

## THE DESIGN OF CATALYSTS

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### INTRODUCTION

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 (ref. 1), coupled to increasing scientific knowledge, have elevated the subject from an art to a science (refs. 2, 3). As a result, it begins to be possible to manufacture a catalyst to a wide variety of given specifications.

Although our capability is far from perfect, this possibility raises new questions. In particular, given that we may know how to prepare a catalyst, it is necessary to ask which catalyst should be prepared. Since this question covers factors such as chemical composition, physical structure and mechanical strength, the answer may well involve optimisation of several non-related parameters. While the bulk of the proceedings of this meeting will be concerned with how to prepare catalysts, this paper is focused primarily on how to decide which catalyst to prepare.

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. This paper describes a general approach to the problem of recognition of which catalyst should be prepared for a given reaction.

The design of a catalyst is discussed in terms of a flow diagram in which means of identification of major and minor constituents of a catalyst are inter-related. Factors influencing the choice of the chemical constituents are considered together with the choice of a support, which often depends more on the desired physical characteristics of the catalyst. Both theoretical concepts and empirical observations can be combined in the overall design to give a limited number of possibilities for experimental testing. Finally, correlation of suggestions from the design with catalyst preparation is considered briefly, with particular reference to impregnation and activation.

As can be seen from figure 1, the interacting requirements of a catalyst complicate the decision. As a result, it is not surprising that most successful catalysts have been developed on an empirical basis. In recent years, however, procedures have been developed to place the selection of catalysts on a more scientific footing. Generally, these involve a theoretical study in which general knowledge of catalysis, arguments by analogy and various theoretical concepts are applied to a particular problem (refs. 4, 5, 6, 7).

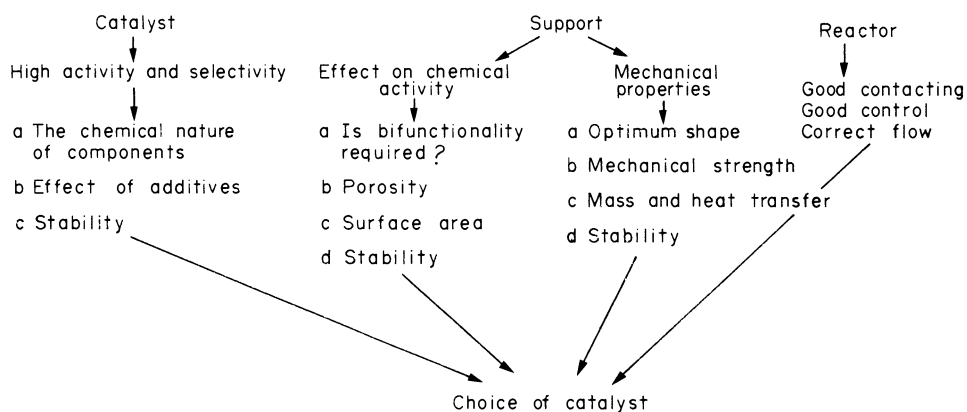


Figure 1. Factors influencing catalyst selection.

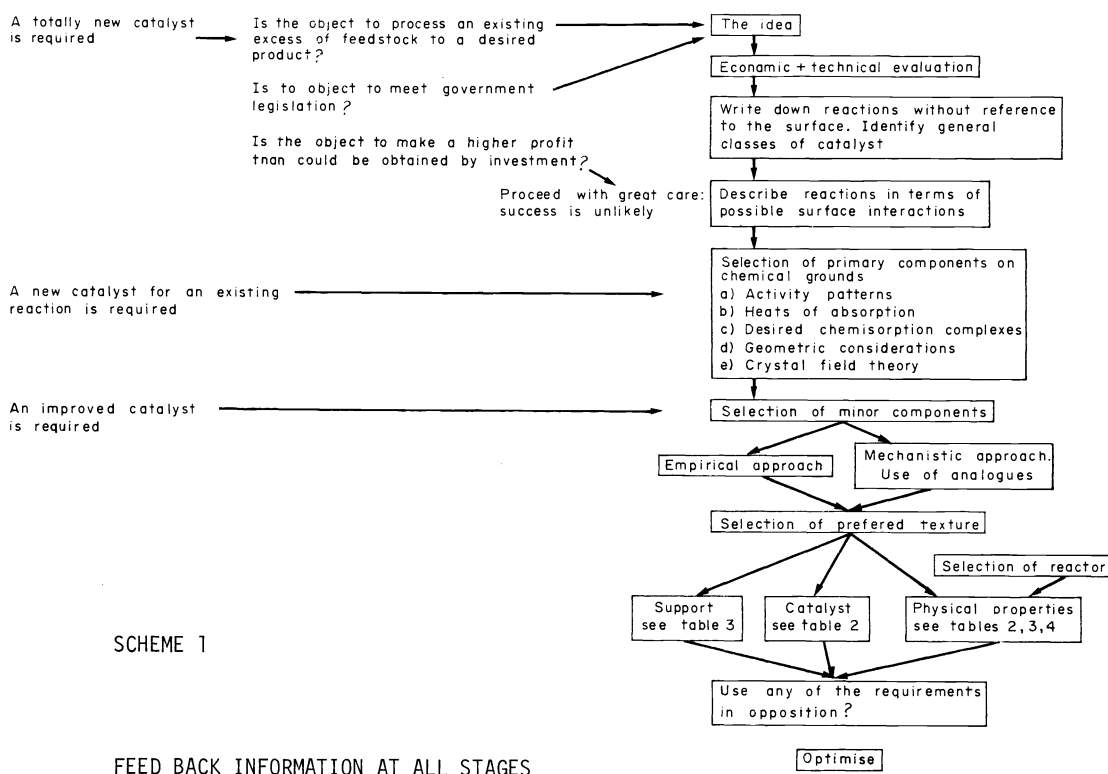
It is regrettable that our understanding of catalysis is still not good enough to guarantee success, but the approach has been found to be very useful in explaining why a given catalyst is active and, in some cases, in successfully predicting new catalysts (ref. 5). Insufficient knowledge is available to be independent of experimental testing, but the approach acts as a valuable guide to experimentation. As a result, the time needed for catalyst identification and testing can be significantly decreased, for the investment of only a short time on catalyst design.

The procedure has been discussed in a few papers in recent years (refs. 4, 5, 6, 7), usually with emphasis on a given reaction. A more general approach is attempted in the present paper, with particular emphasis on those aspects of design that are of interest in the context of catalyst preparation. The broader framework of the complete design is presented in reference 5.

#### Initial stages of the design.

The design process discussed below is summarised in scheme 1, and various entry points to the design are indicated. The extent and depth of a study depends on the effort warranted by a particular application and, in this article, the full design will be discussed.

The starting point for the design requires the definition of the objective and a statement, in the form of a chemical reaction network, of desirable or undesirable reactions which may occur (ref. 16). Thermodynamic and economic calculations can then be used to establish the most attractive route, and general types of catalyst that should favour individual reactions can be identified. This reaction network provides the basic outline of the design, to which it is possible to apply the catalyst selection criteria described below.



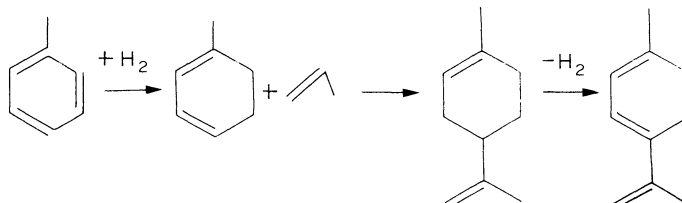
### Selection of the chemical basis of the catalyst: major components

At this point we are concerned with the identification of the major chemical components of the catalyst, and factors such as mechanical strength, surface area and porosity will be considered at a later stage.

Experience has 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 (and possibly to reject) a wide variety of reactions rather than to ignore one totally new approach.

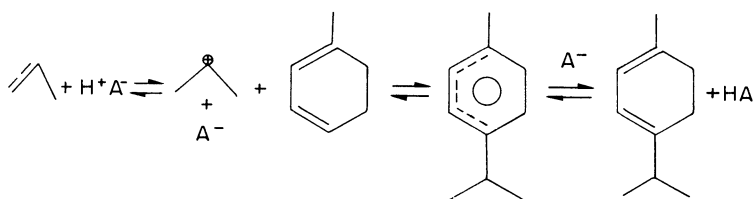
The tools that are used to identify possible catalysts range from empirical observations to theoretically based calculations. The first step in the process is to translate the reaction mechanism in terms of adsorbed intermediates and surface reaction: this allow close definition of what is required from the catalyst.

To illustrate this process it is useful to consider a specific example, such as the production of limonene (ref. 8). This is a member of the terpene family that have considerable importance as solvents. A combination of thermodynamic and economic calculations showed that the reaction sequence was most attractive.

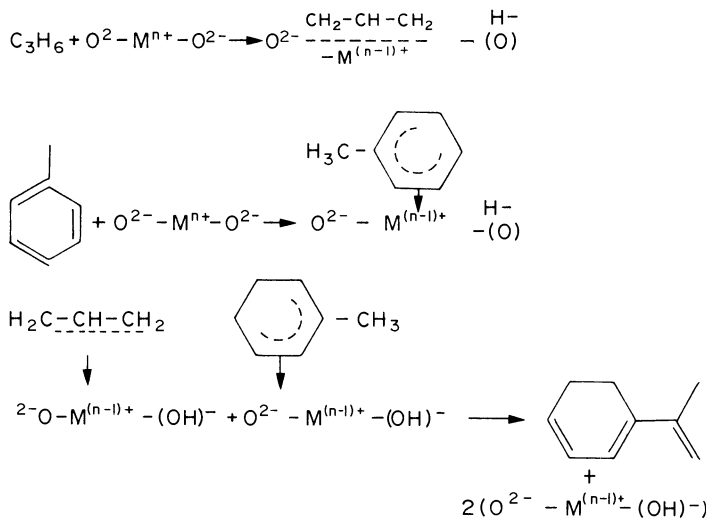


The scheme involves hydrogenation and dehydrogenation (catalysed by metals (ref. 9) or metal oxides (ref. 10)) as well as alkylation. This is normally carried out over acidic catalysts (11), but an oxidative coupling is also possible (ref. 12).

For the acid catalysed reaction the surface reaction may be summarised as (refs. 11, 13).



The surface oxidation reaction, on the other hand, may be written as (refs. 5, 12):



Of course, there will be many other possibilities, but these simplified schemes serve to illustrate the transcription of the reactions to the surface.

It is now possible to discuss different means of identifying active catalysts.

a) Activity patterns. By far the most useful guide, where they are available, are patterns of activity for reactions of the same type. These may vary from the simple pattern well known for the decomposition of nitrous oxide (figure 2) (ref. 10), to the more complicated patterns for hydrogenation (figure 3) (ref. 13) and oxidation (figure 4) (refs. 15, 16). Generally it is possible to find an activity pattern for a class of solids which catalyse a type of reaction. Activity patterns for metals catalysing reactions involving hydrogen are shown in figure 3 and for metal oxides involved in oxidation are shown in figure 4.

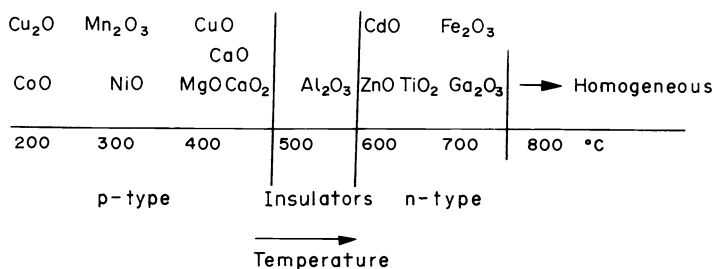


Figure 2. Activity pattern for nitrous oxide decomposition (Temperature at which different oxides catalyse the decomposition of N<sub>2</sub>O).

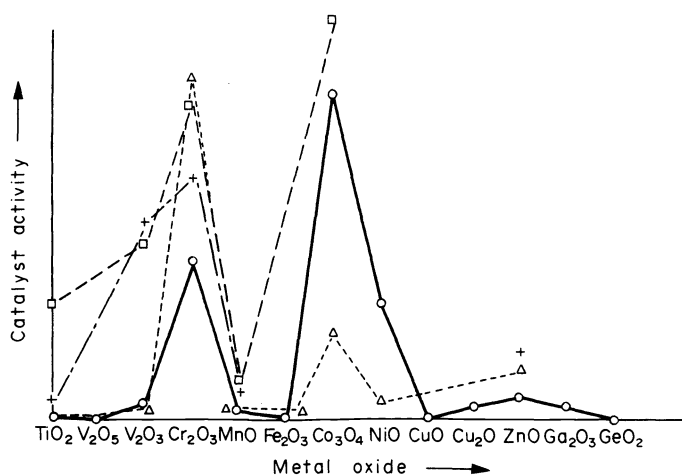


Figure 3. Activity pattern for reactions involving hydrogen

○  $\text{H}_2/\text{D}_2$  exchange at  $80^\circ\text{C}$

+ propane dehydrogenation ( $550^\circ\text{C}$ )

△ ethylene hydrogenation ( $-120$  to  $400^\circ\text{C}$ )

□ cyclohexene disproportionation ( $200$  to  $450^\circ\text{C}$ )

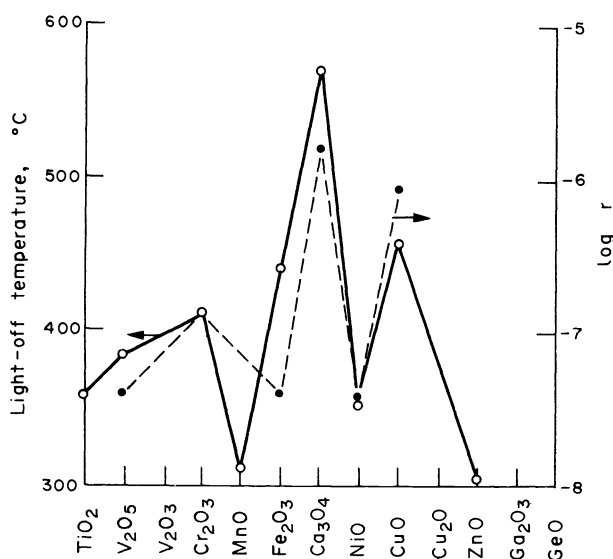


Figure 4. Activity patterns for oxidation

— 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  $300^\circ\text{C}$ .

A less quantitative pattern has been developed for metal oxides involved in acid catalysed reactions (figure 5) (ref. 17), while the activity of a bifunctional catalyst can be established with the aid of diagrams such as figure 6 (ref. 18). The position of the desired compound on the diagram determines the strength of the metal and acid functions desired.

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.

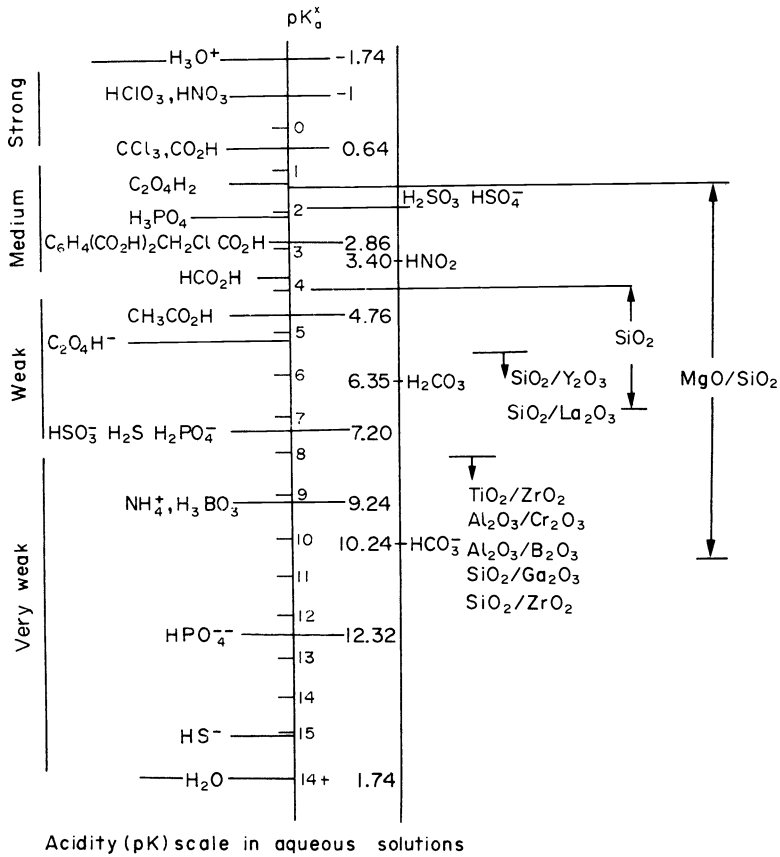


Figure 5. Orders of acidity of different materials.

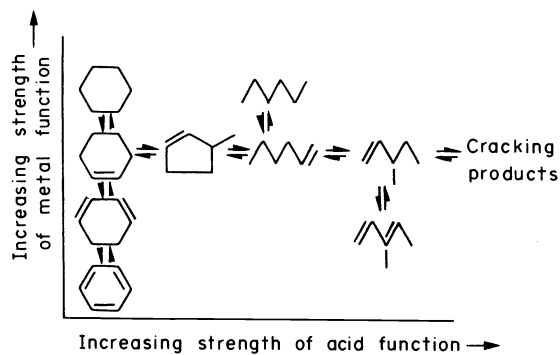


Figure 6. Bifunctional catalysis

**b) Correlations of activity with bulk properties of the catalyst.** In the past there have been several attempts to relate catalytic activity with the bulk properties of solids. Although these have fallen into disrepute with the realisation that the surface may have very different properties to the bulk, it is possible to obtain valuable pointers for catalyst design from the approach. Thus, for example, the concept of percentage d bonding (ref. 19) is open to

severe criticism, and yet these are some systems in which it is possible to relate catalytic activity with this factor (refs. 20, 21). Similarly, attempts to relate adsorption and catalysis with bulk semiconductor properties of oxides have been reasonably successful in explaining some patterns of catalytic activity (ref. 10), and should certainly not be ignored at this stage of the design. However, more accurate predictions should be obtained by considering the gas-solid interface.

c) 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, then 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. Using arguments of this type, it has been possible to identify the most active catalyst for the hydrogenation of nitrogen (ref. 22) and for ethylene (ref. 18), and similar arguments can be used for analogous reactions. Prediction of optimal catalysts does depend, however, on the availability of heats of adsorption data.

A somewhat similar approach has been used for oxidation catalysis, where various properties that indicate the strength of adsorption of oxygen have been correlated with catalytic activity. Boreskov (ref. 23) has measured the heat of adsorption of oxygen on some oxides and have also measured isotopic oxygen exchange between gas and oxides (ref. 24): their results are summarised in figure 7. Moro-oka (ref. 25), on the other hand, relates catalytic activity to the heat of formation of the bulk oxide (figure 8). It will be seen that all of these measurements may have a satisfactory theoretical explanation, even when the authors were not aware of this. Certainly the plots offer a guide to the selection of the most active catalyst, although it must be remembered that activity and selectivity in oxidation are often inversely related.

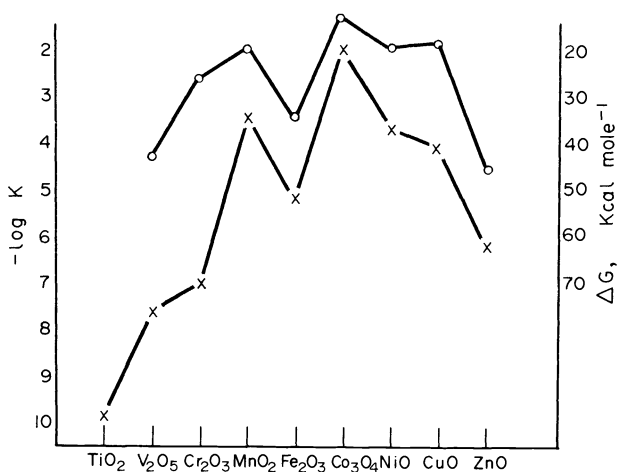


Figure 7. Patterns of behaviour of oxides

○ Metal-oxygen bond energy

× log rate constant for oxygen exchange on the surface

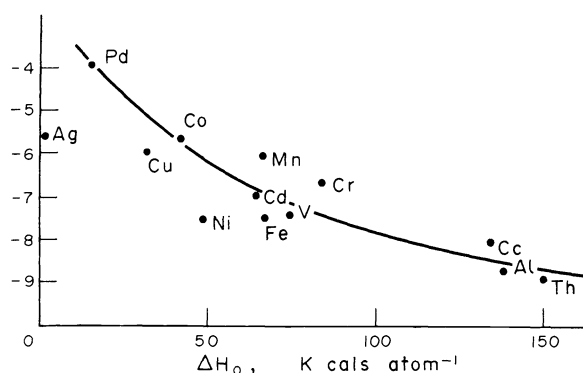
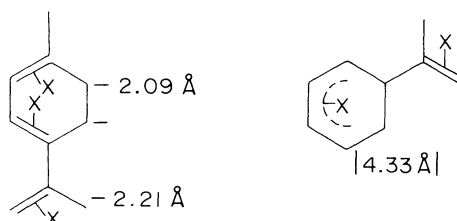


Figure 8. Oxidation of propylene as a function of heats of formation/oxidation atom.

Rates measured at 300°C.

d) Predictions on the basis of geometric considerations. One of the more useful methods of predicting catalytic activity arises from consideration of geometric factors. The concept that the geometry of the catalyst can affect activity has been recognised for many years, and formed the basis of the multiplet theory of catalysis (ref. 26). It is particularly useful in prediction, partially because data is readily available and can be easily applied, and partly because the predictions turn out to be reasonably accurate (refs. 5, 6).

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.

Assuming that the products come from an adsorbed cyclo-olefin and adsorbed propylene, it is possible to generate a table of distances between adsorption centres which are desired or undesired, depending on the modes of adsorption and the reaction path:

Mode of adsorption		Distance between adsorption centres (Å)	
Propylene	Cyclodiene	Desired*	Undesired*
pi-allyl	pi	1.98	2.51
pi	pi	2.15	2.51
pi-allyl	pi-allyl	2.92	1.45, 3.84
pi	pi-allyl	3.26	1.91, 2.13, 3.84, 4.33.

\*In terms of a reaction leading to limonene.

Comparison with the lattice parameters of metals and of metaloxides (figures 9 and 10) gives a strong indication of which metals or metal oxides can be considered and which should be avoided.



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 (refs. 1, 27), but the fact remains that predictions made on this basis are often accurate.

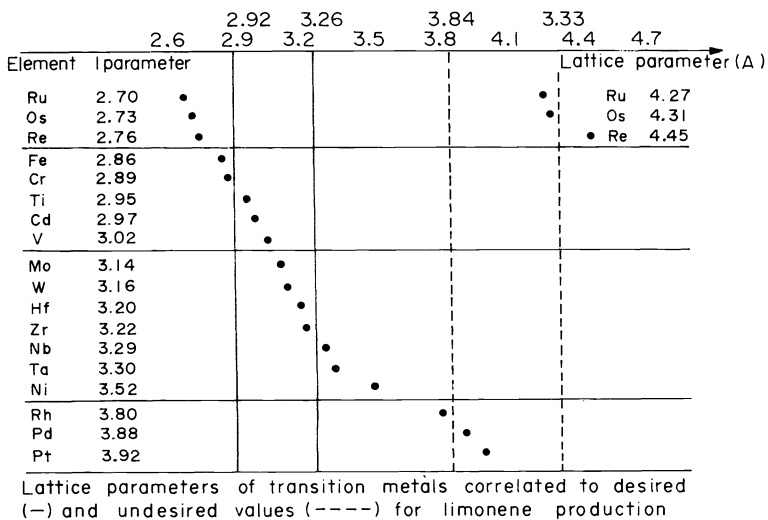


Figure 9. Lattice parameters of transition metals correlated to desired (—) and undesired (---) values for production of limonene.

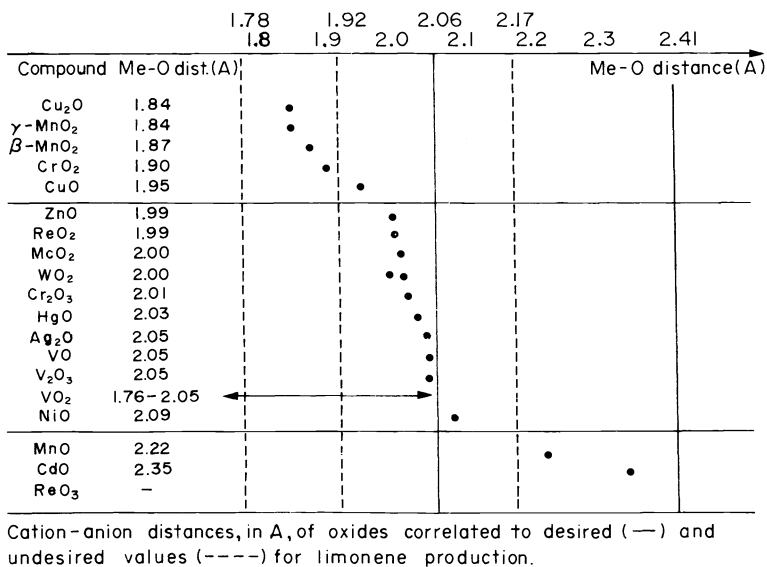


Figure 10. Lattice parameters of metal oxides correlated to desired (—) and undesired (---) values for limonene production.

e) Nature of chemisorbed complexes. Even from the simplified reactions on the surface listed above, 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 from an olefin with an empty sigma ( $dz^2$ ) 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 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), Ti (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 1.

Table 1.

No. of d electrons	0	1	2	3	4	5	6	7	8	9	10	$s^1$	$s^2$
		Ti(3)							Pd(2)		Sn(4)	Zn(1)	Sn(2)
		V(4)	V(3)	V(2)		Fe(3)	Fe(2)		Pt(3)		Sb(5)		Sb(3)
		Cr(5)	Cr(4)	Cr(3)	Cr(2)		Co(3)	Co(2)			Cu(2)	Cu(1)	
		Mo(5)	Mo(4)		Mn(3)	Mn(2)		Ni(3)	Ni(2)		Te(6)		
		W(5)	W(4)										
Adsorption of olefins ( $\pi$ bonded)	+	+	+	+					+	+	+		
(sigma bonded) $d_z^2$					+	+	+	+	+			+	+
Oxygen (radical) ( $\pi$ bonded)		+	+	+	+	+	+	+	+	+	+	+	+
(donor lone pair) (atoms) ]	+	+	+	+	+	+	+	+	+	+	+	+	+

This type of approach is very useful in limiting the number of catalysts that should be considered in the design. It does not take too much time since, once available, such a table is widely applicable.

Similar arguments can be applied to one other, more complex, method of assessing the importance of different chemisorbed complexes. This involves the application of molecular orbital calculations to chemisorption and catalysis. The calculations are complex, and are not to be undertaken lightly. However, several papers have appeared in recent years which assess the probability of finding a given adsorption form on a catalyst (refs. 28, 29). One particular useful review of molecular orbital calculations of chemisorbed molecules and intermediates in heterogeneous catalysis has been published by Beran and Zagrাদnik (ref. 28), covering mainly Russian work up to the second half of 1975. For the normal catalyst design, individual calculations of this type are probably unrewarding: where such information is available, it can be used to good effect.

The dependence of the formation of chemisorbed species on the directional properties of bonds emerging from a surface in an approach which combines the present concept with geometric effects. In an elegant paper covering the possibility of adsorption on different crystal faces, Bond (ref. 30) has considered the fact that  $e_g$  and  $t_{2g}$  orbitals are spatially directed. As a result, location of particular chemisorbed species in positions favourable to reaction can be envisaged, and predictions based on this were found to be accurate. Regrettably, for the catalyst design, this approach is of limited value, in that we know little

about how we should prepare a catalyst with a desired structure, and even less about how we should stabilise that structure during reaction.

There is no doubt that consideration of desired and undesired chemisorbed complexes 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 reactions) and how feasible the proposed surface reactions are. This can only be determined by advanced surface analysis (ref. 1) or, by analogy, from experimental testing of proposed catalysts.

f) Crystal field theory. Relatively modern theories advanced to explain the behaviour of inorganic complexes have been found to offer a good description of chemisorption and catalysis: these include the crystal field and the ligand field theories (ref. 31). 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 ligands, the energies 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. Now the chemisorption of a reactant on a metal ion centre can also be described as the formation of a complex, whether the ion is isolated (say in solution) or is located on the surface of a crystal matrix. Obviously the geometry will be more constrained by the general form of the matrix, but the principle is the same.

The energy changes that occur on formation of such "complexes" depend on many factors, of which the crystal field stabilisation energy is one. The five degenerate d orbitals of the free ion are split by crystal fields of different symmetry, and the amount of the splitting is measured in terms of an energy parameter,  $D_q$ , which

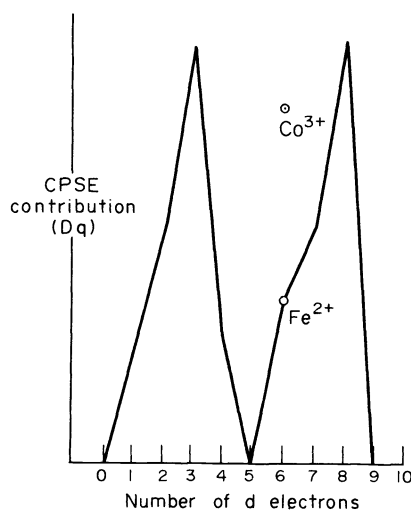


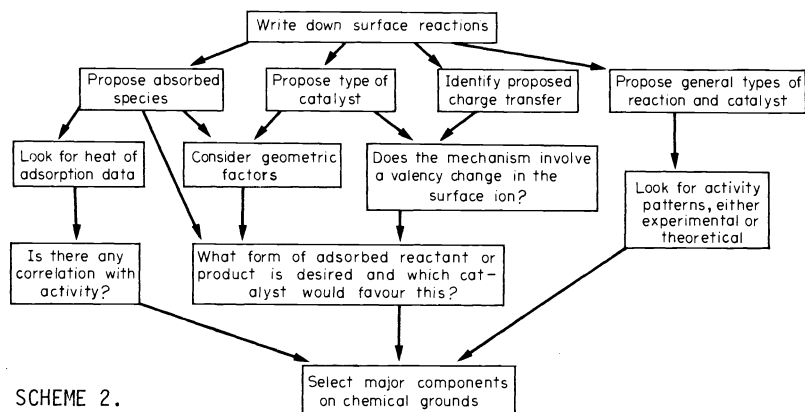
Figure 11. Calculation of crystal field stabilisation energy for strong field complexes.

is usually obtained from optical data. Chemisorption, the addition of a ligand to a complex, results in a change in geometry of the complex, for example from square pyramid to octahedron or from tetrahedron to square pyramid to octahedron. This, in turn, alters the crystal field stabilisation energy and calculations show

that a characteristic twin peak pattern is obtained (figure 11). What is interesting is that this pattern is similar to the patterns of chemisorption and catalytic activity for many metals and oxides (figures 3 and 4). 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. Indeed, if catalysis involves transfer of an electron, rearrangement of the coordination to a different complex (which has the electrons distributed to give overall lower energy) could well be an important driving force for the reaction.

Arguments on this basis provide a useful diagnostic tool for prediction and provide a sound theoretical basis for many of the observed activity patterns. A full description of the approach is given in references 15, 31 and 32 but, for the purpose of design, the information summarised in figure 11 is very useful indeed.

Obviously all the above approaches are very interactive, and the importance of a given approach depends on data that is available. Some idea of the inter-relationships between approaches can be obtained, however, by consideration of the line diagram shown in scheme 2.



SCHEME 2.

Application of the different approaches summarised above can be expected to suggest several possibilities for the basis of the catalyst, and these can only be distinguished by experimental testing. Assuming that the primary prediction has suggested about twenty catalysts, of which two or three are found to be interesting, it is then necessary to consider how the catalytic activity/selectivity can be improved by the addition of minor components.

#### Selection of the chemical basis of the catalyst b) minor components.

The objective of this part of the design is easily stated, in that the catalyst is performing less well in some respect(s) than is desired. The question then is how to improve the performance.

Two approaches are possible. The simplistic approach is easy to apply and often produces results. Thus, for example, if the reaction produces chemicals via a reaction path involving an excess of one reagent (say oxygen), addition of a minor component designed to decrease the amount of oxygen adsorbed is easily carried out (ref. 12). Although such an approach is pragmatic, it usually works.

The second approach is more intellectually stimulating and almost certainly will work: the disadvantage is that it usually takes considerable time and effort.

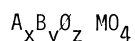
The basis of the method is to delve deeply into the mechanism of the reaction, on the grounds that understanding the mechanism allows optimal fine tuning of the catalyst. This is generally correct, but there is a closed circle in the sense that a catalyst must be of considerable interest to warrant the necessary attention and yet the catalyst may only be of sufficient interest once it has been improved. As a result, detailed studies of this kind are usually carried out only for catalysts which are in current use, but which could be improved.

There are, in fact, two ways of studying the mechanism in order to fine tune the catalyst. The most widely used way is to study reactions on the surface, using recently developed analytical techniques. Of these, electron spin resonance and electron paramagnetic resonance spectroscopy (ref. 33), together with infra red spectroscopy (ref. 34) have proved particularly useful, while electron spectroscopy (ref. 1) holds out much hope for the future. It should also be noted that isotopic labelling experiments, while not fashionable, can be very revealing (ref. 35).

The second method is less direct, but appears to be very interesting. It involves studies of analogues of the catalyst, in which it is possible to control, for example, the location or valency of one of the components of the original catalyst. Several such systems have now been identified, varying from solid solutions to compounds such as scheelites (ref. 36), perovskites (ref. 37), palmierites (ref. 39) and tungstates (ref. 40). The approach and its benefits can be illustrated from a brief consideration of two of these.

The scheelite structure is represented in figure 12 (a). The general formula is  $AMO_4$ , with the M cation being tetrahedrally coordinated to oxygen. About 100 compounds of the general structure have been identified, and some phase diagrams have been presented (ref. 41).

As a catalyst analogue, they are very interesting in that defects, consisting of A cation vacancies, can be introduced in relatively high concentrations (up to one-third of the total of A). Alternatively, it is possible to replace A cations by a second cation, B, to give the general structure



where  $\emptyset$  = defect and  $(x+y+z) = 1$ . As a result, it is possible to generate an analogue which contains two cations at known position and in known coordination, with or without controlled amounts of defects.

This analogue was used to advantage in an elegant study of the oxidation of olefins by Sleight and Linn (ref. 36). Investigating the mode of action of bismuth molybdate, the analogue showed that defects promoted the formation of allyl radicals, while the role of bismuth appears to be mainly to replenish the active site with oxygen. Coupled with other direct observations of the catalyst (refs. 42, 43), the role of additives in the system was established in terms of the various processes that occurred during the overall reaction.

Similar arguments were used to develop perovskite catalysts, but here there is additional interest in that the materials are interesting catalysts in their own right (refs. 37, 38). The crystal structure is very close to cubic (figure 12 (b)), containing large anions (A = La, Nd, Pr, Ca, Sr or Ba) and B ions held in an octahedral configuration. In addition to being useful analogues, this series of compounds is of great interest in the automobile exhaust gas clean up field, where Ru and Rh are stabilised in the perovskite structure.

There is no doubt that detailed studies are needed to understand the mode of action of additives, and that such studies can also be used to predict which additives could be useful. However, the time needed to be invested is high, and one must be sure that the catalyst will be useful before undertaking the effort. Where this is not certain, it is probably best to use a blend of empiricism (based, where possible, on similar catalysts) and as deep a level of thought as is possible, based on the proposed mechanism. This latter process has been illustrated for different catalysts designs (refs. 4, 5, 6, 12).

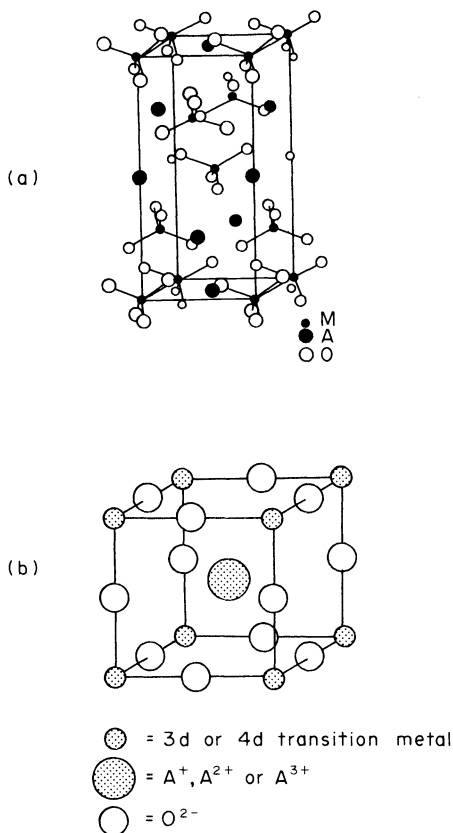


Figure 12. Crystal structures of scheelites (a) and perovskites (b).

#### 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. Micro effects is used as a general term covering the desired crystallinity, surface area, porosity etc of the catalyst, while macro effects covers such factors as pellet size and strength. With a few notable exceptions, macro effects have not received the attention in the literature that they deserve, since mechanical breakdown is a very common cause of catalyst replacement. However, micro and macro effects, although showing individual characteristics, are closely tied together. This is clearly shown, for example, in the case of alumina, where variation in crystallite size, localised variation in phase change or heating, and homogeneity (in crystallite dimensions) were found to have a major effect on attrition and crush strength (ref. 44).

Andrew has presented a good, but too short, review on macro effects in catalysts (ref. 45), in which the desired properties are related by the diagram shown in

figure 1. While correctly identifying physical strength characteristics as being very important, the relation with other factors important in catalysis does not emerge from the review. Thus, for example, the strength of catalysts is related to surface area and porosity, but these factors also have a large influence on activity and selectivity, in that they influence mass and heat transfer in the system.

Considering the problem in terms of catalyst preparation, we would expect that a high surface area should give highest activity. However high surface areas are difficult to prepare, are difficult to maintain (because of the possibility of sintering) and are associated with high porosity. This may introduce mass transfer limitations and will certainly give rise to a weaker catalyst.

The problem can be neatly illustrated by the oxidation of methane to formaldehyde and to carbon dioxide. Formaldehyde is unstable and, at the temperatures needed to oxidise methane, will further oxidise to carbon dioxide very easily. Since both reactions are exothermic, the catalyst temperature will tend to rise and this will favour over-oxidation and catalyst sintering. As a result, it is necessary to remove formaldehyde from the active catalyst rapidly, and to equalise temperature in the catalyst bed at as low a value as possible. This requires a low porosity catalyst with good thermal conductivity. For similar reasons, platinum-rhodium gauzes are widely used for the oxidation of ammonia and novel geometries have been developed for methanation catalysts, including the idea of plating them on the surface of a heat exchanger (ref. 46). A general guide to selection of the properties of the catalyst is given in table 2. It should be emphasised that this table is general, since particular systems may show individual effects. Thus, for example, mass transfer limitations may be desirable, in that they improve selectivity (ref. 47) or even, in some cases, increase rate (ref. 48).

TABLE 2.

THE REACTION PRODUCES	TEMPERATURE CONTROL <sup>a</sup> IS		DIFFUSIONAL EFFECTS ARE		SURFACE AREA <sup>bb</sup> POROSITY <sup>bb</sup>		THERMAL CONDUCTIVITY
	DESIRABLE	UNNECESSARY	DESIRABLE	UNDESIRABLE			
TERMINAL PRODUCTS SUCH AS CO <sub>2</sub> , CH <sub>4</sub> ETC.	✓		✓		MEDIUM	MEDIUM: MAXIMA IN PSD IS 50-100 Å HIGH, PROVIDED TEMPERATURE IS NOT TOO HIGH LOW IF TEMPERATURE RISE IS VERY LARGE	HIGH ANY VALUE
TWO PRODUCTS CONCURRENTLY, ONE OF WHICH IS DESIRED	✓		✓		MEDIUM	MEDIUM: MAXIMA IN PSD AT 50-100 Å	HIGH
TWO PRODUCTS CONSECUTIVELY, THE FIRST OF WHICH IS DESIRED	✓			✓	MEDIUM	LOW POROSITY OR VERY WIDE PORES	HIGH
A PRODUCT, BUT THERE IS A POTENTIAL POISON IN THE FEED OR PRODUCED	✓		✓		MEDIUM	MEDIUM: MAXIMA IN PSD AT 50-100 Å	HIGH
	✓			✓	MEDIUM	LOW POROSITY OR WIDE PORES	HIGH
A VERY HIGH TEMPERATURE RISE	✓			✓	MEDIUM	MEDIUM: PORES MUST BE SUCH EITHER NOT TO ALLOW THE POISON TO ENTER THE PORES OR TO AVOID PORE BLOCKING BY POISON ACCUMULATION	HIGH
	✓				LOW	HIGH POROUS	

<sup>a</sup>FOR ANY REASON: IT IS ASSUMED THAT THE CATALYST IS STABLE AT THE HIGHEST TEMPERATURE LIABLE TO BE OBSERVED

<sup>bb</sup>CONSISTENT WITH DESIRED STRENGTH

The variation in porosity and surface area that can be achieved using a pure catalyst is limited by the preparation methods available and by the fact that such materials tend to sinter rapidly. As a result, it is usual to introduce the desired characteristics primarily through the use of a suitable support. Here, too, there are several other factors which can influence the choice. These may be discussed with the aid of table 3.

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

Table 3. Choice of support

## Chemical Factors.

- Is the support required to show catalytic activity ?
- Are chemical interactions with the catalyst possible ? If so, are these desired or undesired ?
- Can the support interact with reactants or products ? Is this desired or undesired ?
- How resistant is the support to poisoning ?
- Can the catalyst be deposited on the support in the desired form ?
- Does the support induce a particular coordination geometry on the catalyst (52, 53, 54).
- Is the support stable under operating conditions ?

## Physical Factors.

- What is the desired surface area and porosity ?
- What is the desired thermal conductivity ?
- Is the support mechanically strong (45) ? Would this be affected by deposition of poisons, such as carbon ?
- Is the support stable under the operating conditions ?
- What is the desired form of the pellet ?

importance (ref. 49), and that chemical interaction between the support and the catalyst may be desirable (ref. 50) or undesirable (ref. 51). What has emerged comparatively recently is that the support may be able to induce a given geometry on a catalyst without formal chemical interaction, and that this will influence adsorption and catalysis. Such effects have been reported for supported silver (ref. 52) and for supported metal oxides (refs. 53, 54), and may be widely spread. No general guide lines for catalyst design can, as yet, be listed.

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. Both mechanical strength and porosity/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 the latter is given in table 4.

Table 4.

REACTOR	ADVANTAGES	DISADVANTAGES	FORM OF CATALYST PELLETS
GAS-SOLID REACTOR (TUBULAR)	AIDELY USED AND WELL UNDERSTOOD	TEMPERATURE CONTROL MAY BE DIFFICULT	PELLETS. EFFECTIVENESS FACTOR $\sim 0.6$ ; GOOD THERMAL STABILITY
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 TEMPERATURES	MAY BE DIFFICULT TO SEPARATE PRODUCTS AND CATALYST. ALTHOUGH "ANCHORED" CATALYSTS ARE NOW FASHIONABLE (55, 56).	
SLURRY REACTOR	GOOD TEMPERATURE CONTROL	MAY INVOLVE DIFFICULTIES IN GAS-LIQUID-SOLID CONTACTING	

Considerably more is known of micro effects in catalysis, although these may be of more academic interest than applied. This results from the fact that although we begin to know how to prepare a catalyst with a given structure, we know little about how to retain this structure under reaction conditions. This may be illustrated by considering supported metal catalyst.

It is generally desirable to optimise the use of the metal by preparing it in as high a dispersion as possible and, in practice, this usually means depositing the metal in small crystallites on a support. Now, theoretically, this can have other advantages, in that small crystallites are most likely to show geometrical effects (ref. 57) in their catalytic action. The concept of structure sensitive



and structure insensitive reactions is well established (refs. 58, 59), and some assessment can be made of the nature of a given reaction, using the criteria outlined in table 5. Although 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 the probability that a reaction is demanding or is facile. Similarly, on a more theoretically sound base (ref. 57), it can be shown that the number of edge and corner sites on a catalyst will be much higher with smaller crystallites.

Table 5.

## Structure insensitive (facile) reactions may be

- a) addition reactions or elimination reactions
- b) reactions involving a large decrease in free energy
- c) reactions involving reactants with lone pair electrons or pi bonds or strain energy
- d) reactions that do not require a multifunctional catalyst
- e) reactions occurring on an active catalyst whose lattice parameters do not change with dispersion

## Structure sensitive (demanding) reactions

- a) may occur on certain sites, e.g.  $N_2$  chemisorbs only on W(111) and  $NH_2$  is produced only on W(111)
- b) involve single C-C bond breakage
- c) may involve reactants with no lone pair electrons, pi bonds or strain energy
- d) need a multifunctional catalyst
- e) need a less active catalyst whose lattice parameters change with dispersion
- f) may involve reactants with unpaired electrons (e.g. NO).

In practice, there are two difficulties with this approach. With the exception of catalytic reforming, in which the overall reaction involves both facile and demanding reactions (ref. 49), most reactions of industrial interest are, in fact, facile. Secondly, given that a reaction is demanding, it can be very difficult to achieve or to maintain a given geometry in a catalyst prepared on anything but the smallest scale, since reorganisation of the catalyst - either within the particle (ref. 60), or between particles (refs. 61, 62) - is often rapid under reaction conditions - or even during preparation and activation.

Gross rearrangements (sintering) can be prevented to some extent by the use of spacers. Conventionally these involve a high melting point non-deleterious metal salt which is co-precipitated on a support together with the catalyst, thereby acting as a physical barrier to agglomeration. However, there are other forms of spacer, although they are not considered in these terms. Thus, for example, a solid solution not only dictates the geometry of the solute ion (ref. 63) but also acts to separate solute ions. Similarly, an alloy distributes one metal in another, and the resulting effect can be due either to dilution or to chemical or electronic interaction (refs. 64, 65). For the correct properties, one component could also be regarded as a spacer for the other.

The overall design.

A general programme for the design of a catalyst has been discussed above, but this is only part of the overall design process which has been described in detail elsewhere (refs. 5, 6). Although the discussion has been presented only briefly, it does attempt to review the areas important in the context of catalyst preparation.

Before the combination of these ideas with catalyst preparation is considered, it is worthwhile emphasising some points.

Regrettably, we have insufficient knowledge to ensure that the catalyst design is absolutely correct, and experimental testing must be carried out. However, it should be stated that, on the thirty-odd occasions that the author has carried out a catalyst design, the procedure has shown up a catalyst that has been found - either previously or subsequently - to be active for the reaction under consideration. It should be hastily added, however, that several inactive catalysts have also been suggested by the design. As a reasonable assessment, the design procedure offers a guide to experimentation which can often be successful and which requires the investment of only a little time. As the knowledge and experience of the designer improves, so the accuracy of the design can also be expected to improve.

Secondly it is necessary to emphasise the feed back cycle in the design. Experimental testing is necessary at various points, and the results of these experiments can be used to modify the conceptional basis of the design. Thus, for example, if experiments show that reaction path A leads to a more desirable product spectrum than reaction path B, the design can be adjusted to put more weight on reactions of type A.

Thirdly it must be remembered that there are always factors that have not been considered. Catalysis is a complex subject, involving inter-related phenomena from a wide variety of fields. As a result, a set of experiments, carried out for a given reason, may give the "wrong" results because of a second factor which has not been considered. Perhaps the most obvious case of this was work carried out on the design of a catalyst to convert propylene to benzene (ref. 5): at the end of the design it was discovered that changing economics would make the reverse reaction more attractive ! This, again, emphasises the importance of feedback at all stages.

With these comments in mind, it is now possible to consider the interaction of catalyst design and catalyst preparation.

#### Catalyst design and catalyst preparation.

Finally, it is necessary to consider correlation of the suggestions from the design procedure with what can be practically achieved by catalyst preparation. In deference to the main theme of the meeting, this will be limited to impregnation and activation.

Impregnation is widely used as the first step in the preparation of a catalyst, and involves the deposition of a metal salt on a support: this metal salt can be converted into the active catalyst during subsequent processing, activation being one of the major steps.

As with many often apparently simple processes, impregnation may be complex. Three general types may be identified. In the first, the support is soaked in the metal salt solution, and the excess liquor evaporated: this generally leads to an even distribution of metal salt throughout the pore system which can be penetrated by the original solution. This need not include micropores in the support. In the second, it is possible to pre-treat the metal salt in solution before impregnation. Thus, for example, a colloidal suspension of metal could be prepared, subsequent impregnation resulting in the concentration of the colloid at the exterior surface of the support. Thirdly, and perhaps of most interest in the context of control, impregnation could result from a chemical reaction between

the salt and surface groups on the support. This can be illustrated for the preparation of a platinum on silica catalyst.

Silica is known to have a complex surface structure, in which there are a number of different hydroxyl sites of varying reactivity (ref. 66). Impregnation by chlorplatinic acid involves hydrolysis at some of these sites to produce platinum-anion-silica groups at the surface (ref. 67). In these terms, the possibilities of control are large. Thus, for example, chlorplatinic acid can be easily converted to  $(\text{PtCl}_x(\text{OH})_{6-x})^{2-}$  (ref. 68), and the composition of the salt could be adjusted to favour reactivity with only one type of surface hydroxyl group. Secondly, the hydroxyl groups on silica could be poisoned, either with respect to their reactivity (by pre-treating with compounds of different basicity) or with respect to their location (by using bases in which steric effects may limit the penetration of the pore system). As a result, it is possible to deposit the metal salt in varying density and at different locations on the surface.

From the above, it is seen that the amount and location of the catalyst can be controlled, at least in principle, during impregnation, although subsequent processing may redistribute the catalyst (see below). Interaction with the catalyst design is possible in the selection of the active catalyst (major and minor constituents) and in the use of mass and heat transfer considerations to decide where the catalyst should be located. In addition, possibilities of sintering could dictate the desired strength of catalyst-support bonding, although this may be harder to achieve in practice.

In the present context, activation may be considered as the conversion of the as-deposited salt to the desired catalyst by thermal treatment in the presence of a gas: this may, or may not, involve reactions such as oxidation, reduction or sulphidation. The conditions and efficiency of the process are easy to assess, in terms of the nature of the desired conversion, although complete activation may be more demanding than these calculations would indicate (ref. 69).

Two major problems may arise during activation. The first of these involves the rearrangement of the catalyst or the support: either may be desired or undesired. Rearrangement of the support generally arises as a result of phase transformations in the material, causing collapse of pore structure and decrease in surface area. This is often accelerated by impurities (including the catalyst) (refs. 70, 71), and by the ambient gas (ref. 72): during activation, this is usually undesirable. Estimates have been published of the stability of common supports (refs. 44, 45, 70) but, regrettably, these are widely dispersed in the literature and a comparative review is badly needed. However, it is possible to identify conditions under which rearrangement may occur.

Rearrangement of the catalyst during activation may be desired if the catalyst migrates to support surface sites where it can be located more firmly. The resulting catalyst can be expected to be more stable during its working life. If, on the other hand, rearrangement leads to catalyst agglomeration and to decreased surface area or increased particle size, then the process should be avoided. This means either activating under conditions where rearrangement is minimal or, if this is impossible, introducing a second component (such as a spacer) that minimises rearrangement.

The choice of such a component depends, to some extent, on the mechanism of rearrangement. As a general rule, rearrangement can involve surface diffusion

(ref. 73), volume diffusion (ref. 74) or evaporation-condensation (ref. 75), the important process depending on the temperature. Use of a spacer minimises volume diffusion, but surface diffusion or evaporation-condensation can only be prevented by the addition of a second component to the catalyst (as, for example, is the case with Pt/10 % Rh gauzes used for the oxidation of ammonia). It is important to remember that, although a second component may be added to stabilise the catalyst, it may affect the overall catalytic behaviour of the solid.

As a result of recent work on sintering (refs. 76, 78), it is possible to predict with some accuracy the conditions to be avoided. From the viewpoint of catalyst design, however, it is usually sufficient to use the old rule that surface rearrangements are liable to be important at ca. 0.3 x melting point and volume rearrangement at ca. 0.5 x melting point. If conditions are critical, it may be necessary to calculate the temperature rise that could occur in a catalyst bed, and here a simple one dimensional model will usually suffice (ref. 79): the temperature in a pellet is unlikely to rise markedly (less than 20°C) above the ambient in the particular portion of the bed (ref. 80).

The second factor that may be important during activation is the possibility of catalyst-support interactions. These, too, may be desirable (e.g. chromia-alumina (ref. 50)) or undesirable (e.g. nickel alumina (ref. 51)), and this can be established from the design. Fortunately, the conditions under which such solid-solid interactions are possible are usually available (refs. 74, 81, 82), although there has been some consternation in recent years to discover that interaction between platinum and alumina is possible (ref. 83).

Although the purpose of the catalyst design is primarily to decide which catalyst to prepare, it is seen that interaction between the design procedure and catalyst preparation is possible and can be productive. It is certainly possible to recognise which factors are open to control and to predict the probable effects of such control during preparation. Catalyst design is still far from perfect, but it can offer a logical guide to experimentation that can considerably shorten the time needed to develop a new catalyst.

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