

Polymer-Supported Coordination Compounds as Catalysts for Organic Reactions

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INTRODUCTION

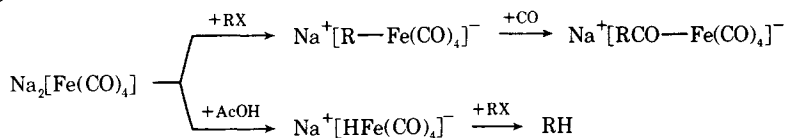
As a pioneering branch of science, organometallic chemistry in its recent astounding growth has overrun the boundaries between inorganic and organic chemistry, focusing on goals of basic import and great applicative interest.

Organometallic compounds in the past two decades have been successfully applied both in stoichiometric organic syntheses through elegant and innovative procedures and in homogeneous catalytic processes (hydrogenation, isomerization, disproportionation, polymerization, hydroformylation, oxidation of olefins). Therefore, the following two research fields may be envisaged as most conducive to applicative developments: (1) stoichiometric organic reactions promoted by coordination compounds; (2) reactions catalyzed by coordination compounds. In these reactions, metal-carbon bonded organometallic compounds are either employed or formed as reaction intermediates and/or activated complexes.

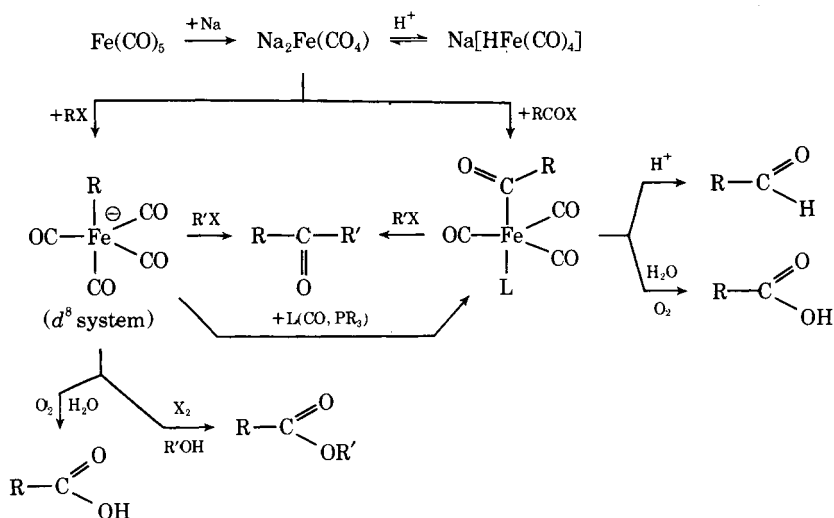
There are described herein some examples illustrating these two facets of research which are meant to provide a general picture of topics of greater current interest rather than a survey of information pieces in these fields.

ORGANIC REACTIONS PROMOTED BY TRANSITION METAL IONS OR COMPLEXES

A most recent example of the use of organometallic compounds in organic synthesis is provided by $\text{Na}_2[\text{Fe}(\text{CO})_4]$, a transition metal complex analogous to Grignard reagents.¹ Disodium tetracarbonylferrate (-2) is a d^{10} system, isoelectronic with $\text{Ni}(\text{CO})_4$, which reacts with alkyl halides and sulfonates to give aldehydes, mixed ketones, carboxylic acids, esters, and amides in high yield (80-100%). These reactions take place via the intermediacy of alkyl-, acyl-, or hydridotetracarbonylferrate complexes according to the reactions

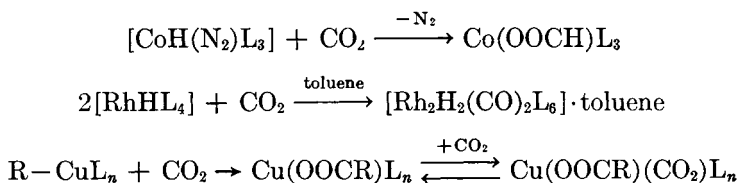


The following scheme summarizes the stoichiometric reactions promoted by disodium tetracarbonylferrate (-2):



The activation of a transition metal-carbon or metalhydride bond has been achieved by addition of a Lewis acid. For instance, the complexes $[\text{Ni}(\text{dipy})\text{R}_2]$, $[\text{Fe}(\text{dipy})_2\text{R}_2]$ (dipy = dipyrityl), $[(\text{H}_3\text{C})\text{TiCl}_3]$, and $[(\text{H}_3\text{C})\text{-Cu}(\text{PPh}_3)_3]$ are decomposed by addition of AlX_3 (X = halide or alkyl) with evolution of alkanes,² whereas $[\text{Ru}(\text{PPh}_3)_4\text{H}_2]$ liberates H_2 in the presence of AlCl_3 . The influence of the Lewis acid on the stability of M-C and M-H bonds may be compared to reactions of olefins in two-component catalytic systems.

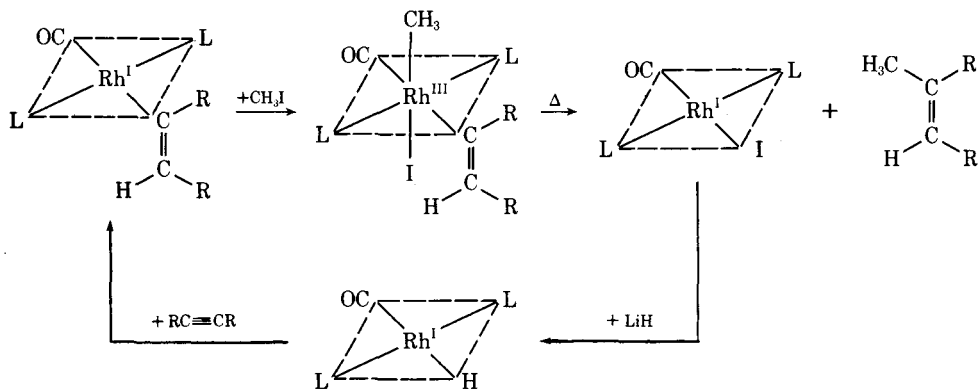
Some promising reactions which have been studied recently involve insertion of CO_2 across M-C and M-H bonds leading to carboxylates:



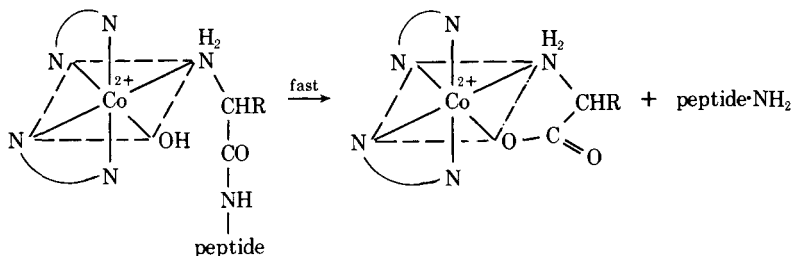
where $\text{L} = \text{PPh}_3$. CS_2 and SO_2 also will activate the M-H bond of some metal hydrides to give CS_2 - and SO_2 -coordinated complexes with cleavage of the M-H bond.

In those metal complex-promoted reactions which take place at a specific site of a polyfunctional organic molecule (regioselective reactions), the metal complex becomes preferentially bonded to one of the several coordinating groupings on the organic molecule. As a consequence, the reactivity of the group that has become attached to the metal will be enhanced or depressed depending on the particular reaction concerned. Preferential coordination may therefore entail selective activation or deactivation of a given functional group in a multifunctional organic substrate.

A clever synthesis of trisubstituted olefins from disubstituted acetylenes involves a series of reactions including the oxidative addition of an alkyl halide to a vinyl-rhodium(I) complex followed by reductive elimination to give a trisubstituted olefin and a Rh(I) halide complex. The latter may be easily converted into a hydride-rhodium(I) complex which gives the starting vinyl-rhodium(I) species through insertion of acetylene across the Rh-H bond³:

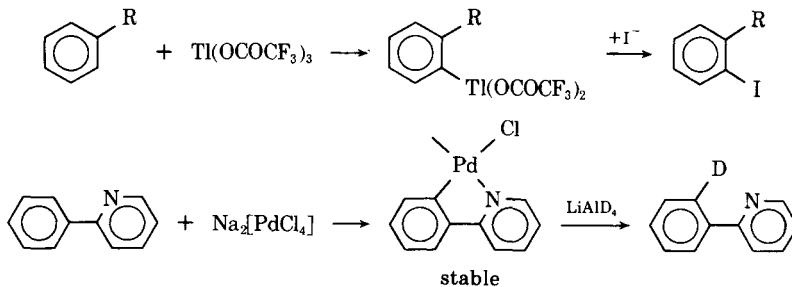


In some cases, formation of a complex is followed by a selective intramolecular reaction, as for the intramolecular chelation reaction^{4,5}:



The nucleophilic attack by the coordinated hydroxyl on the peptide bond is faster by several orders of magnitude than the corresponding reaction between uncoordinate reagents.

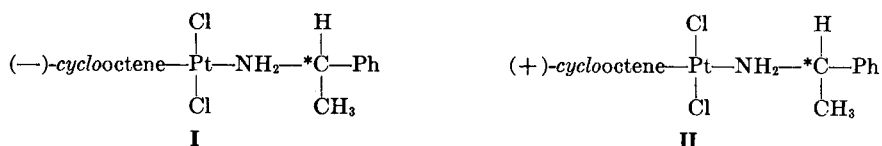
A high degree of regioselectivity may occur also with electrophilic attacks by metal ions. This will happen when the organic substrate bears a functional group that can form a reaction intermediate and/or an activated complex upon coordination to the metal. For instance,



R = CH₃CO₂ or CH₂OH.

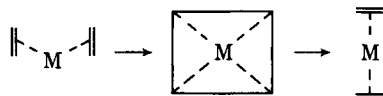
Formation of chelate metal complexes may induce selectivity in organic reactions through a stereochemical modification caused by a limited number of conformations being imposed. Some examples of such conformational effects are provided by reactions of formation of macrocycles, such as the synthesis of corrin⁶ or porphyrins, in which Cu^{2+} and Ni^{2+} are employed to held the tetrapyrrol rings in the correct conformation for cyclization.⁷

Coordination compounds have been also applied in resolving optical isomers through the formation of diastereoisomers. Thus, when a chiral group is bonded to a metal in a complex, it is possible to separate a mixture of enantiomers (i.e., an olefin) through a mixture of two diastereoisomers which may be separated by fractional crystallization. Such is the case for the resolution of *trans*-cyclooctene upon reaction of *trans*- $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PhCH}(\text{CH}_3)\text{NH}_2)\text{Cl}_2]$ with cyclooctene.^{8,9} Ethylene is displaced, and the two diastereoisomers **I** and **II** are produced. Upon crystallization from CCl_4



the less soluble diastereoisomer **I** is obtained, from which (–)-cyclooctene can be set free by treatment with KCN.

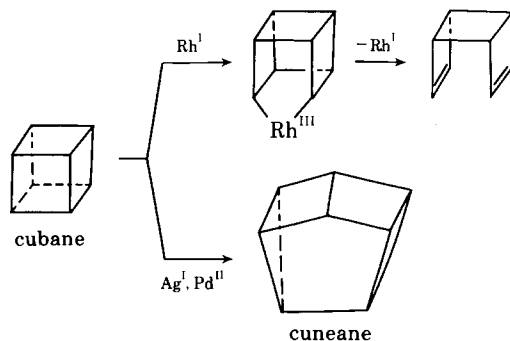
As far as the use of coordination compounds or metal ions in organic chemistry is concerned, a branch of great current interest involves intramolecular rearrangements of organic compounds. Thus, the mode of breaking of the carbon–carbon bond in the metathesis of an olefin may be normally, but not necessarily, adequately rationalized by a *concerted mechanism* involving a four-center transition state¹⁰:



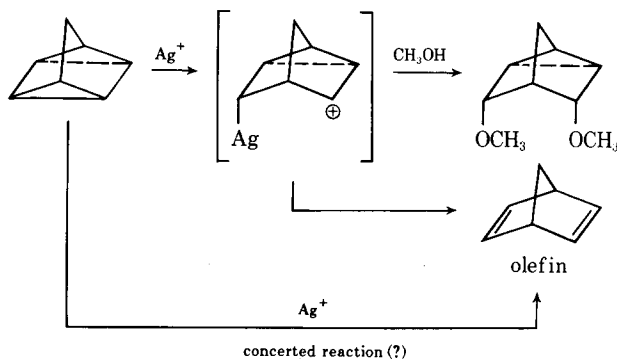
(ancillary ligands involved are omitted). In this description, the transition state is referred to as a “tetramethylene–metal” complex.¹¹

If the aforementioned reaction is viewed as a *concerted reaction*, the formation of the “quasi-cyclobutane” transition state and its subsequent conversion into the bisolefin complex must be looked upon as a $[2 + 2]$ cycloaddition, a “forbidden” reaction for the Woodward-Hoffman¹² symmetry rules. It has been suggested that a transition metal possessing atomic orbitals of the appropriate symmetry can favor the energetics of *per se* forbidden reactions. In other words, in the presence of a transition metal, the process will take place along a new reaction coordinate, thereby becoming Woodward-Hoffman allowed if the symmetry of metal orbitals is considered.¹³

An alternative rationale for the ethylene-cyclobutane conversion catalyzed by rhodium(I) complexes implies an oxidative addition mechanism¹⁴:

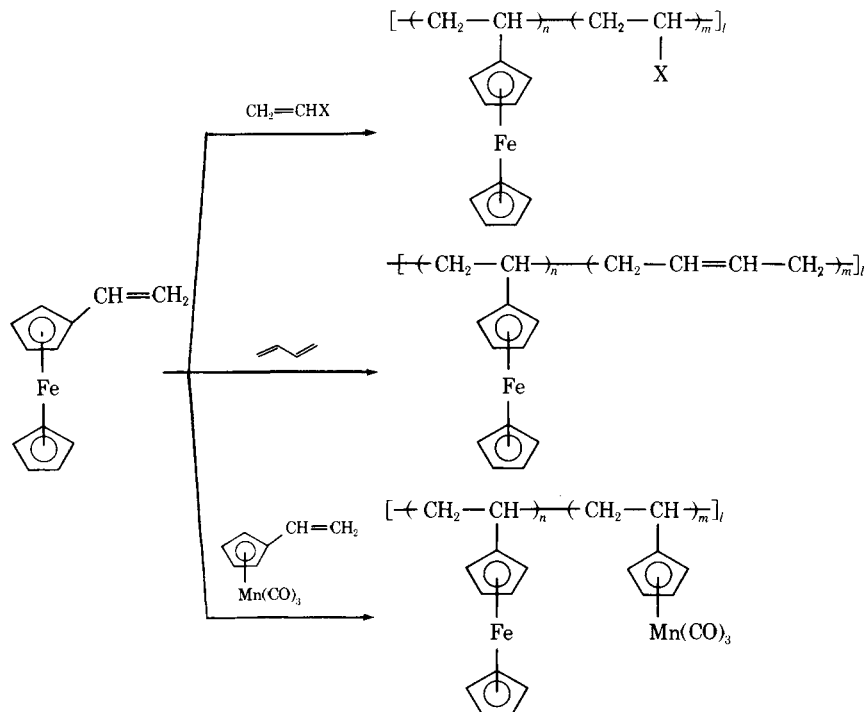
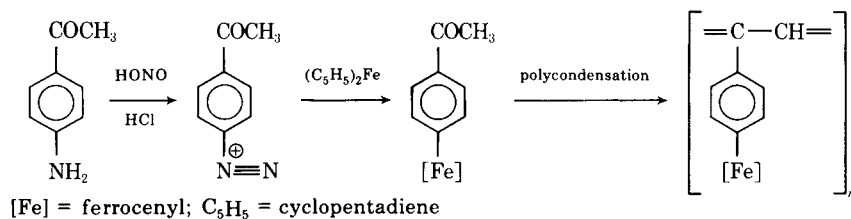


The isomerization of cubane catalyzed by Ag^{I} or Pd^{II} leads instead to cuneane.¹⁴ The varying course of cubane rearrangement in the presence of Rh^{I} , Pd^{II} , or Ag^{I} has been interpreted in terms of (i) the greater tendency of Rh^{I} to undergo oxidative addition and (ii) the intermediacy of a carbocation in the case of Ag^{I} . In the latter case, the reaction is thought to proceed¹⁵ also through a concerted mechanism. The schematic picture for the rearrangement of quadricyclene in the presence of $\text{Ag}^{\text{+}}$ is the following:

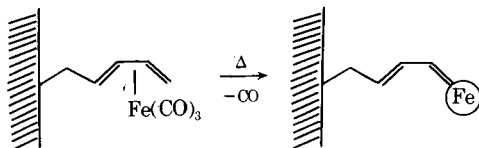


Such a scheme agrees with the experimental findings summarized in Figure 1. Broadly speaking, the stabilization and trapping of labile organic species by metal ions may be rationalized in this context.

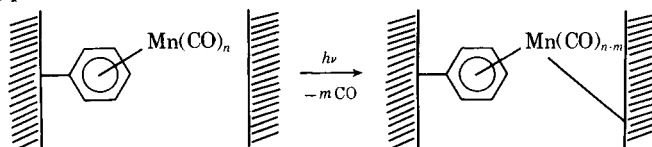
One other field that promises to be rich of implications involves the use of organic polymers containing transition metals. These compounds, though not actually enjoying specific applications, might be the subject of much interest in the near future if, as Hammond¹⁶ foresees, *producing properties* rather than *preparing molecules* is bound to become the basic aim of chemistry. Some examples of preparation of these polymers are^{17,18}:



The following examples illustrate briefly some of the possible applications. A possible magnetic or conducting plastic material may originate from decomposition of a polymer¹⁷:



A new type of chemical adhesion of two surfaces is as follows:



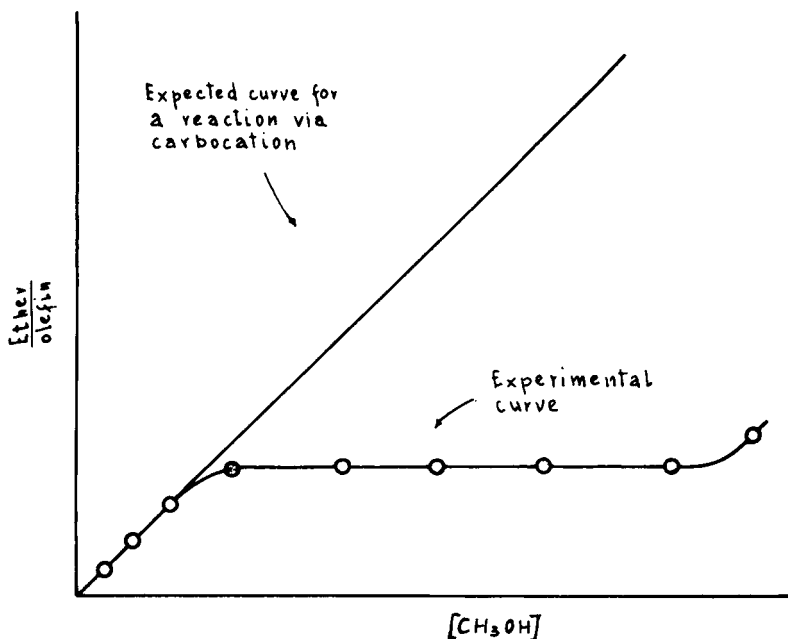


Fig. 1. Ratio ether/olefin for Ag^+ isomerization of quadricyclene as function of CH_3OH as trapping agent.

HOMOGENEOUS VERSUS POLYMERIC MATRIX-SUPPORTED CATALYSIS

In the past few years, studies in homogeneous catalysis by coordination compounds have aroused much interest. The reactions examined are the formation of acetaldehyde from ethylene (Wacker process) and acetylene (in the presence of HgX_2), the hydroformylation (catalyzed by Co and Rh carbonyls), the polymerization of olefins (in the presence of Ziegler-Natta catalysts), the isomerization and disproportionation of olefins catalyzed by complexes of numerous transition metals, and the hydrogenation of unsaturated substrates ($\text{C}=\text{C}$, $\text{C}\equiv\text{C}$, and more recently $\text{C}=\text{O}$ and $\text{C}=\text{N}-$).

The advantage of homogeneous catalysis over heterogeneous catalysis is the greater selectivity which allows the use of relatively milder experimental conditions. However, it brings about some problems in technology related to both the separation of the catalyst from reaction products and its recovery and subsequent recycling. Many research efforts are now devoted to the study of catalysts consisting of coordination compounds immobilized in organic or inorganic matrices.

Although the catalysis by transition metals and/or salts on polymeric organic substrates has been employed since early this century, only quite recently has the use of synthetic organic macromolecules been applied to the immobilization through coordination of metal complexes possessing catalytic properties, along with the advances in supported enzymatic

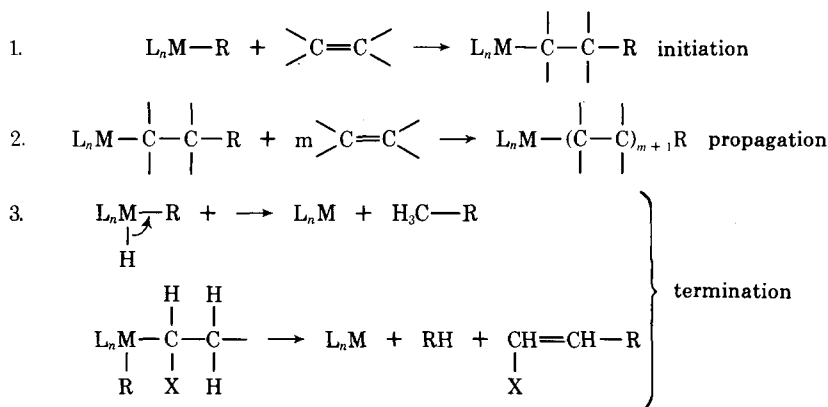
catalysis.¹⁹ To this effect, there have appeared in the current chemical literature several patents and comparatively fewer papers.

Catalytic activity may also be displayed by systems involving transition metal coordination compounds in the presence of polymers. The latter then will act as *inert* supporting materials and their catalytic action will partake of both homogeneous and heterogeneous character. This technique of employing catalysts may entail an increase in specificity and an improvement in the properties of products of catalytic reactions of olefin polymerization, along with an increase in catalytic power and efficiency.²⁰

Before examining some actual examples of application of immobilized homogeneous catalysts, some comparative arguments are required about the features of a metal complex acting as a catalyst either in homogeneous phase or on a polymeric supporting matrix.

This treatment will not involve a general survey of homogeneous catalysis, for which several specialized publications are available in the current chemical literature. Instead, a few example will be described of reactions that have shed light on the mechanism of catalysis and which might be fruitfully employed for a comparative study between homogeneous catalysis and that promoted by complexes immobilized on synthetic organic polymers.

Some alkyl and hydride complexes of transition metals act as catalysts for polymerization, oligomerization, hydrogenation, and isomerization of olefins. Thus, polymerization of vinyl monomers by $[\text{Fe}(\text{dipy})_2\text{R}_2]$, $[\text{Co}(\text{PPh}_3)_3(\text{N}_2)\text{H}]$, and $[\text{Ru}(\text{PPh}_3)_4\text{H}_2]$ takes place through monomer insertion across M-C or M-H bonds as the rate-determining step, followed by propagation via insertion of vinyl monomer across the M-C bond and spontaneous chain termination:



A similar mechanism of "migratory insertion" and elimination may explain the hydrogenation of olefins catalyzed by $[\text{Ru}(\text{PPh}_3)_4\text{H}_2]$.

When using $[\text{Ru}(\text{PPh}_3)_3\text{HCl}]$ and $[\text{Rh}(\text{PPh}_3)_3(\text{CO})\text{H}]$, which are highly selective catalysts for the hydrogenation of monosubstituted olefins, the mechanism appears to involve predissociation of these complexes, thereby providing a coordination vacancy that is only sterically accessible to this kind of olefins.^{21,22}

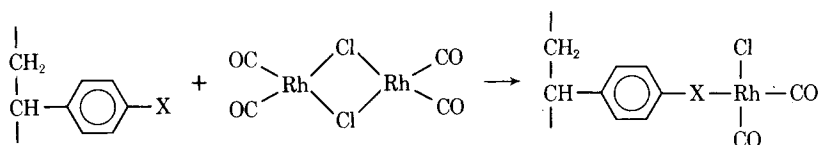
cal environment and the physical interactions between catalytic sites and reactants may be the same in both homogeneous and heterogeneous systems.

As the amount of catalyst employed increases, the efficiency of the homogeneous catalyst decreases, whereas the heterogeneous one maintains its specific activity unaltered. It has been found that at higher homogeneous catalyst concentrations, aggregation and insolubilization of the catalyst occur leading to catalytic inactive species with a decreased surface area, so that the rate of CO absorption reaches a limiting value affected by catalyst solubility. For the heterogeneous catalyst, aggregation is physically prevented by the rigidity of the polymeric matrix, and the rate of CO absorption increases with increasing amount of catalyst. It may be concluded that the use of supported catalysts is conducive to high concentrations of catalytically active species—hence, to high specific activity—even when low solubility allows low concentrations in solution.

HYDROFORMYLATION REACTIONS

The study of hydroformylation reactions sheds some light on the importance of "rigidity" in affecting the selectivity of supported catalysts as compared to their homogeneous analogs. Further, it is also feasible to assess the ability of polymeric matrices to undergo dissociation with possible loss of the metal.²⁴

The most thorough comparative study in this regard is concerned with rhodium complexes from bridge-splitting reactions:

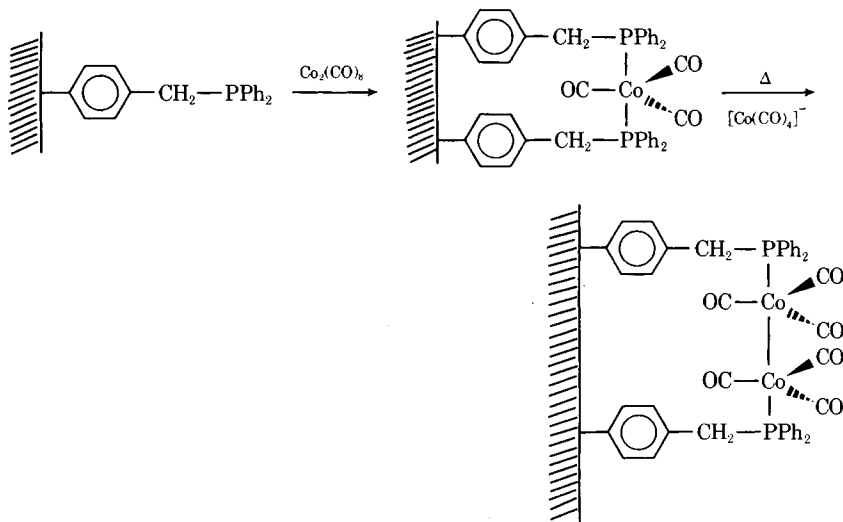


where X = —PR₂, —CH₂PR₂, —NR₂, —CH₂NR₂, and —SH.

Figure 3 shows the relative course of the catalytic process in the presence of homogeneous catalyst versus heterogeneous catalyst. It can be first noted that the two catalytic systems display a different selectivity, as shown by the easier hydrogenation of aldehyde to alcohol by the heterogeneous system. A different type of aldehydes is also obtained, since formation of branched aldehydes is predominant over linear products in the homogeneous system.

A classic hydroformylation agent, Co₂(CO)₈, has also been used on a polymeric supporting matrix²⁵ as seen in the structure on page 2736. The product of this reaction promotes the hydroformylation of cyclohexene under mild conditions (40 psi H₂/200 psi CO; 150°C). At elevated pressures (500 psi H₂/500 psi CO), the ratio of aldehydes over alcohols may be varied by changes in temperature. The catalyst is finally recovered as Co₂(CO)₇ polymer and may be recycled without loss of activity.

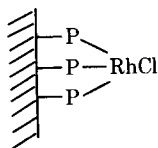
The recovery and recycling of the catalyst is one of the prominent prob-



lems in hydroformylation by cobalt derivatives.²⁶ To this regard, some polymeric cobalt catalysts have been studied, which function in both homogeneous and heterogeneous phase. These are obtained by reaction of cobalt carbonyls with variously crosslinked poly(2-vinylpyridines) with divinylbenzene and can bind the complex $\text{HCo}(\text{CO})_4$ under H_2 atmosphere and release it at the end of the reaction. Recycling without reactant consumption and side product formation becomes then feasible. The advantages of these immobilized catalysts over unsupported ones are a drastically shortened induction period and the reduction to about one fifth of the amount of cobalt required to destroy catalyst-poisoning species.

HYDROGENATION REACTIONS

Catalytic hydrogenations of sundry unsaturated substrates are effected by palladium,²⁷ platinum,²⁷ rhodium,²⁸ and iridium²⁹ complexes supported on polymeric matrices. Palladium, platinum, and rhodium salts deposited on nylon fibers in which bonds between the metal and amide groups are probably formed have been also employed.^{30,31} However, these systems are hardly effective for C=O-containing substrates. A recent paper³² has shown that in the hydrogenation of olefins the supporting polymer is able to discriminate among the various olefins getting in contact with catalytic centers on the basis of steric hindrance and polar character of the olefins. Thus, the results set forth in Table I have been obtained by the use of a polymeric Rh(I) hydrogenation catalyst originating from the reaction of a chloromethylated copolymer of styrene and divinylbenzene:



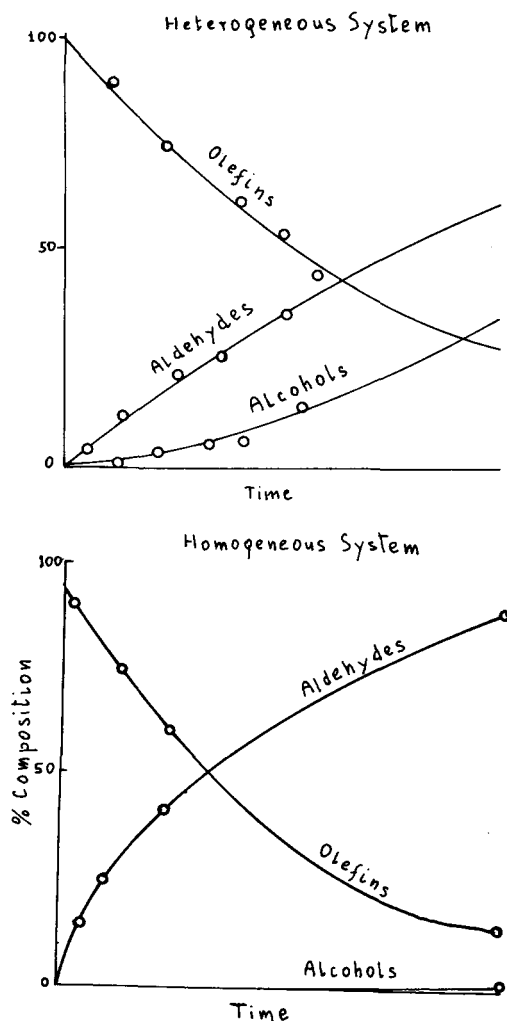


Fig. 3. Catalytic activity of $R_3N + RhCl_3$ (homogeneous and heterogeneous) for the conversion of 2-hexene to oxo alcohol.

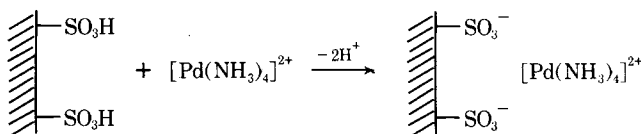
As can be seen in Table I, a relatively rigid and high molecular weight olefin such as Δ^2 -cholestene undergoes a marked decrease in the rate of hydrogen absorption when the catalyst is immobilized on the polymeric matrix. By contrast, the most simple olefin, 1-hexene, is hydrogenated more rapidly by the supported catalyst, indicating that the latter enhances the selectivity of the catalytic center. The hydrogenation takes place mostly at the inside of the polymeric support rather than on the surface, as shown by the less marked difference in specificity displayed by the more hindered olefins. One other advantage is the possibility of recovering and recycling the polymeric catalyst, the catalytic activity being virtually unaltered after ten cycles.

TABLE I
Relative Rates of H₂ Consumption for Various Olefin in the
Presence of Supported and Unsupported [Rh(PPh₃)₃Cl]^a

Olefin (1M)	Relative rate	
	Supported	Unsupported
Cyclohexene	1	1
1-Hexene	2.55	1.4
Δ ² -Cholestene	0.031	0.715
Octadecene	0.485	0.715
Cyclooctene	0.394	1
Cyclododecene (cis and trans)	0.225	0.666

^a 2.5 mM in benzene at 25°C.

High activity and selectivity are maintained by catalysts originating from the reaction of exchange resins with transition metal complexes. Thus, treatment of a basic resin, Amberlite-27-OH⁻, with [PdCl₄]²⁻ gives a solid product whose catalytic activity in the hydrogenation of olefins under ambient conditions is far greater than that of palladium black³³ or of such classic systems as palladium-coated carbon or silica. The selectivity of supported catalysts also is quite high: cyclohexene, styrene, and nitrobenzene are hydrogenated in less than 2 hr without loss of catalytic activity, whereas the benzene ring and keto groups are not hydrogenated. Cationic ion exchange resins have been used successfully as supports for rhodium and palladium complexes. With Amberlite-15 sulfonate, consisting of a styrene-divinylbenzene copolymer, a Pd(II) complex is obtained which may be reduced to Pd(0) by hydrazine:

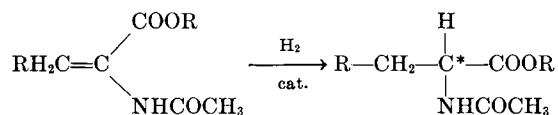


This catalyst hydrogenates selectively 1-hexyne to 1-hexene (95%) and *n*-hexane (5%), as does palladium-coated silica-alumina. The palladium-coated carbon catalytic system favors instead the formation of *n*-hexane over 1-hexene. Complexes of type [Pd(benzonitrile)₂Cl₂] and K₂[PdCl₄] on Amberlite-21 (a porous styrene-divinylbenzene copolymer containing —CH₂—N(CH₃)₂ groups³⁴) have been employed in place of [Pd(NH₃)₄]Cl₂. It has been shown that it is possible to achieve different degree of catalytic effectiveness by changes in the substituents on the phosphorous atom of the polymeric phosphines thereby getting selective reduction of ketones or olefins.⁴⁹ A Rh^{II} species trapped on the polymer has been characterized with ESR spectroscopy, as active catalyst.

ASYMMETRIC SYNTHESSES

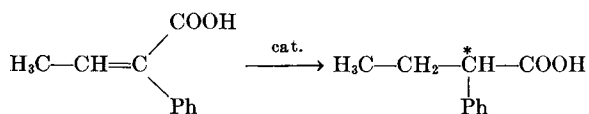
A most promising field of research in the branch of asymmetric syntheses is asymmetric catalysis. Its final goal is to approach as closely as possible to an enzymatic reaction which is completely stereoselective, at least on natural substrates. Many efforts have been focused on the preparation of catalytic systems possessing the same stereoselectivity as enzymes, by the use of simple chiral catalysts. Only in a few cases has an "enzyme-like" stereoselectivity been achieved with soluble rhodium complex catalysts with asymmetric phosphines.⁵²

Comparative investigations of homogeneous and supported catalysis might be concerned with asymmetric syntheses promoted by transition metal complexes having optically active ligands, such as hydrogenation, hydroformylation, and isomerization. Some interesting examples are the asymmetric hydroformylation of styrene promoted by $\{\text{Rh}(\text{CO})_2\text{-}_3(\text{H})\text{-}[\text{P}^*(\text{Me Ph benzyl})]\}$ ³⁵ and the hydrogenation of prochiral substrates³⁶:

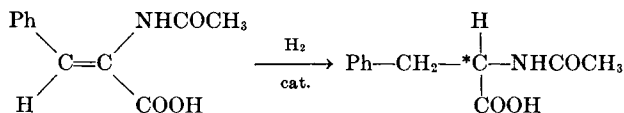


The latter produce α -amino acids with an optical purity sometimes higher than 90%. An important feature of homogeneous catalysts of these reactions is the distance between the central metal and the chiral center in the coordinated ligand.

β -Methylcinnamic acid is reduced to (*S*)-3-phenylbutanoic acid in the presence of $[\text{RhL}_3\text{Cl}][\text{L} = (\text{R})\text{-menthyl}(\text{diphenyl})\text{phosphine}]$ with 60% optical purity³⁷:



By the use of Rh(I) complexes prepared in situ, with chelating phosphines having a β -asymmetric carbon atom relative to phosphorus asymmetric hydrogenation of β -substituted α -acetamidoacrylic acids have been achieved with optical yields as high as 70–80%³⁸:



The methyl ester of α -phenylcinnamic acid has been asymmetrically hydrogenated by palladium-coated optically active polymers consisting of poly(methyl methacrylate) and poly(2-methylbutyl methacrylate). In these reactions, formation of the L-methyl ester predominates in comparison

with those involving palladium-coated poly(methyl metacrylate), whereas the optically active polymers have no influence whatsoever on the symmetric synthesis.³⁹

Polymeric catalysts in asymmetric hydrogenation have been adopted with a view to obtaining models for *hydrogenase*. Cinnamic acid derivatives and various unsaturated amino acids were the substrates. The catalytic activity of these polymeric catalysts is generally higher than that of monomeric catalysts.

The use of metal complexes immobilized on synthetic polymeric organic matrices having coordinated groupings with optically active atoms discloses promising lines of research for the achievement of asymmetric syntheses and stereoselective reactions.

Asymmetric reduction of prochiral olefins by rhodium(I) catalysts supported on asymmetric polyphosphines, have been described recently.⁵⁰ This system proved much less effective than the analogous homogeneous one for which very high optical yields were achieved.

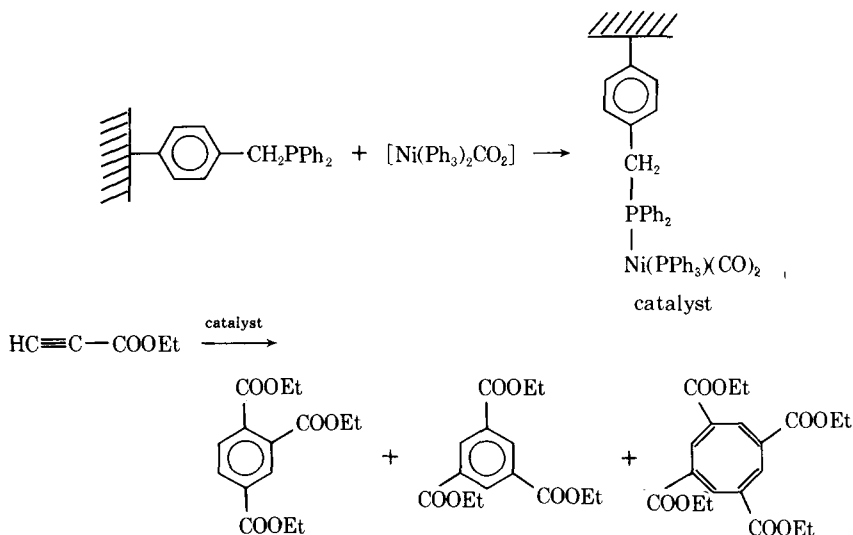
An example of the influence of polymeric character on stereoselectivity is the resolution of racemic mixtures of various optically active species by chromatography on a metal complex immobilized on an asymmetric group-bearing polymer. Thus, the optical isomers of DL-proline have been separated by chromatography on a column filled with an optically active copolymer resulting from treatment of chloromethylated styrene-divinylbenzene with excess of L-proline and subsequent reaction with CuSO_4 . Elution with water gave 50% L-proline and subsequent elution with 1M NH_3 gave D-proline. The resin is easily regenerated by mere treatment with CuSO_4 .⁴⁰ However, the separation of isomers is controlled by thermodynamic factors related to the stability of polymer-Cu-D-proline and polymer-Cu-L-proline systems.

OLIGOMERIZATION

Excellent oligomerization catalysts are prepared by the reaction of poly(4-vinylpyridine) with complexes of type $[\text{Ni}(\text{PR}_3)_2\text{Br}_2]$ ($\text{R} = \text{iPr}$ and Ph), NiCl_2 , and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$. The resulting polymeric species promote oligomerization of various olefins in vapor phase with high yields in the presence of an activator (AlEt_2Cl).⁴¹

Chromium, molybdenum, and vanadium complexes linked to acrylic-methacrylic acid homopolymers or copolymers of these with styrene or methyl methacrylate are effective catalysts for ethylene polymerization in the presence of tris(isobutyl)aluminum.⁴² These catalytic systems are more active than low molecular weight chromium complexes. Catalyzed reactions are the polymerization and copolymerization of α - and diolefins.⁴³

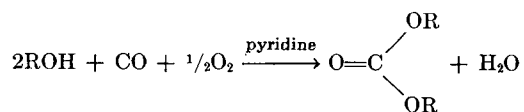
The polymerization of acetylenic monomers of type $\text{EtCO}_2\text{—C}\equiv\text{CH}$ has been achieved with polymeric nickel phosphine complexes resulting from the following reactions²⁵:



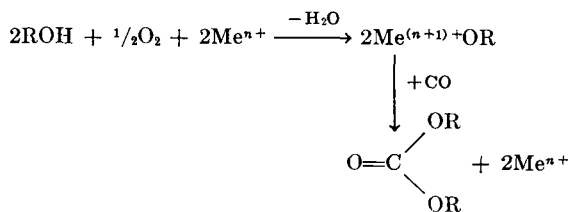
OXIDATION

PdCl_2 supported on a styrene-divinylbenzene copolymer containing $-\text{CH}_2-\text{N}(\text{CH}_3)_2$ groups catalyzes the formation of vinyl acetate along with acetaldehyde and ethylene oxide starting from ethylene, oxygen, and acetic acid.³⁴ Treating this polymeric complex with SnCl_2 gives a bimetallic compound with higher selectivity and catalytic activity.

A reaction which promises to be applicable to intermediate chemical technology has been devised in our laboratories. It involves the oxidative carbonylation of alcohols by CO and O_2 :



At present, phosgene is the starting substrate for the production of alkyl carbonates. This reaction takes place with high yield and selectivity in the presence of copper or nickel complexes as homogeneous catalysts. Amino alcohols, thio alcohols, or amino thiols may be used as the organic substrates. Cyclic carbonates are obtained from glycols and thio glycols. The mechanism proposed involves a redox process with the metal (i.e., $\text{Cu}^{2+}/\text{Cu}^+$):



A systematic study with copper complex catalysts immobilized on an insoluble poly(vinylpyridine) matrix has allowed the optimum experimental conditions for the above reaction to be assessed, while enlightening the possibility of reusing the polymeric catalyst for several cycles with all the advantages pertaining to homogeneous catalysis.

Poly(4-vinylpyridine) was obtained by radical polymerization of 4-vinylpyridine in a degassed closed tube at 50°C in alcoholic medium. The polymeric complex was prepared by treatment of the polymer in methanol with a solution of cuprous chloride in acetonitrile. The pale-yellow jelly-like product was filtered off, washed with methanol, and dried at 50° in vacuo. The catalyst is fed to a reactor in which a stream of CO, O₂, and CH₃OH under pressure can be driven under flow conditions. The carbonylation of alcohols can be effected either in separate stages (by successive cycles of treatment with O₂ and CO) or in a single stage (by simultaneous treatment with O₂ and CO).

In the formation of dimethyl carbonate, the influence of pressure, temperature, and changes in CO/O₂ and Cu/N molar ratios on the per hour production of dimethyl carbonate has been studied (N denotes the monomeric moiety in the polymer). The results indicate that the polymeric catalyst has activity and selectivity comparable to the analogous homogeneous catalyst even after 30 operating cycles.

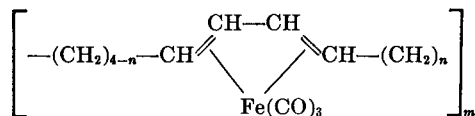
SYNTHESIS OF IMMOBILIZED CATALYSTS

General preparation methods may involve either polymers already containing coordinating groups in the chain (case I) or polymers into which groups must be previously introduced (case II).

In the former case, when the metal complexes to be immobilized are soluble, the reaction of the coordinating polymer with the metal complex is carried out according to usual procedures of organometallic synthesis. The following examples are paradigmatic.

Case I

Iron pentacarbonyl reacts with conjugated double bonds of polybutadiene to give macromolecular complexes via double-bond isomerization:

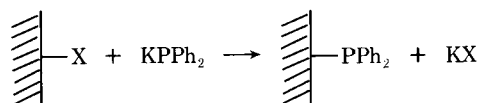


where $n = 0-4$. Among other polychelate agents are polysemicarbazones, polyaminoquinones, Schiff polybases (bis-salicylaldehydes), etc. Exchange resins also fall into this context.

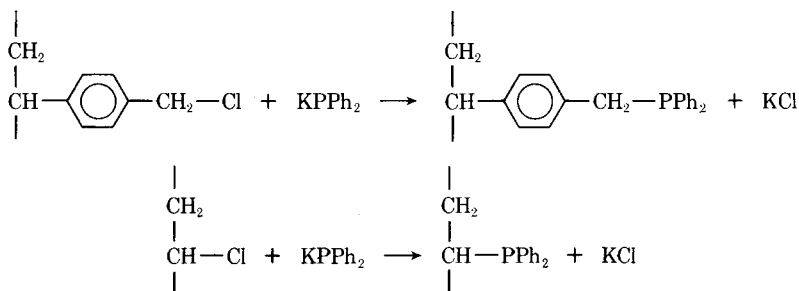
Case II

A typical example is the synthesis of phosphine ligands immobilized on either organic or inorganic substrates.

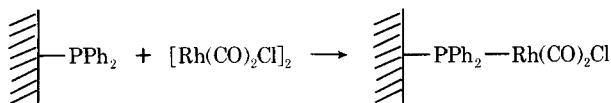
The most versatile technique involves the reaction of a halogenated polymer with an alkali metal phosphide⁴⁵:



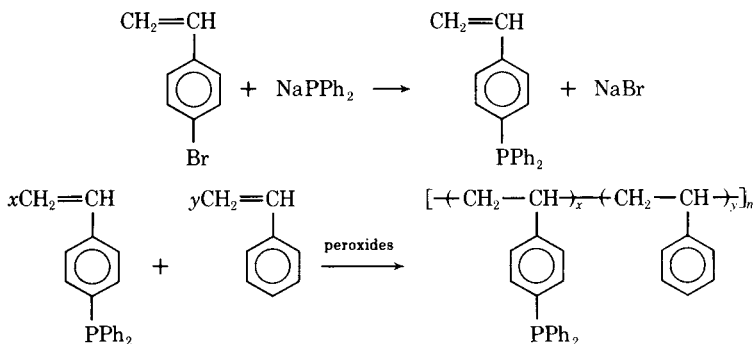
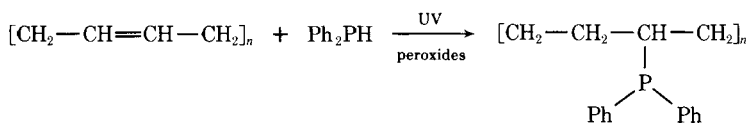
The polymers in this reaction are crosslinked chloromethylated polystyrene (Merrifield resin) and poly(vinyl chloride):



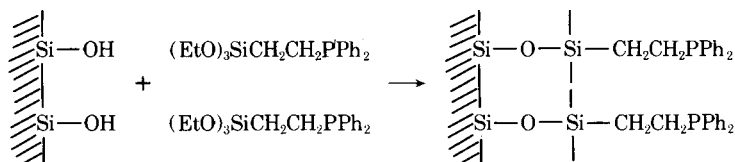
These polymers, once made functional, are treated with metal complexes according to classic procedures, for example, (cfr. hydroformylation):



Other methods are represented by the following reactions^{46,47}:

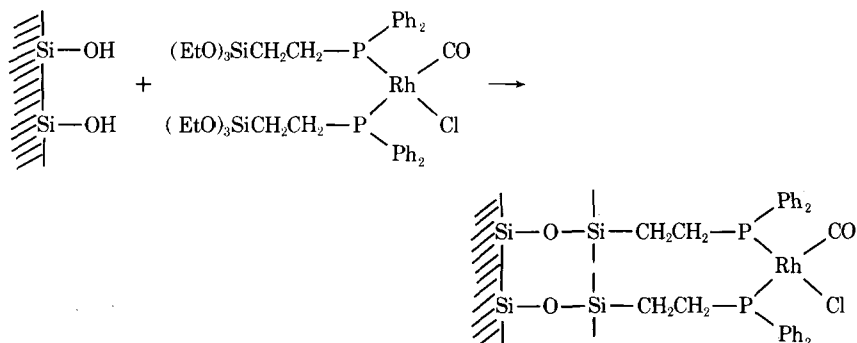


These ligands have been linked also to inorganic supports such as silica, by exploiting the known ability of ---Si---OEt groups to react with the surface of silica to give strong ---Si---O---Si bonds.⁴⁵ For instance, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{---Si(OEt)}_3$ reacts with surface silanol groups according to the reaction

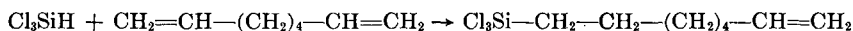


The complex is then prepared in the usual way.

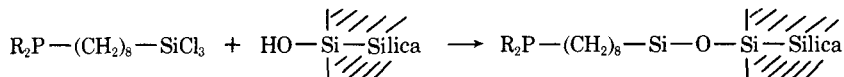
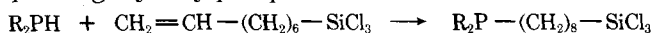
An alternative procedure involves the reaction of silica with the preformed complex:



Silica-bonded phosphine ligands have been prepared by a series of reactions involving (i) selective addition of trichlorosilane to an α,ω -diene to give an ω -alkenyl silane⁴⁸



followed by (ii) reaction of the latter with dialkyl or diarylphosphine to give the corresponding silylalkylphosphine:



The use of these phosphines as ligands in rhodium complexes for hydrogenation and hydroformylation has revealed that a relationship between catalytic activity and chain length is operative: the catalytic activity increases with increasing length of the paraffinic chain.

CONCLUSIVE REMARKS

The polymeric matrix-supported catalysis has, first, the great advantage of allowing the catalyst to be easily separated from the reaction mixture, possibly regenerated, and recycled. Secondly, the induction period at the start is markedly shorter in the case of polymer-immobilized catalysts over homogeneous ones. These latter are also more sensitive to poisoning impurities, since in the former the catalytic site is somehow protected by the organic matrix.

Supported catalysts often display higher catalytic activity than homogeneous ones. For example, the yields of ethylene-propylene copolymerization in the presence of polybutadiene-TiCl₄ are up to five times higher than those with TiCl₄ alone.

The same is true of the catalytic hydrogenation in the presence of rhodium(I) phosphine complexes or in the case of copper catalysts with polydentate ligands for catalytic decomposition of hydrogen peroxide or oxidation of ascorbic acid. This gain in activity may be related to (i) cooperative effects exerted by the polymer which favors the substrate in approaching to catalytic sites through hydrogen bonding or polarities around them, (ii) a different tendency to dissociation of the polymeric complex relative to the monomeric one.

One further advantage of the polymeric catalyst is the maintaining of its catalytic activity over a wider range of concentrations expressed as substrate-accessible catalytic sites.

Although the formation of a metal-polymer complex is not a prerequisite for a gain in activity, catalytically inactive system may become active when such a complex is formed.

As for selectivity, it should be intermediate between those for homogeneous and heterogeneous catalyst for a metal-polymer. However, for the latter, additional selectivity may arise from steric hindrance and/or polar character of the polymeric matrix. The kinetic control of reaction is also more feasible, thereby allowing reaction intermediates to be isolated in some cases.⁵¹

Summing up, the boundary between homogeneous and heterogeneous catalysis tends to dissolve away with the use of complexes immobilized on polymeric matrices. Homogeneous catalysis is likely to find an application in the "fine chemicals" branch, whereas catalysts on organic polymers, also owing to their technologic advantages, seem to disclose even wider fields of application. This greater versatility is also related to the various controlled surface modifications that can be brought on the structure of the matrix itself and to their stability at comparatively elevated temperatures. In this regard, catalysts supported on organic polymers offer distinct advantages over those on inorganic polymers, though being at present more expensive than the latter. However, efforts will have to endeavor at devising novel syntheses of immobilized catalysts and at applying sophisticated physicochemical methods for full characterization.

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