CHAPTER II

THEORY

2.1 Polymeric supports

2.1.1 Reviews of polymeric supports

Polymers are fine catalyst supports. They have been used of three major classes. The first class includes the highly crosslinked resin beads of large surface area called macroreticular or macroporous resins. For example, styrene-divinyl benzene resins with divinyl benzene contents of 5% to 60% of total monomer mixture. The attached catalysts lie mainly in a thin layer at the internal surface, where they are wet by solvents. The high crosslink density prevents rapid diffusion into the core of particle below the internal surface. Usually the surface region is not as highly crosslinked or as rigid as the core.

Swellable, lightly crosslinked, microporous(gel-type) resins constitute the second class. These resins swell in solvents and all of their internal volume is accessible to solvent and reagents. Therefore, they may be functionalized with catalyst sites, giving them the advantage of high capacity.

Unlike macroreticular resins, they must be used with a swelling solvent to permit access to this internal volume. Examples include styrene resins crosslinked with divinyl benzene 1% to 5% of total monomer mixture. Finally, soluble polymers may be employed as supports. Reaction products may be continuously seperated from polymer-supported catalysts by using membrane filtration or by addition of a non-solvent which precipitates the polymer [38].

Since crosslinked polymers are insoluble and non-volatile they are odourless and non-toxic [8]. Most applications have used crosslinked polymer resins as the support, prepared by suspension copolymerization of styrene and divinylbenzene as the crosslinker. Crosslinked polystyrene , with various crosslink densities , surface area and porosity , has received the most attention as an organic support. Variations of the percent crosslink in the support allows an almostcontinual change from solution chemistry to that of usual heterogeneous surfaces. The basic polymer backbone ischemically inert , the polar properties can be modified by controlled functionalization or by preparation of appropriate copolymers [5].

Polymer supports offer several advantages over other catalyst supports. They are easily functionalized, especially when they incorporate aryl groups. Unlike surfaces of metal oxides, polymeric hydrocarbons are nearly inert and are not

expected to interfere in catalysis, which may therefore be associated with a single kind of catalytic group and occur selectively [33].

The highly non-uniform surfaces of metal oxides do not often easily lend themselves to straightforward synthesis of bound organometallics and often complicated mixtures of surface species result. Furthermore, the polymers obtain high densities of sites for binding catalytic groups, and therefore efficient use of reactor volume. Catalytic groups may be dispersed throughtout the bulk of a polymer. Groups supported on metal oxides, in contrast, are restricted to surfaces. However, with high surface area porous solids, high loadings of catalytic groups can be achieved. The polymer supports are unique in being flexible. They may therefore chelate organometallics, giving high ratios of ligands to metal [8].

The choice of a solid support depends on the particular catalyst systems. From a chemical standpoint, the parameters should be considered are inertness to reagent, mobility of the attached species , and polarity relative to reactants and products. The engineering aspects are porosity of the support and diffusion barriers of reactants, surface area, heat-transfer properties , and mechanical and heat stability [5].

Several factors are important for selecting the type of polymer to be used to support a given reactive group. These

include the ease of preparation of potentially suitable polymers with the appropriate functional groups and the ease with which these polymers can be obtained in a good physical form. It is also important that, apart from those groups that it is intended should react, the polymer should be chemically inert under the conditions of use. This is especially important if it is intended to recycle the reactive polymer, since after many reaction cycles even quite small and otherwise unimportant side reactions can seriously impair the capacities and/or physical properties of the polymer. The need for chemical inertness severely limits the use of polymers which contain hydrolysable groups, active OH or NH groups, or easily oxidized or reduced groups. Polymers with such functional groups include poly (acrylate)s, polyesters, poly(acrylamid)s, polyamides (e.g. nylons and peptides), polyurethanes and polysaccharides [8].

Typical organic supports include styrene polymers, poly(amino acid), acrylic polymers, and crosslinked dextrans. Among acceptable inorganic supports are glass, silica, alumina, zeolites, and clays. The active portion of the catalyst must be stable under reaction conditions while being solvated and soluble in the reaction medium.

2.1.2 Preparation of functional polymers

Two approaches exist for the preparation of functional polymers , namely the polymerization or

copolymerization of monomers which carry the desired functionality and the chemical modification of preformed polymers.

2.1.2.1 <u>Preparation of functional polymers by copolymerization</u>

The direct approach and many functional linear polymers can be prepared by free radical, anionic, cationic, coordination or group transfer polymerizations. However, for most purposes crosslinked polymers are more attractive than linear polymers. The preparation of crosslinked polymers in a good physical form is most readily achieved by suspension polymerization. This usually involves suspending droplets of a mixture of water-insoluble monomers in an aqueous medium and the use of an oil-soluble free radical initiator or, suspending droplets of a mixture of water-soluble monomers in a water-immiscible medium and the use of a water-soluble free radical initiator. The latter type of polymerization is usually termed inverse suspension polymerization. Crosslinked polymers prepared by suspension polymerization include those shown in Figure 2.1.
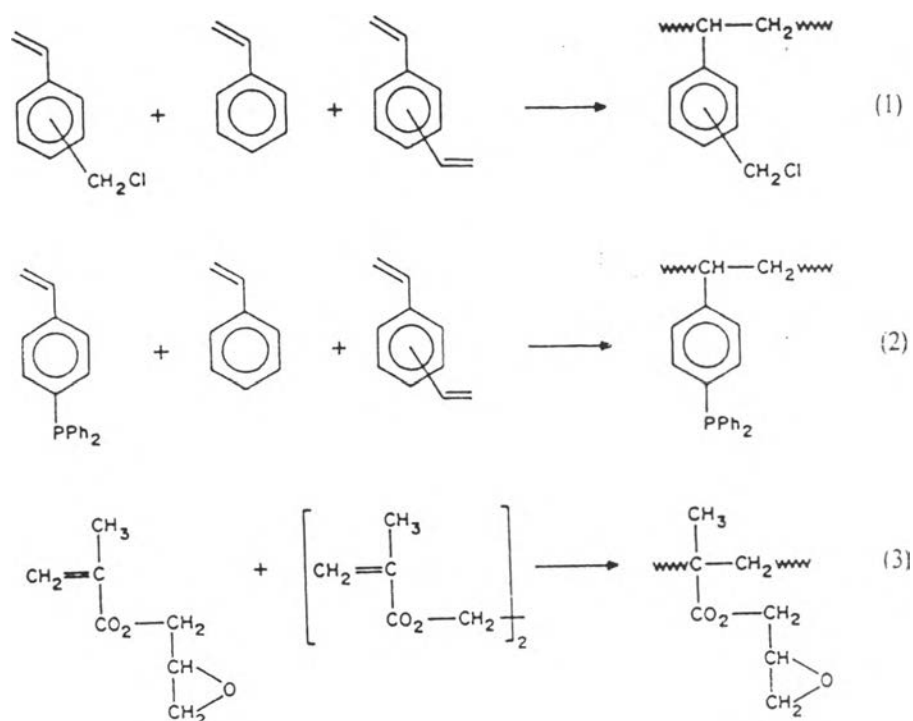
Figure 2.1 Crosslinked polymers prepared by suspension
polymerization

The physical form of the products from suspension polymerization depends on the polymerization conditions. Including such details as the vessel shape , the stirrer size and shape , the stirring speed and the types and concentrations of suspending agents. The optimum conditions for a particular monomer mixture must often be determined by trial and error. By selecting appropriate conditions microporous or macroporous polymer beads can be obtained. The former are prepared using low levels of crosslinking agent. When the product is dried the polymer matrix collapses to give beads with only very small pores (micropores). Macroporous polymers

relatively large amounts of crosslinking agent and additives called porogens. The latter could, for example, be toluene, certain alcohols or linear polymers. Macroporous polymers are relatively rigid. When they are dried the matrix does not collapse; the large pores remain.

2.1.2.2 Preparation of functional polymers by chemical modification of preformed polymers

It is attractive for the preparation of crosslinked polymers because one can start with commercially available microporous or macroporous polymer beads of good physical size and form, with a known percentage of crosslinking and porosity, etc. After chemical modification the final functional polymer generally has essentially the same physical form as the original polymer. However, the reaction conditions used must be carefully chosen to ensure that the reagents can penetrate the crosslinked matrix throughout the reaction. Ideally the reaction used should have no side reactions because it is not possible to remove the polymer-bound impurities resulting from such reactions.

Chemical modification will generally occurs at the more accessible sites of the reactive functional groups should be unavailable for later reactions. Depending on such factors as the rate of the chemical modification reaction relative to the rate of diffusion of the reagent into

the matrix, and whether the group introduced facilitates or hinders the introduction of further group in the vicinity, the functional groups in the final polymer may be clustered or well spaced. Of the many reactions which have been used to chemically modify polystyrenes those summarized in Figure 2.2-2.4 are the most generally useful [8].
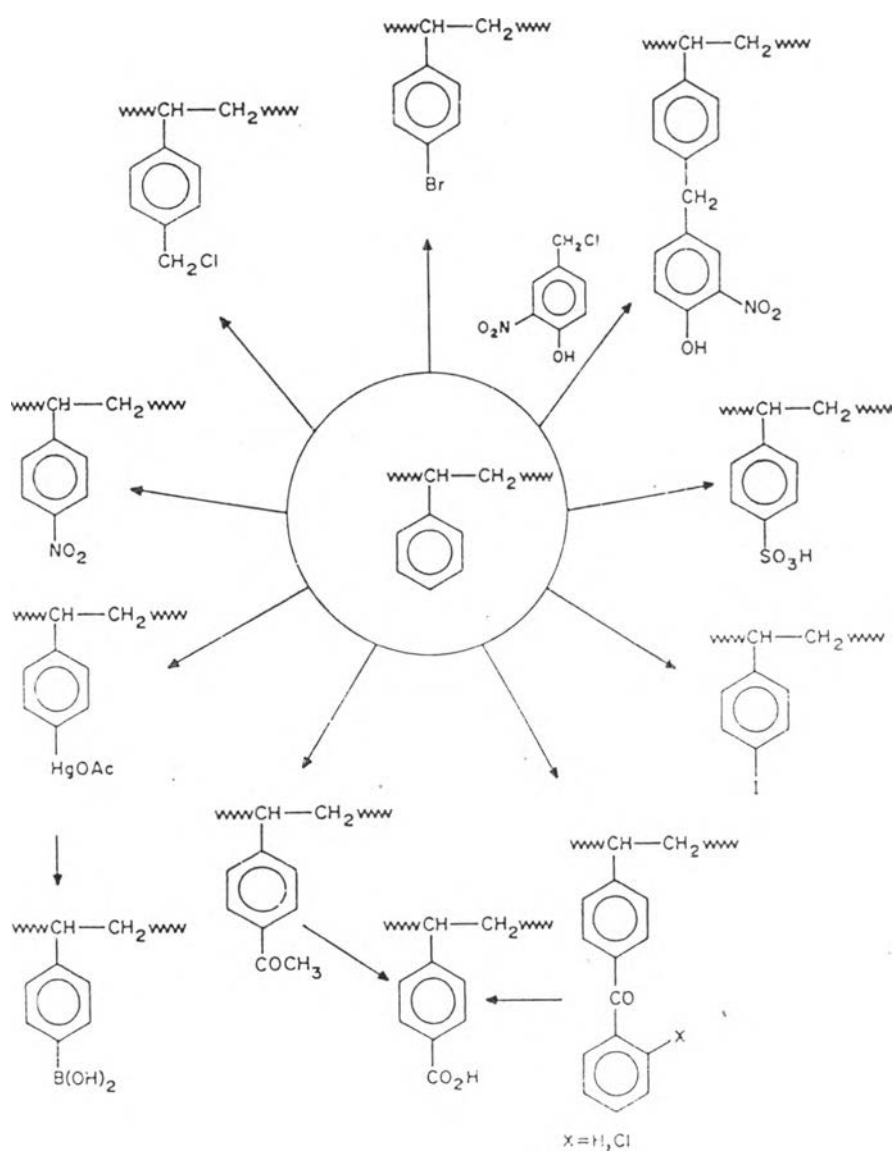
Figure 2.2 Electrophillic aromatic substitution reaction of polystyrene
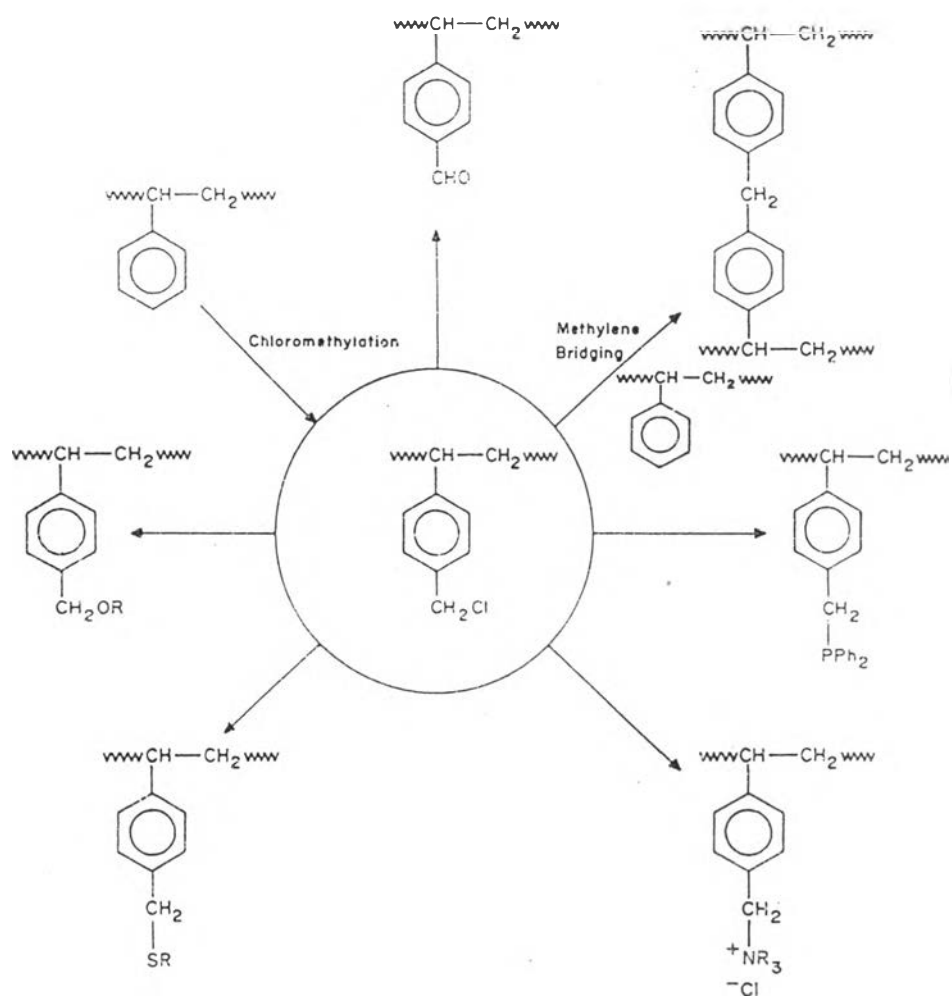
Figure 2.3 Chloromethylation of polystyrene and reactions of the products with nucleophiles

Figure 2.4 Lithiation of polystyrene and reaction of the products with electrophiles

2.1.3 Thermal and mechanical properties of

bead-like supports

The mechanical behavior of gel or macroporous supports might mean the severe limit of using. For instance, gel particles with very low crosslink density , which might be desirable in order to limit the diffusion control of the reactions inside the polymer , are too soft to be handled and cannot be used in a column reactor. On the other hand, macroporous resins with large pore volumes are very brittle and will disintegrate into very fine particles upon attrition in a stirred reactor. In other cases, the swelling-deswelling process which may occur during the life of the supported reagent may cause it to disintegrate into smaller particles.

Wieczonek and coworkers have reported the results of compression experiments carried out on a few single beads, gel-like or macroporous, in the dry state or in the presence of various solvents or liquids. Unfortunately, the results are independent of the size of the bead only above a diameter of about 500 microns, due to imperfect sliding of the sample surface on the plates of the compression apparatus. Assuming Hookian behavior, a penetration modulus, A, was calculated from the following equation:

$$A = \frac{3(2S)^{2/3}}{16\,r^{1/2}}$$

where r is the radius of the bead and S is the initial slope of a plot of $F^{2/3}$ (F force measured) versus the deformation, y. In each test a successive compression, Δy, was imposed and the force was recorded after 30 s of relaxation. The stress at the breaking point can be calculated by the following formula:

$$\sigma_b = \frac{F_b}{\pi \Delta y_b [r - (\Delta y_b/4)]}$$

where F_b and Δy_b are the force and the compression observed at the breaking point.

Styrene-DVB resins are amorphous glassy polymers at room temperature. Their glass transition temperatures have been recently studied using either inverse gas chromatographic analysis or differential scanning calorimetry [8].

2.2 Polymer-bound catalysts

2.2.1 Reviews of polymer-bound catalysts

The following methods have been used to prepare polymeric catalyst:

(a) Functionalization of available crosslinked or non-crosslinked polymers and subsequent incorporation of transition metal complexes.

(b) Homopolymerization or copolymerization of functionalized monomers and subsequent incorporation of transition metal complexes.

(c) Homopolymerization or copolymerization of monomers already containing metal complexes.

(d) Homopolymerization or copolymerization of metal complexes containing polymerizable groups.

Crosslinked polystyrene, which can be prepared in a various physical forms , is usually used as the catalyst support [8]. The ideal group used to bind a metal complex to a support should be chemically inert under the reactions conditions and form a nonlabile link between metal complex and the support. Numerous have been developed for functionalization of polystyrene with suitable ligands as shown in Figure. 2.1.
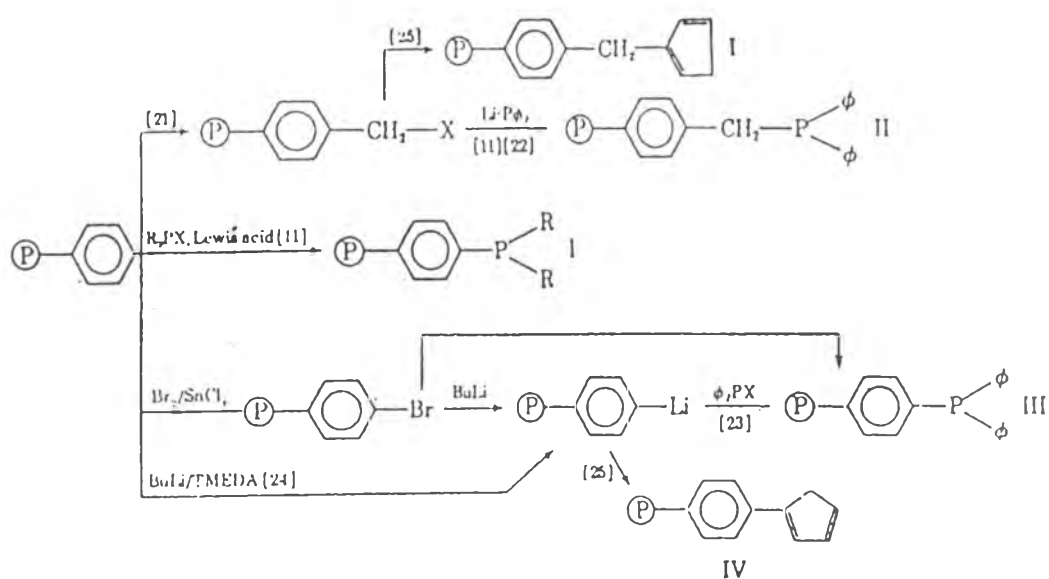
Figure 2.5 Functionalization of polystyrene with ligands

These modes allow linking agents to be attached through either nucleophilic or electrophilic reactions and provide great flexibility in the synthetic design. At least three important analytical factors must be considered for each mode of linking: the percentage substitution, distribution of linking agent in the support, and the structure of the linking agent on the support.

The percent substitution, determined by elemental analysis , indicates the moles of ligand per gram of support. Local concentration of the ligand is important and elemental concentrations are rapidly determined by electron microprobe in a 1-10 micron surface area. By examining a polymer bead half section to be easily find the distribution of a noncarbon ligand inside the polymer. A completely random distribution throughtout the polymer is easiest for model studies; however, for practical applications it may be advantageous to functionalize only the outer polymer volume [5].

The selectivity of the polymer-bound catalyst towards substrates with different sizes can be controlled by the loading of the catalyst on the polymer support and also by the solvent used to swell the polymer. The selectivity increases with decreasing swelling ratio of the polymer in the solvent and, in the more polar solvent, it depends on the separation of the functionallity.

The efficiency of the polymeric catalyst is related to several factors, such as (a) the properties of both catalyst and reactants, since this determine the activation energy of the reaction, (b) the distribution coefficient of the reactants between the solution and catalyst, and (c) the nature of the solvent. The rate of the catalysed reaction depends on the rates of diffusion of the substrate and products within the polymer matrix which, in turn, will depend on the ratio of the molecular size of reactants to the micropore sizes of the polymer and consequently will be related to the degree of crosslinking and the degree of polymer swelling. In other cases, the chemical reaction of the surface or within the polymer granules determines the rate which will depend on the concentration of active sites available at the surface layer of the granule. In the cases where diffusion controls the reaction rate, the polymer can exhibit specificity or selectivity, depending on the molecular of the substrate and micropores of the polymer [37].

2.2.2 Characterization of polymer-bound catalysts

To clearly characterize a low molecular weight compound it is sufficient to give a few physical or chemical data, such as boiling point, melting point, refractive index, and elemental analysis. If two low molecular weight compounds agree in some characteristic properties they are considered identical.

Characterization of macromolecular compounds is much more difficult. Because of the high intermolecular forces, macromolecules cannot be volatilized without decomposition so that boiling points cannot be given. The melting points of crystalline polymers are generally not sharp (frequently, only sintering of softening can be observed) and are often accompanied by decomposition. In addition to elemental analysis, other data have to be determined such as solubility, solution viscosities, average molecular weight, molecular weight distribution, degree of crystallinity.

The fundamental difficulty consists in the fact that polymeric compounds cannot be obtained molecularly uniform in the sence of low molecular weight chemistry. Therefore, macromolecular compounds of like analytical composition may differ, except in structure and configuration, also in molecular size and distribution: they are polymolecular, i.e., they consist of a mixture of macromolecules of different sizes. Thus, it is evident that the term "identical" is practically not applicable to macromolecules. Since there are, as yet, no possibilities to prepare macromolecules of uniform structure and size, it follows that all physical measurements on polymers can only yield average values. Because of the above mentioned peculiarities of macromolecular compounds, the methods for characterizing low molecular weight compounds are frequently not applicable to polymers or can only be used in modified form ; completely new methods of investigation must often be employed.

Even small variations in the molecular structure of a polymer may noticeably effect its properties. Since the structure of a polymer depends upon the conditions of preparation, these must also be specified (e.g., radical polymerization in bulk at 80°C, polymerization with a certain organometallic catalyst at 20°C) in addition to the type of measurement used (e.g., molecular weight by end group determination, crystallinity by infrared spectroscopy, etc.) [35].

Determination of the organometallic structures present in a polymer-supported catalyst is best carried out spectroscopically and, if the supported species are uniform in structure, they can often be characterized quite well by comparison of their spectra with the spectra of molecular analogues. The most easily and widely applied technique continues to be infrared spectroscopy and high quality spectra, especially of metal carbonyls, have been obtained with thin membranes of polymer. The membranes have been frequently used to allow investigations of catalysts in the working state in the presence of gaseous reactants; techniques have also been developed to allow measurement of spectra of catalyst beads in the presence of liquid reactants.

The characterization technique that appears to offer the greatest potential for polymer-supported metal complexes is extended X-ray absorption fine structure (EXAFS) spectroscopy, which can provide detailed structure information about the ligand

environment of the metal. Unfortunately, there have been only a few application of this method of polymer-supported catalyst; the work by Reed and coworkers is the most important. These authors characterized analogues of the Wilkinson alkene hydrogenation catalyst (both in the monomeric and dimeric forms) bonded to phosphine-functionalized poly(styrene-divinylbenzene). The data determined Rh-P and Rh-Cl distances that are in good agreement with the values found for the molecular analogue by X-ray crystallography.

With the increased availability of synchrotron radiation. The EXAFS technique has become accessible to a wide circle of researchers investigation such materials as metalloenzymes and solid inorganic catalyst , typified by metal crystallities supported on high-surface-area metal oxides. Some of the most compelling research opportunities in characterization of polymer-supported catalysts are offered by EXAFS spectroscopy , and the lack of investigations with this technique is symptomatic of the current lack of research on these material.

There are also attractive for the application of NMR spectroscopy to characterize organometallic structure in polymers. In prospect, the method is powerful, but again there have been few application. ^{31}P-NMR spectroscopy has been used to characterize polymer-supported rhodium complexes. The supports were made by homopolymerization of p-styryldiphenylphosphine or

p-styryldicyclohexylphosphine. Each ring of the highly swelled polymer was functionalized with a phosphine ligand, giving a sample with a high signal strength and a nearly uniform environment of phosphorus in the polymer. A series of rhodium-phosphine complexes was formed in the polymer, and their structure were inferred by comparison of the NMR spectra of the polymer-supported complexes and their molecular analogues. With development, the NMR technique may be applied to other polymer-supported catalysts and metal NMR data may become available.

X-ray photoelectron spectroscopy (XPS) has been used to characterize metals in polymers and examples are cited below. The method is most useful for comparison of different forms of a given sample, The data often providing clear evidence of changes in metal oxidation state resulting from catalyst treatment; occasionally the data allows determination of absolute oxidation states.

Polymer-supported catalysts have also been characterized by quantitative electron microscope analysis to determine profiles of metals and other elements within individual beads of catalyst. A particle is sectioned, mounted and tranversed with an electron beam in a vacuum of a roughly 1 m^3 volume of the sample.

Nicolaides and Coville have reported the use of mass spectrometry to analyze volatilized polymers, determining the

degree of crosslinking for poly-styrene-divinylbenzene as well as the degree of functionalization of the chloromethylated polymer. Mass spectrometry appears to be a straightforward and valuable method for the quantitative characterization of polymer supports and catalyst. A related thermal method (temperature-programmed desorption or decomposition involves heating the polymer sample in a continuous stream of an inert carrier gas and analyzing the evolved gas with a mass spectrometer [8].

2.2.3 Catalytic reactions of polymer-bound catalysts

The range of hydrocarbon reactions catalyzed by these complexes with polymer ligands include hydrogenation, hydrosilyl-ation, hydroformylation, acetoxylation, polymerization, and oligomerization. Some catalytic reactions could be shown as follows.

2.2.3.1 Hydrogenation

Hydrogenation is an exemplary reaction that has been widely used in homogeneous catalysis studies. With one of the triphenylphosphine ligands replaced by phosphenated polystyrene , the activity of the complex as a hydrogenation catalyst is much more sensitive to the size of the alkene substrate. This is attributed to restriction of movement of the solution within the cross-linked polymer, indicating that most of the reaction is taking place inside the polymer bead. These

supported complexes are still somewhat less reactive than related unsupported complexes in homogeneous solution. Grubbs et al. report an activity of polystyrene-supported rhodium catalysts at 0.06 times that of an equivalent amount of the homogeneous counterpart , and the difference for the silica-supported catalysts will clearly be rather less.

A necessary feature of a homogeneous catalyst is the existence of a free coordination site on the metal atom which alkene molecules can attach themselves. Often attempts to produce a free site results in polymerization of the complex and removal of the free site ; but if the complex is bound to a rigid polymer there is the possibility that free sites can be produced. Titanocene is a reactive catalyst for alkene reduction, but it rapidly polymerizes to an inactive compound.

Hydrogenation is the addition of hydrogen to an unsaturated moiety. Since the discovery by Iguchi in 1939 that certain rhodium(III) complexes will catalyse the hydrogen reduction of organic substrates, such as fumaric acid, homogeneous hydrogenation catalysts involving most, if not all, of the d-block metals have been studied. Most attention has focused on the Group VIII elements since it is these which generally give rise to the most active catalysts systems. The unsaturated substrate is generally activated by co-ordination and the hydrogen by addition; systems involving oxidative, homolytic

and heterolytic addition of H_2 are known; by careful choice of catalyst system a remarkable degree of selectivity is attainable; many of the catalysts are active under ambient conditions.

2.2.3.2 Hydroformylation

During hydroformylation of a terminal alkene the aldehyde group can add to the end carbon atom giving a linear aldehyde, or to the internal carbon atom giving a branched aldehyde. The amount of each aldehyde is dependent on the catalyst.

2.2.3.3 Hydrosilylation

Hydrosilylation is a reaction of some considerable interest and potential to the organosilicon industry. The usual homogeneous hydrosilylation catalyst is chloroplatinic acid , and its use necessitates the reaction being carried out in inconvenient alcoholic solvents to obtain a homogeneous reaction mixture. Unsupported chloroplatinic acid is a good hydrosilylation catalyst, and rhodium trichloride shows little activity. However, putting these two compounds onto polymer supports has a marked effect on their activity [36].

2.2.4 Some general features of polymer-bound reactions

2.2.4.1 Reaction Conditions

The practical advantages of using polymer-bound catalysts are the fact that they are generally prepared from crosslinked polymers. Such polymers are insoluble in all solvents and, with the sizes of bead commonly used, more than than 99% of the reactive groups are within the beads, for the reactions to take place the low-molecular weight reactants must diffuse into the polymer beads. With microporous polymers diffusion will be very slow unless the reaction solvent swells the beads. The beads must not only be swollen initially but throughout the reaction.

With macroporous polymers access to the functional group within the macropores will generally present no problems, but when functional groups are within the dense and more highly crosslinked regions of the matrix the choice of the reaction solvent will again be important if the functional groups are to be readily accessible.

When diffusion of the low-molecular-weight reactant into and out of the polymer beads is rapid compared with the rate of the reaction being carried out, the low-molecular-weight reactant will become distributed between the polymer phase and the solvent outside. Depending on the position of the

equilibrium, the low-molecular-weight reactants can be concentrated within the polymer bead, and this may lead to faster reactions rates in the low-molecular-weight counterpart, or it can be attenuated, and this may lead to slower reaction rates. The position of the equilibrium obviously depends on many factors, such as the polarity of the polymer and the polarity of the reaction solvent relative to the polarity of the substrate. If the low-molecular-weight reactants can diffuse into and out of the polymer freely throughout the reaction, the reaction will occur uniformly throughout the beads.

If diffusion of the low-molecular-weight reactant into and out of the polymer beads is slow compared with the rate of the reaction being carried out, the reaction will be diffusion controlled and it will, therefore, be slower than the low-molecular-weight counterpart , especially with large reactants. Under these conditions , the reaction will occur initially in the outer shell of the beads and it will gradually migrate inwards. The rate of diffusion obviously depends on many factors such as the extent of swelling and any interactions that the low-molecular-weight reactant may have with the polymer. The distribution of functional groups within a bead can often be determined by using a scanning electron microprobe.

2.2.4.2 Ease of intrapolymeric reactions

Consider functional groups, potentially

capable of reacting together, bound to a linear polymer. With a polymer that exists as a flexible random coil, therefore, any two polymer-bound groups cannot come together and react. If no permanent linkage, which is equivalent to a crosslink, is formed between the groups, eventually every group can react with another. If the linear polymer does not exist as a flexible random coil but is organised in some way, this will limit the extent to which functional groups can react together. ·

With a crosslinked polymer the mobility of the polymer chains, and hence the attached functional groups, is restricted. With lightly crosslinked polymers such as 1% or 2% crosslinked polystyrenes the mobility is not reduced significantly, but as the crosslinking increases a point is eventually reached where a small but significant fraction of the functional groups cannot reach others. At this point a degree of permanent site isolation is achieved. The stage at which it occurs depends on the degree of functionalization and the distribution of the functional groups, the type and distribution of the crosslinks, the extent of crosslinking, the extent of swelling of the polymer matrix, and, indeed, the type of polymer itself, that is whether it is a polystyrene, polyacrylate or polypeptide, etc. It should be noted that even though macroporous polymers have a high degree of crosslinking and, therefore, rigidity, the functional groups may be concentrated near the surfaces of the macropores. Hence, although overall the degree of functionalization may be low, the polymer may behave as though it were high.

Although in most circumstances a substantial proportion of the functional groups bound to a polymer support can react together, the groups are less mobile than their low-molecular-weight counterparts in solution. The reduced mobility is often sufficient to allow other reactions of the functional groups to complete effectively with the intrapolymeric reaction, despite the fact that the functional groups in polymer-supported catalysts are usually confined to a much smaller volume than their molecular-weight counterparts in solution. Under these circumstances a degree of kinetic site isolation is achieved in addition to any permanent site isolation that may be present. The successful exploitation of kinetic site isolation depends on many factors such as the inherent mobility of the polymer chain and the extent to which the swelling solvent and temperature enhance the mobility, the extent and distribution of the crosslinking, the loading of the functional groups and their distribution and the concentration of the low-molecular-weight reactant in the vicinity of the polymer-bound functional group. It should be noted that a functional group bound to the polymer by a flexible 'spacer chain' will be more mobile than a functional group bound directly to the polymer. The mobility of functional groups in polymers has been studied by ^{13}C-NMR and ESR spectroscopy.

2.2.4.3 Microenvironmental effects

Most polymer-bound catalysts are prepared

from lightly crosslinked polymers and are used in good swelling solvents. To achieve swelling the solvents must interact favourably with the polymer chains and, if the loading is high, with the reactive groups. Under these circumstances the polymer-bound reactive groups will usually be surrounded by the swelling solvent and they will have a reactivity just like that of the low-molecular-weight counterpart. Neighbouring groups in the polymer will need to interact strongly with the functional group to alter this situation. This might be the case if hydrogen bonds can be formed. Polar groups present may produce a significant field effect at neighbouring sites. Ionic groups may cluster and clearly this may affect the reactivity of the ionic species. The microenvironment may also be affected if the polymer strongly absorbs low-molecular-weight reactants and products. These various effects are difficult to disentangle and harder still to quantify. Nevertheless, if they can be properly understood they may allow more active and more selective polymer-bound catalysts to be prepared.

The example of reactions concerns a change in the selectivity of a reagent. N-Bromosuccinimide in carbon tetrachloride reacts with cumene to give bromides (I) and (II) with the yields of 89% and 10%, respectively. However, reaction of poly(N-bromomaleimide) with cumene in carbon tetrachloride gives bromides (III),(IV) and (V) with the yields of 13%, 15%, and 48%, respectively. The rationalization proposed for these differences is that the polar nature of the polymer
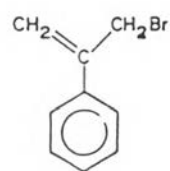
environment for the reaction irrespective of the solvent used and that the initial product (I) is dehydrobrominated to give a product (VI) which then reacts further. In support of this it has been shown that using N-bromosuccinimide in more polar media products similar effects.
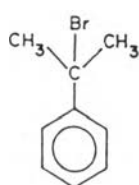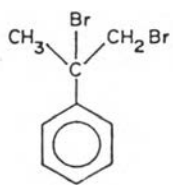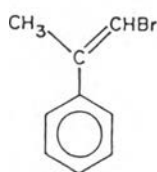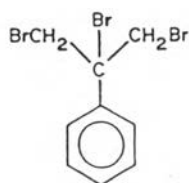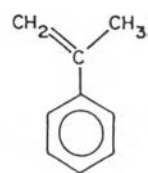

(I)   (II)   (III)

(IV)   (V)   (VI)

2.2.4.4 <u>Steric effects</u>

Functional groups bound to the polymers might be expected to be sterically crowded. In general, this is probably only the case when the functional groups are very close to the polymer backbone. As the functional groups are separated from the backbone by spacer groups, steric effects would be expected to disappear rapidly. Under conditions where the polymer backbone and the functional group interact favourably with the reaction solvent, functional groups bound to the para positions in polystyrene would not be expected to behave any different sterically than their low-molecular-weight analogues.

For example, oxidations of penicillins (VII) and (VIII) to their sulfoxides using polymer-supported peroxyacid (IX) in tetrahydrofuran give , in each case , the epimeric sulfoxides in essentially the same proportions as when m-chloroperoxybenzoic acid is used in the same solvent, and the sodium borohydride reduction of polymer-supported ketosteroids such as (X) in various solvents give essentially the same ratios of epimeric alcohols as in low-molecular-weight model systems.
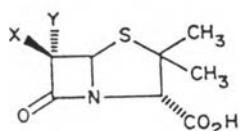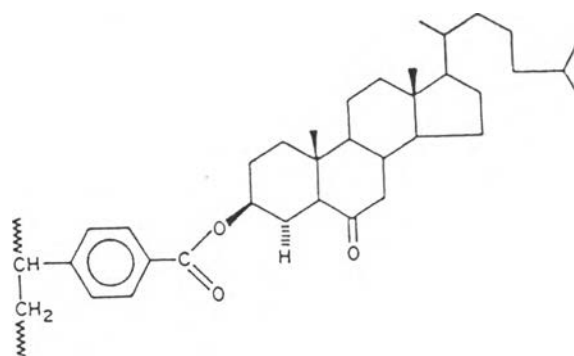
(VII) X=Y=Br (IX)

(VIII) X=H; Y=Cl
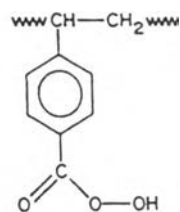
(X)

2.2.5 Stability of polymer-bound catalysts

Analysis of the operating windows in which polymer-supported catalysts will be stable is important for evaluating the possible commercial applications. Catalyst deactivation usually occurs by one or more of the following mechanisms : (i) leaching of the catalyst from the support as a

consequence of the lability of the bond between the transition metal and the functional group of the polymer ; (ii) thermal or chemical degradations of the polymer backbone or functional group under operating conditions and (iii) metal crystallite formation from the organometallic species in the polymer matrix. Examples of each and the consequences of such deactivation are described below.

2.2.5.1 Lability

Loss of the transition metal catalyst will occur if the metal-ligand bond by which the complex is attached to the polymer undergoes dissociation during the reaction. In the early 1970s , Moffat examined poly-4-vinylpyridine as a support for cobalt hydroformylation catalysts. He reported that the rate of the reaction was directly proportional to the concentration of soluble cobalt at reaction temperature. The pyridine-functionalized matrix was clearly functioning as a release agent for soluble cobalt carbonyl.

It is believed that lability problems are inherent to supported organometallic catalysts, since vacant coordination sites are generally necessary for substrates to be coordinated and transformed. It is thus clear that there will always be some concentration of extracted metal present in any process stream flowing over such a catalyst. Batchwise operation may be used to take advantage of equilibrium limitations ;

the equilibrium concentrations of dissociated metal complexes may be extremely small at low temperatures in the absence of substrate. Increasing the polymer-bound ligand : metal ratio and the use of chelating ligands are obvious strategies to limit dissociation ; however, the advantage of minimized metal loss is often compensated by the disadvantage of inhibition of the catalytic reaction by the ligand.

2.2.5.2 Chemical instability

It has generally been assumed that the bonds that link a catalyst to a polymer support are thermally and chemically stable under reaction conditions. The thermal stability of a particular polymer is easily determined by instrumental means, such as temperature-programmed decomposition. However, little information has been available to characterize chemical stability , since prolonged lifetime studies are needed for proper evaluation of slow deterioration of the polymer [8].