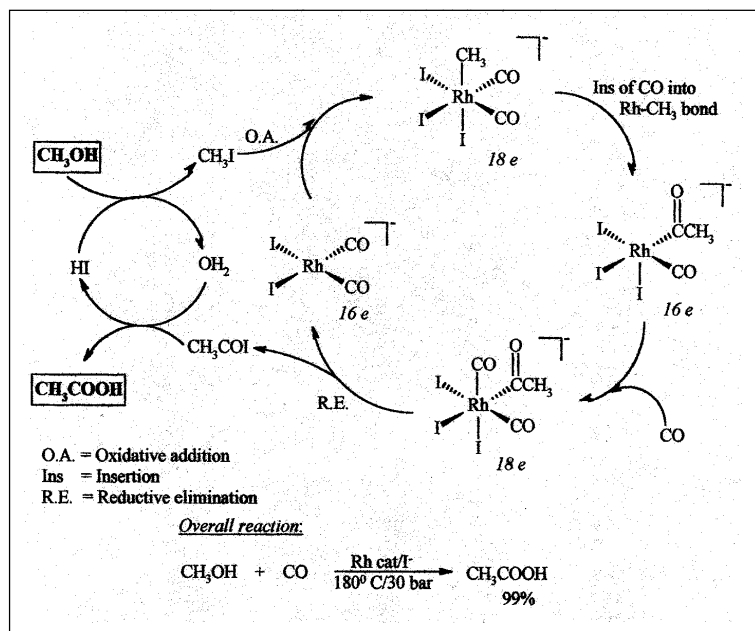


Box 3. Formation of acetaldehyde from *n*-butane.

presence of Co(II) catalysts, it gets converted into 2-butoxy radical, $\text{C}_4\text{H}_9\text{O}\cdot$ which undergoes a β -cleavage of the C-C bond to provide acetaldehyde. These reactions are outlined in *Box 3*. Acetaldehyde is one substrate that can be easily oxidized to acetic acid as will be discussed in the Wacker process later. Other pathways are also possible for the 2-butyl hydroperoxide to generate acetic acid. The overall yields of acetic acid are however moderate.

The production of acetic acid these days is by the Monsanto acetic acid process. The yields are typically 99% of acetic acid. The Monsanto acetic acid process is summarized in *Scheme 1*. A large fraction of acetic acid is converted into acetic anhydride, a very useful acetylating agent. The direct formation of acetic anhydride via carbonylation of methyl acetate has been developed by Tennessee Eastman/Halcon SD. The Monsanto process outweighs the BASF process on all counts for the production of acetic acid.

(ii) Olefin Oxidation: Wacker process for the oxidation of ethylene to acetaldehyde was a great step forward for the production of a variety of organic chemicals. It replaced an expensive feedstock

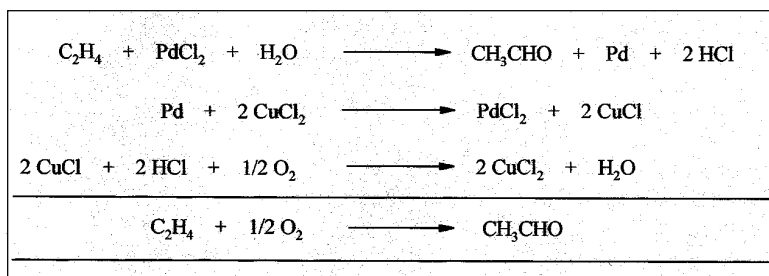


Scheme 1. Monsanto Acetic Acid Process.

like acetylene with relatively cheaper ethylene. Palladium based catalyst is used for this process and has been found to be extremely useful for the formation of a number of compounds. Wacker process is employed for the production of acetaldehyde from ethylene and acetone from propylene in a homogeneous manner, for other products the catalyst is used in the heterogeneous fashion. The homogeneous catalysis has provided a greater insight into the mechanistic details. With the development of the Halcon glycol acetate process and the Oxirane propylene oxide synthesis, the Wacker process is slowly becoming obsolete.

The overall reaction of olefin oxidation is given in *Box 4* and the catalytic cycle is shown in *Scheme 2*. The cycle shows the typical switching of the electron count on the metal between 16 and 18.⁴

As shown in the catalytic cycle, two stages are involved, the oxidation of ethylene to acetaldehyde which results in the reduction of palladium from 2+ to 0 and the copper cycle wherein the palladium metal is reoxidized back to 2+. Single stage process has also been developed. In this process, a mixture of oxygen and ethylene are fed to an aqueous solution of PdCl₂ and CuCl₂ at 120-130 °C and 4 atm pressure. The product gases are fractionated to obtain acetaldehyde. On the other hand, in the two stage process, first oxidation of ethylene is brought about and in the second stage reoxidation of copper salt from 1+ to 2+ takes place in presence of air. Yields greater than 95% are obtained in both processes. In addition to acetaldehyde, small amounts of impurities are also formed. The major products of ethylene oxidation in water, acetic acid, alcohol, or a non-aqueous medium as a solvent are summarized in *Box 5*.

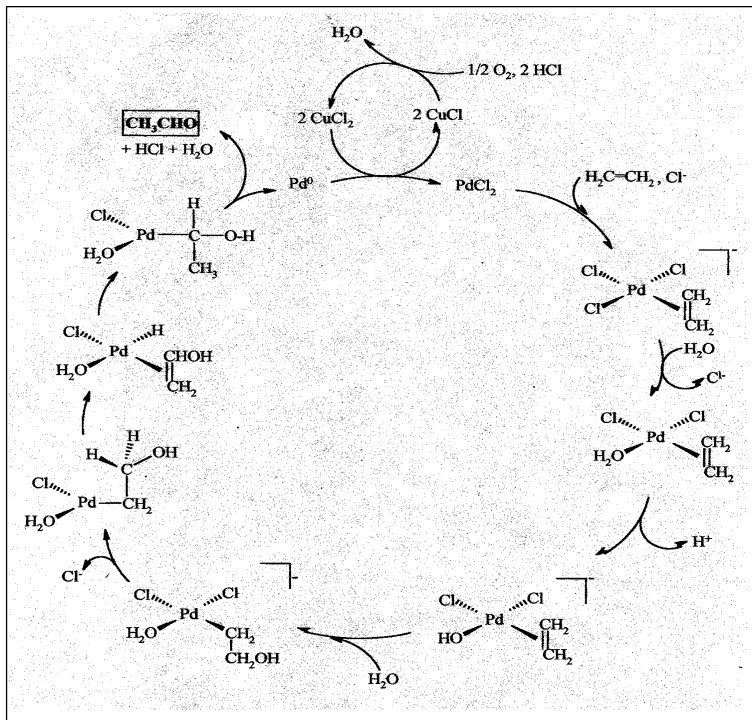


Box 4. Oxidation of Pd⁰ to Pd²⁺ in air using Cu⁺/Cu²⁺ couple.

⁴ It has been known since 1894 that ethylene-chloro complexes of palladium decompose in an aqueous medium into acetaldehyde and Pd metal. However, what was not known until 1956 was that Pd⁰ could be reoxidized to Pd²⁺ in air, mediated by Cu⁺/Cu²⁺ couple. This discovery was a milestone in the development of the Wacker process.



Scheme 2. Wacker Process for acetaldehyde.



(iii) Olefin Polymerization: C-C bond-forming reactions are some of the most useful reactions that find wide practical applications. Most important of these are the polymerization and copolymerization reactions of ethylene, propylene, butadiene, and isoprene. The

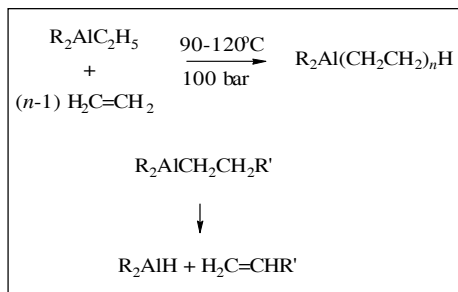
<u>Solvent</u>		<u>Product</u>
Water	$\text{H}_2\text{C}=\text{C} \begin{array}{l} \text{H} \\ \text{OH} \end{array} \longrightarrow \text{H}_3\text{C}-\text{C} \begin{array}{l} \text{O} \\ \text{H} \end{array}$	Acetaldehyde
Acetic acid	$\text{H}_2\text{C}=\text{C} \begin{array}{l} \text{H} \\ \text{OCCH}_3 \\ \text{O} \end{array}$	Vinyl acetate
Alcohol	$\text{H}_2\text{C}=\text{C} \begin{array}{l} \text{H} \\ \text{OMe} \end{array}$	Vinyl ether
Non-aqueous, inert	$\text{H}_2\text{C}=\text{C} \begin{array}{l} \text{H} \\ \text{Cl} \end{array}$	Vinyl chloride

Box 5. Oxidation products of ethylene in various solvents.

polymers obtained using transition metal complexes as catalysts have different properties from the ones obtained via free radical polymerization. Both homogeneous as well as heterogeneous catalysts are being employed in industry for the polymerization of olefins but the heterogeneous catalysts have been found to have some advantages compared to the soluble ones.⁵

The polymerization catalysts have been developed as early as 1950s by Ziegler and Natta independently. Their pioneering work was befittingly distinguished and a Nobel Prize was awarded to them in 1963. Ziegler found that the growth reaction resulting from the reaction of ethyl dialkylaluminum and ethylene competes with the dehydroalumination and was limited to the formation of linear aliphatic compounds with a maximum chain length of about C_{200} , *Box 6*. He also found that a highly polymeric compound was obtained when a mixture of zirconium acetylacetonate and triethylaluminum were used as the catalytic material. He soon realized that a combination of $TiCl_4$ and $AlEt_3$ would be the most effective catalyst and that the polymerization could be carried out at a pressure as low as 1 bar. This was developed into the Mülheim normal-pressure polyethylene process, *Box 7*. This process yielded polyethylene that was quite linear.

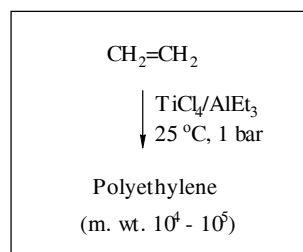
Independently, Natta carried out the polymerization of propylene and created a link between the stereochemical structures and the bulk properties of the polymer, *Box 8*. Ziegler–Natta polymerization is a heterogeneous catalytic process in which fibrous $TiCl_3$, alkylated on its surface, is regarded as the catalytically active species. The proposed mechanism for the polymerization process is shown in *Scheme 3*, although very little experimental evidence exists. Kaminsky and Brintzinger developed a catalyst from a chiral zirconocene halide and methylalumoxane (MAO) that led to the discovery of homogeneous isotactic polymerization processes of α -olefins, *Box 9*. It was found that their catalyst had very high turn over frequencies. This discovery stirred a lot of interest among scientists working in the area of Ziegler–Natta polymerization

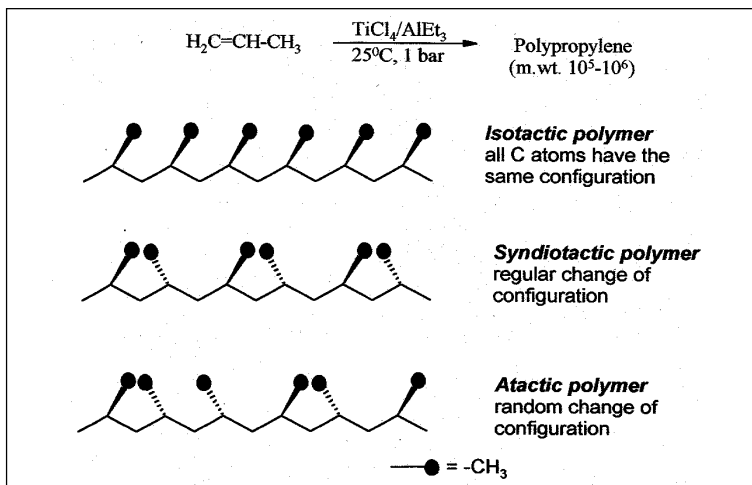


Box 6.

⁵ Depending upon the specific application, polyethylenes with different densities have been produced, the two major kinds are the high-density (linear polymer, density $\cong 0.96$, m.p. ca. $136^\circ C$) and the low-density (highly branched polymer, density $\cong 0.92$, wide melting range) polyethylene.

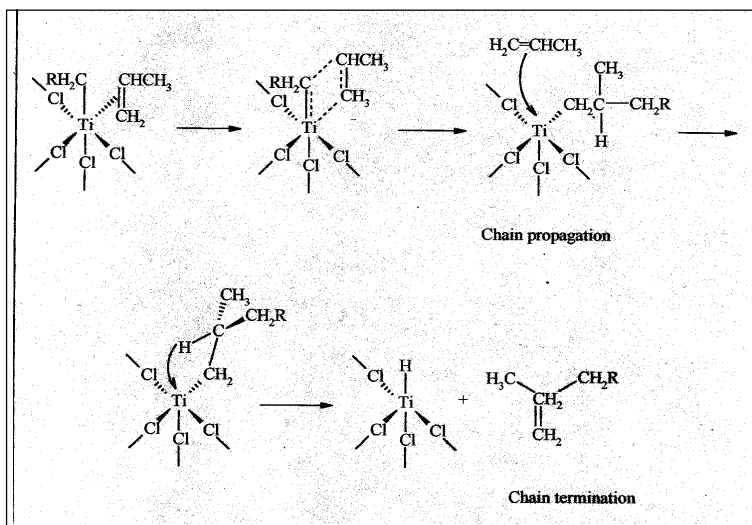
Box 7. Mülheim normal pressure polyethylene process.



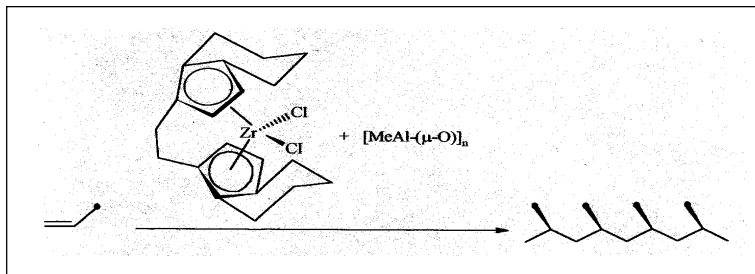
Box 8. Polymerization of propylene.

and their work resulted in a number of novel ansa-metallocenes that have shown high catalytic activities.

Linear α -olefins on a large scale are prepared using nickel catalysts by the Shell higher olefin process. The active catalyst is a nickel hydride species which is generated by reducing a nickel salt in presence of a chelating ligand like diphenylphosphinoacetic acid. The generation of the active species and the chain growth sequence are shown in Box 10. A similar Ni-H species acts as an active catalyst in the dimerization of olefins also.

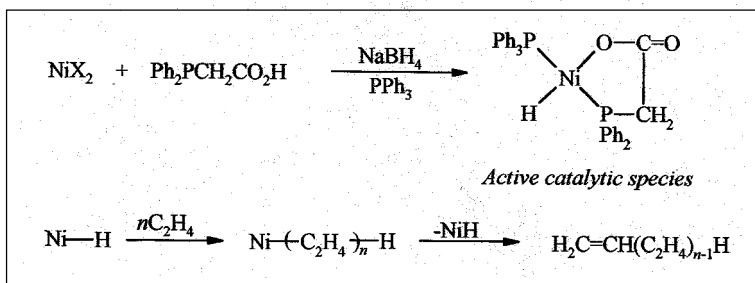


Scheme 3. Ziegler-Natta polymerization.

**Box 9. Kaminsky's catalyst.**

Plastics are usually obtained upon homopolymerization of ethylene and propylene. The ethylene-propylene copolymerization yields polymers that are elastic and are used in many industrial applications instead of rubber. The simple copolymers are often blended with more crystalline polymers as toughening agents. A small amount of an unsymmetrical diene copolymerized with ethylene and propylene provides an elastomer, in which the diene acts as a reactive site due to the presence of the highly reactive double bond and readily copolymerizes to affix the diene to the polymer chain. On the other hand, the less reactive C-C single bonds in the dienes act as cross-linking sites in the 'cure' of the final product. The cured products are essentially saturated, are more ozone-resistant than natural rubber or other synthetic polydienes.

(iv) Olefin Hydrogenation: The most extensively investigated reaction catalyzed by transition metal complexes is the hydrogenation of olefins. It is however, ironic that the active catalysts used for hydrogenation processes in industry are mostly heterogeneous rather than homogeneous type. The only soluble catalyst that is used in industry is the hydrogenation catalyst for

**Box 10. Shell higher olefin process.**

the reduction of an unsaturated amino acid to a precursor of L-dopa drug. Selectivity is a major criterion for the commercial application of hydrogenation catalysts.

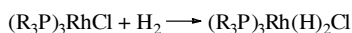
Four classes of hydrogenation catalysts can be identified for practical purposes:

- (a) Wilkinson's catalyst, $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ and the related $[\text{Rh}(\text{diene})(\text{PR}_3)_2]^+$ complexes
- (b) Mixtures of platinum and tin chlorides
- (c) Anionic cyanocobalt complexes and
- (d) Ziegler catalysts obtained as outlined earlier.

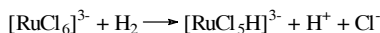
The olefin hydrogenation using Wilkinson's catalyst is the best studied system. A variety of alkenes, alkynes, and other unsaturated molecules have been hydrogenated under mild conditions. In fact, Wilkinson's catalyst is the first complex to serve as a homogeneous hydrogenation catalyst. There are three possible ways by which molecular hydrogen can undergo activation for hydrogenation in a homogeneous solution, *Box 11*.

Three different mechanisms have been demonstrated for Wilkinson's catalyst of which the kinetically dominant one is shown in *Scheme 4*. The mechanisms by which the other systems bring about catalysis differ from the one in the case of Wilkinson's catalyst is the mode of activation of dihydrogen; in the case of platinum catalyst, it occurs by heterolysis and homolysis in that of the cobalt system.

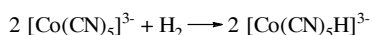
Box 11. Activation of dihydrogen by transition metal complexes.



oxidative addition



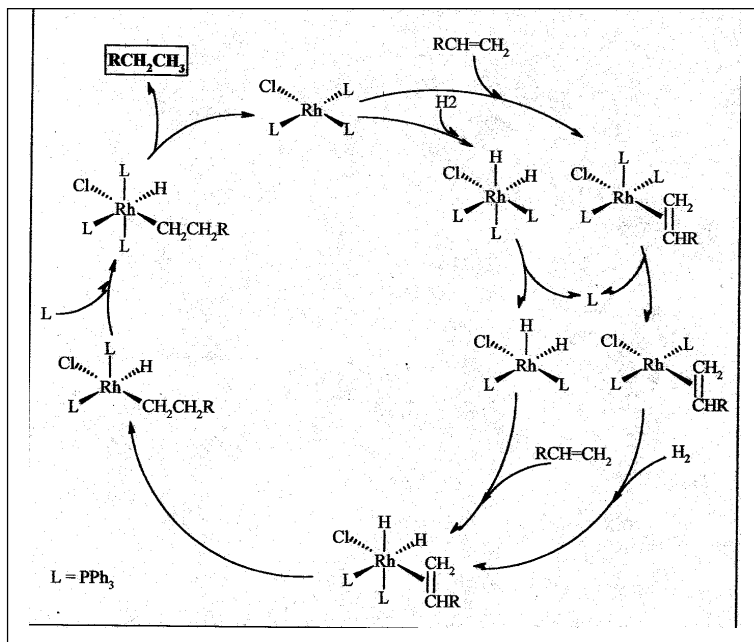
heterolytic cleavage



homolytic cleavage

Heterogeneous catalysts are employed for selective hydrogenation of polyunsaturated vegetable oils to provide shortenings with better

physical properties. The advantage here is the easy separation of the catalyst. On the other hand, when high selectivity is required, homogeneous catalysts are used. The hydrogenation of 1,5,9-cyclodecatriene to cyclododecene, a precursor of dodecanedioic acid and lauro lactam, two commercial polyamide intermediates, can be brought about by certain soluble metal catalysts. This is summarized in *Table 1*.



Scheme 4. Hydrogenation of olefins using Wilkinson's catalyst.

Synthesis of optically active organic compounds from nonchiral starting materials is the most elegant application of homogeneous catalysis. Monsanto Company first commercially employed this asymmetric induction for the synthesis of L-dopa, a drug used in the treatment of Parkinson's disease.

The selective synthesis of one optical isomer of a chiral compound can be achieved by binding a prochiral olefin preferentially in one conformation to an asymmetric catalyst site. By introducing a chiral ligand on the metal, this recognition of the preferred conformation could be achieved. In the synthesis of L-dopa, a

Table 1. Hydrogenation of 1,5,9-cyclodecatriene (CDT) to cyclododecene (CDE).

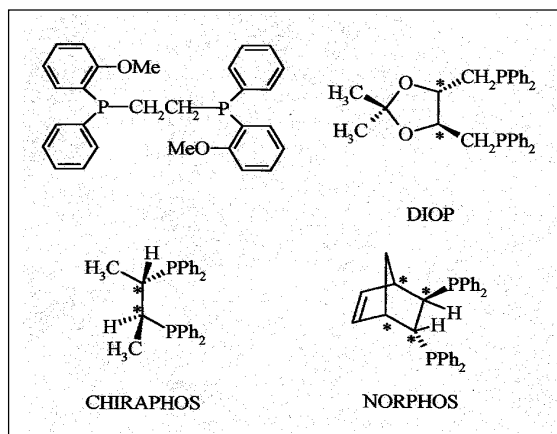
Catalyst	Temp.	Pressure (atm)	Time(h)	Solvent	Conversion of CDT	Yield of CDE
$[Co(CO)_3(PBu_3)_2]$	140°	30	1.7	C_6H_6	100%	99%
$NiI_2(PPh_3)_2$	160°	80	6	CDT	100	99
$[Pt(SnCl_5)]^{3-}$	160°	100	10	Et_4NSnCl_3	99	87
$RuCl_2(PPh_3)_2$	25°	10	30	$C_6H_6/EtOH$	100	87
$RuCl_2(CO)_2(PPh_3)_2$	140°	5	1	C_6H_6	100	98
$RhCl_3(py)_3/NaBH_4$	75°	1	0.1	DMF	100	91

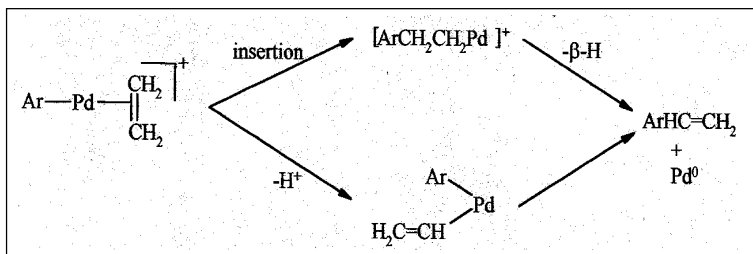
substituted cinnamic acid is the prochiral olefin and a Rh(I) complex bearing an optically active phosphine ligand is used as the catalyst. It has been found that a chelating phosphine gives higher optical yields and provides greater catalyst stability. The optical yields are expressed in terms of enantiomeric excess (ee) of the desired conformation; in this case ee approaches 90%. Examples of chiral chelating diphosphane ligands are shown in *Box 12*.

In pursuit of high optical yields in olefin and ketone hydrogenations, several kinds of chiral ligands have been investigated. It is quite imperative that proper matching of the ligand and substrate are required for the generation of the active catalyst that can provide the desired ee's and this is definitely not an easy task.

(v) Arene Reactions Catalyzed by Metal Complexes: Certain substitution reactions and arene couplings that are difficult to achieve by conventional methods can be accomplished using some Pd(II) and Cu(II) compounds acting as catalysts. In the Pd catalyzed reactions, there seems to be an electrophilic attack of Pd^{2+} on the arene ring. The resulting aryl metal compounds undergo reactions that are well known for metal olefin complexes. An example of an arene-olefin coupling reaction catalyzed by $\text{Pd}(\text{OC}(\text{O})\text{CH}_3)_2$ is the coupling of benzene and styrene to give *trans*-stilbene which is a major product. The mechanism for the reaction of benzene and ethylene, as shown in *Box 13*, proceeds via the formation of an olefin-aryl-Pd⁺ complex. Two pathways are

Box 12. Chelating phosphine ligands used in symmetric hydrogenation catalysis.





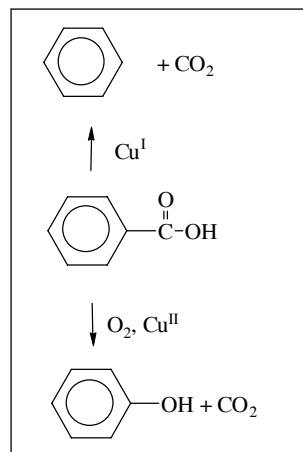
Box 13. Pd catalyzed arene-ethylene coupling reaction.

plausible for the olefin (here ethylene) complex: insertion of ethylene into the aryl-Pd bond resulting in a σ -phenethyl complex which undergoes a β -hydrogen elimination by transfer to the Pd to form an unstable Pd-H⁺ species. The styrene is eliminated and the metal hydride species further degrades into the Pd metal. The second pathway involves the formation of a σ -vinyl complex from the ethylene complex which undergoes reductive elimination reaction to give the styrene. In addition to this reaction, the Pd(II) salts also catalyze arene-arene coupling, oxidative substitution and oxidative carbonylation reactions of arenes. These reactions, however, have not been commercially exploited.

Cu(II) salts also bring about the catalytic oxidations of several aromatic compounds some of which have found their way to industry. The decarboxylation and oxidative decarboxylation of benzoic acid using copper salts give benzene and phenol respectively, *Box 14*. The oxidation of 2,6-xyleneol, an important process in the class of oxidation reactions of arenes, gives a *para*-phenylene oxide polymer by coupling an oxygen of one phenol to the *para* carbon of another. This aromatic polyether is a high melting plastic that has good thermal and water resistance properties. It has found several applications as an engineering thermoplastic. In addition to the palladium and copper catalyzed reactions, certain nickel derivatives, Ziegler type systems, allylcobalt complexes, and arene ruthenium species have also been employed to effect the arene reactions. Although these reactions yield useful derivatives, they have been exploited to a very small extent commercially.

(vi) Catalysis of Condensation Polymerization Reactions: In addition to their use in the synthesis of polymer intermediates,

Box 14. Decarboxylation and oxidative decarboxylation of benzoic acid.



certain transition metal complexes also catalyze the polymerization processes, e.g., manufacture of polyesters, polyurethanes, etc. The preparation of the most widely used synthetic fiber, poly(ethylene terephthalate), sold under trade names such as Dacron[®], Terylene[®], or Kodel[®], employs two different catalysts. The transesterification of dimethyl terephthalate, which is the first step involves either Zn, Co, or Mn acetates as catalyst and is carried out at temperatures of 150-200°C. Antimony compounds catalyze the polycondensation of bis(hydroxyethyl) terephthalate at 250-300 °C. This is the second step in the synthesis of poly(ethylene terephthalate). For both the reactions, the mechanistic details have not been worked out thoroughly yet.

Current and Future Trends in Catalysis

It is possible to rationally design new catalysts to carry out desired reactions with a knowledge of the elementary rearrangements that are known for a given metal atom with certain specific ligands and estimates of thermodynamic and kinetic characteristics for those rearrangements. A lot of research has been and is being pursued on this aspect all over the world and at times met with fruitful results. The improvisations are a response to the demands of the chemical industry.

Some of the current trends in the area of catalysis include the use of new types of feedstocks, preparation of next generation catalysts that combine the practical advantages of both homogeneous as well as heterogeneous catalysts, achieving high yields and selectivities, and development of new reactors and methods.

As the global oil reserves are getting depleted year after year, the search for alternate feedstocks for the production of energy is on the rise. Here I quote Parshall: “according to some the latter part of the 20th century could be a *synthetic gas era* in the history of homogeneous catalysis. This viewpoint may be exaggerated, but four feedstock *eras* can be postulated: 1910-1950 – Acetylene; 1950-1980 – Olefins; 1980-2000 – Synthetic gas; 2000... Biomass”.

The use of biomass, which includes materials such as manure,

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garbage, and other organic wastes for the production of energy on a truly large scale, is purely speculative at this moment. Nevertheless, the use of these materials as feedstocks is not only a means of disposing off the wastes in an economical manner but also a cheap source for producing energy and at the same time helps in conservation of petroleum. The role of transition metal catalysts in such processes at this moment is not clear but it would be worth investigation.

Processes in which a homogeneous catalyst is anchored on to a support for easy catalyst recovery after the catalytic cycle are being and have been carried out for several years now, but more attention will be needed in order to obtain species that have unusual catalytic properties and at the same time show great potential for applications in industrial scale reactions. One other direction in which research efforts are being pursued is the preparation of heterobimetallic complexes. Heterobimetallic systems offer the potential of cooperative activation of small molecular substrates such as CO, H₂, etc. or they could exhibit enhanced activity as observed in certain heterogeneous bimetallic catalytic systems. This area of research also provides an opportunity to study the extent of the metal-metal interactions in such bimetallic complexes that in turn can provide some clues for the design of the so-called next generation catalysts.

The potential of transition metal homogeneous catalysis, especially of enantioselectivity with chiral metal complexes, to provide short, clean, and cost-effective processes is obvious. The selectivity is very important in the pharmaceutical industry for the manufacture of biologically active compounds. At the same time, processes that provide high yield of the desired product are also quite valuable. Cost of pharmaceuticals recently has become an issue due to the ever increasing complexity of new chemical entities and due to pressure on drug pricing. Therefore, cost-effective processing is becoming increasingly important. The focus of research should lie in realizing shorter synthetic routes, e.g., by metal catalyzed C-C bond formation, and since the greater part of new chiral pharmaceutical products is developed in enantiomerically pure

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Enantioselective catalytic transformations, e.g., the reduction of C=C, C=O, and C=N bonds, epoxidation of olefins and C-C bond formation reactions have an enormous scope for research to develop newer and highly efficient catalysts and cost effective production.

form, to provide catalytic processes for establishing chiral centers and thus to avoid resolution processes. Enantioselective catalytic transformations, e.g., the reduction of C=C, C=O, and C=N bonds, epoxidation of olefins and C-C bond formation reactions have an enormous scope for research to develop newer and highly efficient catalysts and cost effective production.

As pointed out earlier, the separation and the recycling of catalysts is an area that is actively pursued which to a certain extent has yielded some reliable solutions. By functionalization of the ligands to make the catalyst water soluble, the transition metal complex can be made to act in a biphasic manner. In this process, separation of the product and the recovery of the catalyst can be achieved by simple decantation. Such methods do really need great attention in the future. One other aspect that needs to be studied is the quantitative investigation of the kinetics of homogeneous catalytic processes. There is a need for newer methods and apparatus for the study and selection of catalysts. Along the lines of newer methods, some work relevant to catalysis has been carried out in *supercritical fluids* (fluids in supercritical state) and the results are highly encouraging. Such experiments perhaps can be realized on a truly large scale in the industries only after preliminary pilot plant scale reactions. In addition, catalysis that can be carried out at low temperatures using catalysts that can be activated using light and catalysis using metal clusters are also noteworthy future trends.

Some Comments on the Industry-Academia Collaborations

Academia is tuned to carry out basic research from which ideas can be derived to build a commercial process in an industry. The industrial R & D relies heavily on the development of products and processes of interest to the company, that is, applied research. It is this very difference that interests the industrial researchers in the outcome of academic research. Maximum benefit can be derived when the two come together and have mutual understanding and stimulating interaction. In order to generate and implement



innovative ideas and discoveries in an industry, the industrialists should keep in close touch with the scientists both at academia and industry and ensure multidisciplinary input into projects.

Conclusions

As pointed out earlier, this review gives an overview of some of the catalytic reactions that are useful, either on a laboratory scale or industrial scale of certain organic compounds. No attempt has been made to include all the catalytic reactions in which transition metal complexes are involved.

Research has come a long way from the time of Werner and Jørgensen, in terms of the growth that coordination chemistry has experienced over the last few decades. Their work was a stepping stone for the development of modern inorganic chemistry which is truly a multidisciplinary one in the present day context. The ever increasing importance of metal complex catalyzed reactions has already been discussed above. A question will however, linger in our minds: what and how much will catalysis with metal complexes achieve in our industrial environment in the next millenium? Since fundamental research in this field is highly dynamic, many new discoveries can be expected in future. Thus capitalization on such progress by industry will and should inevitably follow.

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Suggested Reading

- [1] G W Parshall and S D Ittel, *Homogeneous Catalysis*, 2nd edition, Wiley, New York, 1996.
- [2] Ch Elschenbroich and A Salzer, *Organometallics*, 2nd edition, VCH, Weinheim, 1992.
- [3] D T Thompson, *Coord. Chem. Rev.*, 154, 179–192, 1996.
- [4] R Schmid, *Chimia*, 50, 110–113, 1996.
- [5] K I Zamaraev, *Pure and Appl. Chem.*, 69, 865–876, 1997.
- [6] C de Bellefon, N Tanchoux, S Caravieilhès, *J. Organomet. Chem.*, 567, 143–150, 1998.

