CHAPTER-I

INTRODUCTION

1.1 CATALYSTS AND CATALYTIC PROCESSES.

The phenomenon of catalysis is best described as a boon to chemical industry. The science and technology of catalysis is the cornerstone on which the edifice of modern chemical industry is built. By rendering chemical reactions more facile and providing simplified/alternate routes for them, catalysts offer significant gains in terms of economy, energy and better environment and thus help the industry to prosper. As shown in Table 1.1 decade after decade, newer and improved catalytic routes have ushered in an era of unprecedented growth in the industry (1) whose products have become the mainstay in day to day life. It is estimated that more than 90% of all industrial chemical products are manufactured by one or more catalytic routes. Its applications so far has been only for the production of large volume chemicals, but of recent, it is being extended to the regime of low volume-high value fine chemicals.

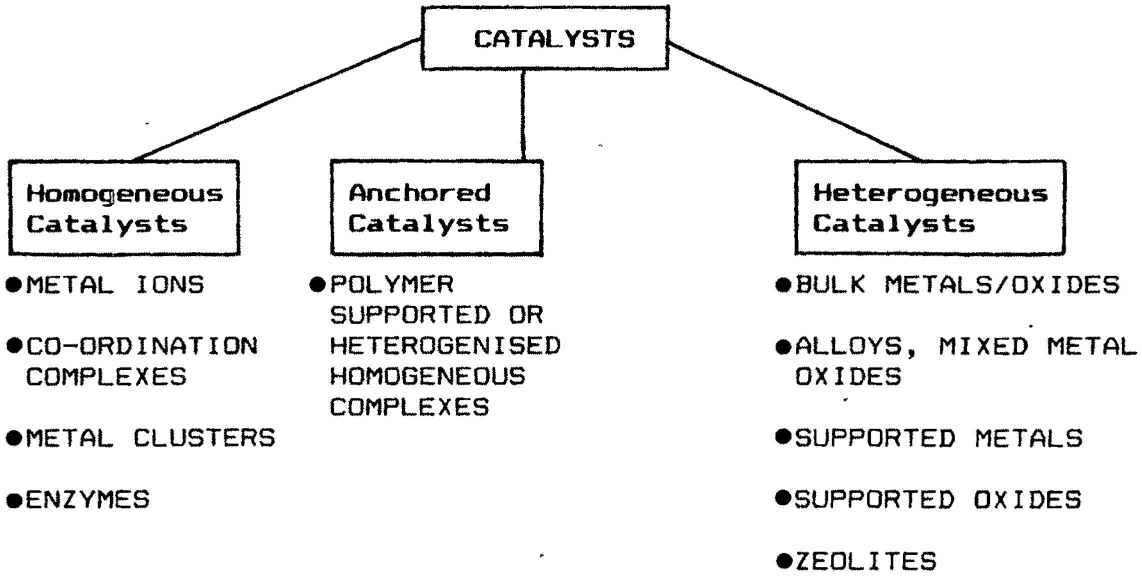
I.2. TYPES OF CATALYSIS/CATALYSTS.

While the classical approach to catalysis has resulted in the broad classification of catalysts into two types namely, heterogeneous and homogeneous, modern developments in science and technology of catalysis have brought in a third type, i.e., anchored catalysts. This third type is essentially a hybrid of the first two and of late gaining importance, since it combines the best features and eliminates the negative aspects of both types. As shown in Scheme I.1. metal ions, co-ordination complexes, metal clusters and enzymes constitute the bulk of homogeneous catalysts. Active metal complexes fixed on inorganic

TABLE I.1

Evolution of Industrial Catalysis

Decade	Example of Process or Product	Example of catalysts
1901-10	Hydrogenation of fats	Ni
1911-20	Coal hydrogenation to liquid fuels	Fe
	Ammonia synthesis	Fe
1921-30	Methanol from synthesis gas	Zn,Cr oxides
	Hydrocarbons from synthesis gas	Fe/Co
1931-40	Fixed bed catalytic cracking	Aluminosilicates
	Ethylene oxide	Ag
1941-50	Catalytic reforming	Pt
	Synthetic rubbers-SBR	Li or peroxides
	" Nitrile	Peroxides
	" Butyl	Al
1951-60	High density polyethylene	Ti or Cr
	Polypropylene	Ti
	Hydrodesulphurisation	Co,Mo sulphides
	Terephthalic acid	Homogeneous Co/Mn
	Hydrocracking	Pt
1961-70	Maleic anhydride	V, P oxides
	Acrylonitrile	Bi, Mo oxides
	Improved catalytic cracking	Zeolites
	Adiponitrile from butadiene & HCN	Homogeneous Ni
	Phthalic anhydride from O-Xylene	V, Ti oxides
1971-80	Methanol from synthesis gas	Cu, Zn, Al oxides
	Acetic acid from methanol & CO	Homogeneous Ni
	Linear low density polyethylene	Ti, Cr
	Alpha olefins via ethylene oligomerisation	Homogeneous Ni,Mo
	Improved hydroformylation	Homogeneous Rh
1981-90	Methanol to gasoline	Zeolites
	Acetic anhydride from synthesis gas	Homogeneous Rh
	Methylmethacrylate from tert-butanol	Mo oxide
	Improved coal liquefaction	Co, Mo sulphides
	Improved coal gasification	Metal salts
1990-	Shape selective catalysis	Metallo silicates
	Chemicals from C1 compounds	Noble metal based homogeneous catalysts
	Catalytic membrane reactors	Membranes containing active elements



SCHEME I.1. TYPES OF CATALYSTS

supports or polymers via functionalisation act as anchored catalysts. A variety of heterogeneous catalysts, namely, bulk metals/oxides/sulphides, alloys, mixed metal oxides, supported metal/metal oxides are widely used. The discovery of Zeolite catalysts has completely revolutionised the phenomenon of catalysis and broadened the horizon of its applications, owing to its unique features like shape selectivity and control of molecular traffic in zeolite pores.

I.3. SUPPORTED METAL CATALYSTS.

In general, supported catalysts are of two types;

(i) Supported base metal catalysts, and

(ii) Supported precious metal catalysts.

Both the types are equally important as industrial catalysts in specific applications. In supported catalysts, irrespective of base or precious metal, the catalytically active material is deposited on an inert or active support in a finely divided form (2). The adsorption of reactants which governs the catalytic activity of a material directly depends on the extent of dispersion of the active species on support. Hence the active species have to be present in a finely divided or micro crystalline form. Since most of the industrial reactions are carried out at high temperatures, these crystallites rapidly sinter and lose the desired high metal surface area leading to deactivation of the catalyst. Hence, they are supported on refractory materials like alumina, silica, clay, carbon etc., having adequate surface area to disperse the material. Some supports may have inherent catalytic properties which may be desired or undesired (3,4). Thermal and mechanical stability of the support materials at the operating conditions are as important as the features of the active species for a specific reaction (5). Finally, mass transfer constraints or diffusion problems forces one to select materials having optimum porosity (2).

I.3.1. Features of Supported Metal Catalysts.

As mentioned earlier, activity and selectivity of catalysts are determined by factors like, state of the active species (metal/oxide/sulphide/chloride), their location, geometry, etc. Hence, a proper way of incorporating the active species in the required form and suitable pretreatments to generate the necessary interaction between the active species and support are also important.

Deactivation of a catalyst can happen because of sintering of metal/support and by poisoning/masking of the active species by impurities in the feed or by some products of reaction which are irreversibly adsorbed. These factors can be controlled successfully by incorporating suitable elements other than the catalytically active ones, hence, modifying the adsorption properties and resistance to poisoning. They are known as promoters.

Hence, the above discussion makes it evident that the purpose of using supported catalysts is to achieve a high specific metal surface area consuming comparatively lesser amount of active material and retain it in the active form for the longer period. In order to achieve this ultimate goal of catalysis research i.e., preparation of a catalyst with (a) optimum activity, (b) maximum selectivity, (c) longer life, (d) easier regenerability & (e) ideal thermal, transport and mechanical properties, the following five aspects are to be considered in detail:

(a) Nature of active species.
(b) Nature of support.
(c) Method of incorporation.
(d) Pretreatments; and
(e) Selection of suitable promoters.

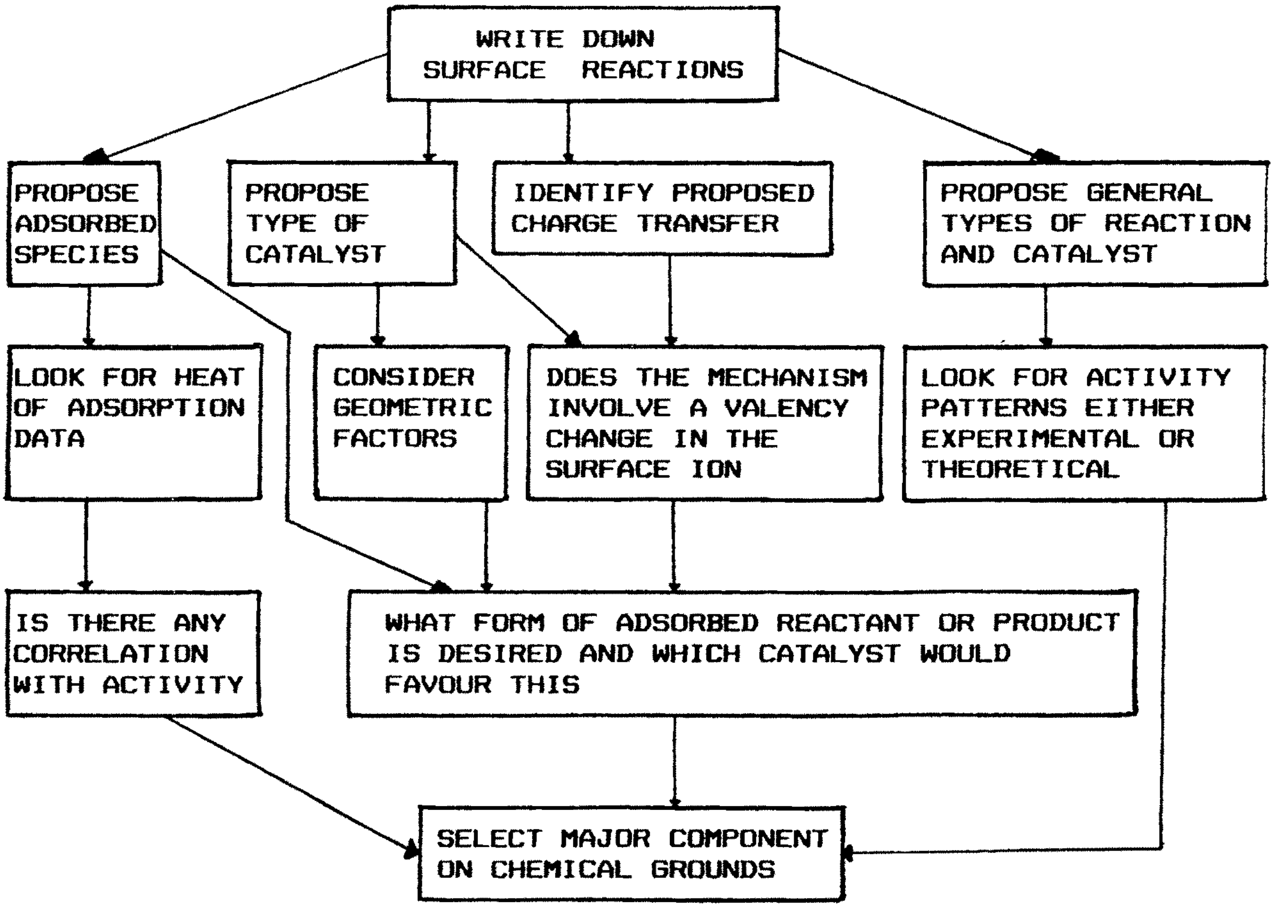
I.4. DESIGN OF CATALYSTS.

The design and development of catalysts with optimum performance which entirely depends on aspects listed above is the challenging job of a catalysis researcher. The progress in understanding the phenomenon of catalysis on a molecular level and the development of theories that describe the interrelationships between preparation - structure - properties - activity of catalysts, have, over a period of time, provided scientific bases for the development of catalysts (6). It is on this basis the choice of active phase, support, promoter, preparation and pretreatment methods could be made.

I.4.1. Active Species.

The choice of active phase to be used for catalysing a particular reaction can be performed only by considering the reaction in detail (2). The major desired reaction alongwith all possible side reactions have to be considered first, without any reference to the surface. Next stage is to recognise the types of reactions and general classes of catalysts, which have been used for each. Then a literature survey covering previous studies on the same reaction, studies on analogous catalyst-reaction systems and activity patterns of relevance can provide the general guideline to the required type of system. Now the next step is to convert the reaction mechanism in terms of adsorbed intermediates and surface reactions (6). This gives information about what is required from the catalyst. Correlating the activity patterns with the surface reactions and considering the bulk properties one can decide upon which system will be appropriate. Moreover, the geometry of the adsorbed molecule, possible charge transfer from or to the catalyst, formation of a bond etc have to be borne in mind. The application of ligand field theory and crystal field stabilisation can lead to valuable predictions in this aspect.

Another important factor is the active phase loading which has to be decided after considering the cost of the metal, solubility of the metal salts and specific activity (7). Moreover,



SCHEME I.2. CHOICE OF ACTIVE SPECIES (Ref 6).

the dispersion and distribution of active species will depend on adsorption properties of the salt solution which also have to be considered and modified accordingly (8,9). The Scheme 1.2 presented here gives in brief, the factors that are to be considered during the choice of active species.

I.4.2. Choice of Promoters/Poisons.

Promoters/modifiers are generally used along with the catalytically active species with an intention to modify the properties of the catalyst in order to achieve better activity, selectivity and stability. This may be effected either by modifying the properties of the support or that of the active species. Alkali metal additives used in dehydrogenation catalyst suppress the acidity of the support, avoid undesired cracking, isomerisation and dehydrocyclisation thus improving the selectivity whereas Sn, In, Re etc increase the activity and reduces coking providing a longer life through an electronic modification of the active species (46,47). Chloride additive improves the aromatisation activity of Pt/alumina reforming catalysts. Generally sulphiding is done in reforming catalysts in order to destroy the highly active centers and reduce coking. This is a sort of desirable poisoning. Thus various additives, modifiers and poisons are used at different stages in the preparation of catalysts. A more detailed review on this topic is given in Chapt.IV.4.

I.4.3. Nature of Support.

The choice of support has to be made on the basis of the properties of the active species, the nature of reaction, transport properties of reactants and products and conditions of reaction. The options for the selection of a support are really wide ranging from naturally occuring materials such as diatomaceous earth, kieselguhr, activated carbon, pumice, kaolin, bentonite, etc to inorganic supports such as alumina, silica, magnesia, zirconia, titania, alumino silicates, etc. The function of a support is to enable a large particle or tablet of catalyst to be made, composed of very small readily sinterable crystals of active phase which are stopped from coalescing by being separated from each other by the support component(2). Hence, a high surface area is an important prerequisite. But high surface area leads to increased dispersion and hence high activity. Loss of selectivity is generally a consequence of high activity and hence one should choose an optimum surface area rather than high surface area so as to maintain optimum activity (10, 11). Again, porosity of the support should be selected in such a way that the transport of reactants and products through the pores should not be restricted. This choice should be made based on the size of the molecules. Increased porosity will have an adverse effect on the mechanical strength, so an optimum porosity should be chosen such that the catalyst is suitable for continuous operations wherein thermal shocks are absorbed and attrition, crumbling/dust formation etc are minimal. Since some of the supports have inherent catalytic activity,selection has to be based on whether this inherent activity is desired or undesired. For example, in reforming catalyst (Pt/acidic alumina), the inherent acidity of alumina is desirable for dehydrocyclisation activity (3) whereas for dehydrogenation of paraffins (Pt/neutral alumina) this is undesirable since it promotes side reactions (4). Apart from this, the support may have some interaction with the active species which may modify the catalytic action. This factor known as Strong Metal Support Interaction (SMSI) helps in many systems to stabilise the active species and improve the activity (12-15,34). Hence the Metal-Support system should be chosen in such a way that the desired SMSI exists. Out of the supports mentioned earlier alumina, silica and activated carbon incorporate most of the desired properties in a modifiable way. But alumina is the most versatile support owing to the preparation variables which can be modified in such a way that the desired surface area, pore size distribution, pore volume, acidity etc. can be achieved (47). In view of such a complex role played directly or indirectly by the support, the choice has to be made judiciously considering the requirements of the reaction and properties of support.

I.4.4. Method of Incorporation of Active Species.

The third step in the design of a catalyst is the incorporation of the species on to the support. Either the support can be in a preformed state or both can be formed together from the solution simultaneously. A number of methods have evolved namely:

1. Equilibrium adsorption/ion exchange/wet impregnation.
2. Pore filling/dry impregnation/incipient wetness.
3. Co-precipitation.
4. Deposition precipitation.

First two are basically carried out on preformed supports whereas in the other two both the support and active species are formed simultaneously from solution. The choice of the method has to be done after considering the properties of the support and adsorbate solutions and the reaction.

1. Equilibrium adsorption/ion exchange/ wet impregnation.

A porous carrier is usually contacted with a solution containing one or more of the suitable metal ions for a period of time, then dried and calcined, to form the final catalyst. The variables in this method are nature of metal salt solution and its concentration, equilibration time (16), the presence of competitive adsorbate ions alongwith metal salt (17-19), pH of the solution etc. The distribution and dispersion of the metal in the resultant catalyst depends on the nature of the solution (metal salt/complex) (20), concentration of the solution and equillibration time (21). Thus, depending on the requirement (uniform/shell/core type distribution) the appropriate method has to be chosen. In solutions like chloroplatinic acid in water competitive anions like chloride are used, which get adsorbed on the highly active centres on the support preferentially, thus forcing the active species into the pores (17). On the contrarary, to prevent the deposition of palladium in the pores of alumina, palladium is impregnated by ion exchange with Na/Ni ions incorporated earlier (2). This way palladium stays on the periphery of the pores resulting in shell type catalyst and selectively catalyses hydrogenation of acetylene to ethylene. Generally inorganic acids like HCl, HNO_3 and organic dibasic acids, aromatic acids containing adjacent hydroxyl and carboxylic groups are used as competitive adsorbates (22).

The amount of the active component that can be impregnated by this method is limited by the adsorption capacity of the support and solubility of the salt. Since it is usually restricted to a monolayer or less, the method is most suitable for precious metals.

2. Pore filling/dry impregnation/incipient wetness method.

This involves the application of a fixed volume of solution, equivalent to the water pore volume, containing the active ingredients onto the support, uniformly and slowly by techniques like spraying. Later on the solvent is evaporated by slow heating. Again as in the case of equilibrium adsorption, dispersion is controlled by the concentration of the solution. The drying procedure is very important in determining the distribution of the active species. High rate of temperature rise will lead to inhomogeneous distribution. A steep rise in temperature causes preferential evaporation of liquid from larger pores. At the same time this concentrated solution will be transported to the dry smaller pores by capillary action. As evaporation progresses, crystalisation of the salt begins in pores still having solution and the crystal size of the metal salt is determined by the amount of the solution present. It is reported that when gamma alumina is impregnated with $CuCl_2$ solution a fast drying results in the migration of $CuCl_2$ to the outer layer of the pellet and hence to uneven distribution (22).

The limitations and advantages of this method are (i) the crystallite size distribution is broad and often reflects the pore size distribution of the support itself, (ii) increased metal loading results in loss of specific surface area (iii) solubility limitation of the salt solution limits the choice of metals narrow, and (iv) leads to concentration gradient across the pellet.

3. Co-precipitation.

This involves the precipitation of support and active precursor together from basic solutions as hydroxides, hydroxy carbonate etc. Experimental parameters such as the nature of the precipitant (ammonia , ammonium carbonate, sodium hydroxide, sodium carbonate etc), final pH of the solution, hydrothermal treatments, aging etc determine the structure of the material formed which is generally a complex one (23). The reducibility and dispersion of the metal depends on this structural modifications.

The reducibility of the catalysts prepared by coprecipitaation are generally low, but they give better dispersion. Lower pressure drop and better transport properties of the catalysts, which generally are achieved by a better control of the pore structure, is not possible in coprecipitation. Due to the low reducibility of these catalysts, separate high temperature reduction rather than in situ reduction becomes necessary and this leads to sintering. This method is especially useful for high loading of metal/metals.

4. Deposition precipitation.

This method involves the precipitation of the active species on to the surface of a carrier, by the addition of alkali to a suspension of the carrier in the metal salt solution.

Precipitated metal salt hydroxides distribute over the support. Base metal catalysts like Ni/silica and Cu/alumina are prepared by this method. The concentration and type of metal salt solution, support to metal ratio, nature and rate of precipitant addition, temperature of precipitation and pH of solution are the factors controlling the distribution and dispersion (24).

The inhomogeneous distribution of the precipitant due to the insufficient stirring will cause local super saturation and nucleation of the metal hydroxide both on the support and in the bulk of the solution giving rise to uneven distribution of the active species during deposition precipitation.

Hence, to avoid this, a modified deposition precipitation method is used,i.e. precipitation from homogeneous solutions(25). This involves the mixing of two solutions under conditions where precipitation cannot occur and then the conditions are gradually changed uniformly throughout the solution to the region where precipitation is permitted. Here, since the conditions of precipitation are approached gradually, the rate of nucleation and hence surface area can be controlled in a better way. This is generally achieved by using, instead of a base, compounds like urea or HMTA which can liberate base on heating by decomposition and cause a pH change (26,27). There are various other methods also like ion release (28-30), change of oxidation state (31), change in solubility (32), reagent synthesis (33) etc to carry out deposition precipitation.

I.4.5 Pretreatments.

Once the active species is incorporated onto the support, the excess solvent has to be removed by drying (22), without adversely affecting the deposited form of the active species. This step is very important in the pore filling/dry impregnation method. A slow uniform heating rate and a minimal required temperature develops a gradientless distribution across the pellet. The dried catalysts have to again undergo a high temperature treatment known as calcination in order to fire the active species on to the support surface firmly (34-36). The temperature of calcination has to be chosen keeping in view, the required species on the surface like chloride, oxide or mixed phases. However, the support characteristics also determine the temperature and duration of calcination. Since, from the mechanistic considerations of the reaction and types of catalyst, the form of the active species required on the surface is known, further treatments are to be designed in such a way that it results in the proper form of the catalyst. If a metal species is required on the surface, the catalyst should be reduced preferably "In Situ" as far as possible. Sulphidation, chloriding etc are steps required in some cases where undesired reactions are suppressed and selectivity for a particular reaction path/product is maximised.

I.5. DEVELOPMENT OF CATALYSTS: FROM ART TO SCIENCE.

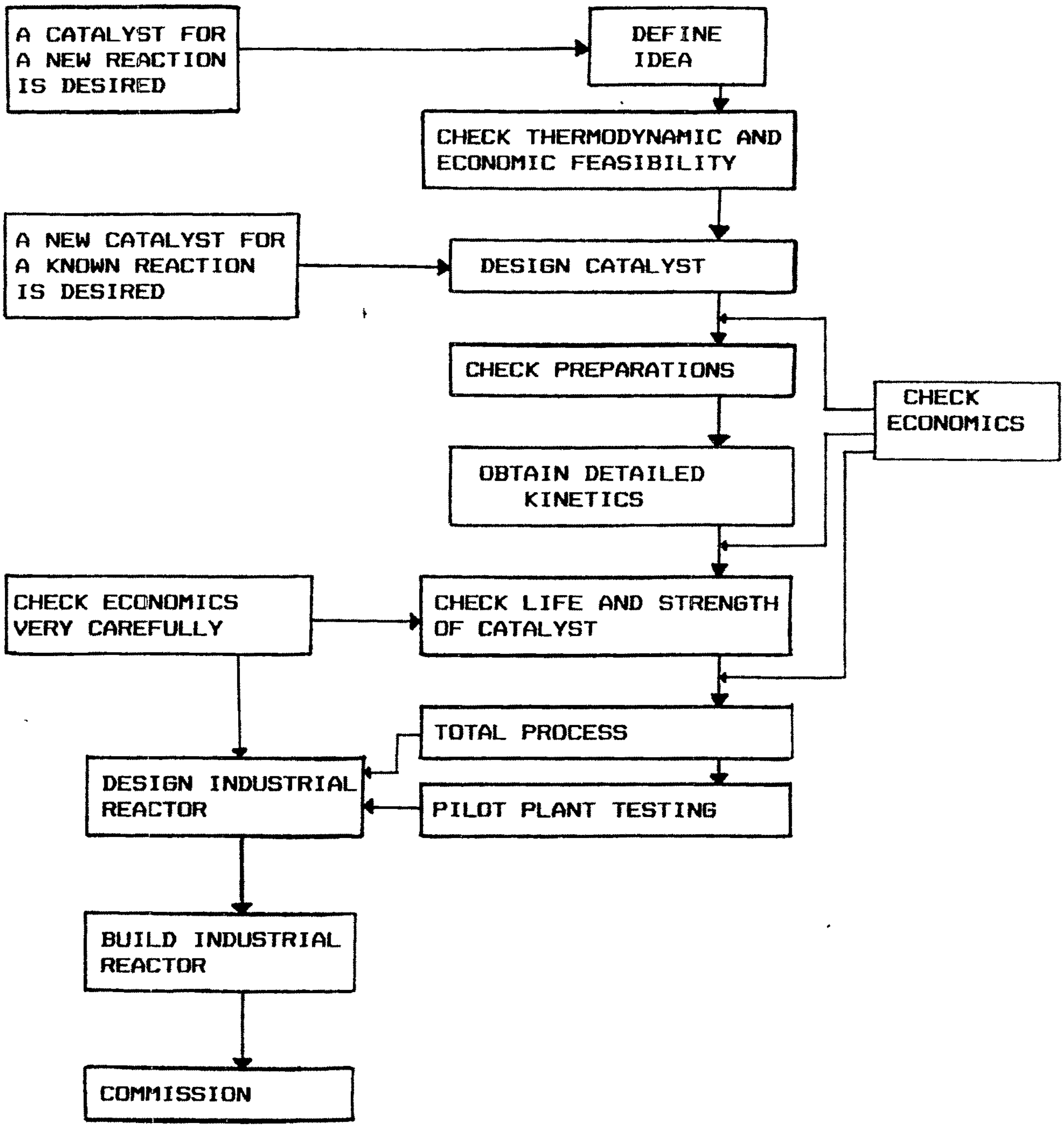
Thus the above discussed general formulation forms the basis of a scientific method of catalyst preparation. The proper identification of the requirements of a particular reaction combined with a deep knowledge of the resources will definitely reduce the time consumed and cost in arriving at a suitable catalyst formulation (5). However, it must be emphasised that it is not possible to select a catalyst on the basis of theory without really finding out its activity, selectivity and stability under the reaction conditions.

Another simple but time consuming way of doing this is by trial and error, i.e., Preparation and field testing of a number of of catalysts and then selecting the best one for the purpose on the basis of performance. This method was mostly adopted by the industrial chemists. This became popular due to the specificity of the reactions and the catalysts. The general rules of catalyst development do not guarantee any absolute success in the task. Thus, the industrial chemists adopted the method of making mysterious formulations and use them as catalysts (37). Hence, even though the preparation and use of catalysts in reactions of industrial importance are as old as the discovery of the reactions, the science behind the phenomena was not well understood. Thus the development of catalysts, rather than growing as a science, developed into a "**Black Art**". Most of the methods of preparation of commercial catalysts are proprietory and patented with minimum information available in the open literature.

But the developments in the last two decades have helped the preparation techniques of catalysts to achieve the approximate shape of a science rather than a proprietory art. Correlation of the activity of a catalyst to its characteristics irrespective of its performance should be possible based on concepts. This is the shape of the comprehensive theory which can rationalise the intricacies involved in the preparation and properties of catalysts. But even now there are many factors and minute details of the characteristics of catalysts and their performance which are not well understood or are in debate. The reason is mainly the inadequate understanding/characterisation of the catalyst. The characterisation of catalysts in the solid state and in a highly dispersed state alongwith a support poses a serious problem. Another important factor is, the surface species existing in the reaction conditions may be different from those existing when the catalyst is exposed to atmosphere or under simulated laboratory conditions. "In Situ" reduction, sulphidation, chlorination etc applied to catalysts during reaction increases its significance. Thus it will be appropriate to characterise a catalyst under "In Situ" conditions (153,167). This introduces serious instrumental limitations in some cases.

There are various experimental methods and techniques like SEM, TEM, ESCA, XRD, EXAFS, IR, UV-Vis, TPR, TPD, H_2-O_2 titration and model reactions which can provide direct and indirect information about the catalyst surfaces and the mode of their action towards catalysing reactions. Combination of a number of these methods can give sufficient and valuable information about the surfaces.

Once a well characterised and assessed catalyst is ready in hand, the next step in the commercialisation process is the understanding of the kinetics of the particular reaction on the



SCHEME I.3. FRAME WORK FOR CATALYST/PROCESS DEVELOPMENT.

catalyst based on which the design of the industrial reactor will be carried out. Scheme 1.3 presents the various stages of commercialisation of a particular process (6). The mass transfer characteristics of the catalyst, exo/endo-thermicity of the reaction, activation energy, the rate limiting/controlling step etc are necessary informations which can be gathered from a detailed study of the kinetics of the particular reaction on the specific catalyst. Remaining part of the job of the process development is mainly in the realm of chemical and mechanical engineers.

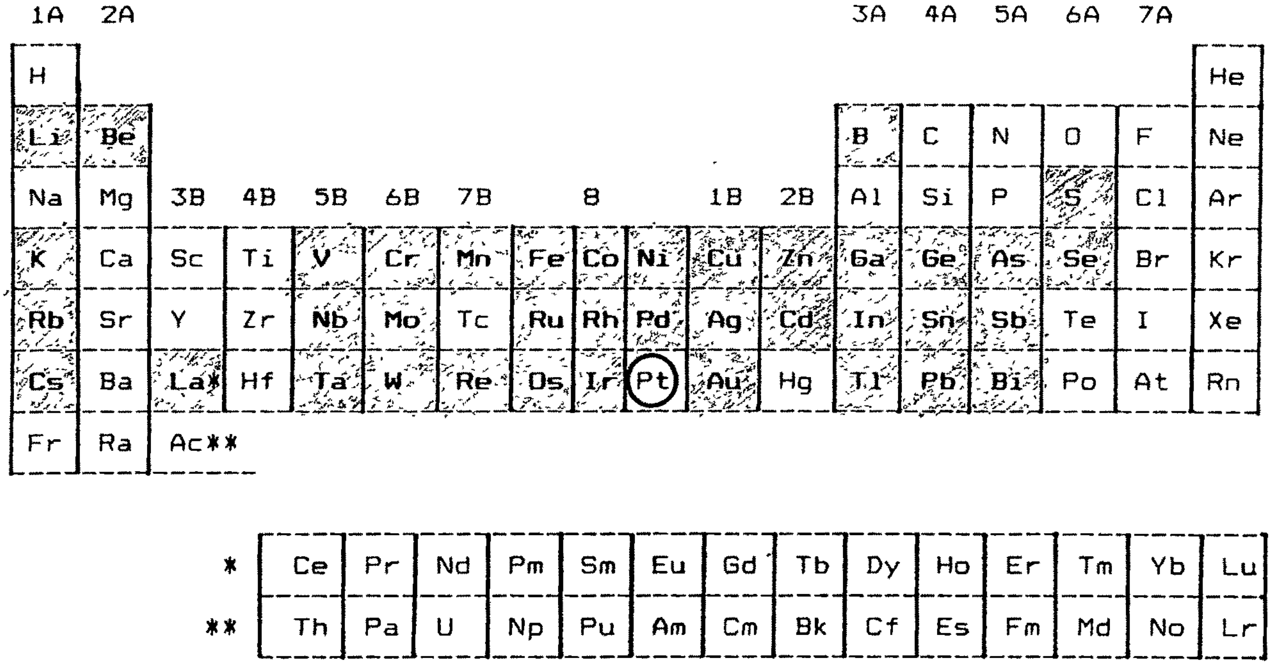
I.6. AIM AND SCOPE OF THE WORK.

Of the various types of catalysts mentioned in Scheme I.1 supported metal catalysts constitute an unique class, most widely used and extensively studied. All the five aspects of catalyst design, namely, active phase, support, promoters, preparation and pretreatments for catalysts of this type have recieved attention of a number of research workers. In the present investigation, emphasis has been laid on two vital aspects, namely, nature of support and role of promoters. To illustrate the influence of support and promoters, a model catalyst-reaction combination has been selected. Selective dehydrogenation of paraffins to monoolefins on alumina supported platinum catalyst has been chosen for a detailed study in view of its industrial application in the manufacture of biodegradable detergents. The n-paraffins, mostly in the range of C_{10} -C_{14} , on dehydrogenation give rise to corresponding mono olefins which are subsequently alkylated with benzene to give alkyl benzenes. Similar catalyst systems are being used also for the dehydrogenation of C_3 and C_4

paraffins to corresponding mono olefins.

In this particular reaction, the pore structure of alumina support is expected to play an important role, since the pores have to allow free diffusion of relatively bigger molecules of C_{11} to C_{14} paraffins and olefins. Though conventional methods of alumina preparation and pore structure modification are known, in this work the spheroidal gamma alumina was prepared by Sol-Gel method and attempts are made to modify the pores by the addition of carboxylic acids, during the preparation of alumina sol. This method is distinct from the addition of acids for peptisation or as filler materials to develop pores. It is expected that added carboxylic acid moieties enter into the sol matrix and change its characteristics. One of the objectives of the study has been to prepare alumina spheroids by the oil drop/sol-gel method and determine the pore structure modifications caused by the addition of organic acids.

Another interesting aspect chosen for study in this work is the role of promoter elements for the conventional Pt/alumina catalysts used for dehydrogenation of paraffins. As can be seen from Figure I.1 a number of elements have been used as promoters for this type of catalysts. The details regarding the composition of promoters and the methods of preparation are available only in patented literature. A number of publications illustrating the possible role of promoters like Sn, In, Tl, Ge, Pb, Ga and noble metals like Re, Rh, Pd etc have appeared from time to time. The promoting action is generally explained in terms of (a) ensemble effect, (b) ligand effect and (c) alloy formation. The promoters are reported to increase the activity



1A	2A	3B	4B	5B	6B	7B	8			1B	2B	3A	4A	5A	6A	7A	
H																	He
Li ▨	Be ▨											B ▨	C	N	O	F	Ne
Na	Mg											Al	Si	P	S ▨	Cl	Ar
K ▨	Ca	Sc	Ti	V ▨	Cr ▨	Mn ▨	Fe ▨	Co ▨	Ni ▨	Cu ▨	Zn ▨	Ga ▨	Ge ▨	As ▨	Se ▨	Br	Kr
Rb ▨	Sr	Y	Zr	Nb ▨	Mo ▨	Tc	Ru ▨	Rh ▨	Pd ▨	Ag ▨	Cd ▨	In ▨	Sn ▨	Sb ▨	Te	I	Xe
Cs ▨	Ba	La* ▨	Hf	Ta ▨	W ▨	Re ▨	Os ▨	Ir ▨	Pt	Au ▨	Hg	Tl ▨	Pb ▨	Bi ▨	Po	At	Rn
Fr	Ra	Ac**															

*	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
**	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Figure I.1. Promoter elements used for paraffin dehydrogenation catalysts (Pt/alumina) ▨

and stablity of Pt/alumina for paraffin dehydrogenation, even under severe operating conditions. However, an unified concept on the action of these promoters is yet to emerge, even in the case of Pt-Sn system, which has been studied in detail. Whether the promoting action is due to ligand effect or ensemble effect is not clear. While some propose Pt-Sn alloy formation the others do not (**152,153,167**). Sn is expected to modify the acidity of alumina and there by influence the electronic structure of Pt (**164**). Studies on the role of Group-III elements like Ga, In, Tl as promoters in Pt/alumina has been studied by Bursian and coworkers (**226**) who could identify and quantify both ligand and ensemble effects. However, according to their report In and Tl, which are isoelectronic have directionally different ligand effects.

Selectivity changes within Ga,In and Tl are not clearly understood. Apparently, there appears to be no firm basis on the selection of promoter to Pt atomic ratio.

In order to obtain a better insight into the role of promoters the following systematic study was planned. Promoter elements were chosen from IB(Ag), IIIA(In), IVA(Sn) and VA(Sb) so as to have a systematic change in electronic configuration. In all the cases Promoter to Pt atomic ratio 2:1 was maintained. Similar alumina support and methods of preparation were adopted except in the case of Pt-Ag system, wherein a double impregnation was carried out.

Detailed plan of investigation include:

(a) Preparation and characterisation of spheroidal gamma alumina by sol-gel technique.

(b) Modification of pore structure of alumina by the addition of carboxylic acids like acetic, propionic, oxalic, malonic, succinic, citric, tartaric and maleic acids.

(c) Preparation of unpromoted and promoted Pt/alumina catalysts (with Ag, In, Sn, Sb promoters separately) and their characterisation by metal dispersion, XRD, TPR, TPO, DRS and ESCA studies.

(d) Evaluation of activity, selectivity and stability of these catalysts for dehydrogenation of n-dodecane.

(e) Elucidation of the role of promoters on the basis of the results of catalyst characterisation and evaluation.

(f) Study the detailed kinetics of dehydrogenation of n-dodecane on a typical promoted catalyst.