



CHAPTER 2

CATALYST DESIGN AND PREPARATION

2.1 Introduction

Although catalysis in both organic and inorganic reaction was recognized more than a hundred years ago, our knowledge of catalytic phenomena is today still largely uncoordinated. The former, catalyst preparations was considered as the art which includes a very extensive "knowhow" of the procedures and experimental techniques employed in the preparation of solid catalysts (10). Realisation of the importance of catalyst preparation to the activity, selectivity and life of a catalyst has led to increasing interest in the scientific basis of different preparations. This, in turn, has led to improved performance, and to the necessity of defining carefully what catalyst should be prepared rather than optimising a catalyst that can be prepared. Know how about the chemical composition alone is not a sufficient guide in predicting the activity of catalysts. In many case, the physical characteristics of the catalysts, such as the surface area, particle size, pore size and crystal structure, determine its activity and selectivity for a specific reaction (11).

The chemical and physical properties of a catalyst are determined by the total history of its preparation. To obtain active catalyst it is important to use established procedure and experimental techniques.

2.2 The design of catalyst (12)

It is well known that the activity and selectivity of a heterogeneous catalyst depends on the inherent activity of the components, on the physical structure of the catalyst and on the operating conditions for the reaction. This has led to attention being focused on catalyst preparation, since this is a major point for control of chemical composition and physical structure of the catalyst. For a long time catalyst preparation was regarded as one of the last strongholds of alchemy, but the advent of modern methods of surface analysis, coupled with increasing scientific knowledge, have elevated the subject from an art to a science. As a result, it begins to be possible to manufacture a catalyst to a wide variety of given specifications.

We may know how to prepare a catalyst but it is necessary to ask which catalyst should be prepared. Therefore, this question covers factors such as chemical composition, physical structure and mechanical strength, the answer may well involve optimisation of several non-related parameters.

The interacting requirements of a catalyst complicate the decision as can be seen from Figure 2.1. It is not surprising that successful catalysts have been developed on an empirical basis. It is regrettable that our understanding of catalysis is still not good enough to guarantee success, but an approach has been found that is very useful in explaining why a given catalyst is active and, in some cases, in successfully predicting new catalyst. Thus time needed for catalyst design can be significantly decreased.

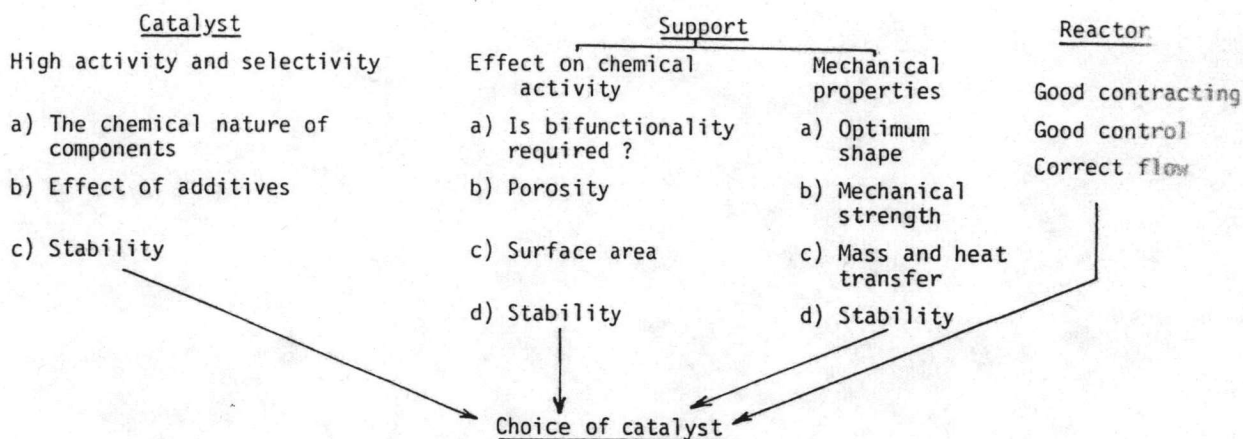


FIGURE 2.1 Factor in fluencing catalyst selection

2.3 Initial Stage of the catalyst design

In Figure 2.2 is a summary of catalyst design process. The starting point for the design requires the definition of the objective and a statement, in the form of chemical reactions, of desirable or undesirable reactions which may occur. Thermodynamic and economic calculations can then be used to establish the most attractive route.

2.4 Selection of the chemical basis of the catalyst : major components

From the experience, it is shown that one difficulty can arise at this point, because of our scientific training, we tend to think linearly, rather than to consider all of the possibilities that exist. It is better to consider a wide variety of reactions rather than to ignore one totally new approach.

The tools sre used to identify possible catalysts range from empirical observations to theoretically based calculations. The first step in the process is to translate the reaction mechanism in terms of adsorbed intermediates and surface reaction; this allows close definition of what is required from the catalyst. For example, the

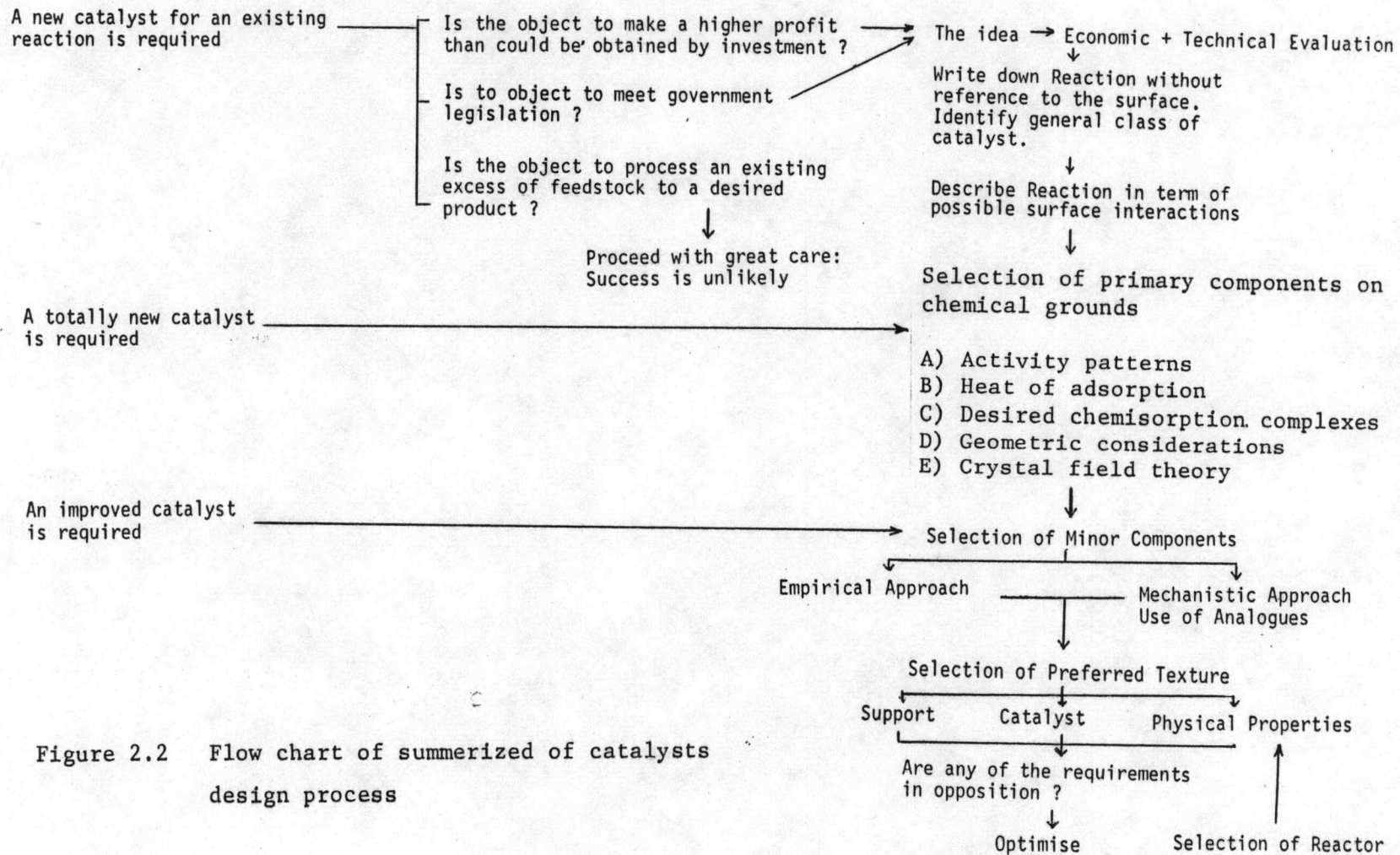
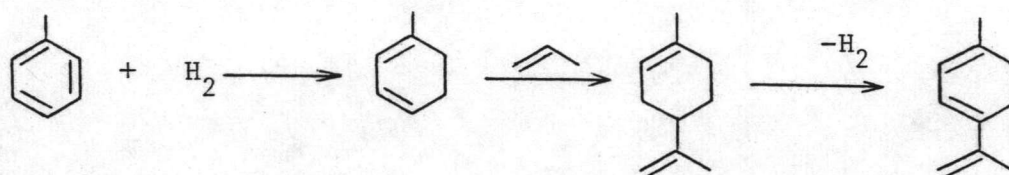
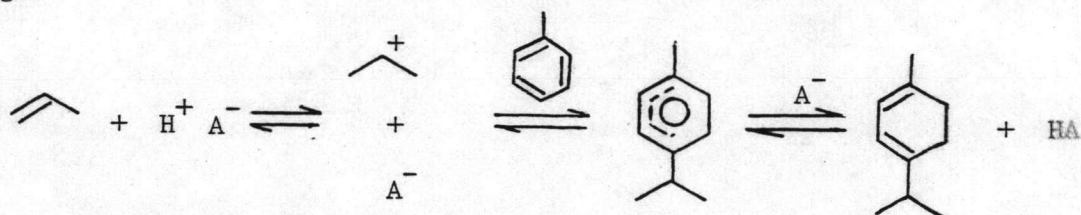


Figure 2.2 Flow chart of summarized of catalysts design process

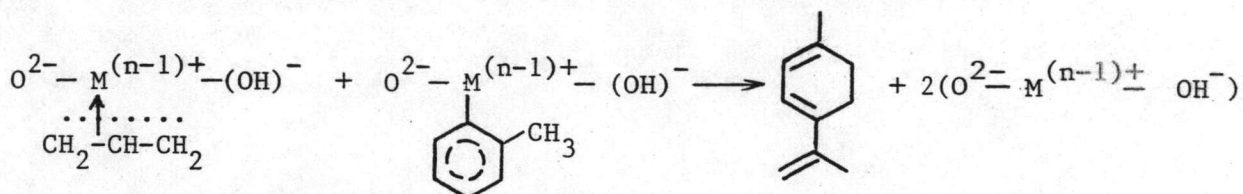
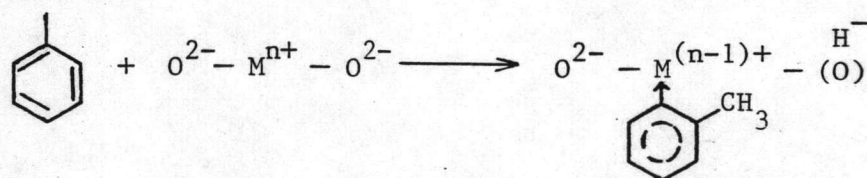
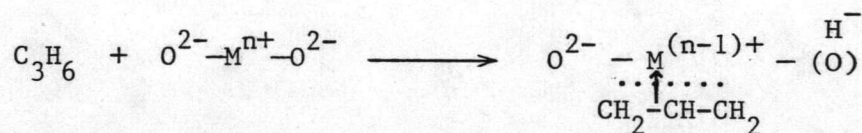
production of limenene which is a member of the terpene family that have considerable importance as solvents. A combination of thermodynamic and economic calculations showed that the following reaction sequence was most attractive.



The reaction path way involves hydrogenation and dehydrogenation as well as alkylation, which is normally carried out over acidic catalysts, but an oxidative coupling is also possible. For the acid catalysed reaction the surface reaction may be summarised as



The surface oxidation reaction may be written as



This is only simplified reaction path way which serve to illustrate the transcription of the reaction to the surface, of course, there will be many other possibilities.

2.4.1 Activity patterns The available patterns of activity of catalysts are the most useful guide for reactions of the same type, and these may vary from the simple pattern well known for the decomposition of nitrous oxide (Figure 2.3) to the more complicated patterns for hydrogenation (Figure 2.4), and oxidation (Figure 2.5). Generally it is possible to find an activity pattern for a class of solids which catalyses a type of reaction.

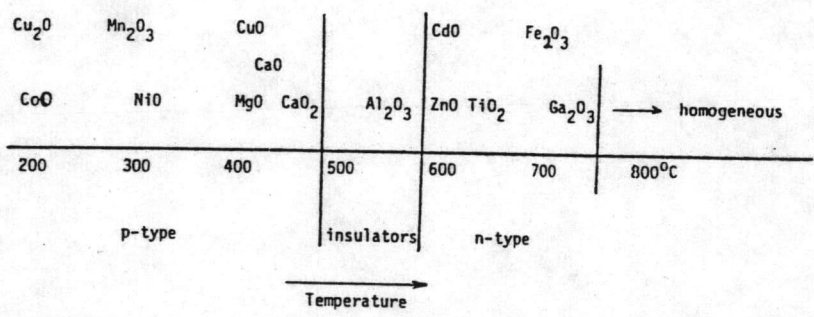


Figure 2.3 Activity pattern for nitrous oxide decomposition (Temperature at which different oxides catalyse the decomposition of N_2O). (12)

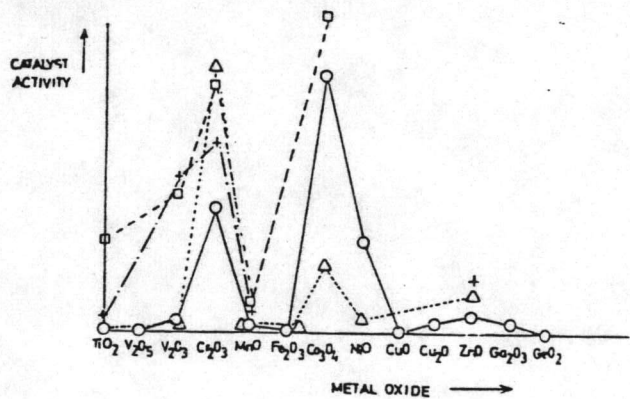


Figure 2.4 Activity pattern for reactions involving hydrogen
 ○ H_2/D_2 exchange at $80^\circ C$
 + propane dehydrogenation ($550^\circ C$)
 △ ethylene hydrogenation (-120 to $400^\circ C$)
 □ cyclohexene disproportionation (200 to $450^\circ C$) (12)

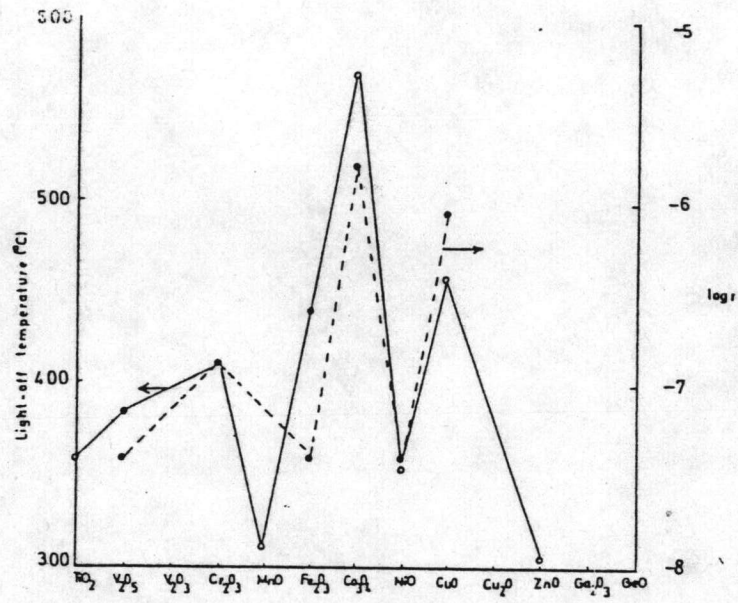


Figure 2.5 Activity patterns for oxidation

— light off temperature for Pt/Rh gauzes doped with metal oxide and used to catalyse the oxidation of ammonia

---log rate of oxidation of propylene at 300°C. (12)

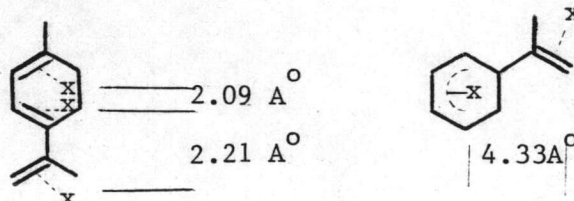
It should be remembered that activity patterns give only an idea of the relative activity of catalysts, unless they refer to the specific reaction in question.

2.4.2 Predictions from heats of adsorption In a few cases it is possible to predict the most active catalyst on the basis of heats of adsorption. This approach is more theoretically justified in that, if adsorption is too strong, a gas will not be displaced from the surface or will not react. If adsorption is too weak, the residence time of the adsorbed gas on the surface will be too short to favour reaction. By using arguments of this type, it has been possible to identify the most active catalyst for the hydrogenation of nitrogen and for ethylene and similar arguments can be used for analogous reactions. Prediction of optimal catalysts does depend, however, on the availability of heats of adsorption data.

2.4.3 Predictions on the basis of geometric considerations

One of the more useful methods of predicting catalytic activity arises from consideration of geometric factors. The concepts that geometry of the catalyst can affect activity has been recognised for many years, and formed the basis of the multiplet theory of catalysis.

Predictions are made on the basis of matching bond lengths of adsorbed species with crystal parameters of catalyst. Thus, for example, alkylation reactions to produce limonene could favour the products.



where x is an adsorption site.

These type of arguments can be easily extended to consider terraces or edges on the catalyst surface. One apparent difficulty lies in the fact that the surface structure does not always mirror the bulk, but the fact remains that predictions made on this basis are often accurate.

2.4.4 Nature of chemisorbed complexes It is obvious that the direction of reaction must be very dependent upon the nature of the adsorbed complex. Since there is usually more than one form of adsorption that is possible, catalysts should be selected which can be expected to favour the desired form.

Thus, for example, the formation of a pi bond requires the overlap of a filled, bonding pi orbital (π) from an olefin with an empty sigma (d_z^2) orbital of a metal if it is to be strong. Back donation from occupied d_{xy} , d_{yz} orbitals of the metal to the empty pi antibonding orbitals (π^*) of the olefin is also desirable. Considering, for example, square pyramidal coordination on the surface, such adsorbed species can only be formed on d^1 , d^2 , d^3 metals if only the d-orbitals are involved in bonding [V(2),(3),(4), T(1),(2),(3), Cr(3),(4),(5), etc.] and on d^8 , d^9 , d^{10} metals when both d- and p-orbitals are involved [Fe(0), Co(0),(1), Ni(0),(1),(2), Cu(1),(2) and Zn(2)].

Similar arguments can be applied to other adsorbed species to produce a table of solids that can adsorb different reactants or products in the desired form. Thus, for example, in considering the oxidation of olefins, possibilities of adsorption of reactants can be summarised as in Table 2.1.

the directional properties of bonds emerging from a surface in an approach which combines the present concept with geometric effects. Regrettably, for catalyst design, this approach is of limited value, in that we know little about how we should prepare a catalyst with a desired structure during reaction. There is no doubt that consideration of desired and undesired chemisorbed complex can be of great importance to a catalyst design. Success depends on how accurately the reaction has been transcribed to the surface (both desired and undesired reaction) and how feasible the proposed surface reactions are. This can only be determined by advanced surface analysis or by analogy, from experimental testing of proposed catalysts.

2.4.5 Crystal field theory The relatively modern theories advanced to explain the behaviour of inorganic complexes have been found to offer a good description of chemisorption and catalysts : these include the crystal field and the ligand field theories. The basis of the theories lies in the fact that d-orbitals are known to have directional properties and, if a transition metal ion is associated with these orbitals can vary. The nature of the ligand and the nature of the complex (high spin or low spin) can obviously affect the energies, but the geometry of the complex, as dictated by the coordination, is very important.

The energy changes that occur on formation of such complexes depend on many factors, of which the crystal field stabilization energy is one. Chemisorption, the addition of a ligand to a complex, results in a change in geometry of the complex. This, in turn, alters the crystal field stabilisation energy. Since catalysis involves

reaction of the chemisorbed complex, either to a new chemisorbed molecule or to a desorbed product, it is not surprising that the same effect can be seen in both cases.

Arguments on this basis provide a useful tool for prediction and provide a theoretical basis for many of the observed activity patterns.

Application of the different approaches summarised above can be expected to suggest several possibilities for the basis of the catalyst.

2.5 Selection of the chemical basis of the catalyst: minor components.

The objective of this part of the design is to improve the performance of the catalyst which is performing less well in some respect(s) than is desired. To improve the performance of catalysts, two approach are possible :

1). Trial and error approach which easy to apply and often produces results. For example, if the reaction produces chemical via a reaction path involving an excess of one reagent (say CO_2), addition of a minor component designed to decrease the amount of CO_2 adsorbed is easily carried out. Although such an approach is pragmatic, it usually works.

2). Mechanism approach : this approach is more intellectually stimulating and almost certainly work. The basis of the method is to delve deeply into the mechanism of the reaction, on the grounds that understanding the mechanism allows optimal fine tuning of the catalyst. The disadvantage is that it usually takes considerable time and effort.

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This is generally correct, but there is a closed circle in the sense that a catalyst must be of considerable interest to warrant the necessary attention and yet the the catalyst may only be of sufficient interest once it has been improved. As a result, detailed studied of this kind are usually carried out only for catalysts which are in current use, but which could be improved.

To studying the mechanism, there are two ways in order to fine tune the catalyst; the most widely used way is to study reactions on the surface by using recently developed analytical techniques. The second method involves studies of the analogous catalysts, in which it is possible to control such as the location or valency of one components of the original catalyst.

2.6 Selection of the preferred form of the catalyst

The morphology of a catalyst is of interest to catalyst preparation for two reasons, which may be called micro and macro effects. For micro effects, it is used as a general term covering the desired crystallinity, surface area, porosity, etc, of the catalyst, while the macro effects covers such factor as pellet size and strength of the catalyst. For example, in the case of alumina, where the variation in crystalline size, localized variation in phase change or heating, and homogeneity (in crystallite dimensions) were found to have a major effect on attrition and crush strength. The strength of catalysts is related to surface area and porosity and these factors also have a large influence on activity and selectivity, in that they have influence mass and heat transfer in the system.

The variation in porosity and surface area that can be achieved using a pure catalyst is limited by the preparation method available

and by the fact that such materials tends to sinter rapidly. As a result, it is usual to introduce the desired characteristic primarily through the use of a suitable support. There are several other factors which can influence the choice of support as shown in Table 2.2.

Table 2.2 Factors that influence the choice of support (12)

Choice of support

Chemical factors:

1. Is the support required to show catalytic activity ?
2. Are chemical interaction with the catalyst possible ?
If so, are these desired or un desired ?
3. Can the support interact with reactants or products ?
Is this desired or undesired ?
4. How resistant is the support to poisoning ?
5. Can the catalyst be deposited on the support in desired form ?
6. Does the support induce the particular coordination geometry on the catalyst ?
7. Is the support stable under operating conditions ?

Physical factors:

1. What is the desired surface area and porosity ?
2. What is the desired thermal conductivity ?
3. Is the support mechanical strong ? Would this be affected by deposition of poisons, such as carbon ?
4. Is the support stable under the operating conditions ?
5. What is the desired form of the pellet ?

Recent studies have revealed that chemical interactions between the catalyst and the support may be more important than was previously thought. Of course, it has been long established that bifunctional catalysis is of major industrial importance and the chemical interaction between the support and the catalyst may be desirable or undesirable. It has emerged comparatively recently that the support may be able to induce a given geometry on a catalyst without formal chemical interaction, and this will influence on the adsorption and catalysis.

However, it is probably the physical properties of the support which are primarily responsible for its selection, provided that these are consistent with desired chemical properties. Mechanical strength, porosity and surface area are important, as well as stability with respect to temperature, etc.

In addition, we have to consider the environment in which the catalyst will be used, both with respect to stability and with respect to the reactor. A general guide to the factors that influence the choice of reactor is given in Table 2.3.

Although we begin to know how to prepare a catalyst with a given structure, but we know little about how to retain this structure under reaction conditions. The concept of structure sensitive and structure insensitive reaction is well established, and some assessment can be made of the nature of a given reaction by using the criteria outlined in Table 2.4. It should be emphasised that this table has no theoretical justification, experimental observations indicate that the greater the number of criteria satisfied by a given reaction, the greater probability that a reaction is demanding or is facile. The number of edge and corner sites on a catalyst will be much higher with smaller crystallites.

2.7 Catalyst preparation.(11)

Finally, it is necessary to consider correlation of the suggestions from the design procedure with what can be practically achieved by catalyst preparation. To obtain active catalysts it is important to use established procedures and experimental techniques. In describing the preparative methods used in catalyst compositing, one assumption is made, namely, that the composition desired to

Table 2.3 Factors that influence the choice of reactor (12)

<u>Reactor</u>	<u>Advantages</u>	<u>Disadvantages</u>	<u>Form of catalyst pellets</u>
Gas-solid reactor (tubular)	Widely used and well understood	Temperature control may be difficult	Pellets. Effectiveness factor, 0.6
Fluid bed	Good temperature control. Useful where catalyst needs frequent regeneration	Bad mixing. Catalyst attrition. Difficult to operate.	Fluidisable particles (e.g. 40-70 microns) good attrition stability
Trickle bed	Allows good gas-liquid-solid contacting. Good temperature control	Difficult to operate. Foaming. Splashing.	Small particles, open porosity, high surface area
Homogeneous catalyst reactor	May give good selectivity at low temperature	May be difficult to separate products and catalyst. Although "anchored" catalysts are now fashionable	
Slurry reactor	Good temperature control	May involve difficulties in gas-liquid-solid contacting	

Table 2.4 Summarized the choice of desired and undesired structure of prepared catalysts (12)

Structure insensitive (facile) reactions may be:

1. addition reactions or elimination reactions
2. reactions involving a large decrease in free energy
3. reactions involving reactants with lone pair electron or pi bonds or strain energy
4. reactions that not require a multifunctional catalyst
5. reactions occurring on an active catalyst whose lattice parameters do not change with dispersion

Structure sensitive (demanding) reactions:

1. may occur on certain sites, e.g. N_2 chemisorbs only on W(111) and NH_2 is produced only on W(111)
2. involving single C-C bond breakage
3. may involve reactants with no lone pair electrons, pi bond or strain energy
4. need a multifunctional catalyst
5. need a less active catalyst whose lattice parameters change with dispersion
6. may involve reactants with unpaired electrons, e.g. NO

catalyze a specific reaction is known. A great many catalysts can be prepared in a variety of ways, while a smaller number can be prepared in only a very highly specialized manner. In the former case, the actual choice of methods may be guided by ease of preparation, homogeneity of the product, stability of the catalyst, and ease of duplication. The various methods of catalyst preparation may generally be considered as a combination of certain unit operations.

2.7.1 Method of preparation

1) Precipitation : This method is frequently employed in the preparation of single and multiple component catalysts. Precipitation techniques are applicable to materials such as the hydrous oxides, sulfides, carbonates, and phosphates. In general, one starts with aqueous solutions of constituents and adds the required precipitating agent. One of the primary problems arising in the preparation of a precipitated catalyst is that of purification from occluded or adsorbed impurities. (To minimize the presence of such impurities, one way, is to carry out the precipitation by mixing very dilute solutions.) Another method is to use ammonia or ammonium salts as the precipitants along with nitrates of the desired metals. The resulting precipitate then requires a minimum of washing, since any adsorbed material remaining can be removed by calcination of the product. The use of nitrates as the source of the desired cations is recommended as a general rule unless otherwise specified. The reason for this is the fact that other anions (e.g., chloride or sulfate) sometimes act as catalyst poisons, if they are present in the final product.

In the case of co-precipitation of two or more components, it is generally desirable to maintain the greatest possible degree of

homogeneity in the product. Since normally the solubility products of the constituents are divergent, it is possible to obtain a decidedly heterogeneous product. Such a situation would exist, for example, if one were to add a solution of aqueous ammonia to a solution of two metal nitrates to coprecipitate the two corresponding hydrous oxides. The ammonia would tend to precipitate with the first one than the other. On the other hand, revising the procedure by adding the solution of the two nitrates to the ammonia solution would tend to give simultaneous precipitation of the two hydrous oxides. It is true that in the latter procedure the pH would change continuously throughout the process of precipitation. If a constant pH is desired, the method would have to be modified. To achieve the goal of precipitating at a constant pH it may be necessary to bring together two streams of the reacting solution in such proportions as to maintain the desired pH.

Alternatively, it is possible to maintain homogeneity of a two component precipitate by dissolving one of the reactants in an acid solution and the other in a basic solution. For example a silica-alumina coprecipitate may be made by mixing dilute solution of aluminum sulfate and sodium silicate. To increase the surface area of the product can be achieved by precipitating the catalytic material on a support material.

2). Gel Formation This particular method of catalyst precipitation is especially suited to those catalysts whose major components are hydrous oxides. In particular those containing primarily silica or alumina are especially amenable to gel formation. The phenomena of gel formation is as mentioned, merely a special case of precipitation. Therefore, precipitation of a catalyst composite in gel form rather than as a coprecipitate does not necessarily result

in a change in specific catalytic activity. However, even when no such change occurs there are frequently major physical advantages to gel formation. In addition, the maximum homogeneity in the polycomponent composites can be produced by gelation. Gels may be prepared not only in aqueous media but also in nonaqueous and mixed media. For example, alcoholates prepared from the various metal chlorides may be dissolved in alcohols and gelled either in the alcoholic or alcohol-water media.

3). Impregnation methods : The simplest possible method of producing a catalyst is the technique of impregnating an active component (or components) on an inactive support. However, in such a simple method of preparation, a number of complicating factors arise. Impregnation of a support normally involves the use of a soluble compound of the desired constituent dissolved in a liquid, which is usually water. The method of impregnation in catalyst preparation can be achieved in many ways which depend on the nature of support and active component.

3.1). Impregnation of granular supports The simplest form of this method may involve the following steps :

- (1) evacuating the support
- (2) contacting the support with the impregnating solution
- (3) removing the excess solution
- (4) drying
- (5) calcination and activation

Frequently it is necessary to add a precipitation and washing steps either before or after drying.

Generally, it is desirable to obtain preliminary information regarding the equilibrium distribution of the solution between the solid support and the impregnating solution. Such information is necessary to establish the quantity and concentration of the impregnating solution required to obtain the desired concentration of the active component on the support.

Evacuation of the support prior to contacting it with the impregnating solution gives more uniform distribution of the active component. An excess of impregnating solution is usually used, and is removed by filtration, decantation or evaporation. However, in many cases the use of excess impregnating solution is undesirable.

Whether a precipitation step is necessary or not depends on the nature of the impregnating compound. If no undesirable compound remains after simple calcination, no precipitation will be required. However, if the impregnating compound involves an undesired component in the final product, it is probably necessary to precipitate the desired constituent and then to wash out the desired material.

3.2) Impregnation of powdered supports : Powdered catalyst supports may be impregnated in a manner entirely analogous to that described for granular supports, with the additional steps of pelleting or extruding to form the final particles. In some cases the active component(s) will be precipitated by the support, it may be advantageous to impregnate with powdered supports. Occasionally, this method may be used where the active component is expensive.

3.3) Vapour phase impregnation : In some case, the active component is a vaporized source, therefore to deposit the active material on a support may be achieved by flow a stream of active

component passing through the support under certain circumstances.

However, there are others techniques which may be applied for catalyst preparation. Examples of these are; 1) thermal fusion, 2) chemical reaction, 3) evaporation of metals.

2.8 Processing operations :

For heterogeneous catalysts to obtain the desired catalyst these following treatments are required :

2.8.1 Washing : The object of this step is primarily to remove impurities from the desired product. Therefore, for this reason many impregnated catalysts need not be washed. The method of washing vary to a great extent, depending on the method of catalyst preparation, and the nature of catalyst, etc.

2.8.2 Drying : In generally, drying techniques are used to insure contain desired physical characteristics in the products. Usually drying is carried out in air with the temperatures varying from 60 to 200^o C. Higher drying temperatures may result in severe fracturing of the gel particles so that the product cannot be tested without being pelleted. Therefore, a safe working range would be from 100 to 150^o C.

2.8.3 Ion-exchange : In some case, especially, when a coprecipitate possesses zeolitic properties, washing alone will probably not be sufficient to remove all contaminating ions. In these case ion-exchanging operation will be required.

2.8.4 Calcination and activation : Calcination and activation take several forms depending on the type of catalyst being prepared

and reaction conditions. In general, the dried catalyst is calcined and activated at the temperature at least as high as those used in the reaction, and is carried out while a large volume of purge gas is passed through or over the catalyst to maintain a low partial pressure of the evolved vapours. These steps represent the final operations in catalyst preparation.

2.8.5 Catalyst forming or sizing : It was stressed that the diffusion of reactants and products, particularly in connection with catalysts having small pores, have the effect in the catalytic reactions. Therefore, it is important to insure freedom from diffusion limitations by sizing of the catalyst.

For the most small scale testing of catalysts in fixed bed reactors, particle sizes between 6 and 30 mesh are used. In some case, if dried catalyst crumbles to a powder, or its structure is too weak to withstand the grinding or sieving operation, pelleting or extrusion is required. These latter operations require specialized equipment and knowhow to obtain the catalyst in desired shape and size.