THE SINTERING AND REDISPERSION
OF SUPPORTED METAL CATALYSTS

by

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CONTENTS

INTRODUCTION

Supported metal catalysts have considerable industrial importance and have been the subject of an increasing number of investigations directed towards the understanding of their structure, activity for various classes of reactions, their deactivation and regeneration etc. The unique and almost atomic distribution of metals on the support make these catalysts fascinating subjects of study from many fundamental viewpoints.

The purpose of this work was to summarize and evaluate the work on sintering and redispersion of supported metal catalysts (Chapters 4 and 5) and also to identify some areas where further work may be done. It was thought that a brief discussion (Chapter 1) about the nature of these catalysts would help in the understanding of their sintering and redispersion.

Since the preparative procedure may affect catalyst properties, including their sintering and redispersion, a brief account of the preparative procedures is included in Chapter 2. The treatment given in Chapter 2 is somewhat empirical; a recently published book on supported catalysts (ref. 252), the first of its kind, contains an excellent account of the preparation and properties of supported catalysts and provides more insight into the underlying chemistry than has previously been available.

A brief description of the commonly used experimental techniques is given in Chapter 3. This should help in recognizing the limitations that are inherent in the sintering and redispersion studies in which these techniques are used for catalyst characterization.

While sintering, ie. growth of crystallites, seems to be a natural process which is thermodynamically favorable, the mechanisms of such growth are not well known. Redisperion, ie. a process whereby the metal surface area increases (probably accompanied by a decrease in crystallite size), is much less well understood and characterized. Sintering is a univeral phenomenon while redispersion is not. These and other topics are discussed in Chapters 4 and 5.

CHAPTER 1

NATURE OF SUPPORTED METAL CATALYSTS

Supported metal catalysts consist of a fine dispersion of a metal or an "alloy" on a supporting surface. The metal is present as very small crystallites and a large metal surface area is thus made available which results in an effective utilization of the metal.

Early catalysts using Ni and Co had metal contents which were typically 10-20%. With the discovery of the great effectiveness of the noble metals in a wide variety of catalytic reactions, catalysts with metal contents 0.05-2% have been developed. The greatest use of these catalysts is in the reforming of gasolines to higher octane values and in the production of aromatics. Supported metals have in the recent years found use in the automobile industry as exhaust converter catalysts. They are also used extensively as oxidation catalysts in pollution control [8].

An introductory description of supported metal catalysts and some of the long known problems in catalysis, which are now being slowly resolved, are mentioned in the following pages of this chapter. Extensive reviews which are available are listed in the bibliography.

1-1. Catalyst Carriers and Their Functions:

Typical supports used for Pt and Pd are: (1) γ or η-alumina, (2) silica-alumina gels, (3) crystalline aluminosilicates (zeolites), (4) active carbon.

A general classification of supports along with examples has been given by Bond [101] and is shown below.

A. Low area-low porosity:

(i) Ground glass

   - (ii) Alundum
   - (iii) Silicon Carbide
- B. Low area - porous
   - (i) Kieselguhr
   - (ii) Pumice
- C. High area - nonporous
   - (i) Silica - Alumina
   - (ii) Titania
   - (iii) Zinc Oxide
- D. High area - porous
   - (i) Clays
   - (ii) Alumina
   - (iii) Magnesia
   - (iv) Charcoal
   - (v) Silica
   - (vi) Asbestos

An extensive discussion of the nature of commonly used supports is given in ref. [252].

The principal reason for using supported metal catalysts is that a high degree of metal-dispersion is obtained and maintained with comparative ease. Some of the advantages in using supported metal catalysts are [102]:

(1) Large metal area for a given metal content resulting in a very effective utilization of the metal.

(2) Sintering of the metal is reduced as compared to a metal film or a metal powder.

(3) Accessibility of the catalyst surface to the reactants may be improved.

(4) Catalytic activity and selectivity may be beneficially modified.

(5) Heat produced in exothermic reactions may be more easily dissipated.

Thus the support constitutes a framework wherein a high dispersion of the active component is maintained due to a separation of the metal crystallites. The support may also lead to increased accessibility of the reactants by virtue of its pore structure.

The support may itself be inert or active, may act in conjugation with the metal or may only modify its activity. Thus, the catalytic activity of a supported metal catalyst may reside in (i) the metal or one of its compounds, (ii) both the metal and the support (bifunctional catalysis), (iii) a compound of the metal and the support.

Thus the role of the carrier may be both physical and chemical. The following list showing some of the functions of a catalyst support is from ref [103].

Functions of a Catalyst Support

Function	Example
Dispersion of active component	Pt on alumina
Catalytic activity	Mo, Cr on alumina
Thermal Stability	Ni on alumina
Mechanical Stability	Silica-alumina

The exact role of the carrier in determining catalyst properties (activity, selectivity) is not known. It is expected that the support may influence the electronic structure or the lattice parameter of the metal thus altering its activity and selectivity. Other interactions [103] between the metal and the support, such as valence induction whereby the active component unites with the lattice of the support may be responsible for the activity as well as the thermal stability of the catalyst, an example is, manganese oxide on alumina.

Thus in the studies of ethane hydrogenolysis over supported nickel and cobalt catalysts, the specific catalytic activity was found to be dependent on the nature of the carrier [104]. The order of effectiveness is: $SiO_2 > Al_2O_3 >> SiO_2-Al_2O_3$ but the variation in activation energy is not large. For ethane hydrogenolysis on Pt, however, substantial variation in activation energy was observed showing that the affect of the carrier may be observed either in the pre-exponential factor or in the activation energy. Instances where the support has no significant influence are also known, for example [250].

The phenomenon of hydrogen spillover from the metal to the support is well known [106]. The hydrogen is dissociatively chemisorbed on the metal and is subsequently transferred to the support, such as silica or alumina. For spillover to occur, the adsorbed species must be sufficiently mobile and moreover, the energy barrier at the metal-support interface must be overcome. Gardes et.al. [108] demonstrated this phenomenon utilizing a mixture of pure alumina and Ni/Alumina. After exposing the mixture to hydrogen at 300°C and then separating the alumina, it was found that the carrier showed activity for ethylene hydrogenation even at room temperature. This activity was much more than could be attributed to the trace amount of Ni which had diffused to the pure support. Hegedus and Petersen [107] discuss such a "capacitance effect" of the η-alumina support in poisoning studies.

Another example of metal support interaction is discussed by Brownlie et.al. [109] for graphite supported Pd catalysts. It is postulated that the formation of a metal-support interface across which electrons can flow, increases the catalytic activity for the hydroisomerization of 1-butene. The support modifies the electron content of the bonding orbitals of the metal in a manner that facilitates the formation of reaction intermediates.

The influence of the support has also been observed in the work on the infra-red spectra of adsorbed species [110] and magnetic measurements [111]. A review of the electronic interaction between the metal and the support and its influence on catalytic activity is given by Solymosi [112].

1-2. Catalytic Activity and Specificity:

Catalytic action is highly specific and only a few factors determining this specificity are understood in detail. Sinfelt [113] has reviewed the broad relationships between the catalytic activities of elements (or their compounds) and their position in the periodic table. The reactions of hydrogenation, hydrogenolysis, isomerization, ammonia-synthesis and decomposition, oxidation and decomposition of alcohols and organic acids have been considered.

Of the various factors discussed, the relationship between catalytic activity and chemisorption properties is of particular interest to us. Broadly, the activity is maximum when the chemisorption of the reactant is fast but not very strong; if the bond is too strong, the surface species will be too stable to undergo reaction. However, if chemisorption is slow, the reaction may be adsorption-controlled. In many hydrogenation reactions, metals such as tantalum, chromium etc. are not active because of the great strength of the reactant-surface bond. For group IB metals, H_2 is not even chemisorbed. Group VIII metals with an appropriate intermediate chemisorption-bond strength are the most effective.

Even for the same solid, the catalytic activity (for a given reaction) of different crystallographic planes may vary markedly; stressing again, the specificity of catalytic action. Variation of catalytic activity with the choice of the metal is better understood than is the variation with different crystallographic planes of the same metal. (This problem is compounded since until recently surfaces with controlled orientations were not utilized; the solid catalysts normally used are polycrystalline and have a distribution of surface orientations.)

The question, ultimately is, "For a particular reaction, what are the factors responsible for the catalytic activity of a solid?" This has been the vital question in catalysis, the answer to which has traditionally been built around three factors, viz., the geometric factor, the electronic factor, and the active centers. As Clark [114] has remarked, these factors are an interim expedient before more basic approaches are possible.

1-2A. Geometric Factors:

The geometric factors are concerned with the relationship between interatomic distances on the metal surface and catalytic activity. According to Blandin's work, the surface arrangement of metal atoms as well as the interatomic distances are important for some reactions such as the decomposition of relatively large molecules. The greater activity of hexagonal lattices and (111) planes of fcc lattices for the hydrogenation of benzene is well known. For ethylene hydrogenation, the catalytic activity varies with the lattice spacing of the metal. In short, catalytic reactions may require very specific configurations of the surface metal atoms. However, in many cases, geometrical arguments do not hold and alternative explanations in terms of electronic factors seem better. As an example [229], the ease of deposition of carbon on the (111) Ni face, in the decomposition reaction $2CO \rightarrow CO_2 + C$, is ascribed to the compatability between the dimensions of the graphite lattice and the (111) Ni face, however no carbon deposition occurs on the (111) face of Cu although a simple superposition is possible.

The geometrical factors can be varied with the choice of the metal or by selecting different crystallographic planes on the same metal. Surfaces with specific crystallographic planes can be obtained by film deposition in suitable environments.

1-2B. Electronic Factors:

The electronic factors in catalysis correlate catalytic activity and the electronic structure of the metals. According to this approach, in the chemisorption process, the rate of formation and the strength of the bond between the adsorbed molecule and the metal depends on the electronic structures of the metal and the adsorbed species. For metals, the bond formation is facilitated by the presence of holes in the d-band (an equivalent explanation can be given in terms of the bond theory). Transition metals which have vacant d-orbitals in the individual atoms, or holes in the d-band (a high d character means few holes in the d-band) are known to be effective hydrogenation catalysts. For reactions where the mechanism involves electron-transfer from the metal, the holes have a negative effect.

Electronic factors have generally been investigated by magnetic studies and by using alloys [115] where variations in the electronic structure (d-character etc.) can be brought about by changes in surface composition without appreciably changing the lattice parameters. Satisfactory correlations have been observed for many systems, however, detailed bonding models are sometimes required to account for observed activities ie. the invocation of the d-character is not essential or sufficient.

The multimetallic or alloy catalysts offer an opportunity to custom-design the electronic structure of the catalysts. In alloy catalysts, the surface tends to be enriched with the component of lower surface energy. The surface composition is usually monitored by chemisorption, work function measurement, auger spectroscopy and photoelectron spectroscopy.

Sinfelt [113,116] in his work on bimetallic catalysts has shown that systems such as Ru-Cu and Os-Cu which have low miscibility in the bulk state may be present as a single phase in the highly dispersed crystallites. Such miscibility has also been demonstrated in "alloy" films on substrates, produced by the simultaneous evaporation of two components [119]. Thus, the search for new catalysts is not limited to systems which exhibit miscibility in the bulk phase.

1-2C. Active Centers:

The role of active centers or imperfections has been postulated since the time of Taylor [118]. It has been proposed that the actual number of active centers (ie. sites which possess catalytic activity) are much less than what is suggested by the surface area. The phenomenon of selective poisoning which results in an almost complete loss of catalytic activity even with a quantity of poison which is a small fraction of the monolayer capacity tends to support this view. Interestingly, the adsorption of reactants may not be significantly altered by the presence of the poison. Several explanations in terms of the interaction of the poison with the surface have been proposed to counter the proposition for the existence of such preferred sites. Such evidence has been found from the dependence of poison resistance on the metal dispersion [117]. In a highly dispersed catalyst, the small amount of poison is taken up by a few small crystallites with little loss in the total active area. In a poorly dispersed catalyst, the poison molecules adsorbed on the large crystallites can, by their mobility and steric hindrance prevent the efficient use of a large surface area on the crystallites.

Active centers would presumably be altered by sintering and if a disproportionate loss in activity as compared to the surface area results, the existence of such centers can be checked. McKee [120] in his work on the sintering of Pt black, found that the decrease in activity for propane cracking is much more than the corresponding surface area decrease and is dependent on the sintering temperature. He postulated the importance of defects and special active sites for the cracking reaction and showed that the results could be explained by assuming an Arrehenius type temperature dependence for the disappearance rate of active sites. Such effects have also been studied by ion-bombardment which can generate defects on the metal surfaces. This and other techniques for studying the role of active centers are discussed in [121].

That geometrical and electronic factors are closely related, is not difficult to imagine; a particular surface geometry would give rise to a unique electronic structure.

In a recent work, Petro, Polyanszky and Csuros [258] discuss the relationship between the hydrogenation activity of Pt, Pd, Ru, Ir and their surface excess free energy. The excess free energy (over the thermodynamically stable state) in catalysts may be due to the presence of lattice defects, irregular crystal growth, presence of nonequilibrium phases and their dispersion etc. The fundamental relationship between excess free energy and catalytic activity is not known, however, it is believed that the free energy influences various physical and chemical properties of catalysts. For catalytic activity, the surface excess free energy, which can be measured by the electrochemical potential, is probably more important.

The bulk metal catalysts were prepared by four different methods in order to study the effect of the preparative procedure on the surface excess free energy and catalytic activity. For the same metal, the catalysts with higher excess free energy were found to possess higher hydrogenation activity. Also, the sensitivity to the mode of preparation was higher for catalysts with higher surface free energy. This relationship between the excess surface free energy and activity did not apply to different metals. The authors found that the heat of sublimation (which is a measure of the bond strength of surface metal atoms in the lattice) followed the same order as the surface excess free energy.

From the above, it is clear that surface excess free energy is not of fundamental significance in the correlations for catalytic activity and specificity, probably because it depends on a large number of factors some of which may not be of direct consequence in catalytic activity. However, its use in the preparative procedures has been demonstrated.

1-3. Structure Sensitive Reactions:

With the advent of sophisticated techniques for surface preparation and characterization, there has developed a great interest in the study of the above factors, particularly the variation of catalytic activity on different crystallographic planes. Boudart labels these geometric factors as structural factors and notes that the fundamental question has been [124]: "How, for a given solid, does the turnover number* change as we go from one plane to the next, or as we look at sites

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* The number of reacting molecules transformed into products per second per surface site.

of different coordination numbers." Reactions for which the activity varies with surface orientation have been called 'structure-sensitive' or demanding while those for which the activity does not vary have been termed structure insensitive or 'facile'.

That reactions can be structure sensitive is to be expected. It is more difficult, however to understand how they can be facile. An increasingly large number of reactions have been found to be facile and many have been verified to be so on highly characterized surfaces as well as supported (or unsupported) catalysts. Boudart [124] has attributed this to the phenomena of surface reconstruction and corrosion due to adsorbtion of the reacting species or due to the reaction itself. In this process of reconstruction, the identity of the original surface may be lost and subsequent reactions would proceed on the newly formed surface.

Such effects have been known for a long time but the details of the two dimensional phase changes are yet to be understood. Boudart has emphasized the promise of surface science in this area.

Structure-sensitivity has generally been studied using supported metal catalysts, supported metal films and single crystals (also metal foils etc.). While metal films and single crystals may have well characterized surfaces, in supported metal catalysts it is not possible to know the surface orientations (statistics) of individual crystallites except as calculated theoretically from models describing crystallite topographies using measurements of surface area and particle size distribution. Structure-sensitivity in supported metal catalysts is thus studied by indirect means ie. by eliminating other variables. For the purpose of structure sensitivity studies, supported metal catalysts are generally divided into three classes on the basis on their dispersion:

(1) Atomic layers

(2) Intermediate or mitohedral zone (10-100 Å)

(3) Crystals >100 Å.

The intermediate or the mitohedral zone is the most informative for structure sensitivity studies since over this narrow range of crystallite sizes, a rapid change in the surface structure is expected. The 'crystallites" in the first group would have unusual coordination numbers while those in the third group would have bulk metal properties (perfect crystal planes). Thus a comparison of catalytic activities of different sized (average) crystallites in the intermediate zone would allow the determination of the effect of structural properties on catalytic activity.

As mentioned before, inferences about structure sensitivity in supported metal catalysts are indirect and it is essential to eliminate other variables in such studies. Some of these have been mentioned by Boudart [123]:

(1) Mass transfer effects.

(2) Metal support interaction effects.

(3) Incomplete reduction of metal.

(4) Effect of impurities.

Mean crystallite sizes can be varied either by varying the methods or conditions of catalyst preparation or by sintering the catalysts. Dorling and Moss [126] have warned that the methods used to vary the crystallite sizes may themselves lead to variation in specific catalytic activity. They have studied such effects for ethylene hydrogenation on Pt/silica catalysts. Among other factors, the size dependency of the efficiency of chlorine removal during catalyst preparation by impregnation of chloroplatinic acid was observed to be of importance.

Boudart [123] originally classified reactions as:

(1) Structure sensitive or demanding reactions: this classification includes reactions where catalytic properties are dependent on the preparation mode.

(2) Structure insensitive or facile reactions: those for which the catalytic properties do not depend significantly on the preparation mode.

As outlined before, apparent-crystallite size effects may arise due to methods inherent to catalytic work and thus the above classification is too broad. Monogue and Katzer [133] have proposed another classification:

(1) Primary structure sensitivity: reactions requiring special sites. Changes in specific catalytic activity are due to changes in the number of such special sites with crystallite size or pretreatment.

(2) Secondary structure sensitivity: reactions which are insensitive to structure under normal conditions but may behave as structure sensitive due to certain secondary factors like self-poisoning. The effect would be due to size (structure) dependent self-poisoning (or deactivation) rather than due to inherent structure sensitivity of the reaction.

(3) Primary size sensitivity: for very small crystallites (or metallic clusters) catalytic activity may depend on the number of atoms in the cluster due to changes of electronic properties with the number of atoms.

Supported metal catalysts generally contain a distribution of crystallite sizes. The question of inference of size (structure)--sensitivity from measurements of average specific activity in such cases has been treated by Luss [128].

In a recent work, Maurel, Leclercg and Barbier [127] have examined apparent crystallite size effects due to the presence of what they call as "demanding poisons" which are adsorbed only on special sites. These poisons had their origin in sulfate impurities in the alumina support.

Extensive work on structure sensitivity in the region of atomic layers (ie. very high dilutions) has been done by Kobozev and co-workers [129]. Their work is generally known as the "theory of active ensembles." Catalytic activity (for a particular reaction) is ascribed to groups of atoms on the support having specific configurations. It is proposed that the metallic atoms are clustered in potential holes on the support due to the heterogeneity of adsorption forces binding the metal atoms to the support. Since the number of atoms in the clusters is small, lattice considerations are not important and the atoms constitute an amorphous phase. Activity patterns are correlated to the number of atoms in the clusters or the ensembles. By a statistical analysis of the probabilities of cluster formation a variation in specific activity with the metal content is predicted. Such variations (maximum-minimum type) have been observed in many reactions. Carra, Ragini and Guella [130] correlated their activity patterns for cyclohexane disproportionation on Pd/Al_2O_3 (30-50°C) on the basis of such calculations with maximum activities observed for η(=no of atoms in the ensemble) values of 4, 10-11, 20-21. A review of Kobozev's work is given in Gilderbrandt [131].

The theory is not very well suited to experimental investigation due to experimental difficulties of characterization and activity measurements in the region of atomic layers.

It is clear that structure sensitivity studies on supported metal catalysts cannot be interpreted unambigiously and thus evaporated thin films [134] and single crystals with well defined surfaces have been used for such studies. This has been made possible, mainly by the use of low energy electron diffraction (LEED), Auger electron spectroscopy (AES)*

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* See Chapter 3

and mass spectroscopy. Using these techniques, catalytic reactions on different surface planes with known surface compositions (AES) can be accurately monitored. The effect of impurities, the surface rearrangements as well as the surface structure of the adsorbed gases can be studied. As a necessity, such studies are conducted at very low pressures. Thus the extension of such studies to practical catalytic systems is not direct, though their value in the design of better catalysts as well as studying reaction mechanisms cannot be denied. Single crystal studies under high pressures are being conducted [134].

1-4. Properties of Very Small Crystallites:

The very small crystallites with their high surface/volume ratios and unusual coordination numbers could be expected to have physical and catalytic properties different from those of the bulk material. J.J. Burton [135] has reviewed some of the experimental and theoretical work on the structure and properties of microcrystallites (<20 Å). It is found that for small crystallites, an icosahedron (five fold) symmetry is thermodynamically preferred to the normal closed packed structures. Microcrystallites melt at low temperatures compared to the bulk material although their lattice parameter is smaller. Moreover, the vibration of the surface atoms can be as large as 25% of the bulk lattice parameter at temperatures as low as half the melting point. This may lead to surface premelting or disordered surface structures on cooling. Refs. [138,139] should be consulted for some additional details.

Kobayashi and Shirasaki [136] have calculated the variation of the step-kink density as a function of crystallite size. They have taken into consideration the stabilizing influence of the support in the expression for the energy required to form a vacancy. By their calculations, they have shown the existence of maxima in defect concentrations; the optimum diameter, Ni(20 Å), Pd(50 Å), Pt(20 Å), Ru(20 Å) agree well with that used in practice. The binding energy of the metal atoms to the oxide support was calculated to be between 2-5 ev/atom (45-120 k cal/mole) which corresponds to a strong metal support interaction (see Chapter 3).

1-5. Surface Science and Catalysis:

Boudart [124], in an attempt to distinguish between surface science and catalysis, remarked that surface science is what appears in 'Surface Science', and catalysis is what appears in 'Journal of Catalysis'. Surface science is increasingly being used in catalysis; the relationship between the two is lucidly discussed by Boudart [124] and Robinson [137].

CHAPTER 2

PREPARATION AND PROPERTIES OF SUPPORTED METAL CATALYSTS

2-1. Introduction:

The most important catalyst properties are: activity and stability (life). In addition to the choice of the metal, factors which influence the physical and chemical structures giving rise to these desired catalytic properties are:

(1) The choice of the metal compound used for preparation and the amount of metal used.

(2) The nature of the support including it's area, pore structure and surface structure.

(3) The detailed preparative procedure, including the pretreatment and reduction conditions.

The above and some of the related factors will be discussed in this chapter. The large number of variables which occur in catalyst preparation are, perhaps, the cause of much confusion in catalysis. Thus, Poltorak and Boronin [180] found that apparently insignificant changes in preparative procedure produced entirely different catalysts. Thomson and Webb [181] propose that the catalyst preparation techniques be standardized in order to reduce the present confusion.

A qualitative insight into the preparative variables can sometimes be obtained by a suitable experimental design procedure; this is briefly discussed by Traina and Pernicone [182] in their review.

2-2. Preparative Procedures:

The most commonly used methods for the preparation of supported metal catalysts are:

(1) Impregnation

(2) Ion-Exchange

(3) Precipitation

2-2A. Impregnation:

In this method, the support is soaked with a solution of the desired metal salt or compound and then dried and calcined at higher temperatures. The catalyst is then reduced with H_2 at an elevated temperature and a fine dispersion of the metal on the carrier is generally obtained.

The amount of solution used is generally not much more than the absorption capacity of the support. When the volume of solution is less than the pore volume, uniform uptake by different pellets must be ensured. The support may be powdered or in a granular form; the former is preferred due to ease of penetration. The support is sometimes evacuated prior to soaking or spraying of solution.

Repeated impregnations with intermediate drying may be used for introducing higher metal concentrations and for introducing more than one component. When used for multicomponent catalysts, the order of impregnations may be important.

A vapor phase impregnation is also possible if the active component can be found in a volatile compound.

Examples:

(i) Pt/Al_2O_3: Platinum or alumina is generally prepared by the impregnation of chloroplatinic acid. The calcination is done at 500-550°C and the hydrogen reduction at ~300°C. Mills, Weller and Cornelius [142] found that the complete reduction to metallic form is possible in 10 minutes. at 245°C in H_2. Similarly, a $Pt/Re/Al_2O_3$ catalyst may be prepared by simultaneous impregnation of chloroplatinic acid and ammonium perrhenate.

(ii) Ni/Silica: Aqueous solution of nickel nitrate may be used for impregnating the silica carrier. Hydrogen reduction is carried out at ~400°C. Re/SiO_2 can be prepared by impregnation by perrhenic acid, drying at ~120°C and reduction in H_2 at ~500°C for ~5 hours.

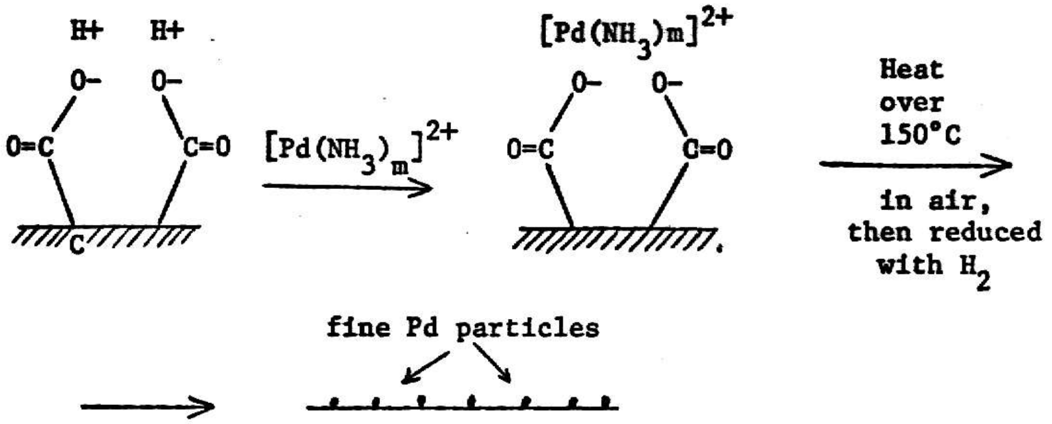
2-2B. Ion-Exchange Type:

In this method, the metal cations are fixed to the support by exchange with ions on the surface of the support in a solution of high pH; the metal uptake being dependent on the pH of the solution. Precipitation at these pHs can be avoided by the addition of enough ammonia or ammine [39a]. The catalyst is then dried and reduced in the usual manner. This method can be used when the metal is present as a cation and the support has sufficient ion-exchange capacity.

Examples:

(i) Pd/Active Carbon: [183]

Cation-exchanged active carbon containing carboxylic groups on the surface is produced by adding nitric acid solution to active carbon and washing until free of nitrate ions. Drying is done at room temperature and at reduced pressure. The hydrogen ions on the surface are exchanged with Pd-ammine complex ions and the catalyst is washed and dried under reduced pressure. Finally, thermal treatment in H_2 at 300°C, in air at 150°C followed by hydrogen reduction at 150°C gives a fine dispersion of Pd on active carbon. The following pictorial sequence is from ref. [183].



A promoter, for eg. Al^{3+} is generally added for thermal stabilty, ie. to prevent Pd aggregation. Pt/silica-gel or nickel on aluminosilicate can be prepared by similar methods.

2-2C. Precipitation:

In this method, a hydroxide or carbonate of the metal is generally precipitated from a solution of the metal salt on the carrier suspended in the solution. In the co-precipitation method, both the carrier and the metal compound are precipitated simultaneously from the solution.

Examples:

Ni/Silica: Nickel hydroxide is precipitated on to the silica carrier by the addition of an alkali. The material is dried and reduced in H_2 at high temperature. For Pt/Al_2O_3, colloidal Pt may be deposited on a freshly prepared alumina precipitate.

In the co-precipitation method, an alkali is added to a solution of nickel and aluminum hydroxides. The precipitate is filtered, washed repeatedly, and then dried and reduced at 500°C. The metal compound is deposited on the support by a combination of adsorption and precipitation. The active component may become embedded in the carrier. Co-precipitated catalysts are generally more difficult to reduce than the impregnated catalysts.

2-3. Preparative Procedures and Dispersion:

To understand the variation of dispersion with the preparation variables, working models for various preparative procedures are needed. Not much mathematical work has been done in this area and thus, most of the following discussion is qualitative and is restricted to the impregnation and ion-exchange methods.

In the impregnation step, the solution is taken up by the support due to capillary forces. If the solute is non-adsorbing, it remains in the pore volume liquid. If the solute is strongly adsorbed, a pore-mouth deposition may take place. If the volume of solution used is equal to the pore volume, the interior of the pellet contains the depleted solvent only. If the solution used is in excess of pore volume, after the above step, the solute will diffuse from the external liquid to the interior. Some redistribution can take place if the solute is reversibly adsorbed. When the volume of the solution used is less than the pore volume, only the larger pores may contain solution and some pores may not be full but may contain only a thick film of solution [184].

Weisz and others [185] have studied the case where the pellet, filled with the solvent, is placed in a large excess of solution from which the solute is gradually taken up by diffusion in the pellet. This is somewhat similar to the case in catalyst preparation where an excess solution is used (see above).

Harriot [186] considered the case where the depletion of the external solution was also taken into account. He also gave numerical solutions of the concentration profiles for the problem of reduction of the impregnated salt (before drying) by putting the pellet in a reducing agent which diffuses into the pellet.

While Weisz and Harroit considered diffusion in a stagnant fluid filling the pores, Vincent and Merill [187] have considered the case of unsteady state liquid impregnation and deposition in a single pore.

$$\frac{\partial C}{\partial t} + \nu_P \frac{\partial C}{\partial z} = D\frac{\partial^2 C}{\partial z^2} + V(C,\theta) \qquad (2.1)$$

with appropriate boundary conditions. Here, C is the solute concentration, D is the dispersion coefficient, νp is the velocity due to capillary uptake, and $V(C,\theta)$ is the rate of removal of solute from the solution. Expression for $V(C,\theta)$ is derived by considering the two cases of mass transfer control or adsorption control. The conclusions are similar to those of Maatman and Prater [188].

The above analyses would be valid for a unimodal pore size distribution of the support. For a bimodal pore distribution, the impregnating solution may be able to penetrate to the interior by excluding one set of pores [279].

The desired distribution of the metal on the support may vary according to the catalyst use [187]. For mass transfer limited reactions, distribution close to the surface may be advantageous. Minhas and Carberry [189] discuss the merits of partially impregnated catalysts for SO_2 oxidation. A subsurface impregnation may be advantageous for reducing attrition losses and the poisoning of the metal component. For minimizing sintering, it is preferable to have a uniform metal distribution.

Redistribution of the active component may take place during drying, calcination and reduction. This is more important for the case of non-adsorbed solute, for the adsorbed solute where the pore volume solute is not too large, as compared to that adsorbed, a uniform impregnation will ensure uniform distribution in the final catalyst.

While use of proper concentrations of the impregnating solution combined with multiple impregnations can yield uniformly impregnated catalysts, a technique that utilizes competitive adsorbates is the simplest. Maatman [188] found that addition of HCl to the chloroplatinic acid solution gives a rather uniform Pt distribution on eta-alumina along with increasing the reproducibility of the preparation. Brennan et.al. [190] suggest the use of aluminum chloride, aluminum nitrate etc. along with chloroplatinic acid. They propose that the presence of additional salts may modify the adsorptive capacity of the alumina or may lead to the formation of Pt-Al complex having a modified affinity for alumina. The catalysts prepared by this technique had 1.5 to 2.5 times the reforming activity of the normal catalysts.

The amount of competitive adsorbate (CA) should be properly chosen, if it is too small, the depletion of CA in the interior will cause strong non-uniform adsorption; if it is too large, the amount of solute in the pore volume may be too large. Moreover, competitive adsorbate may have harmful affect on the activity and selectivity and stability of the catalyst.

The catalyst may be impregnated with the adsorbate (CA) prior to metal impregnation to achieve a similar effect.

Oleck [191] in his patent describes a method of catalyst preparation in which the alumina support is treated with carbon-dioxide prior to impregnation. It is believed that CO_2 pretreatment prevents the adsorption of chloroplatinic acid during impregnation and thus allows uniform distribution of the solution in the pellet. As the CO_2 is removed during heating, the Pt is uniformly adsorbed on the support. Chen, Sagert and Jones [279] have studied the preparation of Nickel-Chromia/Alumina catalysts prepared by the impregnation by different salts. Nickel sulfate and chromic nitrate are strongly adsorbed by alumina while nickelous nitrate, nickelous chloride and chromic acid are weakly adsorbed. Thus when nickel nitrate and chromic nitrate are used together, chromic nitrate is adsorbed at the periphery while nickel nitrate is adsorbed in the interior. When consecutive impregnations are used, the second impregnation can cause the dissolution of the weakly adsorbed salt introduced in the first impregnation (but not of the strongly adsorbed salt). This can be prevented by drying and calcining after the first impregnation.

Increases in surface area (N_2 adsorption) in catalysts prepared from nickel nitrate and from chromic nitrate were attributed to the formation of porous species on the alumina. Since this was accompanied by increased pore volumes, the porous species is not the metallic species and changes in support structure may be responsible for the increases in area and pore volume. However, the support structure, as observed in the scanning electron micrographs, was not appreciably modified.

The problem of redistribution of the pore volume solute during the drying operation is a complex one, partly because of the temperature gradients that may occur in the pellet. The important factors are [184]: the gas temperature and flow, the thermal conductivity of the particle, the heat of vaporization from solution, temperature dependence of interfacial tension, the type of pore interconnections etc. The evaporation starts at the outer periphery; the resulting increase in concentration (at the periphery) causes the diffusion of the solute towards the interior as well as higher local adsorption. The solute may also deposit by precipitation if the concentration exceeds the solubility. The evaporation occurs preferentially from the larger pores due to the higher vapor pressure there, moreover, any liquid evaporated in the smaller pores is replaced by the liquid drawn in by capillary forces from the larger pores [188]. The receding liquid deposits a few layers of solution in the pores.

Since the temperature at the periphery is higher than at the interior and since interfacial tension decreases with temperature, the liquid has no tendency to come to the periphery [184]; if the interior of the pellet is not full, the evaporation in the exterior coupled with this interfacial effect causes the liquid to be drawn to the interior. Thus, the pore volume solute may be preferentially deposited in the smaller pores in the interior of the catalyst. Felenov [192] has discussed the role of drying conditions in obtaining a uniform metal distribution for the case of non-adsorbed solute.

The metal salt used for impregnation is generally converted to an oxide in the drying and calcination stages. The decomposition of the salts on supports, particularly in the presence of interactions, is complex and is accompanied by the evolution of gases. It is generally desirable to use metal compounds with low decomposition temperatures to prevent aggregation during decomposition. Aggregation of mobile species during reduction also leads to lower dispersion. A discussion of these topics is included in the next section.

Dorling and Moss [62] visualize the preparation of impregnated Pt/Silica (no interaction between metal salt and support) catalysts from wholly physical considerations as follows:

The catalyst pores are filled in the impregnation step. In the drying step, the solution is concentrated to a point where the crystallization of the salt begins providing nucleii in the pores still containing solution. On further drying, all the salt in the pore crystallizes out probably as one clump only. Thus the crystallite size obtained on H_2 reduction would be related to the amount of salt deposited in the pore. If the salt solution is very dilute, in the drying step, a number of pores will become empty before the onset of crystallization. In such a case, if the strength of the solution is increased, the number of crystallites would increase, to a point where the number of crystallites is equal to the number of pores. Thus according to this model, the number of crystallites would increase with Pt content up to a certain level; in this range, the Pt area would be proportional to the Pt content. At higher Pt contents, the number of crystallites would be fixed (≈ no. of pores) and the crystallite size would increase with increasing Pt content and thus the Pt area $\propto$ (Pt content) $^{2/3}$.

Some of the above hypotheses were verified by the same authors using Pt/Silica catalysts. At low concentrations, the number of crystallites increased with increasing Pt content and then became constant, giving the area $\propto$ (Pt content) $^{2/3}$. The number of pores/number of crystallites varied from 1-600. The authors proposed that when the nominal pore diameter is small, a large number of pores may remain unused thus giving the high ratio. (The inaccessibility of some pores due to their size or the preferential adsorption of the solvent was mentioned by Maatman [188] who has described a simple technique for finding the effective pore volume for a solute). Moreover, a one-to-one relationship between the number of pores and the number of crystallites cannot be expected without consideration of the pore size distribution, the pore shapes and the pore-system interconnection.

Dorling and Moss [62] also studied the Pt/Silica-gel ion-exchanged catalysts. They calculated the number of surface hydroxyl groups on silica gel as 4.6/100 $Å^2$. For Pt contents less than the maximum uptakes, ie. corresponding to the above mentioned exchange capacity, the crystallite size did not very over a 40 fold increase in Pt content. The crystallites were smaller than in the corresponding impregnated catalysts. To explain the constancy of crystallite size in this case of "adsorption type" catalysts, the authors propose that the exchange sites on the less accessible support areas remain unused, thus even the low Pt content catalysts give the same crystallite size.

The ion-exchanged catalysts are generally more dispersed than the impregnated catalysts having the same metal content. Thus, Wilson and Hall [32] found that ion-exchanged Pt/Silica catalysts had a higher dispersion and a narrower crystallite size distribution than the corresponding impregnated type catalysts.

The variation of metal dispersion or crystallite size with the pore structure of the support is also of interest. Veslov and Lavrentovich [193] have studied this effect for Ni/Alumina catalyst where the main mechanism for metal incorporation is by pore volume filling. The support was assumed to contain spherical cavities with mean radius $r_c = 3Vp/Sc$ where Vp and Sc are the pore volume and surface area respectively. The authors propose that primary crystallites are formed during the impregnation step. When the cell size (r_c) is small, the surface concentration of the metal is low ($C_{sur} = \chi r_c/3$ where χ = concentration of impregnating solution) and thus there is little tendency for aggregation of the primary crystallites. By a mass balance, it can be seen that the number of crystallites per unit cell grow as r_c^3. As r_c increases, the increase in metal concentration and the number of primary crystallites increases their probability of aggregation; thus in this region, the number of crystallites decreases along with their mean radius. Ultimately, there is only one crystallite per cell. Further increase in r_c and hence in the number of primary crystallites does not cause an indefinite increase in the crystallite size but a limiting size is attained and thus the number of crystallites increases. The authors take these results to propose that a favorable carrier structure should contain small pores (r_c < 250 Å) and large pores

(r_c > 1200 Å) ie. a bidisperse structure to obtain a maximum metal area.

Zaidman et.al. [267] have studied the effect of support calcination temperature and the H_2S treatment after the impregnation step. Jawarka-Galas [14] had found that Pt dispersion increased with an increase in support calcination temperature. Pre-sulfiding of reforming catalysts is known to be effective in reducing the excessive hydrocracking. The catalyst can be pre-sulfided by several ways, including that mentioned above.

The catalysts were prepared by chloroplatinic acid impregnation of alumina or aluminum hydroxide and were reduced in H_2 at 500°C. The supports subjected to lower calcination temperatures had considerably lower dispersions and poorer reproducibility, especially for Pt concentrations greater than 0.5%. Pt on aluminum hydroxide had lower dispersions and the particle size increased considerably after 500°C H_2 treatment. Treatment of freshly impregnated alumina with gaseous H_2S resulted in significant decrease of dispersion for supports pre-calcined at lower temperatures; this is explained to be due to the lower stability of the support structure caused by the phase-transformations in the given temperature range which facilitates the movement of Pt and promotes its aggregation. They postulate that upon treatment with H_2S, relatively large platinum sulfide crystals (whose size is related to the pore size) which are weakly adsorbed on the support, are formed. The size of the Pt particles obtained after reduction depends on the size of these crystals.

2-4. The State of Metals in Supported Catalysts:

The variation of dispersion with the preparation variables was briefly discussed in the last section. To understand the variation of dispersion on different supports or on the same support due to variation in metal content, the interaction between the metal-component and the support at various stages of preparation should be known. Such interaction may also be important for the activity of certain supported metal catalysts (see Chapter 1).

The surface chemical properties of the support determine whether any bonding occurs during impregnation with the metal salts, this in turn influences the metal dispersion obtained. For example, the amphoteric Al_2O_3 reacts with H_2PtCl_6 whereas the acidic surface of SiO_2 reacts with basic Pt salts such as $Pt(NH_3)_4Cl_2$ or Pt tetrammine salts. The strong chemical bonding between the support surface and the metal salt influences the decomposition and reduction to the metal and thus affects the dispersion. Such interactions are also important in considering the sintering characteristics of such catalysts.

2-4A. Pt/Alumina:

Pt/Al_2O_3 is an important industrial catalyst and has been the subject of much investigation. The most common preparation technique is the impregnation of alumina by chloroplatinic acid (H_2PtCl_6), a strong acid [216] which reacts with alumina.

McHenry et.al. [25] first proposed that Pt/Al_2O_3 catalysts which were active for dehydrocyclization reactions, contained Pt in a "soluble" form which can be extracted with acetylacetone or dilute HF acid solution. They postulated that this "soluble" Pt was a $Pt\text{-}Al_2O_3$ complex and found that it was highly resistant to a reduction treatment which was ascribed to the stability of the complex. They showed that the dehydrocyclization activity varied directly as the soluble Pt.

Maatman et.al. [217] have studied the reaction between aqueous H_2PtCl_6 and alumina during the preparation of Pt/Al_2O_3 catalysts. They propose the following reaction scheme:

$$nAl(OH)_3\ (s) + 3nH^+\ (aq) + PtCl_6^{2-}\ (aq) \longrightarrow$$

$$\text{"}PtCl_4\ (s)\text{"} + nAl^{3+}\ (aq) + 2Cl^-\ (aq) + 3nH_2O \qquad (2.2)$$

where "$PtCl_4$ (s)" represents the surface species of tetravalent Pt in which chlorine is adsorbed to preserve charge neutrality.

The H^+ of the strong chloroplatinic acid reacts with alumina to release Al^{3+} ions to the solution. The reaction of $PtCl_6^{2-}$ is much less. The authors found that these two reactions were independent and also that for the dehydrogenation of cyclohexane (without H_2), the above reactions affect the activity only through the dispersion. Regarding "$PtCl_4$ (s)", the authors remarked that it is consistent with the concept of tetravalent Pt (IV) ie. soluble Pt. The authors could not prove that the reaction scheme proposed above is correct. There was no affect of a 500°C H_2 reduction of the catalysts stored in air on the cyclohexane dehydrogenation activity. Thus if any soluble Pt was present, it was not affected by the H_2 treatment.

Since there is some unreacted Pt present in the pore volume of the catalyst, which gets deposited on the alumina surface during drying, it was of interest to study its contribution to the total activity for cyclohexane dehydrogenation. The authors found that it does not contribute to such activity, thus suggesting that the only active form is that which is produced by reaction with alumina. However, it may be, as the authors have discussed later, that the Pt which is present in the pore volume sinteres very rapidly, contributing little surface area and hence little activity.

Emarkova and Zaidman [70] have also investigated the nature of "soluble" platinum in Pt/Al_2O_3 catalysts. They stress the need to exclude oxygen while studying the valence state of Pt in Pt/Al_2O_3 catalysts. In agreement with the results of Kluksdahl and Houston [69], they found that the "soluble" platinum content was negligible if oxygen was avoided. The soluble platinum increases sharply after treatment with air even at room temperature; the increase being dependent on the H_2 pretreatment temperature. The soluble Pt is much larger at a low H_2 pretreatment temperature of 300°C than at 500°C and 700°C. The authors compare it to the thin film work where low deposition temperatures give rise to disordered surface structure (vs. epitaxial at higher temperatures; see Chapter 3) which have higher oxygen chemisorption capacity.

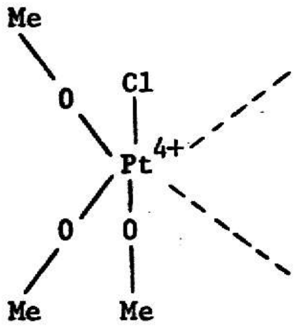
Bursian, Kogan and Davydovan [66] in their study of the state of Pt and chlorine in Pt dehydrocyclization catalysts found that the dried catalyst containing Pt ions of the original compound is completely soluble. Heating in air at 500°C reduced the soluble Pt content to 50% for Pt/Al_2O_3 and ~1% for Pt/SiO_2. This is explained as being due to the decomposition of the initial Pt compound with some formation of Pt-Al_2O_3 complex (soluble) which is stable upto 500°C. H_2 reduction reduces the soluble Pt content to a value determined by the previous treatment with air, the maximum being for air heating at 250-500°C. The authors propose that the soluble platinum is non-homogeneous, one part is stabilized by H_2 treatment while the other part is hydrogen unstable. The formation and decomposition of the hydrogen unstable soluble platinum is postulated to be a reversible process. It is assumed that since γ-alumina has a defect spinel structure, some of the Pt^{4+} cations of the original Pt compound will pass into the available aluminum oxide lattice vacancies; the carrier lattice thus sheilding against reduction to metallic form. This corresponds to the hydrogen-stable form of soluble platinum. The hydrogen unstable form results from the interaction of adsorbed ions of the platinum containing compound with the surface functional groups of aluminum oxide; since this form does not enter the crystal lattice, it undergoes reduction to metal during thermal treatment in H_2.

The atomic ratio of Cl/Pt was found to be 1:1 for soluble Pt. The authors believe that chlorine remains bound to Pt even after H_2 reduction of the catalyst. Chlorine also enters the compound formed between the Pt and the carrier and is therefore a part of the soluble Pt. (Burton [94] in his study on the effect of chlorine in dehydrocyclization of 3-methylpentane by Pt/Al_2O_3 found that the chlorine added as chloroplatinic acid is of a specific type as far as isomer distribution is concerned). The soluble Pt showed specific activity in ring formation and closure reactions but does not catalyze dehydrogenation reactions.

The authors accept the possibility of the hydrogen-stable soluble platinum arising from the formation of an alloy of Pt and Al, the Al coming from the reduction of Al^{3+} released during the reaction of H_2PtCl_6 with Al_2O_3.

Bursian, Kogan and Davydova [67] also studied the state and nature of activity on Pt/Al_2O_3 and Pt/Silica-gel promoted with lithium, sodium and cesium. When the alkali metals are introduced and the catalysts calcined in air at 550°C, the soluble Pt content in Pt/Silica-gel increases sharply, both before and after reduction; for Pt/Al_2O_3 no change is observed. Pt/Alumina and Pt/Silica-gel containing equal amounts of soluble platinum exhibit almost equal aromatization activity. The authors explain that the alkali metals cause an increase in soluble Pt content for Pt/Silica-gel and an increase in the thermal stability of soluble platinum in Pt/Al_2O_3 without changing its content. In both cases it involves the formation of thermo-stable compounds of Pt and the promoter. The migration zone (or mobility) of atoms on alumina is much smaller than on silica-gel which is responsible for the decrease in effectiveness of promoter in Pt/Al_2O_3.

They propose a structure of the complex active center on the surface of Al_2O_3 in which platinum replaces a cationic vacancy in the center of the incomplete octahedron and is surrounded by one chloride ion.



The catalytic activity is associated with the unsaturated coordination bonds. The chlorine increases the effective charge on the central ion which promotes the donor-acceptor interaction of the hydrocarbon ligand electrons and the d-orbital of the central ion.

Kogan, Kiseleva and Burisan [68] have studied the effect of the metal compound used for Pt/Al_2O_3 catalyst preparation on the aromatization activity of hydrocarbons. The compounds used were $[Pt(NH_3)_6](NO_3)_4$, $[Pt(NH_3)_5Cl](NO_3)_3$, $[Pt(NH_3)_4Cl_2](NO_3)_2$, H_2PtCl_6 and $[Pt(NH_3)_6]Cl_4$ (Samples I-V.) The activities for aromatization of n-hexane, methylcyclopentane and cyclohexane and for the decomposition of H_2O_2 were evaluated.

Catalysts with a Cl/Pt ratio of 1-2 in the original Pt compound had a higher dehydrocyclization activity due to a higher concentration of the ionic form of Pt. This ionic form containing Pt^{4+} is formed by the substitution of cations in the octahedral vacancies of γ-Al_2O_3 lattice. The formation of Cl-$Pt \equiv Al_2O_3$ type active center [67] requires the destruction of the coordination sphere of initial Pt-complex compound during calcination. Formation of such active centers is facilitated when the decomposition occurs at low temperatures (II-III). Sample I contained a high concentration of ionic Pt (but) without chlorine and thus had a low aromatic activity. That these effects were not due to variations in the degree of dispersion alone was verified by measurements of H_2O_2 decomposition activity and the cyclohexane dehydrogenation activity.

Neinska, Penchev and Kanazirev [224] investigated the effect of various pretreatments in the preparation of Pt/Al_2O_3 catalysts from an ammonical complex. Larger crystallites were obtained when the catalyst was calcined in N_2 than for the cases where the calcination was in air or H_2. The authors propose that on heating in air, the Pt-ammonia complex decomposes at 250°C and the PtO_2 forms a complex with alumina, as proposed by Johnson and Keith [24]. The complex formation prevents Pt aggregation and a fine dispersion is obtained on reduction. When the catalyst was heated directly in hydrogen, the reduction took place at a low temperature (250-300°C) and thus caused little aggregation. When the preliminary heating was done in N_2, the complex decomposed at higher temperature (350°C) causing the observed aggregation.

Zharkov, Maslyanskii and Rubinov [225] note the considerable disagreement in the literature about the reduction temperature of Pt/Al_2O_3 catalysts. The authors believe that some of the apparent contradictions may be due to variations in the preparation techniques.

Four different catalysts were used. Sample I was prepared by immersing alumina into aqueous chloroplatinic acid to obtain a selective distribution of $PtCl_6^{=}$ in the outer layer of the catalyst granule. Sample II having a uniform Pt distribution was prepared in a similar manner except that acetic acid was added as a competitive adsorbate. Sample III was obtained by treating the catalyst of Sample II with gaseous H_2S after impregnation.

Sample IV was prepared by impregnating alumina with platinum-ammoniate, the Pt being uniformly distributed. After drying, all catalysts (except Sample III) were calcined in air at 500°C.

The catalysts were then reduced in H_2 at different temperatures and the activities for benzene hydrogenation were plotted against the reduction temperature. Well defined maximas were observed; the optimum reduction temperature varied between 350°C and 800°C. The authors propose that the catalysts with higher optimum reduction temperatures have higher thermal stability. They do not explain this but "thermal stability" here probably does not refer to sintering resistance, but to coke deposition, etc. The differences in the catalysts are believed to be due to the different forms of Pt in these catalysts.

2-4B. Supported Nickel Catalysts:

Swift, Lutinski and Tobin [226] have studied the physical and catalytic properties of impregnated Ni on eta and gamma-alumina supports. The catalysts were calcined in air at 500°C for 20 hours after the drying step. After H_2 reduction, the amount of metallic nickel was estimated by CO extraction.

They found conclusive evidence of an association of nickel with the aluminas (probably as nickel aluminate or similar compounds); more with eta alumina than with gamma-alumina. Reduced 2% nickel catalysts contained very little nickel that could be removed with CO or was capable of adsorbing H_2 (ie. metallic nickel). By using a broad line proton nuclear magnetic resonance technique, they found that the number of protons on the support (eta or gamma alumina) alone and in the supported catalysts were the same. Thus the nickel combines with the aluminas without affecting the surface hydroxyl concentration and is held in the lattice. For

Ni/Alumina and Ni/Silica-alumina, this means that the nickel is not only dispersed on the support but also on an ionic nickel phase. The authors propose that alumina probably donates electrons to the metallic phase. The 6% Ni/γ-alumina had considerable amount of metallic nickel after reduction as compared to the little amount on eta-alumina.

For catalysts with the same Ni area, the amount of metallic Ni decreased with increasing support area because the low area supports can combine with less nickel.

For cyclohexane dehydrogenation, Ni/Alumina catalysts are more active than Ni/Silica (cf. their lower activity in ethane hydrogenolysis, ref. [228]). This higher activity is not directly due to ionic nickel since the Ni/Alumina catalysts with this form are inactive. The role of the ionic nickel may be that of accepting or donating electrons to the metallic nickel phase, thus affecting the catalytic properties.

Morikawa, Shirasaki and Okada [183] have summarized the methods of preparation and the properties of supported nickel catalysts. The ease of reduction of the calcined catalysts varied with the method of preparation and the carrier, the alumina supported nickel catalysts being more difficult to reduce than the silica supported catalysts. Also, the nickel surface area in the reduced catalysts was larger for the silica carrier than the alumina carrier. Differential thermal analyis gave evidence for the presence of spinel Ni Al_2O_4. The authors propose that part of the nickel oxide may combine with the support, the remainder is free and can be extracted by treatment with 2N HCl.

Coenen and Linsen [163] studied the structure and properties of impregnated and co-precipitated silica supported nickel catalyst and have discussed the variation of metal support interaction resulting from the types of basic nickel-silicates. The strong metal support interaction requires a balance between a minimum free metal area and a maximum contact area with the support. They postulate that the crystallites are grown epitaxially (see Chapter 4) on the silica surface where the partially reduced basic nickel silicate serves as a matrix for the epitaxy and provides attachment to the support. The crystallites are thus hemispherical (with densest crystallographic planes in the surface) and are attached to the silica with their equatorial plane, the (111) orientation giving the best fit.

The role of metal support interaction in determining the crystallite sizes is qualitatively brought out by their data [163]:

Catalyst No.	Crystallite dia. (Å)	Lattice Const. (Å)	Fraction of Ni as Silicate	$\frac{gSiO_2}{gNi}$
1	45 ± 2.1	3.526 ± 0.001	-	0.47
2	59 ± 2.8	3.521 ± 0.002	0.22	0.50
3	63 ± 2.4	3.523 ± 0.002	0.10	0.45
4	68 ± 4.4	3.525 ± 0.002	0.09	0.46
5	57 ± 1.5	3.522 ± 0.002	-	0.40
6	69 ± 3.8	3.523 ± 0.002	0.10	0.23

Where metal support interaction is low (ie. low silicate), three dimensional hydroxide layers some having little interaction with the support would be formed and would thus sinter rapidly during reduction. This would result in large crystallite sizes and normal lattice parameter. The formation of silicate structure limits the sintering during reduction "to more or less a two-dimensional process, where the silica plates act as dividing walls."

Borisova et.al. [230] have studied the effect of the initial nickel salt and the nature of the support on the particle size distribution in the resulting catalysts. A detailed account of the structure of Ni/Alumina and Ni/Silica catalysts at various stages of preparation, along with its influence on the resulting dispersion is given in ref. [252].

2-4C. Other Systems:

Biloen and Pott [231] have shown that transition metal oxides are more difficult to reduce when supported on alumina than on silica. Lin et. al. [232] point out that part of rhenium in supported rhenium catalysts is present as ReO_3, an intermediate rhenium oxide, and is more difficult to reduce on alumina than on silica. Johnson and Leroy [233] have evidence that rhenium in Pt/Re/Alumina is present as a two dimensional surface complex with alumina which is not reduced under moderate reduction conditions. This was also shown in the work by John Freel [234].

For a 1.8% Re/Al_2O_3 catalyst, Johnson and Leroy [233] had found that on reduction of the calcined catalyst, rhenium is present exclusively as Re^{4+}. However, Webb [235] found that a 3.5% Re/Al_2O_3 catalyst is completely reducible. It was observed that the reduction becomes more difficult when the severity of the calcination is increased. Webb proposed two reasons for this apparent contradiction with the work of Johnson and Leroy. Firstly, for low metal concentrations, the high dispersion facilitates a greater interaction between the metal and the support and consequently low reducibility. Secondly, Johnson and Leroy did not completely exclude water during their reduction treatment which leads to difficulties in reduction. It is concluded that the state of rhenium in low concentration catalysts in systems which are not completely dry is the Re^{4+} state.

Sverdlova et.al. [237] have shown that under oxidizing conditions during catalyst preparation, part of the rhodium in Rh/Al_2O_3 catalysts becomes chemically associated with the alumina support. Interactions between iridium and alumina and in Co-Mo-Al_2O_3 catalysts have been known and are the subjects of recent studies [238, 276].

. Vedenyapin et.al. [239] observed that the mean crystallite size in Ru/SiO_2 (4% Ru) is approximately twice of that in Ru/Al_2O_3. It was found that Ru/Al_2O_3 is more difficult to reduce than Ru/SiO_2. The authors postulate an interaction between Ru and Al_2O_3, the ruthenium ions being captured in the octahedral vacancies of the spinel structure of γ-alumina. This interaction not only stabilizes the metal ions against reduction and agglomeration but also make the metal phase incapable of interaction with the promoter, thus Ru/Al_2O_3 catalysts modified with D-(+)-tartaric acid have no activity for the asymmetric hydrogenation of acetoacetic ester which is found in modified Ru/SiO_2 catalysts.

In a similar work, Klabunaskii et.al. [241] have studied the assymmetrizing and catalytic activity for the hydrogenation of ethyl acetoacetate. They found that the specific hydrogenation activity, the reducibility and the asymmetric activity of the Ru catalysts depends on the nature of the support and the Ru salt used for catalyst preparation. For Ru/Al_2O_3, a low reducibility is accompanied by a high dispersion and hydrogenation activity with little assymmetric activity after modification with D-tartaric acid. Ru/SiO_2 from K_2RuO_4 and $RuOHCl_3$ have similar hydrogenation activity but the former does not exhibit asymmetric activity. The authors say that the Ru/SiO_2 catalysts prepared from $K_2\ RuNO(NO_2)OH$ is difficult to reduce and has a high dispersion and also has high asymmetric activity. However their data show a low specific activity and no asymmetric activity for such catalysts. For Ru/SiO_2 from $RuOHCl_3$, increasing the reduction period increases hydrogenation activity but decreases the asymmetric activity. The authors explain that modification by tartaric acid requires the presence of Ru cations on the support surface; these are decreased by prolonged reduction. The authors believe that the asymmetric reactions may be a useful means for studying the influence of catalysts history on the state of the active phase.

Kozlov et.al. [75] found that for Pd/Al_2O_3 infrared spectra of catalysts containing chlorine differs from those with no chlorine. They attribute this to the formation of a Pd-chlorine complex on the surface of alumina. The sequence of introduction of chlorine, ie. whether introduced with alumina or by adding HCl to catalysts containing no chlorine, did not have any affect on the complex formation. The authors do not give an insight into the possible role of the alumina or the structure of the complex but note that it is not formed on all oxides and that the carrier structure may be important. PdO present in some catalyst samples (due to calcination) was converted to Pd-chlorine complex on the introduction of chlorine. Calicination of the complex containing catalysts resulted in the disappearance of the complex. Although it is difficult to speculate, the change of PdO to the complex may cause a "spreading" of the Pt on the support surface which on heating and reduction may give smaller crystallites, ie. a redispersion effect (see Chapter 5).

Another system where metal-support interaction is of interest, is the supported copper-alumina catalyst used in automotive exhaust control. Summers and Klimish [242] found that the high surface copper catalysts contain copper in the alumina lattice as a six coordinate Cu(II) species, the coordination being probably facilitated through oxygen atoms supplied by alumina or water. The deactivation for CO oxidation is associated with the formation of spinel $CuAl_2O_4$. Also, $CuAl_2O_4$ "catalyzes" the conversion of gamma alumina into the lower surface area form of alpha alumina. Such a catalyzing effect of Pt in the transformations of alumina was mentioned in [277].

2-5. Variation of Dispersion with Metal Concentration and Nature of Support:

Zaidman et.al. [267] have suggested that the factors influencing metal dispersion may be divided into two groups:

(1) The temperature, the surface concentration of metal and the nature of the carrier

(2) Preparation variables: the structural stability of the carrier, the hydration receptivity of the surface, its porosity, the adsorbability of the metal compound, the treatment of the impregnated carrier with chemicals changing the nature of metal compounds.

In this section topics under the first group will be discussed.

It can be expected that the dispersion would fall as the metal loading is increased. Since the total metal area is proportional to the product of dispersion and metal loading, there is some loading where the total area is maximum. This would have meaning if each metal loading is characterized by a unique value of dispersion in a particular preparative procedure. Since catalyst preparation is, to some extent, an art, different persons may obtain varying dispersions with apparently similar procedures.

Zaidman and co-workers [268] in an early work, investigated the system Pt/Al_2O_3 in the Pt concentration range 0.1-2% (by weight) prepared by chloroplatinic acid impregnation. The catalysts were thermally stabilized at 500°C for 6 hours to achieve a constant dispersion, which was characterized by the H/Pt ratio as measured by hydrogen chemisorption. Regardless of the origin of the alumina support, a linear rise in 1/dispersion with increasing Pt concentration was observed. Also, as the specific surface of the support is increased, a shift in the curves toward higher dispersions was seen. The overall dependence was:

$$\frac{1}{H/Pt} = \frac{1}{(H/Pt)_o} + K_t \cdot C\ \text{surf.} \qquad (2.3)$$

with a limiting $(H/Pt)_o$ ratio of 1.5 in this range. The constant K_t characterizes the ability of Pt to aggregate on the support at the temperature of thermal stabilization, C surf is the concentration of metal on the support (g/m^2) and H/Pt is the hydrogen to Pt (total) ratio (atom/atom). A similar relationship for the silver/corundum system which has substantially larger metal concentration and lower values of dispersion was cited by the authors. A constant specific activity as related to H/Pt (≡ surface area) was found for cyclohexane dehydrogenation.

The above work was extended to cover the range 300-700°C in order to study the effect of temperature on the aggregation tendency of Pt on alumina. A similar thermal stabilization at these temperatures was used. Additional heating after such stabilization did not change the dispersion significantly, it was thus assumed that a constant degree of dispersion is characteristic of the metal-support system at a given metal concentration and temperature (and also a preparative procedure). The variation of K_t (crystallization constant) was as follows:

T	K_t (m^2/g)
300°C	3.3×10^3
500°C	7.9×10^3
700°C	13.3×10^3

which can be represented by :

$$\ell n K_t = \frac{\Delta I}{RT} + B;\ \Delta I = -3.95\ \text{K cal/g. atom} \qquad (2.4)$$

The authors put forward the following mechanism for the formation of Pt particles:

On the reduction of H_2PtCl_6, the platinum is in the form of single atoms which, due to their high energy, diffuse on the support surface, leading to collisions and hence larger particles. For a given metal-support system where the interaction is constant, the probability of collisions is determined by the concentration and temperature. This mechanism is similar to that of nucleation and growth of metal films on substrates and therefore a mono-dispersion of Pt particles would be expected. This was confirmed by the size distribution in the electron micrographs.

Zaidman et.al. [269] extended their studies to a lower range of Pt concentrations (0.025 - 0.25 wt%) in the temperature range of 300-700°C. The same linear relationship was found to be valid with a limiting H/Pt ratio of 2.0 at all temperatures. The K_t values in this range were 3 to 8 times the corresponding values in the higher range (0.1 - 2%). Also $\ln K_t$ vs 1/T was not a straight line, however, when the K_t values were fitted into a straight line, a $\Delta I = -1.6$ K Cal/g-atom was obtained. Thus the mechanism of formation of Pt particles is described by the same reationship but with different values of crystallization constant and the "free energy of crystallization:" (ΔI). The authors explained these differences by postulating a lower degree of completion of aggregation in the higher concentration range. Also, the variation in H/Pt ratios at such low concentrations are partly due to transitions from isolated atoms to two and three dimensional structures with different stoichiometries. For Pt/Alumina, the two regions [270]:

Region I: $2 > H/Pt > 1.1 - 1.2$

Region II: $H/Pt < 1.1 - 1.2$

intersect at C surf. ~ 10^{-5} gm/m^2 where the crystallite size is comparable to the critical size of nuclei (6-10 Å) in thim films. In Region II, the activity is proportional to the accessible area; in Region I where all the area is available, the activity is proportional to the stiochiometry of chemisorption.

System of active component + carrier	Compound used to obtain active component	Character of the reaction between the compound containing the active component and the surface of the carrier	Limits of change in the specific surface of the carrier, m^2g	Limits of change in the concentration of the active component, wt.%	Limits of change in the surface concentration · 10^6, g/m^2	Stabilizing temperature of active component, °C	$k_t \cdot 10^3$, m^2/g,	$L_o=(\frac{G}{Me})_o$
Platinum + aluminum oxide	H_2PtCl_6	Adsorbed	200	0.2-2.0	10-100	300	3.3	1.2
The same	H_2PtCl_6	Adsorbed	100-240	0.2-2.0	10-100	500	7.9	1.2
The same	H_2PtCl_6	Adsorbed	200	0.2-2.0	10-100	700	13.3	1.1
Platinum + silica gel	Ammonia complex of platinum	Adsorbed	370	0.7-4.5	10-100	500	4.0	1.2
Platinum + aluminosilica gel	H_2PtCl_6	Not adsorbed	380	0.1-8.0	10-250	500	12.2	1.0
Chromium oxide + aluminosilicate	H_2CrO_4	Assumed to be adsorbed	620-250*	0.1-12.65	10-500	550	12.8	0.5
Chromium oxide + aluminum oxide	$Cr(NO_3)_3$	The same	200	0.5-10.0	10-500	500	4.0	0.62
Iron + aluminum oxide	Trivalent iron salt	The same	200	0.05-13.5	10-675	400	2.0	1.2
Palladium + + aluminum oxide	$PdCl_2$	Adsorbed	200	0.48-18.0	25-750	300	20.0	0.62
Nickel + chrocium oxide carrier	Coprecipitation of salts	—	10-200	0.4-50.0	100-5000	325-600	1.3	2.0

* The data relate to the total specific surface of the catalysts, which, at relatively small concentrations of the active component, does not differ essentially from the specific surface of the carrier.

In another work [271], Zaidman et.al. examined the generalization of their linear relationship for Pt/Al_2O_3 to other systems and related it to other factors such as the reaction between the metal compound and the carrier, the concentration intervals, the temperature of formation and the specific surface of the carrier etc. The authors show that the relationship is valid even for supported metal oxides.

For Pt/Silica-gel, they examined the data of Bensei et.al. [39a] (at 500°C), who had prepared the catalysts by the ion-exchange method and had found little variation of dispersion with metal concentration. A K_t.value of 4×10^3 m^2/g was calculated. The authors state that this shows a small tendency of aggregation (cf. 7.9×10^3 at 500°C for Pt/Al_2O_3 from chloroplatinic acid impregnation). For Pt/Silica-gel prepared by using H_2PtCl_6, which is not adsorbed on silica-gel, an almost linear relationship with a K_t value of 12.2×10^3 m^2/g, showing a greater tendency for aggregation, was found. K_t values for other systems were found by examining data available in the literature. (See Table 2.1).

Low values of K_t are characteristic of systems where the compound containing the active component has a strong chemical interaction with the support. For eg. K_t for Ni on chromium oxide is 2.6×10^3 m^2/g and is independent of temperature. This is consistent with the high-wettability of nickel-chromium oxide system.

The authors point out the limitations of the dispersion concentration relationships to cases where the initial degree of dispersion is lower than the level otherwise reached under steady state conditions; for eg. preparative techniques where large particles are formed in the initial stages, the dependence on concentration would be more complex. Also, the above relationship would not be expected to hold where there is a non-uniform metal distribution on the support and where the actual participating surface is unknown.

The authors compare the "optimum" metal concentrations used for different catalysts and ascribe the variation to different crystallization constants; thus at 300°C, as K_t decreases from 20 X 10^3. m^2/g for a Pd/Al_2O_3 catalyst to 2.6 X 10^3 m^2/g for Ni-chromium oxide catalyst, the "optimal" concentration increases from a tenth of a wt. % to 15-25 wt. %.

A quick check of the data given by Renouprez et.al. [38] for Pt/Al_2O_3 prepared from chloroplatinic acid showed that at 500°C the crystallization constant is 6.2 x 10^3 m^2/g. Similarly, a value of 6.4 x 10^3 m^2/g at 500°C is obtained from the data of Primet et.al. [272] although in this case, the linearity is not obeyed at lower Pt contents. Both these values are satisfactory considering the lower time of H_2 treatments employed.

Cusumano, Dembinski and Sinfelt [250] found that for a 2% Pt/Al_2O_3 catalyst, the hydrogen chemisorption is 10 times greater than for a 2% Pt on Silica-alumina catalyst. The corresponding crystallite sizes were 10 Å and 85 Å. The catalysts were prepared by chloroplatinic acid impregnation.

Kulishkin, Mashkina and Buyanova [273] found that for Pd on different carriers, the crystallization constants at 300°C are:

$$K_{\text{silica-gel}} > K_{SiO_2\text{-}Al_2O_3} > K_{\gamma\text{-}Al_2O_3} > K_{\text{carbon}}$$

with little difference in the last three constants. The catalysts were prepared by impregnating HCl solutions of palladium chloride.

Urisson et.al. [274] have pointed out some data in the literature which do not follow Zaidman's linear hypothesis.

The role of metal-support interaction in obtaining stable iron particles on MgO and in the reducibility of these catalysts has been discussed by

Boudart et.al. [147].

While the variation of dispersion with different perparative techniques and the metal concentration has been discussed, the geometrical uniformity of the crystallite distribution would also be of interest; crystallites present in local groupings would sinter more easily than if they were uniformly distributed. Pt/Alumina does seem to have such local groupings.

In a study of Pt/Alumina catalysts, Kefeli [39b] found that at low Pt concentrations, the average crystallite diameter calculated from electron micrographs agreed well with that from hydrogen chemisorption. At higher concentrations, the decomposition of chloroplatinic acid gives rise to local aggregates of particles which appear as single particles in the electron micrographs causing the discrepency in the average size calculated by the two methods.

Moss [40] using electron microscope, found that a 3% Pt on silica-gel prepared by chloroplatinic acid impregnation, consists of Pt crystallites evenly distributed in the pore structure of silica-gel. For a 5% Pt/alumina catalyst, the crystallites were grouped together as large particles of Pt although its surface area was similar to that of Pt on silica-gel. Herrmann et.al. [11] state that such non-homogeneous distribution on alumina is not expected due to the hetrogenity of the surface density of hydroxyl groups or their acid character.

Considerations such as those of Zaidman and co-workers, although simplistic, signify efforts to introduce some quantitative measure into catalyst preparation. If progress in the field of catalyst preparation is to be made, then, given a preparative procedure and a support of known characteristics, it is necessary to be able to predict the approximate degree of dispersion to be expected. For this, considerable work on the various steps involved in the preparation (vis-a-vis changes in dispersion) by different techniques is required. The dispersion characteristics of coprecipitated catalysts have not been studied in sufficient detail and it seems improbable that Zaidman's linear hypothesis would be applicable.

Zaidman and co-workers take into consideration only the support surface area. The importance of pore size distribution in the impregnation and drying steps was discussed in Sec. 2-3. Dorling and Moss [62] found that for a fixed Pt content, the smallest crystallite size occurs when a large support area is associated with an adequate pore diameter. Paryjczak and Zarzycka [275] found that for Pt on silica or alumina, at low metal coverages, the support area or the pore diameter have no influence on the crystallite size. For higher Pt contents, catalysts with lower support areas and bigger pores had higher dispersion. This is attributed to the "higher structural and energetic uniformity" (with respect to adsorption) of the surface of carriers with larger pores, especially for dilute solutions. Variation of dispersion with carrier porosity for Pt/Charcoal is discussed in [37].

Some of the contradiction in the literature data on dispersion(vs. preparative procedure, nature of support, metal content, etc.) may be due to different reduction procedures employed by different workers. Corolleur et.al. [278] found that the crystallite size in Pt/Al_2O_3 catalysts depends strongly on the hydrogen flow rate in the early stages of reduction. Catalysts with low hydrogen flow rates at low temperatures (50°C) were found to have a mean particle size of 200 Å whereas catalysts subjected to higher temperatures (200°C) have a crystallite size of 60 Å. This is, probably, due to the effect of the water formed, the higher hydrogen flow rate is effective in maintaining a low water content which along with the higher temperature used ensures fast reduction.

The meaning of the "optimum" metal loading as given by Zaidman cannot be taken literally; the metallic surface area in most catalysts continues to rise upto even 10 wt.% metal. Since the highly dispersed catalysts are more prone to sintering, the objective should be a high initial area (activity) combined with adequate dispersion stability (life) instead of a high initial area only. Of course, the thermal stabilization procedure used by Zaidman does take into account this latter factor of stability. The work of Kobayashi et.al. [136] who gave another reason for the use of the low metal contents (to obtain crystallites of specified diameters) was mentioned in Chapter 1. In reforming operations, the choice of the metal content is also dictated by the balancing of cracking and hydrogenation-dehydrogenation activity.

The low activation energies (<5 kcal/mole) for the aggregation process are indicative of a physical interaction between the metal atoms and the support. The sintering mechanism via crystallite migration and collision is discussed in Chapter 4. A theoretical analysis of the formation process as described by Zaidman, could be done by considering all the crystallites to be mono-atomic. It is known that sintering of highly dispersed catalysts in hydrogen has activation energies of 20 kcal/mole, indicating a basic difference between the two processes. It is not known whether the observed degrees of aggregations are consistent with the mobility of single atoms or small clusters on oxide substrates in reducing conditions.

2-6. Alloy and Multimetallic Catalysts:

In principle, alloy and mixed metal catalysts may be prepared by the same procedures as are used for single component catalysts. For example, in the co-impregnation procedure, the carrier is soaked in soluble metal compounds in a desired ratio and is follwed by calcination and reduction as usual. However, the impregnating solution (s) must be compatible in order that alloying may occur, ie. the different components should not deposit in separate regions of the support; this can be achieved by using salts of proper adsorptive capacities. It is possible to have one component ion-exchanged and the other adsorbed and similar variations.

Properties of alloy catalysts have been studied in unsupported systems. Often, it is important to control the compositions in order to achieve optimum activity. At present, the degree of alloying and the distribution of the components in supported metal crystallites is difficult to predict. John Freel [234] found that $Pt/Re/Al_2O_3$ catalyst prepared by co-impregnation had almost unit dispersion with every atom being a surface atom. Since the mean crystallite size is <10 Å and a significant fraction of the metal may be present as individual atoms or two dimensional monolayers, the author questions the concept of alloying, although he offers some evidence of alloying. The study of alloying in supported metal catalysts, which is a topic of current interest, is apparently limited by the experimental techniques available for such studies. The following few studies are taken from recent literature and probably indicate the nature of current work in this field.

Robertson et.al. [214] have studied the formation of Cu-Ni alloys on silica by magnetostatic and ferromagnetic resonance methods. Catalysts were prepared by impregnation, ion-exchange and co-precipitation. In the ion-exchange method, an ammonical solution containing the dissolved hydroxides was used for ion-exchange with silica gel.

Whereas the impregnated and ion-exchanged catalysts exhibited alloying, the co-precipitated catalysts contained the separate metals. The extent of alloying in impregnated and ion-exchanged catalysts was similar; however the ion-exchanged catalysts had a higher dispersion. The magnetic studies are of a limited value in studying the alloy formation because of the small particle size and non-uniform alloying, both affect the magnetization curves. The calcination step caused better alloying at the expense of dispersion. This effect was enhanced at higher nickel loadings, probably due to the higher miscibility of CuO in NiO as compared to that of NiO in CuO. The authors found no evidence of metal-support interaction.

Gomez et.al. [243] have investigated the nature of bimetallic Pt-Pd/ Al_2O_3 catalysts prepared by co-impregnation. A 0.8% Pt-0.2% Pd has a high dispersion and a narrow size distribution while a 0.2% Pt-0.8% Pd catalyst has a lower dispersion and a broad particle size distribution; showing that the presence of Pd causes the formation of bigger crystallites. The authors found some evidence of alloy formation from X-ray diffraction and also from the fact that the turnover number per platinum atom was lower in the bimetallic catalyst as compared to Pt/Al_2O_3. The authors found that chemisorption capacity was conserved in the bimetallic catalyst while the activity was lowered. The authors do not discuss the surface enrichment by Pd but the lower activity could possibly be explained by this effect since Pd has negligible activity for benzene hydrogenation at the temperature of investigation.

The reduction of $Pt-Re/Al_2O_3$ catalysts, prepared by impregnation of H_2PtCl_6 and Re_2O_7, along with several other catalysts was studied by Bolivan et.al. [244]. The presence of Pt greatly facilitates the reduction of Re_2O_7 ie the reduction occurs at much lower pressures and temperatures.

It is postulated that the important step in reduction is the nucleation of the metallic phase which can thereafter activate hydrogen. A migration of Re_2O_7, which has a low melting point and a high vapor pressure, onto the Pt particles via the support surface or the vapor phase is proposed. Evidence of such transport was found in an experiment where H_2PtCl_6/α-alumina and $Re_2O_7/\alpha-Al_2O_3$ (with different particle sizes to facilitate separation) were reduced simultaneously. The $Pt/\alpha-Al_2O_3$ was seen to incorporate some Re during this reduction. It was found that $\gamma-Al_2O_3$ is more efficient in avoiding volatization of the rhenium oxide. The reduction of NiO at 25°C in the presence of Pt is not detectable; this is supposed to be due to the inability of nickel to activate hydrogen under these conditions.

Sovostin et.al. [245] prepared Pt-Re and Pt-Pd alloy catalysts by first introducing Pt or Re from aqueous solution, calcining in air at 500°C introducing Pt by impregnation which is followed by drying and reduction. Crystallite sizes in $Pt-Pd/Al_2O_3$ were higher than in Pt/Al_2O_3 (same metal content) while those in $Pt-Re/Al_2O_3$ were smaller. The authors calcualted a very small value for the crystallization constant of Pt in the presence of Re in the range 0.28 - 2.26%Pt. Evidence of alloy formation was seen from x-ray data.

Engels et.al. [246] found that addition of Ir to Pt catalysts increases the metal dispersion. Zaidman et.al. [247] mention that the highest dispersion of both the metals in $Pt-Re/Al_2O_3$ catalysts is obtained when Pt is introduced first with subsequent drying and introduction of Re. Engels et.al. [248] mention that the metal dispersion in Pt-Re catalysts prepared by reduction of $(NH_4)_2PtCl_6-NH_4ReO_4$ with hydrogen at 500°C increases with Re concentration; Re is believed to have a dispersity increasing and stabilizing effect.

John Freel [234] discusses the properties of Pt-Re alloy catalysts. The high sintering resistance of these catalysts as pointed out by Kluksdahl [249] is also demonstrated, thus even a catalyst reduced at 820°C had a mean crystallite size of only 18 Å. Johnson and Leroy [233] proposed that Re in such catalysts is present as ReO_2 and is associated with the alumina support; the high hydrogenation activity of ReO_2 being responsible for lower coke formation.

2-7. Conclusions:

The areas of interest in catalyst preparation and where further work is needed, were discussed in this chapter. Further work in many of these areas, with emphasis on systems other than chloroplatinic acid-alumina is needed.

Theoretical and experimental work on the uptake and distribution of solute in the porous support structure during impregnation or ion-exchange, is needed. In order to control the metal distribution in the support, and to make catalyst preparation more reproducible, the redistribution of the solute by multiple impregnations (with or without intermediate drying) and during the drying step needs to be studied. The effect of support structure and the solute support interaction on such redistribution also needs to be studied. The resultant metal-concentration profiles can be obtained by electron microprobe analysis. The redistribution during drying is affected by the mechanism of solvent transport, this can be studied by using radioactive tracer techniques [192].

Further work is also needed in the identification of the chemical nature of the metallic species at different stages of catalyst preparation, vix, after drying, calcination and reduction. X-ray diffraction, infrared spectroscopy, x-ray photoelectron spectroscopy and Mössbauer spectroscopy have usually been used in such identification. Studies on the decomposition kinetics of metal salts on different supports and in different environments with the knowledge of the corresponding changes in aggregation and in the support surface chemical properties would help in the design of treatment steps to obtain high dispersions. The changes in aggregation should be related to the presence of mobile species identified by the obove mentioned techniques.

The reduction mechanisms in single and multicomponent catalysts is another area of interest. Common analytical techniques such as thermal gravimetry, differential thermal analysis and volumetry may be used. Optimal reduction procedures, for obtaining the maximum dispersion, need to be developed. It is believed [252] that nuclei for crystallites are formed during the early stages of reduction; the maximum number of nuclei (and thus the highest dispersion) would be possible at high temperatures and in the absence of water. On the other hand, in some works, it is supposed that the number of nuclei are fixed by the support structure with an ideal case of one nucleus per pore [62]. The affect of the reduction procedure on the number of crystallites obtained (and hence dispersion), thus needs to be studied. The reduction process may be studied by using analytical techniques such as thermal gravimetry, differential thermal analysis and volumetry etc. To observe the changes in dispersion during decomposition on supports or during reduction, controlled atmosphere electron-microscopy may be used.

Most of the available work is related to catalysts prepared by impregnation and ion-exchange. The preparation and characterization of precipitated catalysts needs to be emphasized in future work.

CHAPTER 3

EXPERIMENTAL TECHNIQUES

In the study of supported metal catalysts where the changes in the metal dispersion and distribution are important, the experimental methods for determination of dispersion and particle size distribution assume a key role. The methods commonly used for surface area and particle size measurements are discussed below. A brief discussion of some characterization techniques used in fundamental studies in catalysis is also given.

The methods used for surface area and particle size determinations may be divided into two broad categories (i) gas chemisorption methods (ii) physical methods such as x-ray line broadening, small angle x-ray scattering (SAXS) and electron microscopy. Magnetic methods are not discussed.

3-1. Chemisorption Techniques:

Denoting the number of surface metal atoms by Me_s, the total number of metal atoms by Me, and the number of gas atoms adsorbed by its symbol; for the H-Pt pair, we can write:

$$\frac{H}{Pt} = \frac{H}{Pts} \cdot \frac{Pts}{Pt} \quad \text{where } \frac{H}{Pt} \text{ is the adsorption stoichiometry}$$

and Pts/Pt is the metal dispersion.

In the chemisorption technique for determining the surface area of the metal, the metal surface is first cleaned of preadsorbed material by suitable treatment (reduction, degassing at elevated temperature etc.) taking care that the catalyst does not sinter to any appreciable extent. A suitable temperature for adsorption is then selected such that the adsorbate (eg. hydrogen, carbon-monoxide, oxygen) is chemisorbed on the crystallite surfaces while the adsorption on the support is minimized.

The net adsorption on the metal is determined by subtracting the adsorption due to the support only, which can be separately determined by assuming that the presence of metal does not affect the adsorption on the support. In general, the adsorption conditions must be determined for each individual system (to minimize adsorption by support).

The monolayer capacity can be found from the adsorption versus pressure data.

The metal surface area can then be calculated by knowing the stoichiometry of the adsorbent-adsorbate system and the number of surface metal atoms|m^2. The latter is usually obtained by assuming a distribution for the exposed surface planes.

Since supported metal catalysts contain a distribution of particle sizes, a reliable estimate of the surface area can be obtained if the adsorption-stoichiometry does not depend on the particle size. In the early work, it was supposed that the stoichiometry for a supported metal would be the same as that for unsupported metal. It has turned out that adsorption stoichiometries are much more complex. For supported Pt and Pd catalysts, hydrogen has the simplest stoichiometry and is widely used. Oxygen and carbon-monoxide have rather complex stoichiometries but the latter is frequently used in the industry.

For H_2, a constant stoichiometry exists over wide ranges of dispersion. For eg. a unit stoichiometry (H/Pts) has been widely reported in the literature. Stoichiometries greater than 1 have also been repprted. Several reasons have been suggested for this [32], (i) there may be sources of oxygen in the system giving higher hydrogen uptakes (ii) there may be a hydrogen spillover from the metal to the support. Such effects are more pronounced at lower metal loadings due to the low uptakes. However, a different explanation has been given by others [65]. It is supposed that in the region of high dispersions, single atoms, two dimensional arrangements, and three dimensional crystallites may be present in unknown proportions. It is postulated that very small particles on the support have higher stoichiometries. Thus a H/Pt ratio of 2 is taken to indicate the presence of atomic Pt on the surface. Thus, according to this view, different stoichiometries should be used in different ranges of dispersion to calculate the metal area.

Another widely discussed technique for surface area measurements is the H_2 -0_2 titration of Benson and Boudart [22] where 0_2 adsorbed on Pt is titrated with hydrogen. It has however been found that 0_2 chemisorption is not particularly reliable and that changes in adsorption stoichiometry occur with crystallite sizes. For eg., constant oxygen chemisorption was obtained on sintering [98] while the H_2 chemisorption was constantly falling. Thus oxygen chemisorption does not truly reflect the changes in surface area. Such considerations make this technique of doubtful use for sintering studies.

Supported Pd catalysts are more difficult to investigate. Aben [99] has used hydrogen chemisorption for Pd on silica and on alumina. Pope et.al. [85] in their investigations on Pd/Charcoal found that the catalyst sinters even under very mild pretreatment.

Other techniques include the continuous flow method where the gas to be chemisorbed is passed along with an inert carrier gas at a suitable temperature and the concentration of the outlet gas is monitored. In the pulse adsorption method, small volumes of the adsorbate are injected into the inert gas stream passing over the catalyst.

Furrauto [27] in his extensive review, has analyzed the chemisorption techniques for different metal support systems and has listed his recommendations.

3-2. Physical Methods:

3-2A. X-Ray Line Broadening:

This method is applicable for crystallite sizes larger than 50A° though there is mention in the literature of its use down to 35A° or even to 20A° in the case of certain reforming catalysts [28].

The method was first developed by Scherrer [29] and is based on the fact that for crystallites below about 1000A°, the breadth of X-ray reflections, after corrections [30,31] for instrumental broadening, is inversely related to the dimensions of the crystallites giving rise to these reflections. The instrumental broadening may be determined by using a sample where crystallite size is greater than 1000A°.

The intensity of the reflections is proportional to the square of the atomic number; thus Pt produces strong lines. In the case of amorphous supports like silica gel (which do not give rise to a diffraction pattern of their own), those lines are easily detectable. For crystalline supports, the diffraction lines of the support often coincide with those of the metal [34] and while refinements may be used, the method is only of qualitative significance for supports like alumina [33]. For low Pt contents, the lines are weak and a concentration procedure is sometimes used [13,142].

It is noted that when particles on the support are crystalline agglomerates, the line broadening technique still measures crystallite size. The technique is especially suited for routine investigations and requires small sample sizes.

3-2B. Small Angle Scattering of X-Rays:

This technique can be used for particles with dimensions between 40-500A°. It gives the particle size rather than the crystallite sizes as in the X-ray line broadening. The technique is based on the scattering observed in the neighborhood of a direct X-ray beam caused by the hetrogenities in the matter.

The curves of intensity versus diffraction angle are used to determine the particle sizes; a distribution of particle sizes can be obtained by assuming its form (2-parameter), for eg., a log normal distribution [203] is sometimes used for small particles.

Many catalyst supports have scattering centers of approximately the same sizes as the crystallites so that interference between the two is observed. The scattering due to the support cannot simply be subtracted because the two scattering are correlated. The scattering due to the pores can, however, be eliminated either by filling them with suitable quantities of liquids of similar electron density [34] or by destroying the pores by the application of high pressure [35].

Pt-alumina [36,38], Pt-charcoal [37] and Pt-zeolite [100] have been investigated. The technique is simple and does not require much pretreatment. Renouprez et.al. [38] have discussed some of the problems encountered.

3-2C. Electron Microscopy:

Electron Microscopy is becoming increasingly popular as a means of studying supported metal catalysts since the crystallies can be actually observed. The new transmission electron microscopes are capable of resolving crystallites upto 5-10A°. Scanning electron microscopes may be used for larger crystalliets. The selective carbon replica [39] technique has been frequently used for sample preparation. Specimens for transmission electron microscope can be obtained by utilizing an ultramicrotome to cut 300-500 A° sections of catalyst particles embedded in araldite [40] or by using an ion mulling technique [140]. Ruckenstein and Malhotra [91] used a thin non-porous alumina support prepared by anodic oxidation of aluminum foil, which they say is especially suitable for the transmission electron microscope (also see ref. [251]).

Once electron micrographs have been obtained, lantern plates [41], microphotometer or a binocular microscope [39] may be used to determine the particle size distributions from the electron micrographs. Wilson and Hall [32] mention the use of a "Zeiss TGZ-3" analyzer for determining particle size distributions. Some knowledge of interpretation of micrograph images is required.

Apart from particle size distributions, the micrographs reveal the uniformity of the distribution on the support. Some information about particle shapes can also be obtained. Since the samples observed are very small ($\tilde{}10^{-17}$gm[41]), extreme care must be taken to obtain truly representative micrographs. A silica support may be susceptible to sintering [32] in the electron beam while Pt and alumina may react under an electron beam [143]. Flynn et.al. [42] have discussed the limitations of electron-microscopy in the study of supported metal catalysts.

3-3. Discussion:

The different experimental techniques yield different kinds of information. In the interpretation of data, the limitations of the techniques used must be understood.

Use of chemisorption techniques must be accompanied by proper pretreatment of the sample. Adsorption stoichiometries tend to be dependent on catalyst history. This is particularly true for oxygen and thus titrations (H_2 or CO) may not be reliable even though they may be reproducible. In heat treatment studies where the catalyst is exposed to oxidizing enviroments at high temperatures, a proper procedure for reduction, removal of the water formed, and degassing must be established.

There is no standard procedure, however, similar work described in the literature should be consulted. Impurities in the support that cause higher hydrogen uptakes along with all possible sources of oxygen in the system should be identified.

Chemisorption data are generally converted into surface area and surface average crystallite size by assuming a shape for the crystallites and also the complete accessibility of the adsorbate to the adsorbent.

The shape and orientation (surface structure) of the crystallites depends on the environment and thermal history of the catalyst. The manner in which these changes are reflected in the chemisorption measurements is uncertain. Wentrcek, Kimoto and Wise [26] attributed their increased chemisorption values to a surface reconstruction whereby the number of defects or adsorption sites increases without changes in crystallite sizes. However, Flynn and Wanke [49] have disputed this assumption on the basis of their results which show that the titration stoichiometry is a function of temperature and crystallite size. Wentrcek et.al. [44] however believe that the crystal surface reconstruction is responsible for the variations. They point out the variation of 0_2 chemisorption on different Pt faces and the fact that exothermic reactions such as hydrogen and oxygen chemisorption can lead to surface reconstruction. Kikuchi, Flynn and Wanke [45] have shown that hydrogen chemisorption may increase after treatment in oxygen.

It is clear that in studies which include thermal treatment in different environments, the extent to which increased (or decreased) chemisorption values are due to changes in crystallite size, stoichiometry or the orientation of the crystallite surfaces would be difficult to ascertain.

The X-ray line broadening technique is of qualitative significance and may be used to verify the chemisorption data to check if changes in crystallite sizes have actually occured. It is useful where crystallite sizes are greater than 50A°. The small angle X-ray scattering technique seems to be of considerable value in determining particle size distributions. Since the technique is limited to the size range ~40-500A°, some care has to be taken in interpretation, for example, if the catalyst consists of a large fraction of small crystallites <40A° the growth of these small particles would bring them in the range of detection, thus causing an apparent decrease in the mean crystallite size. (This is true for all techniques with a finite range of detection).

In an electron microscopic study, if the support is dissolved during sample preparation, the possibility of changing the crystallite sizes exists. When the crystallites are present as clusters, they may not be distinguishable in the electron micrographs and may thus give unreasonably high crystallite sizes as compared to chemisorption. The uncertainty about the particle shapes may also cause some discrepency between the various determinations. The breakdown of the support structure or the coverage of the metal particles by a thin film of the support [144] may also give rise to difference between chemisorption and SAXS values.

The need for using more than one experimental technique in studies where particle size changes are important can hardly be overemphasised. A parallelism between these techniques must be established even though this may involve some qualitative accounting as discussed above. Excellent agreement has sometimes been achieved with narrow particle size distributions. However, size distributions generally broaden on heat treatment and thus, poorer agreements may be expected.

For alloy catalysts, the measurement of the number of surface atoms of different metals is also of interest. The development of chemisorption (see for eg. [176]) and other techniques for these catalyst (Chapter 1) along with their interpretation is a subject of current interest.

3-4. Other Techniques:

3-4A. Low Energy Electron Diffraction:

Low energy electron diffraction (LEED) is a technique used for the surface structure determination of a single crystal face or an oriented single crystal film, usually in a high vacuum. A beam of low energy electrons (5-500eV) is focused on to the crystal surface and are thereby diffracted. Due to their low energies, the electrons cannot penetrate the surface layers. Most of the electrons are inelastically scattered and are seperated by deacceleration from the elastically scattered electrons which contain the surface structural information. These elastically scattered electrons are impinged on a fluorescent screen to obtain a diffraction pattern whose geometry and intensities are analysed for structure determination. A technique utilizing the inelastically scattered electrons is described next.

3-4B. Auger Electron Spectroscopy:

This technique is useful for surface composition analysis of the first 3-5 atomic layers; however it can be combined with sputtering to investigate further layers, for example, to study the extent and depth of poisoning of a Pt wire by sulfur. The method is based upon identification of atoms from their electronic energy levels. The "Auger-process" is an electron de-excitation process in which the de-excitation energy is transferred to a second electron called the Auger electron. This technique is particularly important for the lighter elements for which the de-excitation through Auger-electron emission is the principal mode of de-excitation, resulting in the failure of X-ray fluoroscence technique.

Vacancies are created by an ionizing electron beam or by other methods. Transitions to these states can occur with the release of appropriate energies. Part of this energy may be utilized for the emission of the Auger-electron. The energy of the ionizing beam is continuously varied to cover the energies of the various electronic levels and the energy distribution of the Auger electrons is analyzed to obtain the desired information. The instrumentation involved is rather simple.

The use of this technique for supported metal and bimetallic catalysts is recent and only a few studies have been made [214].

3-4C. Mössbauer Spectroscopy:

The Heisenberg uncertainty principle requires that the energies emitted and absorbed by an atom be distributed instead of being monocromatic. The conservation of momentum requires the emitting and absorbing nuclei to recoil during transitions. In X-ray emission and absorption, the recoil energy loss prevents the overlap of emission and absorption lines and hence the resonance. The Mössbauer effect consists of the recoil-free emission and resonant absorption of X-rays, the overlap being made possible by the recoil free nature of the transitions. Moreover, the resonance can be affected by small Doppler velocities by moving the source and the sample relative to one another. Although the Mössbauer effect is easily observable in a few elements only, it has a wide potential use in many fields [145].

The spectrum consists of a plot of the absorption versus the Doppler velocity. If the emitting and the absorbing nuclei were in the same chemical environment, the centroid of the spectrum would be at zero Doppler velocity. Changes in electron density around the nuclei such as due to a valance difference between emitter and absorber, cause a shift of the centroid. This is known as the isomer shift and can identify variations of valency states in some cases. The splitting of nuclear energy levels into sublevels due to interaction of an assymmetric electric field with the nuclear quadrupole moment is known as quadrupole splitting. Transitions between these sublevels produce absorption peaks in the Mössbauer spectrum. A similar effect is produced by magnetic fields.

The asymmetric environment of the surface atoms is shown distinctly in the Mössbauer spectrum. Thus the quadrupole splitting can be used as a measure of the dispersion in supported metal catalysts. The use of Mössbauer technique for the quantitative determination of crystallite sizes is described in [146].

The oxidation state of metal atoms in supported metal catalysts can (sometimes) be identified from the isomer shift and quadrupole splitting. The metal support interaction, such as that between α-Fe_2O_3 and silica, alumina and MgO, as varied by catalyst preparation, pretreatment and reduction have been studied [146,147].

3-5. Discussion:

The techniques of LEED and AES are being increasingly applied in catalysis to determine the effect of surface structure on adsorption and reaction. The combination of these two techniques has proved to be particularly useful for studying surface crystallography in different environments. LEED has been utilized in determining the reactivity of stepped surfaces [149], for studying the surface rearrangements associated with exothermic reactions, and other characterstics such as carbon deposition on different surface planes [148]. For example, Joyner, Lang and

Somorjai [215] have studied the structure sensitivity of the n-heptane dehydrocyclization to toluence, by using a combination of LEED and AES, on single crystal Pt. There is indication that such work can be done at higher pressures, to make it more practical [148].

Mössbauer spectroscopy is expected to be extremely useful in catalyst surface (and dispersion) characterization and in the investigation of subtle metal-support interactions, ie. the state of the active species in supported metal catalysts which would also lead to a better understanding of catalyst preparation techniques (for eg. see the recent work of Boudart et al. [147] on Fe|MgO system).

Other commonly used techniques include, mass spectrometry, electron microprobe analysis, X-ray photoelectron spectroscopy, X-ray absorption edge spectroscopy and electron paramagnetic resonance. References for these and the techniques discussed in this chapter are included in the bibliography.

CHAPTER 4

SINTERING OF SUPPORTED METAL CATALYSTS

4-1. Introduction:

The use of supported metal catalysts at high temperatures and their repeated regeneration leads to a decrease in their activity and may also alter their selectivity for various reactions. Such loss in activity or selectivity is loosely termed thermal deactivation. It is generally believed that the reasons for this deactivation may be found among the following:

(1) Decrease in metal surface area due to the growth or agglomeration of the crystallites.

(2) Decrease in the support surface area and/or loss of active constituents or promoters.

(3) Loss of metal due to evaporation, diffusion into the support or its coverage by the support due to the collapse of the support structure.

(4) Chemical association of the metal with the support as in Copper-alumina or Chromia-alumina under oxidation treatment.

(5) Changes in crystal imperfections or surface structure of crystallites. (This would be important, especially for the structure sensitive reactions; some structural changes would be expected to occur due to changes in crystallite sizes itself - see Chapter 1).

The term sintering is sometimes taken to include some or all of the above factors. This is partly because the contribution of the various factors to the overall deactivation is not generally known. However, one of the major problems is the growth of crystallites and the consequent loss in surface area. We shall use the term sintering with this restricted meaning.

The sintering process may be affected by other forms of deactivation such as poisoning and carbon deposition. Also, the sintering may itself affect the poison resistance of a catalyst [117].

In sintering studies, the main purpose is to identify the causes and their importance. For this purpose, simplified systems are used to facilitate interpretation of the effects of a particular treatment. Typically, such studies involve a heat treatment in an appropriate environment, the catalyst being characterized at various stages to determine the kinetics of the process. Most of the studies have been made in oxygen and hydrogen environments at temperatures between 300-1000°C; these are the conditions which a typical hydrocarbon-processing catalyst may be subjected to during its use and regeneration.

These studies would be useful in apriori prediction of sintering rate for a given catalyst-support system in a particular reaction environment and help in the design of stable catalysts. The ability of going from such heat treatment studies to actual processes depends upon the understanding of the additional factors that affect sintering in the actual case. Such studies may also be useful in identifying the nature of active species in supported metal catalysts.

Before discussing sintering studies, it would be of help to delineate the areas of interest as follows:

(1) Causes of sintering: under this the problem of local temperature excursion in small crystallites which has been generally considered to be a contributing factor will be discussed.

(2) The possible mechanisms for the sintering of supported metal catalysts; their similarity with fundamental processes in other fields and the effect of temperature and environment on these mechanisms.

(3) Sintering models.

(4) Experimental studies in sintering.

(5) Studies aimed at improving the stability of supported metal catalyst.

The ultimate purpose of such work is to design stable catalysts or to reduce sintering in the existing processes. There is a great practical necessity for this; for example in reforming catalysts where the agglomeration of Pt crystallites results in a decreased dehydrogenating activity causes a decrease in activity as well as an imbalance in the dehydrogenation/acidic activity ratio [8]. A more stable catalyst would allow a higher severity or increased catalyst life. In view of the great industrial importance of such catalysts, the importance of such studies can hardly be overemphasized.

4-2. Temperature Rises in Crystallites:

The two causes of sintering that have usually been proposed are: (i) exposure of the catalyst to high temperatures in certain environments (ii) the high local temperature excursions on the crystallites due to exothermic reactions, for example during carbon burn-off. In this section we shall discuss the temperature excursions during exothermic reactions, the other topic (i) is discussed in subsequent sections.

There have been a number of attempts to predict temperature rises during carbon burn-off. The early work involved the determination of the temperature differences between the external surface and the interior portion of pellets by the application of diffusion and heat equations. The works of Damköhler,. Prater, and Wei are generally cited [141].

A distinction must be made between the supported metal catalysts (eg. Pt/Al_2O_3) and those which do not contain any metal component (eg. SiO_2-Al_2O_3). Burning off carbon may cause sintering in both cases, however, the heat dissipation and the mechanisms of sintering are entirely different. The silica-alumina cracking catalyst is made up of extremely small particles joined together and their sintering involves particle growth in a manner similar to that in compact powders. Typical supported metal catalysts consist of small metal particles inside the pores of a high area metal oxide. (see fig. 1 in ref. [1]). Simplified geometries are generally used. Only the excursions in supported metal crystallites will be discussed.

Mills Weller and Cornelius [142] recognized that the extremely small dimensions of the crystallites combined with a quick heat release in exothermic reactions could result in appreciable temperature rises.

For the conversion of a single molecule of CO to CO_2 on a platinum aggregate consisting of ten platinum atoms, by a simple heat balance, they calculated a temperature rise of 823°C. They found that conduction to the support is the most rapid mechanism for heat loss and has a characteristic time period of 10^{-11} to 10^{-12} secs while that of the reaction itself is 10^{-12} to 10^{-13} secs assuming it to be of the order of an atomic vibration. Thus the actual rate of conduction is critical to the extent of temperature rise as well as its duration. They pointed out that excessive temperatures could also be reached during the reduction of Pt. ($PtO \rightarrow Pt$).

They observed very large crystal growth when the reaction $SO_2 + O_2$ was carried out on Pt crystallites. This was attributed to "local overheating" and consequent "platinum-mobility". It was also noted that O_2 and H_2, when present simultaneously, can cause severe activity loss probably via decrease in surface area. Since the bulk temperature rose by only 8-10°C, this was attributed to local temperature excursions.

Luss [2] recognized that for typical industrial catalysts, the time between reaction events is several orders of magnitude larger than the time required for energy dissipation. Thus a reaction event which occurs in 10^{-13} sec. is followed by a relatively long period of inactivity ($\sim 10^{-3}$ sec).

Assuming the simplifed geometry of a disc for a crystallite, Luss solved the continuum heat transfer equation for the temperature differential between the crystallite and the support:

$$\frac{\partial \theta}{\partial t} = \alpha \frac{\partial^2 \theta}{\partial x^2} \qquad (4.1)$$

where θ, α and x are the temperature, thermal diffusivity and distance respectively.

Assuming $\theta = 0$ at the interface, an appreciable temperature rise which lasted for a typical reaction time was predicted. It was noted that the concept of temperature rise over such short time intervals may not have a physical meaning. He suggested that it may be treated as an excess energy transfer to the crystallite which may activate the surface diffusion of metal atoms and cause sintering. Two simplified models were suggested to calculate the upper and lower bounds on temperature rise. The author indicated the need for including the probability of several reactions occuring at the same time on various sites.

Ruckenstein and Petty [3] argued that the temperature rise must persist for sufficient time if any sintering was to occur due to crystallite hot spots. They said that the Fourier heat conduction equation cannot be applied to describe the temperature distribution within small platinum crystallites for very short periods, since the temperature fields are not fully established because of the finite velocity of propagation of such fields. The velocity of sound through bulk platinum was taken as an upper bound for the propagation speed. Taking this velocity $c = 2.46 \times 10^5$ cm/sec at 200°C, for a reaction time $t_R = 10^{-13}$ sec, $ct_R = 2.42$ Å which shows that the temperature wave travels distances less than the size of the crystallite in time durations of the order of magnitude of a reaction time. For large crystallites the heat effect is restricted to a region close to the reaction site. Since heat in metals is carried by electrons with a mean free path ~110 Å, for small crystallites, Fourier's law is again not applicable. They propose a modified Fourier's equation:

$$\tau \frac{\partial q}{\partial t} + q = -k \frac{\partial \hat{T}}{\partial r} \tag{4.2}$$

where k is the thermal conductivity, τ is a *relaxation time related to* the thermal diffusivity α and the propagation velocity: $\tau = \alpha/c^2$.

For Ct_r less than the crystallite radius, the conduction to the support is delayed, hence the transient temperature rise may be considered as adiabatic.

Ruckenstein and Petty do consider the possibility of several reactions occuring at the same time on sites of the same crystallite. Citing the work of Sakharov [151] they say that the quick release of energy may cause the nearby sites to be promoted into reaction, ultimately producing a chain of almost simultaneous reactions. They assumed an Arrehenius dependence for the number of such active sites:

$$n_s = n_s^o \, e^{-E/RT_s} \tag{4.3}$$

where T_s is the local surface temperature of an aggregate of particles and E is an activation energy. They assume that surface conduction would be more rapid than conduction into the bulk.

The crystallites are partitioned into two classes (i) the small crystallites which experience large temperature rises and thus may be expected to sinter and (ii) large crystallites which do not experience significant heat effects. The Tamman temperature* is used as the

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*A temperature range near 0.4 T_m (T_m = melting pt.) where the rate of sintering in powders greatly increases, probably via *loosening of surface* defects.

dividing temperature. By a calculation using the special equation (4.2) they show that the finite propagation velocity allows for a prolonged life of a hot spot.

In a similar work, Chan, Low and Muller [4] have shown that for the case of a short reaction time, the finite propagation velocity may contribute to significant temperature rises over and above those predicted by Luss [2].

Steinbrüchel and Schmidt [1] have given a detailed treatment of the mechanism of heat dissipation and the temperature rise in crystallites in supported metal catalysts. Reviewing previous work, they list what they consider to be the inadequacies of such work:

(1) Use of diffusion equation for heat conduction in systems whose dimensions are comparable to the mean free path of their heat carriers.

(2) Use of macroscopic transport coefficients where equilibration between different modes of heat conduction may be incomplete.

(3) Assumption that the reaction energy is released into the catalyst (crystallite) in a time comparable to the vibrational period.

The product molecules formed in an exothermic reaction are in an excited state (electronic or vibrational) and may lose energy to the crystallite in a number of ways, for eg. by the creation of phonons, excited conduction electrons or photons. Thus the mode of energy generation, the time required for energy transmission into the crystallite, and the mean free path of the heat carriers will be important factors in determining the temperature rises.

They point out that for most catalytic reactions only phonon production via the vibrationally excited states is possible. By examining typical phonon production rates they find that the assumption by Luss [2] and others where the oscillator is supposed to lose its energy in a single vibration ($\sim 10^{-13}$ sec), may not be realistic and the times may be of the order $\sim 10^{-11}$ sec.

The consideration of thermal boundary layer resistance at the metal support interface is important, since the main mechanism of heat transport across the metal-insulator interface is the coupling of metal phonons to those of the insulator rather than that of the metal electrons to the insulator phonons. Considering the fraction of the total heat current carried by the phonons in the metal and the transmission and reflection of these phonons at the interface, after some simplifications, the authors arrive at a boundary condition at the interface:

$$\frac{\partial \theta}{\partial x} = f\theta \quad \text{at} \quad x = 0 \tag{4.4}$$

where f is a constant.

Steinbrüchel and Schmidt use Luss' model with the above boundary condition for the case where the mean free path of the heat carriers is smaller than the crystallite dimension. For the very small crystallites there is no temperature gradient, but the temperature is well defined because the time over which appreciable cooling occurs is much longer than the time for collisions of phonons and electrons either with the boundaries or with each other. Using typical values for Pt/Al_2O_3 system, they found that the continuum treatment (with the above b.c.) applies if $\ell > 50$ Å and boundary scattering (uniform temp) applies if $\ell < 10$ Å (ℓ is the crystallite dimension).

The distinction from Luss' work is the introduction of boundary layer resistance, making the cooling slower. They add that the term $\tau \partial^2 \partial / \partial t^2$ added to the continuum equation in [3] and [4] is important only if $t_r < 10^{-13}$ sec which, as said before, is not realistic.

Experimental investigations of temperature rises have been done, among others, by Jech [5] (H_2 - O_2 on Pt-sponge) and Cusumano and Low [6].

In their study, Cusumano and Low [6] used an infra-red radiometric technique to study the surface thermal transients during the chemisorption and reaction of oxygen with nickel-on-silica at room temperature.

In this radiometric technique the temperature rises on the crystallites are obtained by measuring the radiation (at small times) produced by the interaction of oxygen with Ni. The authors argue that the heat loss to the support or the gas is negligible during the short time periods involved.

They found that the temperature rises were affected by the oxygen partial pressure; thus ΔT_{max} for 5.2 Torr and 53 Torr were 144°C and 215°C. Similarly the rates (dT/dt) were higher in the latter case.

Some deviations were observed which were ascribed to the crystallite size effects or catalyst pretreatment. The temperature rises were reproducible for fresh catalysts, however, for catalysts which were used for a second time after degassing and reduction showed decreased values of ΔT_{max} as well as the rates. This is believed to be the result of a decline in activity due to surface area decrease by sintering of crystallites caused by the highly exothermic chemisorption and oxidation reaction.

Decreasing the wt % of nickel is expected to result in a higher dispersion and thus higher activity/gm of metal. The maximum temperature rise for 10, 5 and 1% Ni catalysts were 212, 171 and 137°C. Thus the temperature rise / gm metal are higher for the catalysts with lower metal content. The authors suggest that the temperature rises be carefully interpreted in view of the complex thermal and mass transfer effects involved near the surface.

Luss [2] has mentioned that the quick rise of surface temperature cannot be prevented by change of reactant concentration, however, as is clear from Cusumano and Low's work the reactant concentration does affect the maximum temperature rise, probably due to simultaneous reactions at nearby sites.

The theoretical as well as experimental studies on the hot spots in crystallites have been directed towards showing that extreme temperatures may occur on the crystallite faces or even the bulk. However, there is little indication whether such hot spots do actually cause the sintering of crystallites. Thus, Steimbrüchel and Schmidt [1] say, ". . . we do not consider these calculations in any sense quantitative descriptions of actual systems nor do we imply that local overheating causes sintering."

Ruckenstein and Petty [3] postulate that as the temperature of a group of atoms on a crystallite increases above a threshold value, a detachment occurs and the mobility of these detached particles or atoms on the support results in sintering.

Luss [2] points out that the increased surface diffusion due to temperature rises may cause sintering. Mills et.al. [142] have indicated the possibility of crystallite rearrangements into more spherical forms due to exothermic reactions. Such arrangements have been discussed elsewhere in this report. Mechanisms of sintering based on high surface-diffusion rates are discussed in the next section. While both the above mechanisms are plausible (see next section), there are no quantitative data available for the extent of sintering, if any, caused by such hot spots.

The presence of even trace amounts of carbon is known to severely inhibit the surface diffusion rates, hence the contribution of temperature rises to sintering during regeneration is all the more in doubt. Alder and Keavney [12] studied the regeneration of coked and steam-sintered catalysts. Their measurements do not give a clear picture of the effect of steaming or regeneration on crystallite sizes. This is discussed in Chapter 5. Gruber [23] reported extensive sintering during a laboratory regeneration. Mills et.al. [142] report that burning off coke "restores the catalytic activity showing that no permanent damage to the platinum occurs". However, as they have noted, only a fraction of the platinum is operative, so that a restoration of activity does not prove that platinum has not undergone any change; again an instance of lack of correlation between activity and metal area.

There seems to be little quantitative work where catalysts have been characterized in terms of surface area and particle sizes after carrying out reactions at relatively low bulk temperatures.

4-3. Mechanisms for Sintering:

The three mechanisms generally proposed are discussed below.

4-3A. Particle Migration:

Sufficiently small metal particles may have appreciable mobility and may migrate on the support surface resulting in collisions with other partices with subsequent coalescence.

Very small particles, eg. free atoms or small atomic clusters may possess mobility due to their thermal energy, thus executing random walks on the support surface. The thermal energy must be comparable to the metal support interaction barrier.

Particle mobility has also been explained on the basis of surface self-diffusion on the crystallite faces [150]. It is proposed that if the atomic diffusion over the particle surface is high, ie. $(D_s t)^{1/2}$ (where D_s is the surface self-diffusion coefficient is comparable to the particle diameter, the random diffusion of adatoms on surface may cause accumulation on one side of the particle causing it to advance by an atomic distance. In supported metal catalysts, the differences in curvature at the crystallite boundaries due to irregularities on the support surface or due to the support curvature may cause a surface migration of metal atoms to regions of lower curvature and hence some mobility as discussed above [150].

A quantitative relationship between particle mobility and surface self diffusion, based on the above mentioned concept has been given by Wynblatt and Gjostein [150] . For spherical particles, the particle diffusivity D_p is related to the surface self diffusion coefficient D_s by the expression:

$$D_p = 0.301\, D_s \left(\frac{a}{R}\right)^4 \tag{4.5}$$

where a is the atomic diameter and R is the particle radius. This expression is derived by analogy from the movement of voids in solids such as inert gas bubbles produced in fuel elements due to atomic fission. A similar expression for particle diffusivity of faceted particles (normally present in oxidizing environments), where the process of particle migration is controlled by pillbox type nucleation, is also derived. Anderson [252] has plotted the particle diffusivities versus diameter for spherical and faceted particles for comparison. The diffusivity of faceted particles falls rapidly with size and the particles (Pt) are

are practically immobile once they reach a size of 88 Å [150]. The diffusivity of spherical particles falls rather slowly with size.

In the above expressions of particle diffusivity, no account is taken of the support, thus the expressions would be expected to be valid for weak metal support interaction.

Ruckenstein and Pulvermacher [17] use the evidence of Lyon and Somarjai [152] who observed disordered surface structures on (100), (111) and (110) faces of Pt at about 750°C (which they call "surface-premelting") to postulate that at temperatures higher than the Tamman temperature, the crystallites are in a quasi-liquid state and hence have an increased mobility for migration as a whole on the support surface. Although RP do not explicitly state the cause of the crystallite migration, it can be assumed that the surface premelting would imply high surface self-diffusion (via an increase in diffusable defects) and hence can explain particle mobility as above. These authors [10] also mention the movement of the crystallites due to the thermal motion of atoms at the crystallite-substrate interface.

The evidence of crystallite motion has generally come from studies of thin films on substrates. Bassett [153] observed minor translation of silver islands on graphite and amorphous carbon. Pashley et.al. [154], however, did not observe any translation for silver and gold islands on M_oS_2 substrate. The slight rotation (up to 10°) of the islands during coalescence was, however, observed by both the authors. The coalescing nuclei were seen to rotate to achieve greater alignment. Pashley et.al. proposed that the islands are not acutally mobile and that the apparent translation is due to the liquid like coalescence of the crystallites (on viewing the film under an electron-microscope, rapid disappearance of small crystallites and the simultaneous increase in size of the larger neighbouring crystallites is observed. Sometimes it appears as if the larger crystallite swallows the smaller one and in this process changes its orientation).

Masson et.al. [155,260] found that gold islands (10-30 Å) on KCl substrates exhibit Brownian movement even at 70°C. The authors propose that the crystallites are mobile if they are not in epitaxial order (see Section 4-4). During translation, the crystallites acquire an epitaxial order by rotation whereby the movement stops. They propose that surface self-diffusion or some special atomic configurations at the crystallite-substrate interface facilitate such motions. It has been observed [156] that no such rigid motion is observed for epitaxial particles. Bassett [153] has, however, observed such motion even for epitaxial particles. Models based on lattice mismatch or misalignment have been developed to explain the mobility of large crystallites [157].

Metois et.al. [260] derived an expression for crystallite mobility in which the activation enthalpy consists of two terms, a term which is independent of the crystallite size and another which is proportional to the contact area. The model explains their experimental observations for migration of aluminum crystallites on KCl substrates. From their experimental data, it is seen that at temperatures ~190°C, D_p values for crystallites up to 30 Å are ~10^{-12} cm^2/sec. The size dependence varies with temperature. At 160°C, a 10 A crystallite has a D_p value (10^{-13}) ten times that of a 20 A crystallite (10^{-14}) but at 190°C, they have the same D_p value ($10^{-12.2}$). It is seen that the migration is a low activation energy process (~20 R cal/mole at 190°C).

Other workers have postulated that the mobile behavior of the crystallites may be related to the gas contamination of the substrate surface. For eg. Thomas and Walker [158], using different metals on a graphite substrate noted the mobility of certain metals and the immobility of others under apparently similar conditions. They also noted the strong influence of environment on the mobility of some particles which in some cases was associated with channel formation. They proposed that oxide covered particles may require little shear to move on gas covered substrates. Thus gas contamination can facilitate crystallite movement even in the presence of a strong metal-support interaction. Stowell [161] considers crystallite migration possible only under contaminating conditions.

Using Pd/graphite catalysts prepared by evaporation and impregnation, Brownlie et.al. [109] noted the formation of large crystallites above 350°C. They propose that movement takes place over a layer of adsorbed gas and that its cessation and the consequent decoration takes place due to the formation of a metal-substrate interface in a manner similar to that proposed by Webb [159] . During the hydroisomerization of 1-butene at 43°C, the particle size of the evaporated catalyst increased considerably while in the impregnated catalyst only some changes in shape took place.

In a recent work, Baker and France [160] using Pd/graphite (evaporated) observed mobility of Pd particles on graphite in an oxygen environment at 850 C. In another work, Baker et.al. [164] observed movement of Pt, Pd/graphite in oxygen; this movement is related to the catalyzing affect of these metals on the $C-O_2$ reaction and results in catalytic etching of the support. It seems to the present author that the carbon deposited on the support and metal-support boundary may induce crystallite movement during carbon burn-off.

Phillips et.al. [162] observed mobility of gold on carbon and silicon-monoxide substrates. This, and other works on crystallite migration are discussed in the section on sintering studies.

From the above discussion, there is indeed, experimental and theoretical evidence of crystallite migration on substrates. Most of this evidence has come from thin film studies which are highly characterized and where physical phenomena are relatively well understood. Even thus, the results are not unequivocal and are sometimes very sensitive to the conditions of deposition, the heating environment and the presence of contaminants. A direct extension of these results to infer crystallite migration in supported metal catalysts does not seem to be feasible. The widely different support morphologies and the rather complex nature of the preparative procedures for supported metal catalysts, which leads to a lack of understanding of the structure of the metal support interface in these catalysts, make such an extension more difficult. If metal atoms are produced during the stage of preparation, the process of nucleation and growth in supported catalysts may be, at least qualitatively, similar to that in thin films; recognizing again the limitations due to the support structure. Coenen et.al. [163] have proposed that in the Ni/silica catalysts, the crystallites are grown epitaxially (Section 4-4.) on the silica surface with the partially reduced nickel silicate serving as a matrix and also providing attachment to the support. Baker et.al. [164] found that Pt/graphite prepared by evaporation and from chloroplatinic acid exhibited similar movements.

For diffusion of gold particles on a KCl (100) substrate in the temperature range 60-130°C, the D_o (pre-exponential factor) and the activation energies (E) are [165]:

d = 13 Å : $D_o = 10^2 - 10^6\ \mathrm{cm}^2/\mathrm{sec}$
$E = 26 - 30$ KCal/mole
at 130 C, $D_p = 10^{-11}$ to $10^{-15}\ \mathrm{cm}^2/\mathrm{sec}$
d = 24 Å : $D_o = 10^{-4} - 1\ \mathrm{cm}^2/\mathrm{sec}$
$E = 14\text{-}18$ KCal/mole
at 130 C, $D_p = 10^{-13} - 10^{-17}$
(d is the average particle diameter)

Baker et.al. [164] found an activation energy of ~85 KCal/mole for channel formation by a 20 Å Pt crystallite on graphite at 750°C in 5 Torr oxygen. Typical channeling rate for such a particle is 1000 Å per second.

For Pt at 600°C, the diffusivity of a 50 Å particle as predicted by equation (4-5) is $10^{-14}\ \mathrm{cm}^2/\mathrm{sec}$ with a mean displacement of 3300 Å in 5 hours [150]. For a 20 Å particle, D_p is $10^{-12}\ \mathrm{cm}^2/\mathrm{sec}$ under the same conditions. In another work [261] Wynblatt and Gjostein found that a 75 Å particle migrates less than 100 Å on alumina in 16 hours at 1000°C in H_2.

It can be seen that in thin films, the crystallite diffusion coefficients even at low temperatures (<300°C) are higher than those given by equation (4-5) or the actually observed values at higher temperatures (>500°C) (See Table 4-1). This shows that there is a basic difference between the two systems as far as crystallite mobility is concerned.

TABLE 4-1: CRYSTALLITE DIFFUSION COEFFICIENTS

System	Crystallite size	Temperature	D_p (cm^2/sec)	Activation Energy (kcal/mole)
Gold/KCl [165]	13 Å	60-130°C	10^{-11} to 10^{-15}	26-30
(Thin film)	24 Å	60-130°C	10^{-13} to 10^{-17}	14-18
Al/KCl [260]	10 Å	160°C	10^{-13}	~15
(Thin film)	10-30 Å	190°C	10^{-12}	20
Pd/graphite [164]	20 Å	750°C (5 Torr Oxygen)	10^{-11}	—
Iron/graphite [288]	120 Å	740°C (5 Torr Oxygen)	10^{-11}	15
Pt/? [150]	20 Å	600°C	10^{-11} to 10^{-12}	same as for surface self-diffusion
	50 Å	600°C	10^{-14} to 10^{-15}	
Pt/Alumina [10]	10 Å	500°C (H_2)	10^{-17}	—
Pt/Al_2O_3 [261]	75 Å	1000°C	10^{-17} - 10^{-18}	—

4-3B. Surface Migration of Atomic Species:

For large crystallites which are too sluggish to migrate or are trapped into the support structure, atomic or molecular species may detach and migrate on the support surface, attaching to other crystallites on collision. The process is visualized as being similar to the ripening or coarsening of precipitates in contact with saturated liquid or solid solutions. Thus it is supposed that each crystallite equilibriates with a particular concentration of atomic species; the smaller crystallites having higher concentrations as given by the usual Gibbs-Thompson relationship. This size dependence causes the larger crystallites to grow at the expense of the smaller ones.

While the process is easy to understand for the case of precipitates, its application to supported metal catalysts has often been criticized on the basis of unfavorable energetics for the detachment process. Flynn and Wanke [16] discuss this aspect and explain such escape of metal atoms on the basis of increased metal support interaction in oxidizing environment.

4-3C. Interparticle Transport Through the Vapor Phase:

This mechanism is similar to the above except that the atomic or molecular species are transported through the vapor phase instead of by surface diffusion. This mechanism can be possible only under suitable temperature and environment conditions. For example, Pt may form volatile oxides if placed in oxygen atmosphers at high temperature. With a Gibbs-Thompson type size dependence for the vapor pressure, sintering can proceed by an evaporation-condensation process. Such a mechanism has also been proposed for the crystallite growth in unreduced catalysts [62].

The two systems of interest here are the Pt-oxygen and Pt-chlorine systems. These are briefly treated in terms of known bulk compounds in Appendix 1.

4-4. Film Formation and Growth Phenomena:

A number of fundamental concepts that may be important in the sintering of supported metal catalysts can be borrowed from studies on the formation and growth of metal films on substrates for which a large body of literature exists. It must, however, be recognized that film studies pertain to relatively highly characterized systems as compared to supported metal catalysts where characterization is much more difficult. By characterization here is meant:

(1) Precise knowledge of the support structure, its physical-chemical characteristics, the impurities and the residual gases in the system.

(2) The ability to monitor processes of formation and growth by visual or other sophisticated techniques.

In the studies on film formation and growth, the three important processes that occur are:

(1) Diffusion and nucleation into crystallites on the substrate, of atoms incident from a high temperature source.

(2) Surface self-diffusion of deposited material.

(3) Diffusion at the internal surfaces such as grain boundaries which are formed by the coalescense of crystallites.

The importance and relevance of the above concepts in supported metal catalyst sintering is outlined below:

(1) Diffusion of atomic species on substrates: this is important in the models which are based on Ostwald ripening type mechanisms. Such considerations include the interaction of metal atoms (single or small clusters) with the substrate in different environments.

(2) The surface self-diffusion of metal atoms: this phenomenon is

of primary importance in considering the coalescence rates of crystallites in contact and in the migration of crystallites on substrates since surface self-diffusion has been utilized in explaining the mobility of large crystallites on the support. The affect of the environment and the impurities on the rates of surface self-diffusion of metals (eg. Pt, Pd, Ni) would be of particular interest.

(3) The interaction of microscopic crystallites with the substrate and the effect of environment on this interaction. This would of interest in the mechanism of crystallite migration.

(4) The shapes and surface structure of crystallites in different environments is of interest since it affects the growth process of crystallites (faceting etc.)

(5) The metal bonding at the crystallite surface and the metal substrate bonding in different environments is used to discuss the energetics of escape of atomic species from the crystallites to the substrate in Ostwald ripening type models.

In addition, the familiar problem of nucleation may also be important. Zaidman et.al. [264] postulate that atomic species are generated during the reduction step in the preparation of supported metal catalysts and that the nucleation occurs in a manner similar to that in thin films.

4-4A. Interaction of Atoms and Crystallites with Supports:

The following (Sections 4-4A, B, C) have been largely taken from references [52, 259, 262, 263].

The interaction of small clusters or individual metal atoms with the substrate governs their mobility. This interaction is studied indirectly by contact angle measurements or directly by measuring the adhesion of metal films by a mechanical method.

A number of studies have confirmed that the interaction between the metal and substrate has a physical character with a typical heat of adsorption of ~5-20 KCal/g atom. However, in the presence of oxygen this interaction may be modified. In oxidizing environments, the metal ions can be strongly bonded to the oxidic substrate. According to Pask and

Fulrath [265], the oxidation may involve the incorporation of the surface metal atoms into the substrate structure.

Substrate surfaces are generally hetrogeneous i.e., the bonding energies of metal atoms and crystallites vary over the surface. The metal atoms could be strongly adsorbed on sites where the coordination with the substrate is maximum, the bonding strength increases with increasing surface roughness on an atomic scale. The strongly bonding sites may be concentrated in definite substrate regions or there may be a uniform distribution of isolated sites depending on the substrate preparation and treatment. Impurities can give rise to strongly bonding sites by producing surface lattice distortions giving high coordination number adatoms. Electron bombardment may also give rise to temporary strong bonding sites.

Considering the migration of individual atoms on substrates, the activation energy (Esd) must be smaller than Ea, the heat of adsorption; Esd may be 10-50% of the bonding energy with the surface. Thus the mobility of metal atoms on non-metallic surfaces would be very high. It would be expected that mobility of metal atoms in oxygen atmosphere would be lower, however, there is little evidence for this.

For the migration of metal crystallites on substrates, the activation energy would be determined by the variation of their interaction with position on the substrate. The number of atomic metal-substrate contacts (~200 for a 50 Å crystallite) and the degree of "registry" between the atomic arrangements in the crystallite and substrate surfaces would determine the activation energy for surface migration of the crystallites.

The concept of epitaxy was mentioned previously. The essence of this concept of growth is the interfacial reaction between the deposit and the substrate. The nature of such interaction is highly sensitive to the conditions in the initial stages of nucleation. Under suitable conditions of deposition rate and substrate temperatures, the crystallites have either definite orientation relationships with respect to the single crystal substrate or certain preferred orientations. However, considerable reorientation can take place during the latter stages. While such rearrangement can easily take place when the crystallites are small (<10 Å), with increasing size it rapidly becomes difficult and the clusters grow (or decay) with the same atomic arrangements.

Another important concept of interest is surface pseudomorphism. If the deposition occured by monolayers, the structure of the first few monolayers would be expected to be influenced by the substrate lattice. This constraining of the deposit lattice, to match the substrate lattice misfit is small (<0.2%), and interfacial bonding is strong, the deposit will strain to match the substrate lattice exactly up to several hundred angstroms of film thickness. After this thickness, the misfit is accomodated by misfit dislocations. According to a well accepted theory, a spherical crystallite on a substrate can be coherent, ie. have surface pseudomorphism only if their size does not exceed a critical value [262].

Amorphous structures can be produced by ensuring low adatom mobility or by the codeposition of incompatible systems. Presence of oxygen would decrease the mobility of oxidizable vapor material.

Some of the experimentally known facts about epitaxy have been listed by Chopra [262]: (i) a particular value of lattice misfit or the best-fit geometrical matching of lattice is neither a necessary or sufficient condition, (ii) pseudomorphism or constraining of the lattice of the deposit by the substrate, if present, is not required for obtaining epitaxial growth (iii) epitaxy appears at the earliest stages of film growth by 3-dimensional nucleation, although orientation changes with subsequent growth may also result by recrystallization on coalescence of differently oriented nuclei, (iv) for a given material and suitable deposition conditions such as a low rate and high deposition temperature, epitaxy, or at least partial epitaxy, is generally possible on single-crystal substrates of a variety of crystal structures and different types of atomic bonds. The orientation, degree of perfection, and the deposition conditions required for epitaxy do, however, vary with different substrate materials for the same deposit and vice versa.

To emphasize that psuedomorphism is not essential for epitaxy, it is known that even the smallest crystallites (<20 Å) may exhibit epitaxy, although their interface is too small to accomodate any misfit dislocations. To consider the interaction of a microscopic crystallite with the substrate, a constant adsorption energy based on a single atom is not realistic. A single atom may sit exactly at the adsorption center; if a second atom is attached, and if the cohesive interaction (metal-metal bond) between these two atoms is stronger than the depth of the adsorption center, the difference in the bond length of these two atoms and that between two adsorption centers may cause both the atoms to shift their location to a position of lower total energy. Hence the adsorption strength of the pair may be much lower than that for a single atom. In a similar manner, the interaction between a microscopic crystallite and the substrate may be lower than what is suggested by the adsorption strength of a single atom. As mentioned before, models of crystallite migration based on such weak interactions have been developed [157].

The structure of supported metal catalysts has rarely been discussed in terms of these concepts of epitaxy and pseudomorphism. Ruckenstein [289], in an effort to explain miscibility of Cu-Os on silica catalysts, uses the concepts from thin films, in particular the assumption of coherency. It is mentioned that amorphous supports would produce an amorphous deposit. Pseudomorphism is generally exhibited when growth occurs by monolayers. Such growth is not expected in supported catalysts, hence the concept cannot, probably, be applied directly to supported catalysts.

4-4B. Coalescence of Crystallites in Contact:

The coalescence of two crystallites in contact leads to a smaller surface area and hence a gain in inter-metallic bonding, making this a thermodynamically favorable process.

The chemical potential of metal atoms in a positively curved parts of the surface is higher than of those in flat or negatively curved parts and hence the atoms tend to migrate to the latter regions. For two contacting crystallites, the migration of metal atoms is due to the formation of a negatively curved surface at the point of contact.

The material transport may take place by volume or surface diffusion. For two contacting spheres of radii r, the growth rate of the neck radius x (0.3r) is given by:

$$\frac{x^n}{r^m} = A(T)t \tag{4.5a}$$

where $n = 5$, $m = 2$ for volume diffusion

$n = 7$, $m = 3$ for surface diffusion and

A(T) contains transport parameters.

The observed rates of coalescence of contacing crystallites suggests that surface migration of atoms is the dominant mechanism. This is discussed in the next section. The kinetics of coalescence of cap-shaped crystallites on interacting and non-interacting supports has not been theoretically studied.

4-4C. Surface Diffusion:

Surface diffusion proceeds by the migration of vibrating surface atoms from one lattice position to other. The fundamental equations used for surface diffusion work are [167]:

$$D = \frac{P\,a^2\nu}{2\,\alpha} \quad (\alpha = 2 \text{ for surface diffusion, } 3 \text{ for bulk, } 1 \text{ for line}) \tag{4.6a}$$

$$J = -D\,\frac{\partial C}{\partial x} \tag{4.6b}$$

$$\langle X^2 \rangle = 2Dt \text{ for one dimensional random walk} \tag{4.6c}$$

$$D = Do\ \exp\ (-E/RT) \tag{4.6d}$$

Here: a = interatomic distance

ν = vibrational frequency ($\sim 10^{13}$/sec)

P = probability of a jump ($P \ll 1$)

D_o = term containing all the temperature independent terms of the first equation.

E = activation energy for surface diffusion.

C = concentration, J = flux

X = displacement

E, the activation energy defines the temperature dependence of $\Gamma = P\nu$, the jump frequency and is a measure of the net energy required to move atoms from one position to another. Since surfaces are hetrogeneous and atoms can move to a variety of sites, E depends on the dominant type of surface sites between which the atomic transport takes place.

A model of a surface structure which is frequently used is the terrace-ledge-kink model [166] (see Fig. 6 in 166), there are atoms in ledges, at kinks in the surface and others adsorbed on the surface. The activation energy for diffusion (E) would depend on the relative contributions of different kinds of atomic transitions which can depend on the concentration of atoms at different sites. Both D_o and E would be expected to vary with the surface plane. Recently, Rhead [167] has stressed the interactions between diffusing atoms which causes a decrease in both D_o and E. In mass transport phenomenon like coalescence, the activation energy includes the formation of the diffusing defect as well as its migration. The activation energy for surface diffusion on fcc metals may vary from 1/4 to 1/2 of the sublimation energy depending upon the mechanism of diffusion.

Rapid, liquid-like coalescence has been observed for metal crystallites that are not too large and is characteristic of weak interfacial interaction. The time required for coalescence of two equal crystallites varies approximately as the fourth power of their radii. Thus, from experimental data, it has been found that at 300 to 450°C, liquid-like coalescence ends at a particle dimension (parallel to the substrate) of about 1000 Å.

Non-metallic deposits do not display liquid-like coalescence. It is expected that strong bonding to the substrate, as in an oxygen atmosphere, would impede the denudation of the support and hence the coalescence.

The data on surface self-diffusion which is of prime importance in coalescence phenomenon, are full of contradictions, probably due to the effect of contaminants. Gjostein [168] has shown that a plot of the diffusivities versus the reduced reciprocal temperature (absolute melting point/temperature of experiment) yields a common curve for all metals, the departures being attributed to the effect of contaminants. This yields a diffusion coefficient of 3×10^{-4} cm^2/sec at the melting point. A change in the slope (ie activation energy) near 0.75 Tm has been noticed for fcc metals. Several theoretical arguments utilizing different mechanisms of diffusion have been proposed to explain this observation.

Adsorbed gases and impurities can strongly affect the coalescence of contacting metal crystallites. Migration of atoms on a metal surface completely covered by an adsorbed gas is expected to proceed more easily than on a clean surface. On the other hand, the mobility of metal atoms originating from sites in the surface is decreased by the adsorbed gas. For sparsely covered surfaces, the mobility of adatoms will decrease if the interaction between adatoms and gas molecules is attractive. It is however difficult to predict the effects of adsorbed gas at temperatures where the gas molecules themselves are mobile.

The surface migration of metal atoms dissociated from ledges in the metal surface leads to coalescence. If the impurity atoms can strongly adsorb at ledges, this will severely impede the transport of metal atoms from sites in the metal surface. A relatively small number of impurity atoms can fill up the ledges completely. The ledge coverage by impurity atoms decreases at high temperatures (due to their mobility); thus decreasing its effectiveness.

However, for oxygen adsorbed on copper, an increase in self-diffusion rates has been observed at high temperatures. With oxygen, both the pre-exponential foactor and activation energy may be decreased. The effect of adsorbed gas is complicated by the possibility of a chemical reaction between the gas and the metal.

Rhead [167] gives the effect of adsorbed contaminants on the surface diffusivities as a function of the contaminant partial pressure. This enormous increase in surface self-diffusion coefficients due to the contaminants has been termed as "catalyzed surface diffusion." D_s values of ~1 cm^2/sec (c.f. 3×10^{-4} cm^2/sec at melting point for pure metals) have been observed at moderate temperatures. A steep rise occurs near

$D_s = 3 \times 10^{-4}$ cm^2/sec. The author proposes two explanations:

(1) The formation of a surface compound or alloy which has less strongly bound atoms. A decrease in diffusivity would occur if it has higher binding.

(2) The surface compound may melt to form a two dimensional liquid.

Work on surface self-diffusion in the presence of halogens shows that halogens do promote surface self diffusion though the discontinutiy in the activation energy and the surface melting is not observed.

For Au in H_2, Gjostein [169] found that surface diffusion is negligible below 800°C, while Gequzin et.al. [169] found appreciable mobiltity even at 500°C. This has generally been attributed to the effect of contaminants.

When the region between the crystallites has been filled, the resulting configuration has a grain boundary which separates the two particles. The grain boundary migrates out of the metal-lattice by shifting through one of the particles, thus reducing its surface area and the coalesced particle assumes its equilibrium shape.

4-5. Sintering of Unsupported Catalysts:

The sintering studies of unsupported metals in different environments provide information about the metal-environment interaction and its effect on various diffusion phenomena. The important processes occuring in the sintering of unsupported metals would probably be similar to those for fine metal powders. Surface and volume diffusion would be important, the former being particularly important in reacting environments. While such results may be useful for the extensions to supported metals, the absence of the support should be recognized; thus inferences to the coalescence step in the crystallite migration model are valid only for weak metal-support interaction.

Finely dispersed blacks of group VIII noble metals can generally be obtained [266] by the reduction of the metal salts by formaldehyde or sodium borohydride. Extreme care has to be taken to wash out the impurities.

The relatively high thermal instability of such systems presents experimental difficulties but also lends to an easy interpretation of the effects of treatment conditions. The present discussion is limited to Pt blacks.

McKee [120] in his study of sintering of unsupported Pt/black in H_2 at 150-200°C found the relationship $S = Kt^{-0.11}$ where K is a function of temperature. A large decrease in area was noted on reduction of the chemisorbed oxygen layer. This was attributed to the local heating caused by the reaction:

$$PtO + H_2(g) \rightarrow Pt + H_2O \text{ (ads)}; \Delta H - -42 \text{ KCal/mole} \qquad (4.7)$$

No sintering was observed for the unreduced metal, i.e. the chemisorbed oxygen inhibits the growth process which is supposed to proceed by vacancy migration. The sintering procedure is not well described.

Khassan, Fedorkina and Emel'yanova [170] studied the sintering of Pt black in vacuum (2×10^{-5} Torr) in the temperature range 300-700 C.. Along with the surface area and x-ray diffraction measurements, the activity for H_2O_2 decomposition and cyclohexane hydrogenation were monitored.

At all temperatures, the activity and surface area initially decreased monotonically and then leveled down to steady state values; the steady state values decreasing exponentially with temperature. Second order sintering kinetics was observed:

$$-\frac{dS}{dt} = k_s S^2 \qquad (4.8)$$

The specific activity for both the above mentioned reactions did not change with sintering.

The activation energy for the sintering process was found to be 18.4 Kcal/mole which is of the same order of magnitude as the recrystallization energies on the surface of solids. The authors propose that the sintering of Pt-black in vacuum is a direct consequence of the recrystallization occuring on the surface as a result of temperature induced migration of atoms.

In another investigation, Khassan, Atyakoheva and Emelyanova [171] studied the sintering of Pt-black in air at 300 and 600°C. As in vacuum, heating of Pt-black in air at these temperatures leads to a monotonic decrease in area and activity; however, at 300°C, the steady state is achieved faster in air than in vacuum. At 600°C the steady state is achieved in approximately the same time (20-30 minutes). The steady state surface areas and activities at both temperatures were higher in air than in vacuum. At 300°C the activity in vacuum decreased by a factor of 5 and by 1.7 in air. At 600°C the corresponding values are 112 and 30.

The activation energy for sintering in air is 5 Kcal/mole. According to the authors, the lower activation energy in air shows that air facilitates some surface processes which lead to sintering of Pt-black. This statement should be interpreted carefully since the extent of sintering in air is lower. By a rough comparison it can be seen that the initial sintering rates at 300°C in air and vacuum are comparable; however the inhibiting effect of oxygen begins to appear at later stages.

Hassan [172] has also investigated the sintering kinetics of unsupported platinum black catalysts in nitrogen, oxygen and hydrogen at

300-600°C. From activity and surface area determinations, it was found that the sintering rate in different environments varies as:

$$H_2 > \text{vacuum} > N_2 > O_2$$

The high sintering rate in H_2 is explained due to its cleaning effect by reduction of surface oxides. The inhibition to sintering in O_2 is attributed to the formation of an oxide layer. The results in vacuum are intermediate and can be explained by oxygen contamination.

The sintering rates in O_2 and H_2 were second order:

$$-\frac{dS_{pt}}{dt} = K_s S_{pt}^2 \tag{4.9}$$

The activation energies of the sintering process in H_2, O_2 and N_2 were found to be 2.9, 2.7, and 19 Kcal/mole respectively. The high activation energy in N_2 was explained on the basis of formation of NO_2 on the surface (from initially chemisorbed oxygen) with its desorption being the rate controlling step.

The inhibiting effect of oxygen in the sintering of Pt-blacks is also discussed in [90].

Baird, Paal and Thomson [173] have investigated the sintering of Pt-black catalysts in H_2, He, air and ethylene as a contribution towards understanding the relationship between thermal treatment of Pt in different environments and its surface and catalytic properties. The temperatures used were in the moderate range (~360°C).

Heating in helium, air or vacuum caused negligible sintering. Pretreatment with H_2 (room temperature) followed by heating in helium caused some sintering which was uniform, as shown by the electron micrographs. Heating in hydrogen alone (at ~360°C) caused extensive and non-uniform sintering. Negligible sintering was observed when oxygen was preadsorbed at room temperature followed by introduction of hydrogen without heating. Pretreatment with air at elevated temperatures (360°C) followed by heating in hydrogen caused considerable sintering. Kinetic data is not given.

That oxygen-hydorgen reaction does not cause extensive sintering by itself can be argued on the basis of the above results; thus the sintering is primarily due to hydrogen. When a hydrogen layer is formed at room temperature and heated in helium, it results in uniform sintering. At higher temperatures it attacks more selectively. The pretreatment with air at elevated temperature causes a "loosening" of the Pt structure by the migration of oxygen into the Pt but causes little sintering by itself. Subsequent H_2 treatment causes greater sintering due to this loosening which may also be enhanced by the oxygen-hydrogen reaction. When used for hydrocarbon reactions, the carbonecous deposits protect the metal from sintering.

The authors conclude that under the conditions (~360°C), Pt/H_2 behaves as a very mobile system (in terms of material transport) and that hydrogen can transform the structure of Pt and hence affect the active centers.

In an extension of their work, Baird, Paal and Thomson [174] found that oxygen can remove carbonecous deposits more efficiently than hydrogen and that water causes sintering if the surface is not preadsorbed with hydrogen. The role of water too is explained in terms of oxygen removal. For Pt-black treated with hydrogen, the effect of water may be as:

$$\text{Pt-H(s)} + H_2O(g) \rightarrow \text{PtOH(s)} + H_2(g) \qquad (4.11)$$

Since subsequent heating in helium does not show sintering, the role of surface hydroxyl groups or oxygenated species in sintering was discounted.

The emergence of carbon, from within the Pt-black to the surface, inhibits the sintering process. The extent of its emergence is proposed to be temperature dependent, a reversal in the observed trend of sintering at high temperatures (> 360°C) is thus explained. The standard treatment was heating the sample to the required temperature in static air in 30 minutes, maintaining the temperature for 20 mins, purging by He and followed by H_2 flow for 60 minutes. A bimodal particle size distribution was obtained at 420°C, the extent of sintering in this case being lower than that at 300°C. In a variation of this treatment at 420°C where static air was replaced by a flow of air and the hydrogen treatment omitted, the crystallites obtained corresponded to the more sintered fraction of the bimodal distribution obtained previously. Unless the flow of air causes a pronouned difference in carbon removal (versus that of static air), this result is difficult to understand. Moreover, H_2 causes extensive sintering and its omission only could not have led to lower sintering.

The authors did not discuss the role of carbon in their first work [173] although from this work it is found to be important even at 200°C.

Santacesaria and Gelosa [175] have studied the influence of the pretreatment conditions of Pt-black catalysts on their activity and selectivity, for the hydrogenolysis and skeletal isomerization reactions of n-hexane. While these effects are of interest, only their results on sintering characteristics will be considered here. They followed the sintering behavior by measurements of volume contraction of the solid. They too found no sintering in helium atmosphere while hydrogen had a marked influence. A room-temperature adsorption of H_2 prior to heating caused sintering, as was noted in [173]. They used two heating cycles:

P_1: heating in a flow of hydrogen to 300°C in 1/2 hour,

P_2: hydrogen adsorption at room temperature (1 hour) followed by heating to 300°C in a helium flow (1/2 hour).

The sintering rates in the two cases are similar, except for a relative displacement of the P_2 treatment to higher temperatures. They summarized the pretreatment as follows:

$$\begin{array}{l}\text{structural}\\ \text{modification without}\\ \text{oxygen removal}\end{array} \xleftarrow{P_2} H_2 \text{ chemisorption} \xrightarrow{P_1} \begin{array}{l}\text{structural}\\ \text{modification}\\ \text{with partial}\\ \text{oxygen removal}\end{array}$$

Since oxygen treatment was not done at elevated temperatures (it could have come only from room temperature adsorption), it must have been present only on the surface and can be removed by H_2 chemisorption. The above scheme is thus not clear. The authors have apparently concluded this from the similarity in the selectivity versus time behavior for catalysts which had been pretreated with oxygen (300°C) and those with P_2 treatment.

4-6. Miscellaneous Studies:

The influence of hetrogeneous reactions on surface rearrangements and surface transport is well known. Surface rearrangements are known to occur at temperatures as low as 200-300°C. Bond [101] postulates that the surface rearrangements could be due to: (i) a higher surface temperature than the bulk facilitating atomic transport. (ii) The adsorbed species weakening the binding of surface metal atoms to those below and hence causing the migration of the former.

Macrae [177] made an early study of surface rearrangements on Ni due to oxygen chemisorption by using low energy electron-diffraction.

Norris and Parravano [178] have investigated the affect of a chemically reacting environment on surface transport phenomena. They monitored the sintering of Pt microspheres (155 to 195μ) in contact by the growth of the neck radius while heating in He, H_2, and O_2 in the temperature range 850-1020 C. Surface rearrangements were observed with a metallurgical microscope. Striae (thin and narrow grooves) formation and faceting occured in both H_2 and O_2 but changes in surface topography occured in O_2 only and increased with increasing oxygen partial pressure, helium had no such effects. Using and expression for neck diameter X versus t ie. $(\frac{X}{r})^m = Kt$ (r is particle radius), they found m values between 12 and 18 which are greater than those for non-reactive sintering.

Extremely high transport rates were found in hydrogen atmospheres. These did not change appreciably with temperature, showing that transport in hydrogen is a low activation process. At 900 C, they calculated a Ds value of 7×10^{-8} cm^2/sec. It is proposed by the authors that transport in H_2 occurs by the surface migration of vacancies created with H_2.

$$2\ Pt + H_2 \rightleftharpoons 2\ (Pt\text{-}H) + \square_s \qquad (4.12)$$

where $\square$s is a vacancy.

On addition of oxygen to H_2, the transport rate decreased, probably due to the reaction between oxygen and Pt-H complex. Subsequent addition of oxygen increased the transport rate, probalby due to thermal activation of mass transport (H_2O was produced). In pure oxygen, the transport is only local and has been ascribed to the "pinning" of surface vacancies by oxygen. Very little sintering was thus observed in pure oxygen. The surface rearrangements due to this local transport are believed to be due to the formation of unstable PtO_2 with low escape probability which causes back-scattering. This also results in the observed faceting in oxygen.

Ushakov et.al. [294] discuss the formation of a stable Pt-H compound ($PtH_{0.6}$) in highly dispersed Pt/Alumina catalysts at high temperatures in H_2 (500-1250°C). This is accompanied by a decrease in the lattice parameter of Pt as seen from the x-ray diffraction patterns. The possible role of such a compound in the sintering of supported catalysts was spectulated but not defined.

4-7. Sintering Models:

4.7A. Models Based on Surface Migration of Atomic Species:

This mechanism was described in Section 4-3B. The transfer of materials from the smaller crystallites to the larger crystallites is facilitated by the different concentrations of the atomic species surrounding the crystallites. Since the attachment/detachment phenomenon is similar to that of vaporization or the dissoulution of solid particles; the Gibbs-Thompson relationship has been widely used to give the size dependence for the equilibrium concentration of atomic species on the substrate surrounding the crystallites.

The approach used for models using this mechanism is typical of that used in Ostwald ripening which is the name given to the growth of solid particles in a solid or liquid medium via atomic or molecular transfer In this growth process, the concepts of nucleation and growth from the solution (medium) are not important but "ripening" (growth of some particles and dissolution of others) via the solution is of interest; the supersaturations being generally low. This process is important for eg. in the growth of precipitates or particles in dispersion-strengthened materials.

The models to be considered here are those developed by Chakravarty [84], Wynblatt and Gjostein [150] and that of Flynn and Wanke [16].

Since these models, particularly the first two, are similar to those in Ostwald ripening, a brief discussion of Ostwald ripening is given below.

The main steps in the development of Ostwald ripening models are as below:

(1) A distribution function f(R,t) is defined such that f(R,t) dR gives the number of particles at time t having radii between R and R + dR. A continuity equation applicable for low supersaturations is next considered:

$$\frac{\partial f(R,t)}{\partial t} + \frac{\partial}{\partial R}\left(F(R,t)\,\frac{dR}{dt}\right) = 0 \qquad (4.13)$$

A rigrous derivation of this equation is given by Kahlweit [253]. Dunning [254] derives it by a simpler method.

(2) The conservation of the solute gives:

$$C_I(o) - C_I(t) = \left(\frac{wd}{M}\right)\int_0^{\infty} f(R,t)R^3 dR \qquad (4.14)$$

where w is a shape factor, M is the molecular weight and d the density of the crystal. $C_I(o)$ and $C_I(t)$ are solute concentrations initially and at time t. If the variation in the average concentration of the species in the solution is neglected and particles are assumed spherical, then:

$$\frac{4}{3}\int_0^{\infty} f(R,t)R^3 dR = \phi = \text{constant.} \qquad (4.15)$$

(3) Given an initial particle size distribution and a solution concentration, the objective is to find the variation in particle size distribution and the concentration in the solution at various times. Thus the continuity equation (4.13) must be solved subject to the restraint (4.14) or (4.15). This can be done by a numerical method. Asymptotic analytical solutions can be obtained if one of the two steps of diffusion or reaction (ie interface transfer) is assumed to be limiting.

(a) Interface or Reaction Controlled Growth:

The driving force is taken to be the difference between the equilibrium concentration (C_R) as given by the Gibbs-Thompson equation and the actual average surface concentration C* which is the equilibrium concentration for a particle of critical radius.

$$\frac{dR}{dt} = -K_T \, \Omega \, (C_R - C^*) \tag{4.16}$$

where K_T is a transfer constant and Ω is the molar volume of the solid phase.

(b) Diffusion Controlled growth:

In this case:

$$\frac{dR}{dt} = - D\Omega \left(\frac{dC}{dR}\right)_R \tag{4.17}$$

where D is the diffusion coefficient of the solute. To obtain $(dC/dR)_R$, the steady state problem of diffusion from an infinite medium of concentration C* to a sphere of radius R is considered. Thus

$$\frac{dR}{dt} = D\Omega \, \frac{C^* - C_R}{R} = \frac{\gamma C_o D\Omega^2}{R_g TR} \left(\frac{1}{R^*} - \frac{1}{R}\right) \tag{4.18}$$

where γ is the surface free energy, C_o is the equilibrium concentration at a planar interface, R_g is the gas constant and R* is the critical radius, ie. the radius of the particle which is neither growing nor dissolving.

The expression for dR/dt obtained above must now be substituted in (4.13). The variation of C* due to variation in R* is generally neglected but Dunning [254] has avoided this assumption for the case of diffusion control.

The asymptotic solutions can be obtained analytically and the particle size distribution is found to become stationary and also independent of of the initial particle size distribution. The solutions are given below [338]. Here $\bar{R}$ is the average radius, ρ is R/R^* and $R^*(o)$ is R^* at $t=o$.

1. Reaction Controlled:

$$R^* = \frac{9}{8}\bar{R} \; ; \quad R^*(t)^2 - R^*(o)^2 = \left(\frac{K_T C_o \gamma \Omega^2}{R_g T}\right) t$$

$$f(\rho,t) = \frac{\rho}{(2-\rho)^5} \exp\left(\frac{-3\rho}{2-\rho}\right) \quad \text{for } o<\rho<2 \qquad (4.19)$$

$$f(\rho,t) = 0 \qquad \text{for } \rho>2$$

2. Diffusion Controlled:

$$R^* = \bar{R} \; ; \quad R^*(t)^3 - R^*(o)^3 = \left(\frac{8\gamma C o D \Omega^2}{9 R_g T}\right) t$$

$$f(\rho,t) = \rho^2 \left(\frac{3}{3+\rho}\right)^{7/3} \left(\frac{3/2}{3/2-\rho}\right)^{11/3} \exp\left(\frac{-\rho}{3/2-\rho}\right) \quad \text{for } 0<\rho<\frac{3}{2} \qquad (4.20)$$

$$f(\rho,t) = o \qquad \text{for } \rho > 3/2$$

We first discuss the models developed by Chakravarty [84] and by Wynblatt and Gjostein [150]. The two models are similar, although the latter authors claim that their approach is physically more realistic.

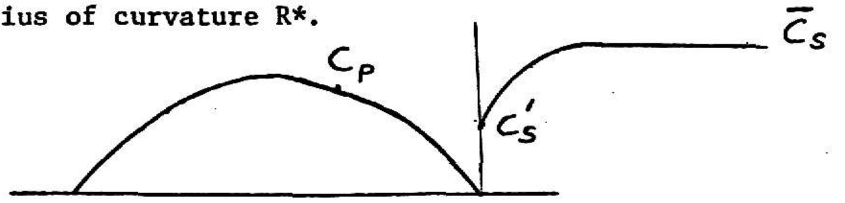
The particle geometry in both the cases is taken to be that of a spherical cap with a radius of curvature R and a contact angle θ.

Thus the crystallite volume is given as $\frac{4}{3} \Pi R^3 \propto_1$ and the exposed area as $4 \Pi R^2 \propto_2$ where

$$\propto_1 = \frac{2 - 3\text{Cos}\theta + \text{Cos}^3\theta}{4} , \quad \propto_2 = \frac{1-\text{Cos}\theta}{2} \qquad (4.21)$$

General equations are first developed which are later simplified for the two limiting cases of interface or surface diffusion control. The two steps are first considered separately.

(1) Surface diffusion: It is assumed that the substrate has an average adatom concentration of $\overline{C}_s$ which corresponds to the adatom concentration on the substrate in equilibrium with a crystallite of a critical radius of curvature R*.



For $\overline{C}_s$, Wynblatt and Gjostein give the following Gibbs Thompson equation:

$$\overline{C}_s = C_s^{eq} \exp \left[\frac{2\gamma\Omega}{R_g TR^*}\right] \tag{4.22}$$

where C_s^{eq} is the atom concentration on the *substrate in equilibrium* with an infinite-size crystal. Chakravarty following Mullins [255] gives the Gibbs-Thompson equation as:

$$\overline{C}_s = C_s^{leq} \exp \left[\frac{2\gamma\Omega}{R_g TR^*}\right] \tag{4.23}$$

where C_s^{leq} is the adatom concentration on the substrate corresponding to the equilibrium vapor pressure P_{eq} of the film material at T. C_s^{leq} is obtained by equating the adsorption and desorption rates:

$$\frac{P_{eq}}{\sqrt{2\Pi m_c k_T}} = C_s^{leq} \nu_s \exp \left(- \frac{\Delta G_{des}}{R_g T}\right) \tag{4.24}$$

where ΔG_{des} is the activation energy for desorption of adatoms from the substrate, ν_s is the vibrational frequency of an adatom on the substrate m_o is the mass of an adatom and k is Boltzmann's constant.

Wynblatt and Gjostein obtain C_s^{eq} by first considering the adatom concentration (C_p) on the crystallite at the edge or boundary:

$$C_p = C_p^{eq} \exp \left[\frac{2\gamma\Omega}{R_g TR}\right] \tag{4.25}$$

where C_p^{eq} is the adatom concentration on an infinite size particle. To get C_s^{eq} (on the substrate) from C_p^{eq} (on the particle), a transfer constant

$$\beta = \frac{\nu_p}{\nu_s} \exp\left(-\frac{H_{ps}}{R_g T}\right) \tag{4.26}$$

where ν_p/ν_s is the ratio of the vibrational frequency of an atom on the particle to that on the substrate and H_{ps} is the difference in bond energy of an atom on the particle and on the substrate is used.

$$C_s^{eq} = \beta C_p^{eq} \tag{4.27}$$

Comparing C_s^{eq} of Wynblatt and Gjostein and C_s^{1eq} of Chakravarty, it is found that:

$$C_s^{eq} = \frac{\nu_p}{\nu_s} \exp\left(-\frac{H_{ps}}{R_g T}\right) C_p^{eq} \tag{4.28}$$

$$C_s^{1eq} = \frac{1}{\nu_s} \exp\left(\frac{\Delta G_{des}}{R_g T}\right) \frac{P_{eq}}{\sqrt{2\Pi m_o kt}} \tag{4.29}$$

which are similar. C_p^{eq} will contain an activation energy term involving metal-metal bonding.

The adatom concentration on the substrate at the crystallite edge is taken as C_s' (unknown). By considering surface diffusion of adatoms, an application of Fick's law gives the flux (J_p) as:

Wynblatt and Gjostein: $$J_p = \frac{2\Pi D_1}{\log(L/R \operatorname{Sin}\theta)} (\bar{C}_s - C_s') \tag{4.30}$$

Chakravarty: $$J_p = \frac{2\Pi D_1}{\log L} (\bar{C}_s - C_s') \tag{4.31}$$

where D_1 is the diffusion coefficient of the diffusing atomic species on the substrate. The difference in the demoninator is due to a fixed screening distance L (distance from the particle center to the point where the concentration is the same as the average concentration on the substrate) taken by Wynblatt and Gjostein compared to LRSinθ by Chakravarty.

Both seem to be arbitrary.

(2) Interface Transfer:

Wynblatt and Gjostein first correct C_p to obtain the atom concentration (C_R) in equilibrium with a crystallite of radius R:

$$C_R = C_p \beta \tag{4.32}$$

where $\beta = \frac{\nu_p}{\nu_s} \exp(-H_{ps}/R_g T)$ as before.

The atomic flux at the interface (J_i) is proportional to the difference between C_R and C_s' ie.

$$J_i = 2\Pi R \mathrm{Sin}\theta .\ a.\ \beta'(C_s' - C_p \beta) \tag{4.33}$$

where $\beta' = \nu_s \exp(-H_m^s/R_g T)$ and H_m^s is the activation energy for adatom migration on the support, a is the atomic spacing in the crystallite.

Chakravarty argues that the rate of atom transfer at the interface is proportional to the surface area and local adatom concentration. Thus

$$\text{Rate of atom attachment} = 4\Pi R^2 \alpha_2 \beta^* C_s' \tag{4.34a}$$

$$\text{Rate of atom detachement} = 4\Pi R^2 \alpha_2 \beta^* C_R \tag{4.34b}$$

$$\text{or } J_i = 4\Pi R^2 \alpha_2 \beta^* (C_s' - C_R) \tag{4.34c}$$

where β^* is a constant (see below).

Again, the forms of the two expression (4.33) and (4.34c) are similar except for the effective areas and β^*. The expressions for C_s' and C_R are also different as stated before. Chakravarty obtains an expression for β^* by considering the equilibrium between a crystallite of radius R with its adatom population:

$$4\Pi R^2 \alpha_2 C_R \beta^* = 4\Pi R^2 \alpha_2 \frac{\nu_p}{a^2} \exp\left(-\frac{\Delta G_1(R)}{R_g T}\right) \tag{4.35}$$

(rate of attachment) (rate of detachment) where $\Delta G_1(R)$ is the activation energy for desorption of a single atom from a crystallite of radius R. Letting $R \to \infty$

$$\beta^* = \frac{\nu_p}{a^2 C_s^{1eq}} \exp\left(-\frac{\Delta G_1^\circ}{R_g T}\right) \qquad (4.36)$$

where ΔG_1° refers to a flat surface. Considering the activation energy term present in C_s^{1eq}, the overall activation energy for β^* is that of desorption of an adatom from the substrate. The activation energy for surface migration is much smaller than that for desorption and hence this does not seem satisfactory.

The unknown concentration C_s' can be eliminated by equating the two fluxes J_p and J_i. Also, since

$$\frac{d}{dt}\left(\frac{4}{3}\Pi\, R^3 \alpha_1\right) = J_p \Omega \; = \; J_i \Omega \; , \qquad (4.37)$$

an expression for $\frac{dR}{dt}$ can be obtained. Finally, by substituting $\frac{dR}{dt}$ into the continuity equation, the asymptotic solutions for limiting cases of diffusion and interface control satisfying the conservation restraint can be obtained.

For both limiting cases, Chakravarty obtained universal distribution curves which are asymmetric δ-function types and are independent of the initial size distribution. In both the cases there are finite cut off points for particle sizes. For surface diffusion control, the maximum particle size in the final distribution is 1.33 times the critical radius which is identical to the mean radius. The rate law for this case is:

$$R^*(t) = R^*(o)\left[1 + \frac{t}{ts}\right]^{1/4} \qquad (4.38a)$$

where $$\frac{1}{ts} = \frac{4D_1 \Omega^2 \gamma C_s^{1eq}}{9.5 \log\alpha_1 kT} \qquad (3.38b)$$

For interface control, the cut off radius is twice the critical radius and the growth law is:

$$R^*(t)^2 = R^*(o)^2 \quad [1 + t/t_i] \tag{4.39a}$$

where
$$\frac{1}{t_i} = \frac{\alpha_2 \, C_s^{1eq} \, \gamma\Omega \, \beta^*}{\alpha_2 kT} \tag{4.39b}$$

Wynblatt and Gjostein obtained slightly different results:

Diffusion control:

$$R^*=\overline{R};\ R^*(t) = R^*(o) \quad [1 + K_D t/R^*(o)^4]^{1/4} \tag{4.40a}$$

where
$$K_D = \frac{27 D_1 \beta C_p^{eq} \gamma\Omega^2}{64 \log(L/R\mathrm{Sin}\theta) \alpha_1 kT} \tag{4.40b}$$

The cut off point is at $R/R^* = 4/3$.

Interface Control:

$$R^*=\overline{R};\ R^*(t) = R^*(o) \quad [1 + K_I t/R^*(o)^3]^{1/3} \tag{4.41a}$$

where
$$K_I = \frac{4\mathrm{Sin}\theta.\ a.\beta'\beta \ C_p^{eq} \gamma\Omega^2}{9\alpha_1 \ kT} \tag{4.41b}$$

with the cut off at $R/R^* = 3/2$.

Flynn and Wanke [16] have proposed a model for the sintering of supported metal catalysts based upon the escape of individual atoms (or molecules) from the crystallites, their rapid migration over the support surface and finally their capture by other crystallites on collision. The migrating species may depend on the environment.

The smaller crystallites equilibriate with higher concentration of surface atoms; however, for a practical range of crystallite diameters, they find that the size effect on the rate of loss is not important and thus model the rate of loss from the i^{th} crystallite as:

$$\frac{dL_i}{dt} = A \exp\ (-Ea/R_g T) \tag{4.42}$$

where A = pre-exponential factor

Ea = activation energy for atoms (molecules) moving from crystallite to support.

L_i = atoms lost by crystallite i.

The rate of capture of atoms (molecules) by crystallites has a linear size dependence:

$$\frac{dG_i}{dt} = \frac{\alpha v}{N_t} \frac{F_s}{S_o} D_i \quad \text{where} \tag{4.43}$$

α = sticking probability of atoms colliding with crystallite (collision accomodation coefficient).

v = velocity of atoms on the support surface.

N_t = total number of metal atoms in all crystallites.

S_o = support surface area per metal atom.

F_s = number of metal atoms migrating on support surface.

G_i = Atoms gained by crystallite i.

D_i = Effective collision size of crystallite i.

Thus, for the ith crystallite:

$$\frac{dN_i}{dt} = \frac{\alpha v F_s}{N_t S_o} D_i - A \exp(-Ea/R_g T) \tag{4.44}$$

where N_i - no of atoms in crystallite i.

The above equation shows that large particles grow at the expense of the smaller ones; the reduction of surface energy being the driving force.

The dispersion of the catalyst is defined as:

$$D = \frac{F_s + \sum_{i=1}^{m} N_{si}}{\Sigma N_i} \tag{4.45}$$

where N_{si} = number of surface atoms on crystallite i and m is the total number of crystallites.

For certain low values of the parameters $\frac{\alpha v}{S_o}$ and $\frac{Ea}{RT}$, the migrating atoms may accumulate on the support in the initial stages of sintering, giving rise to a redispersion effect. This will be discussed in greater detail in the next chapter.

The model is not suitable for a power law fit. The sintering is extremely sensitive to particle size distribution and thus the n value in the power law changes continuously; possible values of n range from 2-13 or more. In general, n in the power law equation ($-\frac{ds}{dt} = KS^n$) increases with increasing $\overline{R}$. Narrow distributions are more stable, moreover, unimodal distributions are more stable than biomdal distributions with the same mean size. The sintering kinetics are also affected by the metal content (see Section 4-10).

The model developed by Flynn and Wanke is different from those of Chakravarty and Wynblatt and Gjcstein in that the attachment and detachment processes are considered independently while in the latter, they are considered as the reverse of each other. Otherwise it is similar to the case considered by Chakravarty where $\overline{C}s$ is constant throughout the substrate and the growth law is:

$$\frac{dR^*(t)^3}{dt} = \text{const.} \tag{4.46}$$

with a universal distribution similar to that for diffusion control. Chakravarty, however, considers this situation to be unlikely except in the intial stages of sintering.

4-7B. Crystallite Migration Model:

Here, we shall only discuss the works of Ruckenstein and Pulvermacher [10,17,55,280] who have developed models for sintering kinetics of supported metal catalysts based on the random surface migration of crystallites and their coalescence after collision.

The basic population balance equation is:

$$\frac{dC_k}{dt} = \frac{1}{2} \sum_{i+j=k} K_{ij} C_i C_j - C_k \sum_{i=1}^{\infty} K_{ik} C_i \qquad (4.47)$$

where C_i is the number of crystallites per unit support area containing i metal atoms (or units) and K_{ij} are rate constants dependent upon the mobility of the crystallites and their coalescence rates.

K_{ij} are obtained from consideration of collision rates between various particles by a diffusion equation in cylindrical coordinates, using a time scale θ which is order of magnitude smaller than the time for the overall sintering process. The collisions are considered over a time interval θ_o in which no appreciable modification of the particle size distribution takes place.

Two limiting cases are considered; the sintering controlled case in which the limiting step is the coalescence of the crystallites and the diffusion controlled case where the surface migration of the crystallites is limiting.

In the sintering controlled case, the rate constants K_{ij} are independent of the small scale time; in the diffusion controlled case, the K_{ij} have a weak dependence on the small scale time after a short time.

$K_{ij} = 2\Pi R_{ij} \propto_{ij}$ for sintering control

$K_{ij} = \frac{4\Pi D_{ij}}{\ln 4T}$ for T>>1 in the diffusion controlled case.

where $R_{ij} = r_i + r_j$, r_i = radius of particle i, $\propto_{ij}$ is the reaction rate constant for the coalescence process and $T = \frac{D_{ij}\theta}{(R_{ij})^2}$. For practical values of D_{ij} (= $D_i + D_j$), the time dependence of K_{ij} is weak. Using an inverse power law dependence for D_i, the crystallite diffusivity,

$$K_{ij} = C\,[r_i^{3m} + r_j^{3m}] \qquad (4.48)$$

Numerical solution of the population balance equations showed that for both the limiting cases, the surface area variation could be expressed as:

$$\frac{dS}{dt} = -KS^n \qquad (4.49)$$

where n = 2 or 3 for coalescence control.

n = 4 or higher for diffusion control.

Using a continuous representation of the population balance and introducing a similarity transformation, the asymptotic behavior of the particle size distribution can be obtained. For the diffusion controlled case, the solution after a short time can be represented by similarity variables. For sintering control, a similarity solution does not exist, however, a family of curves which are close together and are parameterized by a dimensionless time are obtained; thus the similarity transformation is approximately valid. These considerations show that the initial particle size distribution is not important and the exponent n depends only on the controlling process. Moreover, the particle size distributions (PSD) are unique and do not depend on the initial distribution .

Numerical solutions for the two limiting cases have shown that PSD's for diffusion controlled case are narrower than that for the sintering controlled case. This could be used as a criterion for determining the limiting step.

The authors have also developed a model where the support hetrogenity is taken into account [10]. In this model, some of the crystallites are immobile due to the presence of strongly interacting sites on the support. In this case, an equilibrium size distribution is strongly dependent on the initial distribution. There are two more parameters in this model; the probability p of formation of a mobile particle on collision of two mobile particles and q, the probability that the collision between a mobile and a trapped particle will result in a mobile particle.

In another work [55], Ruckenstein and Pulvermacher consider the effect of the pore structure of the support on the sintering kinetics of supported metal catalysts.

Two cases are considered. In both cases, the diffusion coefficient D_i is taken to be inversely proportional to the crystallite - support interfacial area S_i. In the first case this relationship is taken even for crystallites with equivalent diameters larger than the pore diameter; in the second case D_i is taken to be zero when the equivalent diameter of the crystallite is equal to or larger than the pore diameter. A constant pore diameter is considered and macropores are neglected. Both of the above models give similar time dependence of surface area which may be significantly different from that on a planar substrate. When the ratio of the crystallite diameter to the pore diameter is high ($>\frac{1}{2}$), the first model gives the exponent n in equation (4.49) which is very different from that for a planar substrate. For example, a decay exponent $n = 3$ was obtained (for $D_i \propto 1/r^2$) compared to the expected $n = 6$ for a planar substrate

TABLE 4.2: SINTERING MODELS

MODEL	GROWTH LAW	REMARKS
1) Crystallite migration and coalescence. (spherical particles; higher exponents for faceted particles)	$-\frac{ds}{dt} = KS^n$	1a) $2<n<8$ 1b) For crystallite migration controlling, $n = 4 + m$ where m is the exponent of the size dependence of D_p, the crystallite diffusion coeffiencient (ie. $D_p \propto \frac{1}{R^m}$) 1c) For sintering control, $n = 2,3$ depending upon the size dependence of α_{ij}, the reaction rate constant for the merging process. 1d) Variations in exponent possible by considering surface hetrogenity and affect of pore sizes.
2) Surface diffusion of atomic species (Ostwald ripening) (spherical particles; higher n values for facted particles)	$-\frac{ds}{dt} = KS^n$	2a) $n = 3$ for interface control, $n = 5$ for surface diffusion control, $n = 4$ for vapor transport.
3) Surface diffusion of atomic species (Flynn and Wanke [16])	power law not suitable	3a) If power law is used, n increases with increasing particle size.

4-8. Sintering Studies:

There are few sintering studies where the effects of variables such as time, temperature, environment and the crystallite size distribution have been systematically investigated. In the following, some of the sintering studies are discussed according to the environment used for heat treatment. Most of these are related to Pt/Alumina but a few studies for other systems are also included. The two recent reviews by Wanke and Flynn [95] and Wynblatt and Gjostein [150] on this subject should be consulted. Some of the experimental work has also been discussed in references [10,198].

The sintering of supports is discussed first.

4-8A. Sintering of Supports:

The catalyst supports may sinter during thermal and hydrothermal treatment leading to changes in surface area, pore volume, surface acidity and crystalline structure etc. Since impurities strongly affect sintering rates in gaseous environments, the sintering characteristics may vary extensively, depending upon the support composition.

The sintering of silica, silica-magnesia, alumina is discussed in [324]. The sintering of alumina and magnesia is also discussed by Cutler [285] and Vleesschauwer [287]. The thermal and hydrothermal treatment of alumina is discussed by Ciapetta and Wallace [48] who also give some of the original references. Here we discuss the work of Kozlov, Lazarev, Mostovaya and Stremok [277] who investigated the structural changes of alumina in Pt/Alumina catalysts with Pt contents between 0.1 and 3 wt.% over the temperature range 600-1200°C in air (6 hours), using x-ray diffraction. The temperature ranges over which the phases are stable are:

γ-alumina (600-800°C); θ-alumina (850-950°C); α-alumina (above 1050°C). In the higher Pt content catalysts (1-3%), the transition temperatures from γ to θ and θ to α were lower than in the lower Pt content catalysts. Thus the authors believe that Pt "catalyzes" the phase transitions of alumina. For the 1 and 3% catalysts, Pt lines appeared on heating to 600°C; for lower Pt contents, the lines appeared above 850°C. At about 1000°C, Pt lines appeared in all samples. The initial carrier is γ-alumina and hence highly dispersed Pt is formed by the introduction of Pt atoms to the vacant octahedral sites whereas small crystallites which are amorphous to x-rays are formed on the alumina surface. On the formation of θ-alumina, which has a crystal lattice different from γ-alumina, the Pt atoms in the γ-alumina sites are displaced and are able to aggregate. Thus, structural transformations are accompanied by changes in dispersion.

Above 1000°C, the Pt lines are found to disappear. The authors believe that this may be due to the volatization of the PtO_2 formed. It can also be due to the coverage of Pt crystallites by the support or due to the formation of x-ray amorphous (<50 Å) crystallites, in effect a redispersion.

The silica, silica-alumina and carbon supports cannot be used in steam containing environments at even moderately high temperatures. Sintering of porous silica in aqueous environments can take place even below 100°C. The mechanism involves the dissolution of silica from the surface and a recondensation of the silica in the solution with the hydroxyl groups on the surface [286]. When a silica-alumina cracking catalyst is heated in steam at ~500°C, the growth of larger particles at the expense of the smaller ones is observed. This is similar to the sintering observed in aqueous environments at 80°C. The Ostwald ripening (dissolution - recondensation) process described above, allows a change in surface area without a corresponding change in the pore volume causing an enlargement of the pores. Thermal sintering, for example in dry air, would cause a decrease in both the support area and the pore volume with little variation is pore size. The sintering rate for the dissolution-condensation mechanism would depend on the pH of the solution, this was experimentally verified by Okkerse [286].

4-8B. Studies with Pt/Alumina:

Herrmann, Adler, Goldstein and Debaun [11] made a quantitative study of the sintering kinetics of Pt/alumina catalysts, prepared by chloroplatinic acid impregnation, in air between 564 and 625°C. Catalysts with varying Pt and chlorine contents were studied using H_2 chemisorption, line broadening and soluble Pt content.

For a wide range of chemisorption capacities, a second order decrease of chemisorption capacity with respect to the remaining capacity ($\equiv$ surface area) was found. An activation energy of 70 Kcal/mole was determined. Values of the rate constant K were between 1-120 $(\mathrm{cc\ H_2/gPt})^{-1}\mathrm{hr}^{-1}$ with 20 being a typical value at 625°C. The sintering rate is not affected by the platinum content (0.3-0.8%) or the chlorine content of the catalysts. The hydrogen reduction procedure used by these authors is similar to that of Adler and Keavney [12] which has been criticized [98] for its short duration.

Maat and Moscou [13] also found a second order sintering rate during heat treatment of a 0.6% Pt/Al_2O_3 commercial catalyst in air at 780°C. A 15 fold decrease in area in the first 17 hours was observed as compared to a 5-6 fold decrease in the first 18 hours observed by

Herrmann et.al. [11] at 625°C. The two are in approximate agreement (considering the activation energy).

McCarthy et.al. [194] sintered their 0.035% Pt on low area α-alumina (BET area = 5 m^2/g) support in air at 700°, 750°, and 800°C and observed second order sintering kinetics with an activation energy of 60 KCal/mole. In this case, a 15 fold decrease in area occurs in less than 10 hours at 800°C.

Spinder, Ratner and Kefeli [200] studied the sintering of Pt on silica-alumina (% Pt?) at 800°C for 15 hours in air, vacuum and helium. The initial particle size distribution was narrow with a mean particle size of ~40 Å. Sintering rates in vacuum and helium were similar and caused less growth (50 Å) than in air (60 Å). The particle size distribution narrowed on vacuum sintering but widened on sintering in air. Sintering for 15 hours in air caused a less than 4 fold decrease in area (chemisorption) while in vacuum (15 hours) the loss was ~30%. The fresh catalyst which had been reduced at 500°C in H_2 had considerably lower Pt area than in [11]; some sintering may have occured in the reduction step or it may be due to the lower sintering resistance of $Pt/SiO_2Al_2O_3$ compared to Pt/Al_2O_3.

Huang and Li [195] studied the sintering of large Pt crystallites (1500-3000 Å) on single crystal alumina substrates of surface orientatins (0001), $(2\overline{11}3)$, $(11\overline{2}3)$ and $(11\overline{2}0)$ in oxygen containing atmospheres at 900°C. For all runs in air (½ and 1 atms.) a fourth order dependence of average particle size (5th order for surface area) with time indicating surface diffusion control in the Ostwald ripening mechanism [84] was found. The sintering kinetics is sensitive to the substrate orientation, for eg., the rate constant on $(11\overline{2}3)$ surface was about 15 times of that on $(2\overline{11}3)$

surface showing that surface diffusion is controlling. However, from a plot of the experimental particle size distributions against those predicted by surface diffusion and interface control, no conclusion about the limiting step could be made. Sintering rate was significantly lowered on decreasing the oxygen partial pressure, thus emphasizing its role in growth processes.

Wynblatt and Gjostein [196] studied the sintering kinetics of Pt (deposited by evaporation) on a thin alumina substrate in air and in a 2% O_2 in N_2 environment at 700°C. Higher growth rates in air compared to those in 2% O_2 were attributed to the participation of some oxides in the vapor or surface diffusion processes. Refering to the equation

$$\overline{R^n} - \overline{R^n_o} = Kt \tag{4.50}$$

which is obtained for various sintering models ie. surface diffusion with $n = 2, 4$; vapor transport with $n = 3$, particle migration with $D_p \propto 1/R^4$ with $n = 7$; they observed two important facts:

(1) A high n value (=12) at low oxygen pressure, indicating inhibition of particle growth.

(2) Low values of n at high oxygen pressure (air) and a steep rise in particle size, with some particles growing very large as compared to others. The authors call it as "morphological instability" which they believe is related to whisker growth. A similar but more pronounced instability was observed by the authors in another work [197] at 800°C in air.

The high n values at low oxygen pressure are attributed to the formation of facets which require "pill-box" type nucleation before growth can occur and can therefore inhibit growth rates in Ostwald ripening mechanism. The inhibition due to facets for the particle migration was also mentioned, it can probably be explained as discussed in Section 4-3A. To describe an exponentially decreasing growth rate, they propose the growth law:

$$R^{n'} \frac{dR}{dt} \propto \exp(-AR/R_g T) \qquad (4.51)$$

which gives increasing values of n when put in the form of equation (4.50). However, this increasing value of n is not characteristic of low oxygen pressures where n is high but constant. Huang and Li [195] had also observed faceted particles but had n = 4. In their review, Wynblatt and Gjostein [150] analyze several experimental studies from the viewpoint of facet inhibited growth and morphological instability. In particular, they explain the low n values of Maat and Moscou [13] and Herrmann et.al. [11] (in air) by proposing that only a small fraction of particles grow in the rapid mode.

Khassan et.al. [171] observed maximas and minimas in catalytic activity for the decomposition of H_2O_2 and the surface area when the Pt-alumina catalysts were heated in air at 300-600°C. The authors do not believe these maximas and minimas to be characteristic of the sintering process but attribute it to a "non-reproducible effect of gases, mainly oxygen" in the measurement of surface areas and activities. Although the authors do not give any insight into these effects, it may be conjectured that maximas and minimas arise due to sintering and redispersion occuring alternately, at least at higher temperatures.

In their studies of Pt-alumina catalysts, Flynn and Wanke [50] observed sintering and spread of size distribution after 16 hours in oxygen treatment between 550° and 700°C. At (~) 550°C, a 4.76% Pt catalyst sintered noticeably while a 2.03% Pt catalyst did not show any change in dispersion, thus showing the importance of metal loading on sintering.

In the sintering of the 2.03% Pt catalyst, the addition of a small amount of presintered catalyst with large crystallites caused on appreciable increase in the extent of sintering on a 16 hour oxygen treatment at 575°C. The authors interpret this as an indication that the atom-migration mechanism may be operative since the expected low mobility of the large crystallites cannot account for the above mentioned effect via a crystallite migration mechanism; no mathematical insight for such a distinction is, however, provided.

Facing numerous experimental difficulties, the authors studied the effects of reduction and sintering on individual particles by recording electron micrographs of the same area before and after the treatment. Even at 300°C, H_2 reduction caused particle growth though some particles remained stationary. The authors also observed some localized affects due to the close proximity of many Pt particles which gives rise to unusual growth. The observations were not found to be significantly conclusive with regard to the mechanism of growth (crystallite migration versus atomic diffusion).

Ganguli et.al. [201] studied the sintering of a 0.6% Pt-alumina catalyst between 600 and 800°C. They observed second order sintering kinetics at 700°C and their results are similar to those of Maat and Moscou [13]; hower, the initial decline is much faster. Moreover, the alumina support sintered considerably during the heat treatment; this may have resulted in some crystallites being covered by the support as well as caused higher sintering rates by the transport of the crystallites by support movement.

Gruber [202] in his sintering study of Pt-alumina catalysts (0.6 and 0.7%) in hydrogen at 500°C found a linear log-log relationship between surface area and time. The catalysts, prepared by chloroplatinic acid and TPH (tetraamino platinum hydroxide) had high stability and lost half their chemisorption capacity in 1500 hours. On fitting a power law (4.49), n = 6 is obtained [10].

In another study [23], Gruber sintered TPH prepared Pt-alumina catalysts in hydrogen at 500°C upto 12 hours. A 60% decrease in chemisorption capacity occured in 1200 hours with a 35% decrease in the first 72 hours. A power law fit of n = 8 is obtained in this case.

Kirklin and Whyte [203] sintered their 0.6% Pt on n-alumina catalyst in hydrogen for about 2 hours. The catalysts were characterized by SAXS. Fitting data into a second order curve (4.49) they observed an activation energy of 8 Kcal/mole in the region 450 -700°C. It is interesting to note that the catalyst loses more than half its area in 2 hours even at 450°C. The particle size distribtuion broadened considerably on heating.

Hughes, Houston and Seig [204] found that a 0.4% Pt-alumina catalyst loses two-thirds of its chemisorption capacity in 1000 hours when heated in hydrogen at 485°C. Their data can be fitted into an eighth order power law.

Renouprez et.al. [38] found surface area losses of 15, 30 and 30% on heating a 3.7% Pt-alumina catalyst in vacuum for 6 hours at 600°, 700° and 800°C.

Somarjai [35] studied the sintering of 0.5% and 5% Pt/η-alumina in air and hydrogen environments at 400-700°C. The particle sizes were followed only by SAXS. The authors state that growth in air was much higher than in hydrogen, however, from their plots it appears that the initial growth rate in hydrogen is higher than in air. Moreover, the growths in oxidizing and reducing environment after 100 hours are comparable in magnitude, at least at 600°C. A limiting particle size observed after extended heating, particularly in the reducing environment is attributed to the limitation of SAXS in detecting smaller particles rather than being a physical phenomenon. The activation energies, calculated on the basis of time elapsed to attain a given radius at different temperatures, were 20 and 52 Kcal/mole in reducing and oxidizing environments respectively.

Armstrong et.al. [256] studied the deactivation of several Pt and Pt-alloy (Ru, Rh, Pd, Ir) on alumina catalysts for the H_2-0_2 reaction. This reaction is utilized for ignition in space vehicles, the Pt containing catalysts facilitate ignition at temperatures as low as -195°C. The standard treatment was 30 minutes in a 15% steam, 85% hydrogen mixture at 1000-1200 F, this being typical of operating conditions. Hydrogen chemisorptions losses were 60-75% in 30 minutes at 1200°C. The activity was measured by the minimum temperature at which the H_2-0_2 mixture could be ignited. Although the Pt-alloys had better stability than Pt alone in such measurements, the other metals (except high wt % Ir) were inferior when used alone. The alloy catalysts are of widely different metal contents so that a comparison of sintering characteristics is not possible. Changes in activity, due to the above mentioned treatment, do not correlate well with the changes in metal surface area (hydrogen chemisorption). It seems that changes in support characteristics, such as the concentration of surface hydroxyl groups, due to the steaming are more important; the support takes up the water formed on the crystallites which would otherwise inhibit the H_2-0_2 reaction,

The mechanism or kinetics of metal sintering in steam has not been studied and is complicated by the fact that the alumina supports sinter extensively in such environment. The loss of chemisorption capacity in the above study may have been due to the partial collapse of the support structure (thus covering the Pt crystallites) or by metal sintering due to changes in support area and structure.

Mills, Weller and Cornelius [142] also studied the effect of steam on Pt-alumina catalysts. They note that the loss in activity for chclohexane dehydrogenation is larger when oxygen is included along with steam than for steam alone. Steam below 370°C was not found to be harmful. Surface area measurements were not included.

The effect of steam on Pt-alumina catalysts was also studied by Adler and Keavney [12]. Steaming in 0.35 atmp. at 705°C for 5 hours decreased the adsorption capacity of a cogelled catalyst by 80% and that of the impregnated by 50%. The X-ray line broadening results for this case did not agree with the hydrogen chemisorption values showing that even after mild steaming there is still a considerable fraction of platinum in a highly dispersed form which is not visible to the x-rays. The catalyst thus has a bimodal distribution. The severely sintered catalyst (latm. steam, 750°C) contained large crystallites (250 Å) and thus provides evidence for crystallite growth.

4-8B. Other Systems:

Nakamura, Yamada and Amano [209] sintered their Pt-charcoal catalysts at 650°C upto 72 hours in a stream of hydrogen. Results given for a 0.5 wt % catalyst show that the area/gm. Pt decreases by a factor of 2.5 in 72 hours, with a 1.6 fold decrease in the first two hours only. On fitting a power law (4.49), $n = 2$ is obtained in the initial period, followed by a high value (8-9) later.

Bett, Kinoshita and Stonehart [198] have studied the crystallite growth of Pt (5-20%) on graphitized carbon black on heat treatment in nitrogen and hydrogen at 600°C. In order to arrive at a mechanism of the sintering process they analysed the various growth models for atomic diffusion and crystallite migration and noted that while the resultant equations are all of the form:

$$\frac{1}{S^n} = \frac{1}{S_o^n} + Kt \tag{4.52}$$

(S_o is the initial area), the constant K is proportional to the metal content (Ø) for the crystallite migration model but is independent of Ø for the atomic diffusion model. As pointed out by Wanke and Flynn [95], the assumption for the atom migration model is correct only if the build up of atomic species on the support is small. They further state that for high metal loadings, the rate of capture is larger than for low metal loadings thus giving a lower build up of migrating species. However, since the metal contents used by Bett et.al. are sufficiently high, the build up may not be important and the assumption of these authors may, after all, be correct.

While sintering of 5 and 12% catalysts was gradual, there was a catastrophic initial decrease in surface area for the 20% catalyst. In a manner similar to that of Phillips et.al. [162] (see later) they proposed that the stabilization of the metal nuclei occurs at "trap-sites" which are not necessarily major step locations. For the 20% catalyst at 600°C, the trap density is exceeded, thus giving rise to an unstable distribution of particles during preparation which causes the rapid initial sintering. Neglecting the initial decline, they found that their results conformed to a crystallite migration model (K proportional to Ø) with n = 4 obtained as a fit.

At 700°C, even the 5% catalyst behaved in a manner similar to the 20% catalyst at 600°C (ie. rapid initial decline). This can be explained on the basis of a temperature dependence of the trap-site density. From a single temperature data [162] they calculated an activation energy of 41 KCal/mole.

The work of Bett et.al. serves to emphasize the importance of the support surface structure (in terms of sites available for stabilization of metal crystallites) in sintering studies.

Bett, Kinoshita and Stonehart [199] have also recently studied the sintering of Pt on graphitized carbon black in the presence of various liquids. In agreement with the work of Connolly et.al. [208], they find that in the presence of liquids, significant sintering takes place even at 100-200°C in contrast to the high temperatures (600°C) required for gas (H_2) phase sintering. Rapid sintering in the first one hour is followed by a low sintering rate. Fitting their data into a power-law, they found n values of 11-13 and activation energy ~ 21 Kcal/mole with H_3PO_4 as the liquid medium. Catalysts with 5% and 20% Pt showed little difference in their sintering behavior; thus the authors favor the Ostwald ripening mechanism with nucleation barrier in the interface transfer step for explaining their high n values. The strong influence of the liquid environment on the sintering process is intriguing. The possibility of a dissolution-redeposition mechanism was ruled out by the observed insensitivity of sintering rates to variation in applied potential. The possibility of area loss due to dissolution of platinum oxide into H_3PO_4 was also eliminated by experiments.

The authors note that the sintering rates of Pt black in air and in liquids are of similar magnitude, thus liquids probably do not enhance surface diffusion of Pt. The authors propose that liquids facilitate the transfer of atoms from the crystallite surfaces to the support. The highly disordered surface of graphitized carbon black can provide strong binding sites to the adatoms to make the transfer energetically favorable. The atoms on the support can migrate and cause sintering as in the Ostwald ripening mechanism. The details of the mechanism whereby the transfer rate is enhanced and the activation energy lowered in the presence of liquids is not clearly discussed.

Pope et.al. [85] in their study of Pd/charcoal catalysts found that even very mild pretreatment (H_2 at 25 C for 2 hours) causes significant sintering in some catalysts. Extensive sintering is observed for catalysts with high Pd contents or those where the distribution consists of localized Pd aggregates as seen under the electron microscope.

Brinen et.al. [218] studied the variation of dispersion with metal content for Rh/charcoal catalysts. The observed that dispersion (~0.1) was independent of the metal content (3-12%). This was attributed to the fact that even a 15 min. hydrogen treatment at 400°C increases the crystallite size from <40 to 75 Å while a 5 hour hydrogen treatment increases the size to 235 Å.

The relatively high unstability of these catalysts [85,218] raises questions about the significance of the initial dispersion which would probably be lost very rapidly during use in hydrogen atmospheres.

Baker and France [160] have studied the heat treatment of evaporated Pd/graphite in argon, oxygen, hydrogen, ethylene and acetylene (5 Torr). They used controlled atmosphere electron-microscopy to monitor the particle formation and growth. Pd was first deposited as a thin layer by evaporation and then heated in various environments. The temperature at which the Pd particles nucleated to form crystallites depended on the environment; being highest for argon. The shape of the resulting particles was not, however, sensitive to the environment. After the crystallites had formed, subsequent heating caused their growth. They system was maintained at each temperature for 5 minutes. It is noticed that the growth in argon is minimal.

Particle mobility was observed only in an oxygen atmosphere above 850°C. The tremendous growth at this point is noticeable. Where particle mobility is absent, the growth is attributed to surface diffusion or vapor transport of molecular species, the effect of environment being explained as in [16] ie. due to differences in the ease of escape of molecular species, their diffusion rates and the different temperature rises due to exothermic reactions. None of these were explained.

It is significant that at low temperatures, the growth in acetylene is higher than in oxygen. The case of H_2 was complex, due to its reaction with Pd. Addition of ethylene, however, removed these complexities (not described). Also, growth in acetylene and ethylene at high temperatures was inhibited due to carbon deposition. It is interesting to note the very high growth rates in the present study as compared to those in usual supported metal catalysts (for eg. [35]).

Another work of Baker et.al. [164] on the catalytic oxidation by Pt and Pd of the C-O reaction where particle growth, movement and etching was observed was mentioned in Section (4-3A).

Baker, Harris and Thomas [205] have also made a direct observation of mobility of iron particles on a graphite substrate using controlled atmosphere electron microscopy. The gaseous environments were, CO, CO_2 and Ar (5 Torr). Iron particles (40-100 Å) were nucleated by heating a deposited film. The particles nucleated at ~700 C in all the environments but their subsequent behavior was different.

In CO, the particles were irregularly shaped and their motion was not random but was either vibrational around a fixed point or rotary, though some particles would execute jumps on to sites vacated by other particles. Cooperative motion between a group of particles was observed. Coalescence on collision was not observed and the particles seemed to avoid each other. Isolated particles suffered larger displacements than those in groups.

Completely different behavior was observed in CO_2 and Ar, the particles executed random walks and coalesced to form larger particles. The reason for this difference in behavior is not known; the authors proposed that the electron beam probably produces some species from CO which adsorbs on graphite and/or the crystallites, causing the strange behavior.

The mean displacement for a 200 Å particle at 740°C (in CO?) is of the order 4000 Å/sec with characteristic D_p values of 10^5 nm^2/sec and activation energy of 15 KCal/mole.

The authors have emphasized the importance of controlled atmosphere electron microscopy for studying phenomena on surfaces. However, if the electron beam causes complication, the application of such studies to actual systems would be difficult. Electron beam induced movements have been studied in thin film work but their application to sintering studies is not obvious.

Wanke and Dougharty [290] in their studies on Rh/Al_2O_3 catalysts found that catalysts prepared from rhodium trichloride do not require a long reduction time. Heat treatment of fresh catalysts at 750°C in hydrogen or vacuum caused little sintering. A 5% Rh/Al_2O_3 catalyst lost half its chemisorption capacity in 3 hours at 700°C in oxygen and 5/6th in 8 hours (700°C, O_2).

Carter, Cusumano and Sinfelt [206] in their study of crystallite size effects sintered a 10% Ni/silica-alumina catalyst in H_2 for 1 hour at 370-700°C. The dispersion falls off rapidly near 400°C followed by a slow decrease. A four-fold decrease in the metal area occurs in 1 hour at 700°C in H_2.

Hughes, Houston and Seig [204] studied the sintering of Rh/alumina (0.3% Rh) and Ni/alumina (3% Ni) after heat treatment in N_2 at 1650°F. While the Rh catalyst retained 1/3 rd of its initial area after 72 hours, the Ni catalyst retained less than 1/10th.

Lawson and Rase [117] studied the effect of hydrogen reduction conditions on the activity and poison resistance of 1% Ni on sodium Y zeolite (aperture 13 Å). Nickel crystallites were observed on the outer zeolite surface after high temperature reductions. The authors explain this on the basis of surface diffusion of individual nickel atoms; the agglomeration inside the pores would be minimal since crystallites cannot probably migrate in such small pores. It was found that agglomeration and the consequent loss in poison resistence could be prevented by a prolonged low temperature reduction, however, it is more effective to introduce the irreducible Cr_2O_3 or $Cr(CO)_6$ in the gas followed by O_2 treatment. The action of Cr_2O_3 is not discussed but the data clearly show an increased poison resistance and hence higher dispersion in such catalysts.

Kubo et.al. [207] discuss the variation of disperson and particle size distributions with the calcination temperature for Pt-NaY and Pt-NH_4Y. Whereas high calcination temperatures produced large crystallites in Pt-NaY, the effect in Pt-NH_4Y was minimal.

In discussing the sintering of zeolite supported catlysts, the nature of the initial dispersion must be kept in view. Gallezot et.al. [100] discuss the two kinds of Pt dispersion in Y-zeolites where, depending on the pretreatment temperature, Pt is either dispersed atomically in the sodalite cages or as agglomerates in supercages. The Pt crystallites in the supercages are stabilized due to their close fit. These crystallites can sinter only when the cages collapse at ~900°C. The Pt dispersed atomically in the sodalite cages does not chemisorb hydrogen, hence hydrogen chemisorption results must be carefully interpreted.

Mashchenko et.al. [281] have discussed the decomposition of $[Pt(NH_3)_4^{2+}]$ introduced into the NaY zeolite by ion-exchange and postualte the formation of a surface compound $(Pt-H)^+$ (which is present in certain local positions (?) in the zeolite structure) on heating in vacuum at 300-400°C. The authors believe that the formation of this compound may be a prerequisite for obtaining a high platinum dispersion on further reduction; the decomposition of $[Pt(NH_3)_4^{2+}]$ itself in a hydrogen environment may give rise to lower dispersion.

Pt sintering in 0.5% Pt-decationated type Y zeolite was studied by Weller and Montagna [9] during their oxygen chemisorption studies at high temperatures (475 ,525°C). The H/Pt ratio in the fresh catalysts was 1.97. Reduction in flowing hydrogen at 300°C followed by evacuation at 550°C lowered this value to 1.50 indicating sintering. An exposure to oxygen followed by the same reduction and evacuation gave a higher H/Pt ratio (1.68) which the authors interpret as a redispersion. Subsequent cycling in oxygen and hydrogen caused sintering; after 5 cycles, the H/Pt ratio had fallen to 0.88. The Pt-aggregation was confirmed by Pt lines in the x-ray diffraction pattern. The diffraction pattern also showed that the cycled catalyst support had lost 35% of its original crystallivity. The Pt sintering is partly related to the structural changes in the zeolite support.

Phillips, Desloge and Skofronick [162] have studied the sintering of gold islands (crystallites) on carbon and SiO at 260° and 450°C in vacuum (10^{-7} to 10^{-9} Torr). The electron micrographs clearly show various stages of coalescence of two islands which were not previously in contact. They observed that particle growth was accompanied by a spread in the size distribution.

The authors proposed a growth mechanism wherein the islands are normally located in "trap-sites" (potential holes) with a binding energy (E_o) which is independent of the island size. This binding energy is also the activation energy that is required for an island to become mobile. Once mobile, the islands, which are treated as a two-dimensional gas, execute random walks and coalesce on collision with stationary islands, the collisions between mobile islands being neglected. Using a gamma distribution for particle sizes, they derived two basic laws:

$$(1) \quad \bar{R}^{7/2} = 1.82\gamma t + \bar{R}_o^{7/2} \tag{4.53}$$

where $\gamma = \frac{3\phi R_1}{2\Pi D}$, ϕ = mass of metal per unit area of support, D = density of the metal and $R_1 = \left(\frac{3kT}{D}\right)^{\frac{1}{2}} \exp\,(-E_o/kT)$

$$(2) \quad \bar{R}^2 - \bar{R}_o^2 = 7.1[\sigma^2 - \sigma_o^2] \tag{4.54}$$

where $\sigma^2 = \bar{R}^2 - (\bar{R})^2$ is a measure of the distribution width. (4.55)

The experimental plots of $\bar{R}^{7/2}$ versus time were linear, the constant 7.1 in equation (4.54) was found to vary between 5-30, the variation for carbon being smaller. The activation energies (E_o) were found to be 30 and 35 Kcal/mole for carbon and SiO substrates which is consistent with the lower growth rates on SiO.

As mentioned by Flynn and Wanke [16], some of the micrographs in this work are strange in that larger particles seem to be travelling much faster than the smaller ones. However, this may not necessarily be the case, the nature of the tracks due to the larger particles may be different from that of smaller particles, thus giving the above mentioned impression.

The sintering of Pd catalysts prepared by the cation-exchange method has been discussed by Morikawa et.al. [183] and Furuoya et.al. [257]. The authors attribute the loss in activity on heating in air to changes in the lattice imperfections of the Pd particles (qualitative sintering) and to the growth of Pd particles (quantitative sintering). The Pd existed in the original catalysts as Pd metal.

The Pd on silica-alumina catalysts were calcined in air for 2 hours at 300-700°C and were subsequently reduced in 300°C hydrogen for 2 hours The crystal imperfections, as seen in the x-ray diffraction pattern, were not changed by this treatment. The average crystallite size incrased from 50 Å to 100 Å at temperatures above 500°C. Since there is little difference in the activity or surface area of catalysts sintered at 500° and 700°C, it can be concluded that the sintering is a low activation energy process.

Heating the same catalysts in air at 300°C followed by reduction in hydrogen at varying temperatures (200-500°C) brought about no growth of crystallite sizes but large changes in activity and crystal imperfections. The authors conclude that heating in hydrogen causes qualitative sintering.

Examination of the mechanism of crystallite growth in air by x-ray diffraction (?) led the authors to believe that the diffusing species is produced by oxygen chemisorption on Pd. The exchange of Al^{3+} or Th^{4+} on to the support was found to be useful in inhibiting Pd growth.

The authors [183] state that growth of Pd crystallites also occurs in the course of the hydrogenation reaction. The mechanism of such growth (in the absence of oxygen) was not discussed.

Williams, Bulter and Hammonds [219] studied the sintering of Ni/alumina catalysts in hydrogen-steam atmospheres. These catalysts with only 25% alumina cannot probably be regarded as being similar to the usual Pt/Al_2O_3 catalysts. The fresh catalyst had Ni crystallites < 100 Å while the catalysts sintered in hydrogen-steam mixture (9:1 by volume) at 500°C and 25 atmp. had crystallites between 300 and 3000 Å. Loss of nickel and support surface areas were roughly parallel; thus the authors state that the sintering of the nickel crystallites is caused by their coalescence when they are brought together during the sintering of the alumina from the γ to the α-form. However, the collapse of the support structure is not supposed to cover the nickel crystallites. It is seen that the sintering in hydrogen is much less than in steam-hydrogen mixtures.

A copper catalyst stabilized by alumina can sinter in the presence of halogens. Chlorine forms a volatile surface compound with copper and particle growth via the vapor transport mechanism or the surface diffusion of atomic species, causes the particles to grow from 100 to 10,000 Å in a few hours even at 200°C [293].

The structure of the common ammonia synthesis catalyst is different from that of typical supported metal catalysts. The formulation and structure of this catalyst is discussed in ref. [292]. Magnetite (Fe_3O_4) is the main component, the other components being typically: 0.8% K_2O, 2.0% CaO, 0.3% M_gO, 2.5% Al_2O_3, 0.4% SiO_2 and traces of TiO_2, ZrO_2 and V_2O_5. The spinel structure of Fe_3O_4 consists of a cubic packing of oxygen ions with the Fe^{2+} and Fe^{3+} ions being located in the interstices. The unreduced catalyst contains large crystallites. All the oxygen is removed during the reduction; however no shrinkage occurs. This results in a porous iron structure. During reduction, dissolved Al_2O_3 and M_gO come out of the solution and are distributed in the porous structure, tending to separate and stabilize the crystallites against sintering. The catalyst sinters in the presence of oxygen and steam. A temperature of ~550°C is considered as an upper limit in this regard. Chlorine can cause sintering in a manner similar to that described for Cu/alumina catalyst.

4-8C Deactivation of Automotive Exhaust Catalysts:

The thermal deactivation of automotive exhaust catalysts is of great practical concern. Loss of metal and support area by agglomeration, loss of metal by evaporation and incorporation into the support, solid state phase changes in the support components etc. lead to decline in activity and changes in selectivity for different reactions.

Moii, Juebrich, Johnson and Chloupek [210] have examined the modes of deactivation of exhaust catalysts in actual performance using a test milage of 15,000. Causes of deactivation include severe losses in support surface area and pore volume, phase changes in the support components and poisoning by lead, phosphorous etc. In addition, the CO chemisorption capacity decreased from 0.02 cc/gm to as low as 0.0008 cc/gm. This was verified by x-ray line broadening measurements which gave mean crystallite sizes of 112-500 Å compared with 77 Å of the fresh catalysts. There seem to be large discrepencies in their chemisorption and X-ray measurements.

It is significant to note that catalysts which experienced extreme temperature rises, as evidenced by their low cordierite/mullite ratios, do not show corresponding extremes in chemisorption capacity or the Pt crystallite sizes.

Liederman et.al. [211] have reviewed some of the work on this subject. In a performance test of 25,000 miles at a maximum temperature of 1450°F with unleaded fuel, they found a rapid decrease of the activity for oxidation of CO and C_3H_6 while the activity of C_3H_8 oxidation decreases gradually. Calcining the catalysts in air at 1400°F for 5 hours decreases the hydrogen chemisorption by 50% while aging 25,000 miles causes a 90% decrease. The chemisorption capacity of catalysts aged for 5,000 and 20,000 miles is the same. It is interesting to note that catalysts which have been calcined at 1400°F for 5 hours in air prior to 20,000 miles aging show higher CO chemisorption than those which had not been calcined. X-ray line broadening results gave average crystallite size of ~500 Å for the 5,000 and 20,000 miles aged catalysts. This is in contrast to the values calculated by chemisorption (~2000 Å). The electron micrographs showed large crystallites of dimensions upto 5000 Å. No soild state changes in the support component were observed. The authors believe that the growth of crystallites is the primary cause of deactivation below 1400°F.

In another work [212], Voltz and Liederman present some CO chemisorption and X-ray line broadening results supported by electron micrographs to show that thermal treatment in air between 1400-2400°F leads to significant crystallite growth:

Calcination temperature, °F	CO Chemisorption, Calcined 2 hours	CC(STP)/gm Calcined 72 hours
Fresh (as received) - 0.0296		
1400 °F	0.0016	0.0015
1800 °F	0.0010	—
2000 °F	0.0011	0.0012
2200 °F	0.0004	0.0005
2400 °F	<0.0001	<0.0001

It is seen that the loss of Pt area is complete at 2 hours. These catalysts contained 0.42% Pt but its distribution over the support is not known. The changes in activities for different reactions are complex, for example, even though a large decrease in CO chemisorption occurs after 2 hours calcination at 1400 °F, the catalytic activity for CO and C_3H_6 oxidation does not change significantly.

Miyazaki [213] using Pt-alumina catalysts for aging upto 200 hours found that the deactivation occured primarily in a surface layer of the support. Using results from microfocused X-ray diffraction studies, the author proposes that initially the platinum in the surface layer is "alloyed" with the alumina support and possesses a disordered crystalline arrangement. Deactivation occurs due to changes in orientation in this layer, probably due to a redistribtuion of the phases in this active layer.

4-9. The Design of Stable Catalysts:

The stability of supported catalysts as varied by (i) the metal component, (ii) the support structure and wetting and (iii) the addition of promoters, is discussed below.

4-9A. The Metal Component:

The relative stability (sintering resistance) of different metals has been discussed by Wynblatt and Gjostein [150]. If crystallite migration is the controlling mechanism and crystallite mobility is based on surface self diffusion, the stability would be in the inverse order of the surface self diffusion rates; which, in the absence of impurities, are in the same order as the melting points. On this basis, the order, proceeding from the least stable, is:

$$Ag<Cu<Au<Pd<Fe<Ni<Co<Pt<Rh<Ru<Ir<Os<Re \qquad (4.56)$$

Since impurities are invariably present, the effect of the environment would be dependent on the efficiency of impurity removal. This may vary with the nature of the metal.

When the diffusion of atomic species is the dominant mechanism for sintering, the important factors are: (i) the ease of escape of atomic species from the metal to the support, (ii) the ease of migration of these species on the support.

For the escape of metal atoms to the support, the activation energy barrier at the metal-support interface is not known. The barrier would probably be less than the heat of sublimation of the species on the metal surface. If metal oxides are present on the crystallite surface, the barrier may be smaller, since oxides may have lower sublimation energies. For the present discussion, the energy diagram for rhenium is shown in Fig. (4.2).

Wynblatt and Gjostein [150] postulate that the stability series in oxygen environments can be based upon the magnitude of enthalpy change for the reaction:

$$M(s) + O_2(g) \rightarrow MO_2(g) \qquad (4.57)$$

Metals with low enthalpy change for the above reactions should have higher stability. On this basis, they propose the stability series in oxygen environments with atomic migration as the dominant mechanism:

$$Os<Ru<Ir<Pt<Pd=Rh \tag{4.58}$$

In the Fig. (4.2), the enthalpy change for (4.57) is the sum of steps (3) and (4). The reason why the heat of sublimation of the oxide is not taken as the activation barrier may be that the oxidation reaction $M_{(s)} + O_2 \rightarrow MO_{2(s)}$ could provide some of the heat necessary for sublimation.

In the above, no account is taken of the metal support interaction. Flynn and Wanke [16] proposed that the increased metal support interaction in oxidizing atmospheres facilitates the escape of atomic species. This corresponds to a large enthalpy change in step (5) in Fig. (4.2). If the metal (oxide)-support interactions for different metals were of the same magnitude, the series (4.58) would be corect. Similar series could be constructed for chlorides and other compounds.

Alloying of a metal with another metal which is higher in the order of stability, would increase its stability. It is interesting to note that the stability series for crystallite migration based on surface self diffusion (reducing atmospheres) is approximately the converse of that for surface migration of atomic species (oxidizing atmospheres). Thus, alloying for lower sintering in hydrogen may lead to higher sintering during regeneration in oxygen atmosphers. However, the new bimetallic and multimetallic catalysts have adequate regeneration stability. The performance of these catalysts is discussed next.

Polymeric residues produced by the stripping of hydrogen atoms from the alkane structure or by other decomposition reactions are produced in the catalysts during reforming. It is known that catalysts such as

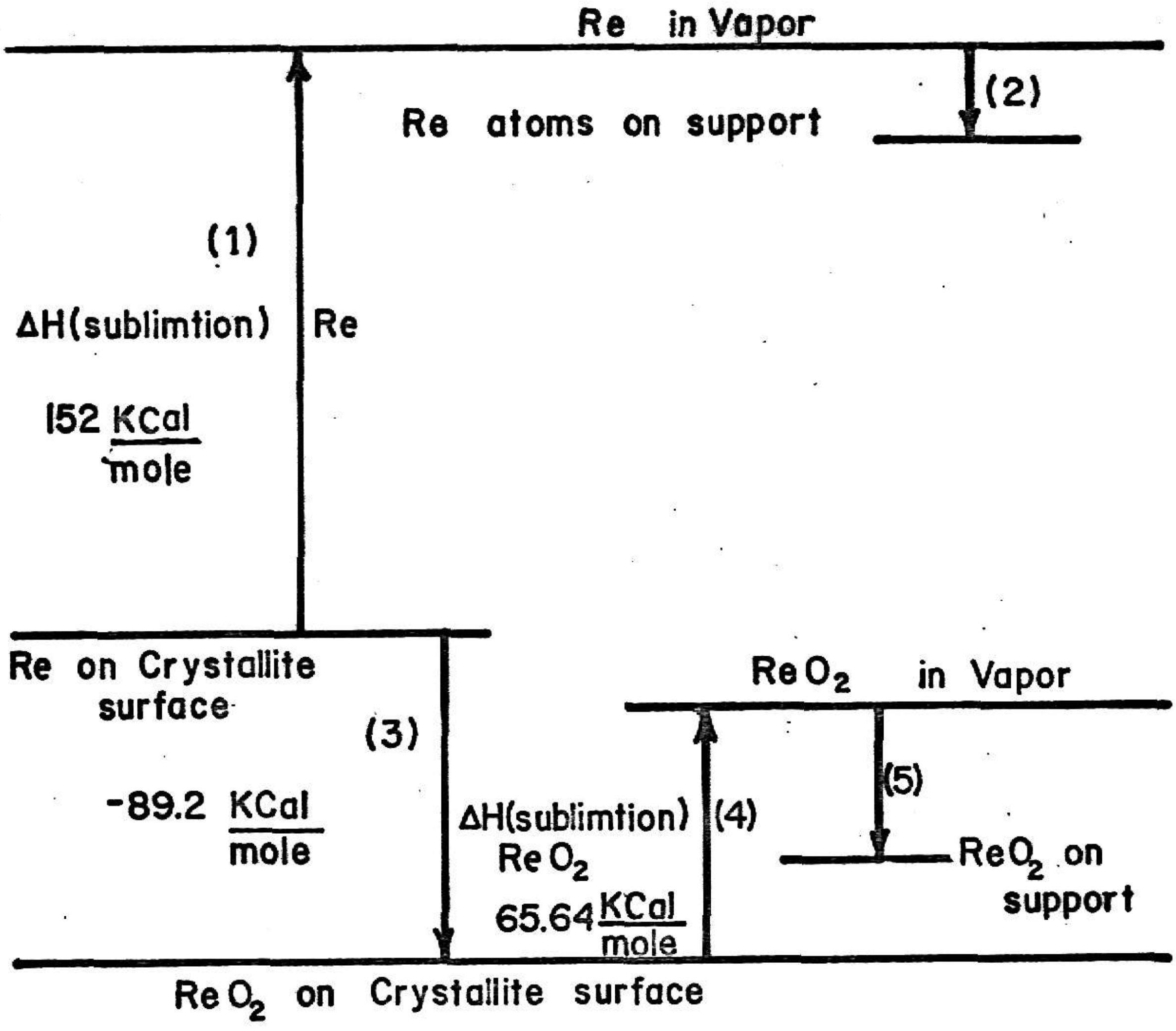

Re in Vapor
(2)
Re atoms on support
(1)
ΔH(sublimtion) Re
152 KCal/mole
Re on Crystallite surface
(3)
-89.2 KCal/mole
ReO2 in Vapor
(5)
ΔH(sublimtion) ReO2
65.64 KCal/mole
(4)
ReO2 on support
ReO2 on Crystallite surface

Fig. 4.2

Pt/Re/Alumina can be used at low pressures and more severe conditions. Due to their resistance to coking, these catalysts have longer on-stream time before regeneration. In addition, they seem to have higher sintering resistance and lower tendency for the "annealing" of active centers (see Chapter 5). Thus, Pavlov and Levinter [283] atrribute the beneficial effect of rhenium to "the formation of inter-metallic structures which possess a smaller tendency to recrystallization (annealing?) and a greater stability.

The original patent for the Pt-Re alloy catalysts was filed by Kluksdahl [249] who found that Pt-Re catalysts, though causing excessive hydrocracking in the initial stages, have superior stability in terms of yield-octane number selectivity when sulfur is excluded from the feedstock.

In the catalysts prepared by impregnation and subjected to a 850°C reduction, evidence for alloy formation was obtained from x-ray diffraction. From the bulk phase diagram for Pt-Re, it is seen that only one phase with the fcc Pt structure exists below 40% (at <1750°C) whereas the hcp Re can also be observed above 40% Re. In the supported catalysts, only fcc Pt structure was observed below 50% Re while the hcp Re could be observed above this concentration.

The Pt-Re catalysts had smaller crystallites than the corresponding Pt catalyst. This may be due to the lower aggregation tendency of Pt-Re on alumina (also see Section 2-6). The higher sintering resistance of Pt-Re catalysts was also shown by the fact that the dehydrogenation activity of these catalysts falls off more slowly with increasing reduction temperatures than the Pt catalysts.

The Pt-Re alloy has a higher melting point than Pt; moreover, the addition of Re to Pt decreases the lattice spacing of the latter. These factors may be responsible for the higher sintering resistance of these catalysts.

John Freel [234] pointed out the excessive temperatures used by Kluksdahl to show alloying in his catalysts. He (Freel) found very high dispersions in catalysts which were reduced at moderate temperatures. Since the term "alloy" for such catalysts has doubtful meaning, Freel argued that the sintering resistance of these catalysts could not be due to alloy formation. While there is merit in this arguement, it can be stated, as before; that the presence of Re inhibits the growth of the crystallites or else that the small initial sintering produces alloy crystallites smaller than 20 Å, with little change in dispersion.

In a recent work, Bursian et.al. [282] studied the crystallization and sintering of Pt, Pd, Pt-Re and Pd-Re on silica gel under coking conditions (aromatization reactions). The catalysts were prepared by impregnation. The coke deposited was 4-5 wt %.

It is seen from their results that under the conditions (see Table 4.3) Pd sinters less than Pt. However, the crystallization (annealing) is significant in Pd but, is negligible in Pt. It can be seen that the addition of Re inhibits the sintering of Pt catalysts; for Pd, it inhibits both the sintering and the crystallization (as measured by the intensities of the diffraction patterns). For example, whereas the crystallite size after coking was 780 Å in a 2% catalyst, in a 2% Pt, 0.8% Re catalyst it was 360 Å.

TABLE 4.3 Ref. [282]

Amount in Sample (wt%)		S/S_o .100% (% Crystallinity)		Crystallite Diameter d (Å)	
Pt, Pd	Re	before coking	after coking	before coking	after coking
5 Pd	-	40	95	390	480
5 Pd	2	40	50	330	420
-	2	100	105	110	100
2 Pt	-	105	105	520	780
2 Pt	0.4	40	40	420	480
2 Pt	0.8	40	40	470	360

4-9B. Support Structure and Wetting:

Wynblatt and Gjostein [150] demonstrate how substrate concavities with dimensions comparable to crystallite dimensions can stabilize the particles with respect to growth by crystallite migration or by atomic diffusion.

The microstructure of commonly used supports has not been examined in detail. Faulkner et.al. [291] have shown that some of the structural features can be studied by using scanning electron microscopy and using ion-milling for sample preparation. Studies of support structure as obtained by different preparation techniques and treatments would enable the understanding of the relationship between support structure and sintering. The strong influence of the orientation of the support on the growth via atomic diffusion was observed by Huang and Li [195]. The above mentioned work would require the identification of broad micro and macro-structural features of the support along with an understanding of their role in particle stability.

Since the crystallite diffusion coefficient (Dp), based on the surface self-diffusion of atoms, varies inversely as the fourth power of the crystallite diameter; increased wetting with the accompanying increase in effective particle diameter, would reduce crystallite mobility.

Wynblatt and Gjostein [150] give a thermodynamic arguement to propose that increased wetting also reduced the growth via interparticle transport of atomic species. For two particles of given volumes, the difference in chemical potentials, which is the driving force for growth; decreases with increasing wetting. That increased wetting lowers the rate via atomic diffusion can be seen from the kinetic equations (4.40) and (4.41).

Ruckenstein [132] discusses the role of wetting in the stabilization of bidimensional metal dispersion on the support. It is shown that there exists a critical radius $r_c = 5\delta/(1-\text{Cos}\theta)$ (where δ is the diameter of the metal atom and θ is the wetting angle of the metal on the support) such that for radii less than r_c, the bidimensional dispersion is more stable. The roughness of the support having curvature greater than r_c would favor growth by providing the nuclei for growth.

The possibility of modifying the wetting angle by the use of surface active species was mentioned by Ruckenstein and Pulvermacher [10]. Using Youngs equations for wetting angle and Gibbs equation for surface excess concentration they derived a condition which allows for increased wetting in the presence of the impurity. The possibility of increasing metal support interaction by the addition of interfacially active species which may dissolve in the support was also mentioned. They speculate that the higher stability of the bimetallic catalysts may be a result of the increased wetting due to better registry and lower surface tension at the metal support interface. Although some examples are given, there seems to be little work on the wetting and adhesion of alloys on substrates of practical interest in catalysis. In the case of strongly adsorbed solute or for catalysts prepared by ion-exchange, where high metal support interaction exists at the preparation stage, an incomplete reduction at the interface would stabilize the crystallites against migration.

4-9C. Role of Promoters:

The role of halogens and alkali metals in modifying catalyst stability is discussed below.

The halogens such as chlorine and flourine enhance the Lewis acid strength of the alumina surface and increase its activity for acid catalyzed reactions such as the skeletal isomerization of olefins and cracking reactions of hydrocarbons [252]. The halogens may be added to the catalyst by treatment with HCl, HF, NH_4Cl etc. before or after the impregnation. Some halide is introduced into the carrier on the decomposition of chloroplatinic acid. The role of halogens in Pt-Al_2O_3-halogen catalysts was briefly discussed in Chapter 2.

Ciapetta and Wallace [48] note that Pt-Al_2O_3-halogen catalysts have a higher thermal stability and regenerability. Hermann et.al. [11] found that though the chlorine content affected the initial dispersion to some extent, it has essentially no effect on the sintering kinetics. Webb [20] has indicated that halogen containing catalysts are somewhat more susceptible to high temperature degradation. Hall and Lutinski [53] found that Pt is more easily sintered on a flourided alumina base during catalyst preparation. In the studies on heating of unreduced catalysts [142,62], the rapid growth processes have generally been accounted in terms of the movement of chloroplatinic ions or the vapor transport of volatile chlorides.

The recent work of Baker et.al. [160] is of interest in this regard. Compared to preparations on alumina by vacuum evaporation (Pt/alumina) or from tetrammine platinous hydroxide, particle growth from a chloroplatinic acid preparation was significantly lower. Interestingly, they found that they could induce this behavior (i.e. the increased stability) in Pt/Alumina by treating it in HCl at room temperature after having heated it in oxygen at 500°C. This has led these authors to believe that chloride ions have a dramatic effect on the behavior of

Pt supported on alumina and that it inhibits the growth of Pt particles on alumina. These authors also compare their work with that of Dorling and Moss [62] who used chloroplatinic acid/silica. They explain the difference by suggesting that chloride ions may not exert the same influence on platinum supported on silica as they do on Pt/Alumina.

While the role of halogens in catalyst sintering has not been resolved, it may be visualized in terms of wetting. Additional work in this area is necessary.

The effect of introduction of alkali metals, which supress coking and cracking and which act as promoters in aromatization (dehydrocyclization), on the sintering resistance of Pt catalysts does not seem to be well understood. It was postulated by Bursian et.al. [71] that alkali metals stabilize the x-ray amorphous (highly dispersed) form of Pt. Kozlov et.al. [277] using chloride free catalysts with promoter conentrations to completely supress catalyst acidity, correlated the activity for n-hexane dehydrocyclization to the presence of platinum particles 40-80 Å in diameter. They propose that the alkali metals interfere with the migration of Pt particles which may be mobile under the operating conditions or in the oxidation-reduction treatment used for obtaining the original catalysts. The stabilization of supported Palladium catalysts by the addition of Al^{3+}, La^{3+} etc. was discussed under sintering studies (Section 4-8).

It is felt that in some of the above discussed works, the activity measurements, being indirect means of catalyst characterization, do not constitute sufficient evidence for the stabilization against sintering by alkali metals. More direct studies such as sintering of metals in promoted catalysts during heat treatment in H_2 may bring out the mode of action of promoters.

4-10. Discussion:

The topics of interest in sintering studies are: the effects of environment (oxygen, nitrogen, hydrogen, steam, vacuum), the temperature, the nature of the support, the metal content, the particle size distribution and the preparative procedure. Also of interest are the sintering models and the studies aimed towards determining the sintering mechanisms under different conditons.

Sintering rates in oxidizing environments are generally higher than in reducing atmospheres. Thus, for Pt/Al_2O_3 and Rh/Al_2O_3, extensive sintering may be observed in oxygen between 500-700°C [50,290] in a few hours whereas the sintering in hydrogen at these temperatures is minimal [23,202,204,290]. Below 500°C, the sintering of Pt/Al_2O_3 is very slow [39a]; the data of Kirklin and Whyte [203], who noted a 50% decrease in area in 2 hours at 450°C, being an exception. Growth in oxygen generally increase with increasing oxygen partial pressure [195]. Growth in nitrogen and in vacuum is minimal even at 800°C [38,200]. Baker, Thomas and Thomas [51], however, found that, for an <u>evaporated</u> Pt/Alumina catalyst, the growth in 2 Torr nitrogen is higher than in 2 Torr oxygen. Although the growth in oxygen is complicated by the loss of Pt by volatile oxides, the sintering rates in oxygen and nitrogen are still comparable below 700°C. It is felt that the nature of sintering in such systems is different from that in typical supported catalysts. Appreciable growth occurs even in 5 minutes at temperatures above 600°C.

In discussing the effect of temperature on sintering rates, it is noticed that for Pt/Alumina, the activation energies in oxidizing atmospheres range from 50 to 70 kcal/mole [11,35,194] while for reducing atmospheres, the values are typically between 8 to 30 kcal/mole [34,38,203].

The effect of environment on the sintering of Pt/Alumina is also seen in the values of the decay exponent in equation (4.49). The exponent (n) is typically 2 in oxygen atmospheres [11,13,194,201], while in hydrogen it is generally greater than 6 [202,204].

The strength of the sintering models can be discussed in the light of the above facts. The main weakness of the crystallite migration model due to Ruckenstein and Pulvermacher [17] is its inability to explain the low n (~2) values and the high activation energies in oxygen environments at high temperatures. The model gives n=2 for the case of coalescence controlled sintering. Normally, coalescence is a very rapid, low activation energy process. In the sintering studies of Pt blacks, it was seen that the activation energy in oxygen is ~5kcal/mole. If coalescence was the controlling step in the sintering of supported catalysts at high temperatures in oxygen, the temperature sensitivity of the overall process should be similar to that of the coalescence step. ie. it should be low. Thus, the coalescence controlled sintering cannot explain the strong temperature sensitivity observed in practice.

In making a comparison of the relative magnitudes of coalescence and crystallite diffusion rates, it is observed that the inter-crystallite separation in low concentration catalysts may be several hundred angstroms and the crystallites would require time periods of the order of an hour or more to cover such distances. On the other hand, the time period for coalescence may be of the order of a few seconds or less. The low mobility in oxygen, coupled with a strong metal support interaction may make coalescence slower and may also make possible somewhat higher values of activation energies (since the coalescence of the crystallites on the support requires it's partial denudation). However, on these same accounts of low metal mobility and strong metal-support interaction, the crystallite diffusion would itself be impeded. It is thus seen that the coalescence controlled sintering does not satisfactorily explain experimental results in oxygen at high temperatures. On the other hand, the high activation energies and the low n values are consistent with the Ostwald ripening mechanism with the controlling step being the loss of atoms from the metal to the support.

In reducing atmospheres, the diffusion controlled cyrstallite migration model seems to be satisfactory, both with respect to the exponent of the sintering rate and the observed low activation energies which could be attributed to the process of migration due to surface self-diffusion.

The modification of the crystallite migration model to consider surface hetrogenity and also the effects of pore sizes [10,55] may give results significantly different from that of a planar substrate. Only a few cases have been examined, for the particular case of crystallite migration control, the impeding of crystallite motion by the pores gave a decreased exponent n (=3) compared to n (=6) for a planar substrate. More cases would have to be examined before predicting general trends.

The model of Flynn and Wanke [16] is not amenable to easy application because of the absence of a rate equation and the predicted sensitivity to the particle size distribution. It is true that sometimes the experimental results do not obey a power law and that an increasing exponent with an increasing particle size is observed [196,209]. However, the fact that similar sintering rates, for the same system, have been found by different investigators [11,13,194,201], with probably different particle size distributions, tends to discount the possibility of a strong influence of the particle size distribution. If catalysts are prepared by the impregnation technique, the macropores would contain large crystallites; which according to this model would strongly influence the sintering kinetics. This would tend to make sintering results less reproducible than they seem to be.

Flynn and Wanke's model is able to predict a redispersion effect, however, redispersion seems to be a much more complex process than they suggest. Moreover, it is not known whether the model would be valid under the conditons of a large buildup of atomic species on the support which is necessary for redispersion.

Particle size distributions are generally found to broaden during sintering. There is no evidence to the contrary, except in the vacuum sintering study by Spindler et.al. [200]. Information on particle size distributions is rarely available and mechanistic conclusions based on such information are more difficult to make as compared with sintering kinetics or activation energies. This is especially true for porous substrates where the fraction of stationary particles or those with impeded motion are not known aproiri. The limitations of the experimental techniques are also a contributing factor.

Herrmann et.al. [11] found no influence of the platinum content (0.3-0.8%) on the sintering rate in air. Flynn and Wanke [50] did notice an influence of the metal content on the sintering behavior of Pt/Al_2O_3 catalysts (2.03,4.06%) in air. Comparing the sintering of the 0.6,0.7 and 1.1% Pt/Alumina catalysts, used by Gruber [23,202] Wanke and Flynn [95] found no logical influence of the metal content on sintering. Bett, Kinoshita and Stonehart [198] on the other hand, noted the effect of the metal content on the sintering behavior of Pt on graphitized carbon black (5-20%). These authors interpreted this dependence of sintering rate on the metal content in terms of the crystallite migration model. The crystallite migration model of Ruckenstein and Pulvemacher [17] has not been analyzed for the effect of metal content, however, the dependence is expected to be similar to that in Smolchowskii coagulation and thus the remarks of Bett et.al. (see Section 4-8C) are probably correct. The fact that Flynn and Wanke [50] noted such a dependence for Pt/Al_2O_3 in oxygen, where sintering is expected to proceed by atomic migration, combined with the observation that the metal content seems to be important only for higher loadings, it can be proposed that at high metal conents, the crystallites are non-uniformly distributed on the support and thus the local effects, whereby crystallites in close proximity or in contact can sinter rapidly, may be important. It is noted, however, that similar catalysts (Pt on graphitized black) did not show a metal-content-effect in liquid environment [199]. Thomas [8] states that Pt aggregation is related to the platinum concentration, the low concentration Pt catalysts (0.4-0.6%) can operate at conditions which may be too severe for the high concentration catalysts (?).

That the support has considerable influence on the sintering rate can be seen from the fact that Pt, Pd and Rh on charcoal catalysts are unstable [85,209,218] in hydrogen even at moderate temperatures while the corresponding alumina supported catalyts are stable [23,290].

The aggregation tendencies of metals on different supports, during catalyst preparation was discussed in Chapter 2. It was stated that the low activation energies in Zaidman's work were probably due to the aggregation of the salt (instead of the metal). The sintering behavior of a metal on different supports may be different from that of its salt. Moreover, the aggregation of the salt or the partially reduced metal involves one to two dimensional and two to three dimensional changes while that in a reduced catalyst involves mostly 3 dimensional aggregation (this point must also be kept in view when comparing the sintering characteristics of catalysts with high initial dispersions to those with low initial dispersions).

The fact that the predicted stability series for oxygen environment is approximately opposite to that for reducing environment was mentioned in (Section 4.9). A similar trend can probably be predicted for different supports. A support that stabilizes the metallic species would cause higher sintering by the atomic migration mechanism (oxygen atmosphere) but lower by the crystallite migration mechanism (reducing atmosphere) and vice versa. Thus it would be expected that Pt/Silica would sinter less rapidly than Pt/Alumina in oxygen atmosphere, but more rapidly in a hydrogen atmosphere.

Areas in which further work may be pursued are identified below.

(1) The influence of the support structure on the sintering kinetics.

Supports with varying surface areas and pore structures may be obtained by calcination in air, steam sintering or by varying the support preparation procedure. The study may also include the characterization of the structural features of the support by electron microscope, apart from the surface area, pore size distribution and x-ray measurements. Support structures are usually dictated by considerations of selectivity and mechanical strength. The introduction of sintering as an additional variable may help in the better design of supports. It is expected that the support pore structure would have a greater influence on the mechanism of growth by crystallite migration than on the atomic diffusion mechanism, unless the surface migration of the atomic species is controlling.

(2) The sintering characteristics of various metals in the stability series mentioned in (Section 4-9).

Such experiments may be helpful in identifying or verifying the mecahnisms of sintering, such as atomic migration in oxidizing atmospheres and crystallite migration in reducing atmospheres. Correlations of stability with the metal properties such as melting point, the heat of sublimation of metal or the metal oxides, the surface self diffusion rates for metals, the known metal support interactions etc. should be sought. The trends in surface self diffusion rates may be obtained by using metal balcks. The starting catalysts should have comparable dispersions, as emphasized previously. Such work may also include the study of sintering characteristics of the same metal on different support.

The sintering characteristics of alloy and cluster catalysts also need to be studied. It is known that growth can be modified by using metals that are structurally incompatible. Addition of a small amount of such a metal, may be helpful in obtaining higher stability, provided that influences on the activity and selectivity are tolerable. Again, correlations of the above mentioned nature should be sought.

(3) The sintering characteristics of catalysts prepared by different techniques, with comparable initial dispersions. Ion-exchanged catalysts are believed to be more stable than those prepared by impregnation. If the metal in these catalysts is present in a reduced form as three dimensional crystallites, the difference in stability could only be due to different crystallite-support interactions, probably due to different

interfacial structure. Thus, it would be of interest to see whether ion-exchanged catalysts are also more stable in oxygen environments.

(4) The sintering kinetics in the presence of steam, chlorine and the normally encountered poisons in reforming. Such studies would help to extend the heat treatment studies in pure environments to those encountered in practice during operation and regeneration.

Reforming and other hydrocarbon processing catalysts operate under conditions where some coke deposition generally occurs. In a Pt/Al_2O_3 reforming catalyst, most of the coke is deposited on the acidic alumina but some coke is also deposited on the Pt crystallites which reduces their chemisorpiton capacity and activity. Most of the sintering studies have been performed in pure hydrogen atmospheres with clean catalysts; the effect of the presence of coke on the metal and the support needs to be studied. From the sintering studies on Pt blacks, it is known that even a trace amount of carbon may greatly inhibit the sintering, probably through a decrease of surface diffusion rate. If particle migration based on surface diffusion is the controlling mechanism, the sintering should be greatly reduced. On the other hand, Flynn and Wanke [16] mention that the presence of carbon at the metal support interface would facilitate the transport of atomic species from the metal to the support, in a manner similar to that of hydrogen spillover. A similar effect was observed in liquid environments [199]. Thus it would be of interest to study the sintering kinetics in H_2 in the presence of coke and observe the rates and activation energies involved to arrive at mechanistic conclusions on the influence of coke.

A possible experimental procedure would be to prepare fresh catalysts and sinter them in hydrogen for various times at different temperatures.

Coke depositon (say <1%) on similar catalysts, followed by sintering in hydrogen would enable the comparison of the two series of catalysts. Characterization may be done by x-ray diffraction or by small-angle x-ray scattering. If only small amounts of coke are deposited, and long time intervals for sintering in hydrogen are chosen, a careful carbon burn-off may be practiced to make the chemisorption measurements possible. A carbon burn-off procedure that does not cause appreciable sintering may be arrived at by initial experimentation. A pretreatment procedure to be used before chemisorption measurements would also have to be used in such a case.

CHAPTER 5

REDISPERSION OF SUPPORTED METAL CATALYSTS

5-1. Introducation:

Deactivation of industrial catalysts for hydrocarbon processing is due to the agglomeration of the metal crystallites, deposition of carbon and other residues, poisoning by arsenic, lead, sulphur and copper compounds etc. and the loss of promoter etc. In dual functional catalysts, such as the reforming catalysts, where the support has a catalytic function, these affects are important for the support also. Thus the alumina support in a reforming catalyst loses its surface area due to sintering of the support particles and also its acidity by chloride loss due to the presence of basic nitrogen compounds and water in the feed. The sintering of the support may, in addition, cause changes in diffusivities and hence catalyst selectivity.

The process of regeneration or reactivation of reforming catalysts, as it is used in the industry, serves a number of purposes including carbon burn-off, removal of poisons and replacement of the support acidity by chloride addition. An "oxygen-soak" using high concentration oxygen or air at 480°C is sometimes used, supposedly to retard crystallite growth during subsequent usage [8]. The regenerated catalysts are known to have performance (activity and selectivity) similar to the fresh catalysts, however, a catalyst that has been regenerated a number of times has to be discarded or sent for recovery of the precious metal.

As said above, the restoration of catalytic activity and selectivity may be due to a number of complex factors. A large number of patents which describe new methods for regeneration or reactivation of hydrocarbon processing catalysts are issued each year. It is difficult to follow the effects of such regeneration techniques since only rarely are the catalysts properly characterized in terms of areas or particle sizes. In many reactions activity does not always correlate well with the metal area [78], thus the effect of these procedures on the metal dispersion is not known. Normally a sintering of the catalyst during regeneration would be expected (see Chapter 3), however, with Pt, Pd etc. various processes [7,9,12,14,18,19,23,24,46,47,50,63,91] among them treatment with oxygen and gaseous chlorine, have been found to achieve a reactivation of the spent catalysts which apparently includes a redispersion of the metal on the support. Redispersion has also been observed during the course of chemisorption studies, usually after an oxidation-reduction cycle [9,12,23].

5-2. Survey of Redispersion Work:

An early mention of redispersion occurs in U.S. patent 3,134,732,[18] filed July 17, 1953 and accepted May 26, 1964. This work relates to nobel metal catalysts dispersed on metal oxides and deals specifically with platinum on alumina. The invention comprises a reactivation process for spent reforming catalyst consisting of oxidation to remove carbon, and treatment with a halogen gas followed by reduction with a hydrogen containing stream. It is noted that one of the reasons for deactivation is increased size of the platinum crystals. Platinum crystallite sizes were measured by X-ray diffraction and found to be <50°A for the fresh catalyst, >200°A for the spent catalyst and again <50°A for the reactivated catalyst. The authors note that the experimental data indicates that the reactivation is more than a restoration of halogen content. The chlorine content of the fresh catalyst is reported to be 0.23%, of the spent catalyst, 0.19%, and of the reactivated catalyst, 0.13%. Suggested halogen treatment and conditions were quite broad with temperatures from ambient to 1250°F and Cl_2 pressures of up to 200 psi. It was mentioned that the preferred time interval of treatment was of the order of several minutes but that this can be varied to obtain the desired degree of dispersion.

Along the same line is U.S. Patent 3,117,076 [19] filed August 31, 1959 and accepted January 7, 1964. The proposed method employs the contacting of deactivated Pt-alumina catalyst with gaseous Cl_2 at elevated temperature. It is stated that this procedure not only reactivated the catalyst but upon further treatment with an aqueous media serves to re-distribute the platinum on the support. No crystallite size measurements were made. It was indicated that increasing or restoring the chlorine content was not the cause of the reactivation. Typical chlorine treatment conditions were for one hour at 950°F and one atmosphere. Such a redistribution in an aqueous media causing redispersion is also described in ref. [92].

Much more quantitative work on redispersion using various oxidation-reduction cycles is available than exists for the halogen treatments. One of the early references is U.S. Patent 3,011,068 [20], filed May 21, 1956 and accepted December 5, 1961, in which a process following carbon burnoff, involving an oxygen soak and subsequent reduction is described. The following depicts how the author visualized the effects of the treatment.

> "While the nature of catalytic activity and the mechanism of catalytic processes are difficult to discern in most cases, I suggest that the decrease in activity of platinum-type hydroforming catalysts may be due to a reorientation process through annealing of the platinum or palladium crystallites during exposure to the hydroforming temperature range, whereby the crystallites are caused to assume an unstrained state. In the unstrained state, the catalytic metals might be expected to be sluggish in their ability to bring about oxidation, reduction, and the several reactions involved in the hydroforming process. In treating the catalytic metal by exposure to oxygen at high temperature according to my new process, the metallic bulk tends to be increased because the oxides thereof are less dense (as much as 20 percent less) than the metal; and when the oxides are thereafter subjected

> to reduction, the resulting shrinkage produces strains or rifts in the oxide and in the regenerated metal centers. If, after the oxygen soaking period, the catalyst is cooled rapidly to a temperature below the recrystallization point of the catalytic metal or of any oxides formed therefrom, the said strains or rifts may be accentuated and fixed therein. My tests have demonstrated that the catalyst, after treatment in these ways, exhibits the same hydroforming characteristic as when it was freshly prepared."

The recommended oxygen treatment is with a gas containing O_2 at partial pressures above 0.4 atmospheres and at a temperature of approximately 1000°F for a period of 1 to 24 hours. It is noted that a catalyst which has become severely deactivated requires higher temperatures, oxygen partial pressures and/or a longer exposure time than a catalyst which has suffered less severe deactivation. Most of the tests of the proposed procedure were on spent catalyst from a reforming environment. It was found that a catalyst deactivated by heat treatment in helium could also be reactivated.

U.S. Patent 2,879,232 [21] filed January 25, 1957, and accepted March 24, 1959 is similar to the above. In it a method of reactivation in which the catalyst is subjected to a mild oxidation to remove the readily oxidizable carbon and then subjected to a more severe oxidation, quickly quenched and then reduced is described. Neither surface area nor particle size distributions were determined and the process is viewed very much as in 3,011,968 [20]..

In U.S. patent 3,278,419 the authors Coe and Randlatt [7] describe a process for reactivating halogenated Pt/Al_2O_3 catalysts. The authors believe that the reactivation process includes a redispersion effect. The three main steps are:

(1) Chlorine pretreatment step: A few hours (~48) before regeneration, chlorine is introduced along with the hydrocarbon feedstream either

as gaseous Cl_2 or as low b.p. compounds such as trichlor ethylene and ethylene dichloride in amounts varying from 20 to 200 ppm by wt. Water is introduced along with chlorine to control the quantity adsorbed (Cl_2/H_2O ratio between 0.0002 to 0.050). The Cl_2 rate and the Cl_2/H_2O ratio are determined by the amount of chlorine desired finally. The authors prefer to prechloride the catalyst to 0.8 - 1.1% by wt.

(2) The carbon burnoff step: At the end of the prechloriding step, the reactor is purged with N_2 and then the burnoff is started, controlling the oxygen content ($<1\%$ by volume) to maintain temperatures between 700-900°F. During the last stages the oxygen content is increased to achieve a gradual transition up to 900 - 1000°F which is the "reactivation" temperature.

(3) Reactivation: The chlorided and decarbonized catalyst is reactivated by maintaining it in a flow of oxygen (at least 20% by volume) at a high temperature (900 - 1000°F) for about 8 hours. A small amount of water (~500ppm) is used in the gas-flow and this is believed to greatly enhance the redispersion of platinum. The amount of water used should be controlled to avoid excessive chloride losses.

The authors state that chlorine is responsible for the redispersion of platinum which occurs during the reactivation step. The amount of chlorine in the oxidizing environment which in turn is controlled by the water content in the reactivation step, is supposed to be an important factor. The authors do not propose any mechanism but state that the reactivation (ie. redispersion) is due to "interactions between the chlorine, the air, the water content of the air and the temperature."

The authors describe a set of experiments which show the importance of the pre-chloriding step. However, since these experiments do not include any physical characterization of the catalyst (the measured variable is the temperature required for a particular octane number), the claim of redispersion is not validated.

In an intersting variation decarbonized Pt/Al_2O_3 catalysts were impregnated with dilute HCl and this was followed by the reactivation (step-3) at 950°F for 8 hours. The increase in the H_2 chemisorption, value over that of spent catalysts varied greatly with the water content in this step. The authors state that ". . . H_2O content greater than 100 ppm-mole H_2O greatly enhances the degree of platinum redispersion at all chloride levels, thereby increasing the available area of platinum surfaces, ergo catalytic activity as well."

While it is difficult to interpret the meaning of their increased H_2 chemisorption values, it is noted that the authors do not report data on catalytic activities for the corresponding H_2 chemisorption values, although they do <u>state</u> a paralle effect (see above).

A "reactivation" with oxygen is also reported by Adler and Keavney [12]. This work dealt with platinum-alumina reforming catalyst prepared by both impregation and cojelling. In most of the above references the effects of the oxygen or chlorine treatments were determined by comparing activities as measured by the resulting octane obtained from a given naptha charge. In this study the effects were determined by the physical measurements of H_2 chemisorption and X-ray line broadening. As a part of this study the catalyst was sintered by steaming and then reactivated in O_2 at 620°C and 60 psig for two hours. The sintered catalysts showed significantly decreased H_2 chemisorption capacity and after the oxygen treatment a part of the capacity was restored. The cogelled and impregnated catalyst responded differently to both the steaming and the reactivation. For mild steaming the cogelled catalyst lost more of the chemisorption capacity than did the catalyst prepared by impregnation. Similarly the cogelled catalyst regained more of its H_2 chemisorption capacity as a result of the oxygen treatment than did the impregnated catalyst. The results under more severe steaming did not follow consistently. The cogelled catalyst lost slightly less of its chemisorption capacity under severe steaming than under mild, while the impregnated catalyst showed more sintering as would be expected. After severe steaming neither catalyst responded significantly to the oxygen treatment.

Adler and Keavney related the adsorption data to particle size by assuming either a monolayer of platinum atoms or a three-dimensional hexagonal pyramid and it was further assumed that the adsorption of hydrogen atoms occurs at the interstices of the platinum surface. Considering the monolayer approach, the number of interstices, I, were determined from the volume of hydrogen adsorbed and then by assuming the monolayer to consist of n rows of platinum atoms containing alternately n and n-1 atoms a relation was developed between n and I and between n and T, the total number of platinum atoms in the monolayer. Thus the adsorption volume yielded

$$\begin{tikzcd} I \arrow[r] & n \arrow[r] \arrow[dr] & \text{size} \\ & & T \end{tikzcd}$$

A similar approach was utilized with the hexagonal pyramid where the mean dimension was taken to be the distance between opposite sides of the base.

The particle sizes were also measured by means of X-ray line broadening and compared with the adsorption measurements. The general trends predicted were usually the same though the actual values predicted were not in particularly good agreement. The results did show very high dispersion of the platinum on the support and indicated a decreased particle size as a result of the reactivation process. The authors however interpreted the results as follows:

> "On the one hand, we do not believe that the results obtained on the reactivated catalysts should be taken to indicate a decreased Pt particle size. Considerations of energetics would rule out the possibility of a platinum particle of over 200 A° dissociating into 20 A° particles as might be indicated for the cogelled catalyst containing 0.30% Pt. Instead, we interpret the apparent decrease in size after reactivation as due to a disruption of the platinum lattice by oxygen atoms. These are removed by subsequent hydrogen dosing, leaving fissures in the sintered particle. These fissures are then responsible for an increase in Pt surface area which accounts for increased H_2 sorption. At the same time, the degree of ordering in the lattice is reduced and this accounts for the line broadening results."

Gruber [23] subjected a platinum catalyst to an oxidation-reduction cycle and then used hydrogen chemisorption to determine the effect of the cycle on the dispersion. With highly dispersed catalyst no significant effect was found, however, for the sintered catalysts, a significant increase in dispersion as measured by H_2 chemisorption was found. In the study the catalysts were prepared by both tetramminoplatinum hydroxide and chloroplatinic acid impregnations. It was concluded by Gruber that while the halogen may be partly responsible for the regeneration of the catalyst prepared with chloroplatinic acid, the increase in dispersion of the catalyst prepared with tetramminoplatinum hydroxide must be due to the reaction with oxygen.

Johnson and Keith [24] note the considerable evidence that Pt surface area is an important factor in the activity of reforming catalyst but also note that McHenry [25] postulated that the active component of these catalysts consisted of a Pt alumina complex the extent of which can be measured by the amount of Pt soluble with the alumina in aqueous hydrofluoric acid or acelylacetone. In their experimental work Johnson and Keith treated spent catalyst with air for various time durations and conditions and then after reduction in H_2 measured the surface area by CO chemisorption and also the amount of soluble Pt and found an excellent correlation between the two. It was suggested that the complex exists in oxidized form and is desirable not per se but because it leads to high dispersion upon subsequent reduction.

They also found that as the severity of oxidation treatments was increased a limit was reached such that an area decreased resulted from the treatment. To explain this the reaction

$$Pt + O_2 \rightleftharpoons PtO_2 \rightleftharpoons PtO_2 \ . \ \text{alumina}$$

was suggested with the idea that as the temperature is increased the equilibrium shifts to the left forming the metal with the ultimate result of increased crystallite size. (See Table 5.1)

Wentrcek, Kimoto and Wise [26] subjected a supported platinum catalyst to a series of oxygen exposures and found the area to increase after each exposure. The area in the work was determined by a CO titration technique based on the reaction

$$O_{(s)} + 2CO \rightarrow CO_{(s)} + CO_2$$

It was suggested that the same surface reconstruction that results in increased hydrogen chemisorption capacity after treatment with oxygen also causes the increased CO chemisorption.

Redispersion was also found by Weller and Montagna [9] after treatment with oxygen and subsequent reduction. Their results indicate that the redispersion occurs during the reduction step. These authors found the redispersed catalyst to be more resistant to sintering than the original preparation.

In a recent study on the sintering of Pt/Al_2O_3 catalysts, Flynn and Wanke [50] have found evidence of redispersion on a commercial 0.5%

Pt catalyst after it was heated for 16 hours in air at 450°C - 600°C; at higher temperatures the catalyst showed sintering. The redispersion was characterized by increase in uptakes of hydrogen and oxygen; that of H_2 being much greater than of oxygen. They point out that the H/O ratio increases with increase in dispersion so that their results do indicate the presence of smaller particles. For a similar commercial catalyst (0.3%Pt) they found no evidence of redispersion but noted extensive sintering when subjected to similar treatment. They did not discuss this discrepency since the catalysts were surface coated type and exact Pt contents in the outer region were not known. Their efforts to investigate whether redispersion is a transient process [16] did not succeed. They also found slight redispersion in the lab-prepared catalysts when they were heated in air at 550°C.

Baker et.al. [164] in their controlled atmosphere electron microscopic study of oxygen-graphite reaction catalyzed by Pt and Pd found that the metal particles supported on graphite sometimes split up into smaller fragments. Such splitting was also observed during the oxidative decomposition of chloroplatinic acid on graphite.

In a recent work, Ruckenstein and Malhotra [91], using Pt/Al_2O_3 catalysts prepared by depositing Pt on a nonporous alumina obtained from anodic oxidation of an aluminum foil, found that heating in air at 600°C for 24 hours followed by slow cooling gave rise to strong sintering whereby the mean crystallite size increased from 31 Å (fresh sample) to 107 Å. However, reheating this catalyst to 500°C for 24 hours followed by slow cooling gave a redispersion effect and the crystallite size decreased to 41 Å. A lower redispersion was observed when the second heating was at 400°C. Rapid cooling after the second heating causes the crystallites to disappear, i.e. either they evaporate or become smaller than the resolving power of the microscope (∿5 Å).

The authors attribute the splitting to the formation of a metal-support complex in the presence of oxygen; the mismatch at the interface due to this complex causes a strain in the crystallites which causes the splitting. Since redispersion is associated with the formation of the complex, it can occur only below the decomposition temperature of the complex.

Examples of redispersion of some other supported metal catalysts can be found in the patent literature. For example, coke burn-off followed by reduction and subsequent halogenation-reduction treatments is claimed to redisperse iridium into crystallites smaller than 12 Å [73]. A similar procedure is described in [74] where catalysts containing Ir are oxidized to convert the Ir into large oxide crystallites which are redispersed into smaller crystallites on reduction. The authors in [73] suggest that oxygen should be excluded during halogenation in order to prevent agglomeration.

Kozlov et.al. [56,75] suggest that oxygen treatment of Pd catalysts containing chlorine converts it into a complex with chlorine and alumina. Reduction of the complex transforms it into a highly dispersed state to a finer distribution on the carrier surface. A redispersion process for supported Pd is also described in [76].

The work of Bremer, Muche and Wilde [82] on Cr_2O_3-K_2O/Al_2O_3 is of interest in that it emphasizes the effect of the interaction of the active component with the support (in this case, with the promoter K_2O also) on its sintering, regeneration and activity.

The catalysts which were prepared by impregnation had 20% Cr_2O_3 and 4% K_2O on a γ-alumina support. The activity of these catalysts is attributed to Cr ions which are a result of a strong interaction of chromia with η or γ-alumina.

The sintering was done by heating in a flow of hydrogen for 5 hours. in the temperature range 300-900°C. The regeneration consisted of an oxiation treatment: heating at 570°C for 5 hours in an oxygen flow, followed by a 1 hour reduction in H_2 flow at 500°C. Optical reflection spectroscopy, oxygen chemisorption and EPR were used for catalyst characterization.

The regenerated samples show a poorer reflection spectra than the aged samples and thus contain highly dispersed Cr_2O_3. Two kinds of sintering are identified by the authors: (i) a reversible sintering process, below 650° - 750°C where Cr_2O_3 crystallites grow, (ii) an irreversible sintering process above 650° - 750°C where some clusters of Cr_2O_3 form solid solutions with the support.

The authors regard the regeneration process as an oxidative decomposition of Cr_2O_3 clusters resulting in their redispersion on the support. However, the Cr_2O_3 from the solid-solution cannot be redispersed (hence the name 'irreversible'). The authors note that irreversible sintering does not affect the activity (dehydrocyclization of n-hexane) of the <u>aged</u> catalysts since the surface area of Cr_2O_3 does not change because of its strong interaction with the support.

The fact that a redispersion of the reversibly sintered part does occur was also verified by surface area measurements.

In the discussion following this paper, Delmon pointed out an apparent discrepency. In their work (Delmon et.al. [83]) they had postulated that Cr_2O_3-Alumina solid solutions are the true dehydrogenating phases and that the free Cr_2O_3 has little catalytic activity, the present authors however attributed the irreversible sintering (or 'aging') to the formation of such solid solutions. However, the formation of solid-solution does not affect the catalytic properties, it only decreases the regeneration ability. As the authors explained, even small crystallites have strong interaction with alumina and possess catalytic activity contrary to Delmon's suggestion. The irreversible aging is postulated to be due to the penetration of Al^{3+} ions into the crystallites and would supposedly not affect their size and the exposed Cr_2O_3 area. It seems that there is a difference of opinion between Delmon and the present authors about the nature of the active species; however both attribute activity to an interaction of Cr_2O_3 with alumina.

The role of K_2O was not discussed except that it was pointed out that it is important for the oxidizability and hence the regeneration-ability of the catalysts.

It would have been interesting if the authors had investigated the effect of successive sintering and regeneration cycles wherefrom their hypotheses about the nature of irreversible sintering, the active component and the possible mechanisms of regeneration (redispersion) could have been clarified. The variation in aging and regeneration-ability with metal content would also be of interest.

The foregoing and other mentions of redispersion are summarized in Table 5.1. As discussed before, some authors regard the regeneration procedure to activate the sites that have been annealed during usage, the opposite of so called "qualitative sintering."

TABLE 5.1 SUMMARY OF PREVIOUS WORK

Authors	Catalysts	Experimental	Dispersion Characterization	Results
Kearby et. al. [1953] U.S. 3,134,732 Ref. [18]	Pt/Al_2O_3	Carbon burn-off in air or O_2 contg. atmosphere (700-1100°F), halogen treatment (Cl_2) (7 catalyst wt.%); Cl_2 strip-off and H_2 reduction.	1. X-ray diffraction 2. Octane numbers of reformed naptha	Reactivation is more than a restoration of halogen content. Deactivated catalyst has crystallites > 200 Å while the reactivated catalyst has size < 50 Å Believe that apart from removing poisons, the halogen treatment brings about a re-distribution of the Pt crystallites by decreasing their size and thus resulting in higher surface areas and activity.
Webb [1956] U.S. 3,011,968 Ref. [20]	Pt/Al_2O_3	Carbon burn-off followed by severe O_2 treatment (~1 atm 950°F) and H_2 reduction at 600-1000°F.	Activity as measured by octane number	1. Believe that loss of hydroforming activity is due to annealing of the crystallites whereby they assume an "unstrained" state; the oxidation - reduction treatment "regenerates" the active centers. 2. Catalyst subjected to accelerated deactivation in helium can also be reactivated by this procedure. 3. No mention of crystallite size changes.

Authors	Catalysts	Experimental	Dispersion Characterization	Results
Coe and Randlatt [1956] U.S. 3 278,419 Ref. [7]	$Pt-Al_2O_3$ $-Cl$	(i) Chlorine pretreatment step, prechloride to 1% Cl (ii) Carbon burn-off in 1% O_2 (iii) Reactivation in a 20% O_2 flow at 1000°F for 8 hours with controlled amounts of H_2O.	(i) Temperature required for a given octane number (ii) H_2 chemisorption measurements in one case	(i) Believe that the reactivation includes a redispersion of the metal - Increased H_2 chemisorption shown in one case (ii) Optimum amount of H_2O needed in the reactivation step (3) to achieve a high redispersion.
Malo et.al. [1957] U.S. 2, 879,232 Ref. [21]	Pt/Al_2O_3	Carbon burn-off, severe oxidation at 950°F followed by quenching and high temp. H_2 reduction 600-1000°F.	Activity as measured by octane number	Reactivation of active centers by oxidation - reduction treatment. Similar to 3,011,968. No mention of crystallite size changes.
Brennan et.al. [1959] U.S. 3,117,076 Ref. [19]	Pt/Al_2O_3	Carbon burn-off in O_2 contg. gas followed by oxidation-reduction cycles: oxidation: air at 100 psig. at 1050°F Red: H_2 at 100 psig. at 950°F followed by Cl_2 treatment at 950°F. Cl:Pt : 4:1 other treatments (eg. aqueous) optional.	Activity as measured by octane number	Halogen treatment after oxidation - reduction improves the activity. Believe that halogen treatment redistributes Pt on the Al_2O_3 support.

Authors	Catalysts	Experimental	Dispersion Characterization	Results
Adler and Keavney [1960] Ref. [12]	Impregnated and cogelled Pt/Al_2O_3 catalysts	1. Slow carbon burn-off 2. Mild sintering in steam- 705°C, 0.35 atm H_2O, 5 hours. 3. Severe sintering in steam- 750°C, 1atm H_2O 5 hours. 4. Reactivation of sintered catalysts: 620°C in a static O_2 atmosphere - 2 hours, p = 60 psig	X-ray line broadening, H_2 adsorption	a. Impregnated catalysts contain Pt monolayers, cogelled catalysts have aggregates. 1. Coke burn-off causes partial recovery of adsorption capacity. 2. Sintering (steaming) causes greater loss of adsorption capacity for cogelled catalysts. 3. Oxygen reactivation partially restores adsorption capacity for the mildly sintered catalyst. Little improvement for severely sintered. Increased adsorption capacity is not taken to imply a decrease in crystallite size.
Gruber [1962] Ref. [23]	Impregnated Pt/Al_2O_3 catalysts. 1. Tetra-amino Platinum Hydroxide. (TPH) 2. Chloroplatinic acid. (CPA)	Several Catalysts including those sintered in H_2 at 500° for 0-1200 hours subjected to oxidation-reduction treatment: Two H_2 adsorptions (250°C) followed by 2 oxygen adsorptions (350°C, 150 mm pO_2). Evacuation after each adsorption.	H_2, O_2 Chemisorption	Sintered catalysts showed significant redispersion as measured by H_2 chemisorption. No affect on fresh catalysts. Redispersion in TPH believed to be due to reaction with oxygen; for CPA the halogen may have some contribution in the redispersion of Pt.

Authors	Catalysts	Experimental	Dispersion Characterization	Results
Johnson and Keith [1963] Ref. [24]	Commercial impregnated Pt/Al_2O_3 catalysts.	Heat treatment at different temperatures (427°-650°C) and oxygen partial pressured (0.015-1 atmp). Reduction in flowing H_2 at 480°C for 12 hours after oxygen treatment.	Pt solubility in aqueous HF, CO adsorption, H_2-D_2 exchange.	Redispersion and sintering observed (after reduction) under different treatment conditions. Surface area as measured by CO adsorption after H_2 reduction is paralleled by Pt solubility in oxidized state. Postulate that redispersion proceeds via a platinum alumina complex that exists in the oxidized state (McHenry) and gives highly dispersed Pt on reduction. When oxygen partial pressure > dissociation pressure, sintering takes place. Critical temperature for oxygen partial pressures of 0.21 atmp. and 1 atmp. were 510°C and 580°C.
Maat and Moscou [1965] Ref. [13]	Pt/Alumina	Heat treatment in air (muffle furnace) at 780°C; 0-72 hours H_2 reduction at 450°C.	H_2 chemisorption Electron - microscopy	1. Second order sintering rate as found by Herrmann et.al. 2. Mention that a lab scale regeneration causes a part of the platinum to be redispersed into crystallites of 10-20Å diameter as seen by electron-microscope. (See discussion following ref. 13).

Authors	Catalysts	Experimental	Dispersion Characterization	Results
Jaworska-Galas and Wrzyszcz [1966] Ref. [14]	Pt/Al_2O_3	Oxidative regeneration of a used reforming catalyst at 480°C in air. H_2 reduction at 480°C ~3 hours	O(S) - H_2 titration	1. Pt surface area (as measured by titration technique) after regeneration was $197 m^2/g.Pt$ compared to $145 m^2/g.Pt$ of fresh catalyst and $101 m^2/g.Pt$ of the used catalyst. 2. Redispersion attributed to oxidation of bulk platinum (Gruber) which leads to greater dispersion on reduction include the possibility of chloride having a contribution to redispersion.
Emelianova and Hassan [1968] Ref. [46]	Dilute Pt/Al_2O_3	Heat treatment in vacuum at 300-800°C.	Low temperature H_2 chemisorption, also H_2O_2 decomposition activity	1. Sintering observed only upto 400°C, at higher temperatures, quenching the catalyst gives a redispersion effect. Slow cooling causes sintering. [c.f. ref. 16]. 2. Postulate that the above includes a reversibility of the sintering phenomenon: a thermal dissociation of the "subcrystalline phase*" (microscrystallites). *subcrystalline phase: crystallites which do not yet have the bulk properties.

Authors	Catalysts	Experimental	Dispersion Characterization	Results
Spindler and Kraft [1968] Ref. [47]	Pt/Al_2O_3	Heat treatment in air and H_2 at 500° and 600°C.	O(s) - H_2 titration, X-ray diffraction, Pt solubility.	1. Highly dispersed Pt is converted completely to the soluble form by air treatment at 500°C increasing the Pt dispersion in this process. 2. Mechanism of fedispersion explained via complex formation [Johnson and Keith]. 3. At temperatures above 500°C the oxides of Pt start to decompose and in addition to oxidation of small crystallites, growth of large crystallites is observed. 4. Soluble Pt may consist of various Pt forms including non-stoichiometric Pt-O compounds.
Weller and Motagna [1971] Ref. [9]	Pt/Al_2O_3 (impregnated and Pt Zeolite (type Y) catalysts.	Adsorption-desorption studies of O_2 on Pt at 475°C and 525°C. Oxygen partial pressures: 5-40 cm Hg.	H_2 chemisorption qualitative X-ray diffraction patterns.	(i) Pt/Al_2O_3 sinters during oxygen treatment but redispersion is obtained on H_2 reduction. Catalysts stabilizes against sintering after a few cycles. (ii) Pt-Zeolite sinters regularly with each cycle; less stable t than Pt/Al_2O_3. (iii) Since the redispersion obtained after reduction is highly stable, they postulate the existence of

continued

Authors	Catalysts	Experimental	Dispersion Characterization	Results
Weller and Montagna [1971] (cont)				stabilizing complex after the reduction step. (versus the complex in oxidized state c.f. Johnson and Keith)
Wentrcek, et.al. [1973] Ref. [26]	Pt/Al_2O_3 Pt/carbon	1. Surface area by O/CO titration. 2. Affect of repeated O(s) chemisorbed - CO titration at room temperature on Pt dispersion (Pt/Al_2O_3).	O(s) - CO titration	1. 10% surface area increase after five O(s) - CO titrations. Postulate that oxygen treatment causes Pt surface reconstruction leading to higher CO chemisorption.
Flynn and Wanke [1975] Ref. [50]	Pt/Al_2O_3 a) Two commercial catalysts 0.3% 0.5% Pt	1. Catalysts sintered for 16 hours in O_2 at different temperatures. 2. Electron microscopic study of catalysts before and after reduction and heat treatment - viewing single particles.	a) H_2 and O_2 uptakes b) Electron Microscopy	1. For a 0.5% commercial catalyst evidence of redispersion after heating in air at 450° - 600°C for 16 hours as measured by gas uptakes. Also noted nominal redispersion for lab prepared catalysts on heating at 550°C in O_2. 2. Agglomeration found during reduction; at least some particles remain fixed during reduction and heat treatment.

Authors	Catalysts	Experimental	Dispersion Characterization	Results
Ruckenstein and Malhotra [1976] Ref. [91]	Pt on non-porous alumina by deposition	1. Heating at 600°C for 24 hours followed by slow cooling. 2. Second heating at 500°C for 24 hours with slow cooling.	Electron Microscopy	1. Sintering observed in step 1 and redispersion in 2. 2. Redispersion in oxygen atmosphere due to strain caused by complex formation.

5-3. Redispersion Models:

They only existing model which predicts a redispersion effect is that due to Flynn and Wanke [16]. The model was developed for the sintering process by the atom migration mechanism but for certain low values of the parameters $\frac{\alpha\nu}{S_o}$ and $\frac{E_a}{RT}$ (see pg. 114), the accumulation of the migrating atoms on the support in the initial stages of sintering gives rise to a transient redispersion. This corresponds to a case where the overall rate of loss of atoms by all the crystallites is greater than the overall rate of capture If the catalyst is cooled at this stage, the migrating species may be fixed on the support as individual atoms or as small clusters.

The factors which affect the extent of build up on the support surface are: the migration velocity (ν), collision accomodation (α), activation energy for escape from particles to crystallite surface (E_a), temperature (T) and the metal loading (S_o). The first three factors (ν, α, E_a) may be influenced by the heat treatment environment. Since the capture (probably loss too) of atoms is size dependent, the particle size distribution (PSD) would also influence the redispersion. The important variables which could be of interest in an experimental study are: 1) environment, 2) support, 3) PSD, 4) temperature, 5) metal loading.

The interpretation of the model in physical terms is quite simple: redispersion occurs when an ease of escape of atoms is accompanied by a low accomodation or sticking coefficient giving rise to a one-way flow of atoms. It can be seen however, that the parameter values which give a high redispersion may eventually lead to higher sintering rates. The case where significant redispersion is shown (see Figure 5, Ref. [16]) has an $\frac{\alpha}{S_o} = 2 \times 10^7 m^{-2}$. For a 0.5% Pt catalyst, this gives an extremely low accomodation coefficient ($\sim 10^{-12}$). While faceting or some similar nucleation barriers on the crystallite surfaces may give rise to low accomodation coefficients, the α values used to show a redispersion effect are not physically realistic.

The sintering model developed by Ruckenstein and Pulvermacher [10] does not account for the phenomenon of redispersion. The authors however, treat it separately and give a qualitative argument considering wetting as a contact angle phenomenon.

The spreading coefficient as it is usually defined is:

$$X = \alpha_{sg} - \alpha_{ss'} - \alpha_{s'g} \qquad -(5.1)$$

where α_{sg} = metal - gas surface tension

$\alpha_{s'g}$ = support - gas surface tension

$\alpha_{ss'}$ = solid - solid surface tension

At equilibrium:

$$\frac{\alpha_{sg} - \alpha_{ss'}}{\alpha_{s'g}} = \text{Cos}\theta \leq 1 \qquad -(5.2)$$

In solid-liquid systems $X > 0$ only means that the liquid will ultimately form a thin film. The kinetics of spreading of liquid drops on solids has been given by a number of authors (for eg. see 79,80,179). The kinetics of "spreading" of solid crystallite on a substrate has not been treated; RP, however, take eqns (5.1) and (5.2) to postulate that the crystallites would breakup in an appropriate environment.

The work of Emelianova and Hassan [46] (see Table 4.1) is of interest in that they observed redispersion when a catalyst undergoing heat-treatment in vacuum at temperatures above 400°C is quenched. Sintering was observed on slow cooling. While this conforms somewhat to the redispersion model by Flynn and Wanke, the authors explain this qualitatively on the basis of dissociation of crystallites.

5-4. Discussion:

From the foregoing, there appears to be sufficient evidence to assume that redispersion does occur and to warrant a systematic study of the phenomenon. Most of the previous studies have found redispersion in the course of sintering studies, thus the conditions under which redispersion occurs are not well understood and are often conflicting with those of sintering; although as mentioned by Wanke and Flynn [95], redispersion in oxygen environments is restricted to temperatures in the range of 400 to 620°C. An illustration of the difficulties involved can be found in the work of Flynn and Wanke [50] in which they were able to redisperse on 0.5% commercial catalyst but could find no evidence of redispersion for a 0.3% catalyst.

The phenomenon of redispersion probably involves complex interactions between the metal, support, and the environment. Johnson and Keith [24] and Weller and Montagna [9] utilize the concept of complex formation to explain the redispersion and the stability of the metal dispersion.

Ruckenstein and Malhotra [91] propose that complex formation at the interface causes strains in the crystallites which results in their splitting (redispersion). Since the redispersion is associated with the complex formation, the decomposition temperature of the complex (at a given oxygen pressure) as given by Johnson and Keith (see Table 5.1) defines the limiting temperature. To explain why sintering occurs at lower temperatures, the authors propose that the complex formation requires a high temperature (ie. to have a sufficient rate). The role of the two heatings employed by these authors is not clear. Since the temperature for the first heating (600°C) is higher than the decomposition temperature of the complex (at 0.21 atmp 0_2), one assumes that complex formation does not take place in this stage. This is in turn confirmed by the fact that extensive sintering occurs in this step. Heating at 500°C alone also causes sintering, although one would expect complex formation in this step. The reason why heating at 500°C after the initial 600°C heating causes redispersion is not clear. From the present knowledge, redispersion appears to occur under very restrictive conditions ie. deviations from the known conditions under which it occurs, result in extensive sintering. It remains to be seen whether redispersion is a more general phenomenon and whether it can be applied to catalysts with different histories. For this, the mechanism of redispersion has to be established. Complex formation alone is inadequate, for then redispersion would be much more common; moreover it does not even explain all the results of the present authors (Ruckenstein and Malhotra).

In some of the works [12,20,21] reactivation is believed to be due to the production and fixing of "strains and rifts". Although it is supposed to be due to oxygen-platinum interaction, this can also be explained by assuming that the strain is caused by the metal-support complex formation and that it leads to higher activity without the crystallites being split.

That halogens may have a role in the redispersion process was mentioned in [14,23]. If chlorine takes part in the complex formation, it would affect the decomposition temperature and thus the conditions where redispersion is possible. Baker, Thomas and Thomas [51] found that on heating chloroplatinic acid/alumina in 2 Torr. oxygen above 800°C caused the crystallites to decrease in size. Moreover, such behavior could be induced in Pt/alumina by heating in 2 Torr. oxygen at 500°C, treatment with H Cl at room temperature followed by reheating in 2 Torr. oxygen at 900°C. The work of Burton [94], who found that in Pt/Al_2O_3, the role of chlorine originating from chloroplatinic acid was unique, was mentioned in Chapter 2. The role of chlorine in soluble platinum was also proposed in [67]. Thus it could be postulated that chlorine is present in a complex form and that it can be introduced in evaporated Pt/Alumina by the method given by Baker, Thomas and Thomas. These facts are consistent with the stabilizing effect of chlorine in Pt/Alumina catalysts, thus HCCl is often used in reactivation procedures [eg. 58].

It is possible that only crystallites above a particular size are able to split or redisperse and this may explain the necessity of sintering prior to the redispersion as in [91,46,51]. However, Emelinova and Hassan [46] proposed the splitting of microcrystallites (<20-50 Å).

The redispersion of catalysts involving a "redistribution" in an aqueous media is mentioned in [19,92]. In these, the first step probably consists of the formation of a water soluble compound such as a chloride which is in turn spread over the support in an aqueos media, for eg., by the application of steam. The further steps may be considered equivalent to those in normal catalyst preparation.

Chemisorption techniques have generally been used to study sintering and redispersion. The difficulties encountered in the interpretation of such measurements vis-a-vis the changes in dispersion were mentioned in Chapter 3. The magnitude of error in these techniques may sometimes be comparable to that of the changes observed in dispersion.

There is need for further work which would emphasize catalyst characterization during various stages of the treatment. The work of Ruckenstein and Malhotra [91] is a significant contribution in this direction. The variables one might investigate in making such an effort are: (1) the choice of the catalyst, (2) the choice of the preparation technique and the metal content, (3) the thermal history of the catalysts to be redispersed, this would include the extent and nature of the sintering that has occured, (4) the choice of the various redispersion processes given in literature, (5) severity of treatment (time, temperature, partial pressure), (6) cooling and reduction procedures.

To start with, Pt/Al_2O_3 should probably be studied with a combination of electron-microscopic and H_2 chemisorption techniques. A support that is suitable for transmission electron microscopic study and which does not undergo transformations during the treatments in the redispersion process should be used. Choices for 2,4,5 and 6 may be indicated by previous work. Some trial and error procedures may be required and a proper set of experiments based on the available information (temperature and pressure ranges, order of various treatments) would be necessary to obtain reproducible results. In addition to the above listed factors, the effect of multiple sintering - redispersion cycles would be of interest.

Since redispersion has been closely associated with metal-support interaction, it would be logical to investigate whether redispersion is possible in systems with no known interactions. Catalysts prepared in the different techniques (evaporation, impregnation with different salts) and with varying degrees of interaction should be studied to bring out the differences. Controlled atmosphere electron microscopy may be advantageously used where the treatments are possible.

Some of the work on redispersion in other systems was mentioned in this chapter. Since metal-support interactions are known to be present in many systems (see Chapter 2), similar experiments should be extended to cover these also. The regeneration of Amoco's bimetallic catalyst [97] includes a "rejuvination treatment which redistributes the active metal and restores the active site." The redispersion of such catalysts also needs to be studied.

APPENDIX 1

The surface species present on the metal crystallites are important in considering surface diffusion rates and for crystallite growth by vapor transport or surface diffusion of atomic species. At the cost of redundency, the affect of gaseous environment on surface diffusion is repeated here:

(1) Change in composition of the gaseous phase may affect the diffusion mechanism, for eg. by changing the number of vacancies on the crystallite surface.

(2) If a material A is covered with a film of B, whose lattice has higher mobility than of A, sintering would be facilitated by the formation of B. If the lattice of B has higher energy than of A, a gas phase that facilitates the removal of B, favors the sintering process.

The surface species also determines the ease of escape from the crystallite surface to the support as well as the growth by vapor transport. Surface thermodynamics of the systems of interest (Pt-O, Pt-Cl) are not known, thus most of the following discussion is in terms of bulk compounds.

A. Pt-Oxygen System:

Weller and Montagna [9] have reviewed some of the chemistry surrounding the Pt-oxygen system. They found that very little is known about the thermodynamics or even the existence of oxides of platinum.

Using the adsorption-desorption of oxygen, they determined the dissociation pressure of PtO as 11 and 21 cm Hg at 475° and 525°C. Thus surface oxidation was observed below these pressures while bulk oxidation is observed at higher pressures. This was in agreement with the calculated values which themselves were very sensitive to the values of thermodynamic quantities used in the calculation.

Other recent studies include that of Chaston [295] who postualted that the high temperature oxide is PtO_2 which decomposes into metal and oxygen at higher temperatures. The dissociation temperature of solid PtO_2 is between 550-770°K in one atmosphere oxygen. Loss of platinum is prevented due to the high boundary layer resistance. Some data on volatization rates is given.

PtO is a strong oxidizing agent and can be prepared in bulk by heating Pt under 8 atm of oxygen at 420-440°C [86]. PtO_2 can be prepared by heating Pt powder in oxygen at 450°C and 150 atmps, the PtO formed can be dissolved in aqua regia. Original references for thermal and catalytic properties of platinum oxides are given in [86]. A bibliography of surface reactions of oxygen with Pt is given in [89]. Pt-oxygen interactions in titration techniques are discussed among others, by Akthar and Tompkins [43].

B. Pt-Chlorine System:

Some of the better known chlorides of platinum are Pt_3Cl_3, $PtCl_2$, Pt_6Cl_2, $PtCl_3$ and $PtCl_4$. The preparation, properties and regions of stability of these chlorides are given by Hartley [86]. Some of the data from this work are given below.

Pt_3Cl_3 has been described but is probably a mixture of Pt(II) and Pt(IV) chlorides. $PtCl_2$ can be prepared by direct chlorination at high temperatures, by the chlorination of PtO_2 at 500°C, by the thermal decomposition of $PtCl_4$ above 350°C or by passing chlorine over H_2PtCl_6 at 500°C. Pt_3Cl_3 is reported to be formed in the gas phase on heating platinum dichloride. At higher temperatures it decomposes into Pt and Cl_2. $PtCl_4$ can be formed from Pt metal and chlorine at high temperatures, by chlorinating $PtCl_2$ at 275°C or by heating H_2PtCl_6 (alone or in chlorine).

Landsberg and Schaller [87] have studied the kinetics and equilibria of Pt-chlorine system and report reaction rates per unit area of metal as a function of temperature and pressure between 470° and 880°C and chlorine pressures of 152-760 Torr.

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1. General Reviews on Catalysis by Metals, particularly on Supported Metal Catalysts:

   15, 28, 60, 61, 64, 72, 88, 93, 101, 113, 114, 122, 123, 124, 125, 131, 137, 220, 221, 222, 229, 252, 298, 308, 310, 317, 318, 320, 323, 325, 327, 337, 347, 350, 362

2. Catalyst Preparation:

2A. General Principles: 102, 103, 131, 182, 184, 185, 186, 187, 188, 192, 266, 279, 356

2B. Pt/Al_2O_3: 14, 33, 53, 68, 142, 188, 190, 191, 217, 224, 225, 226, 267, 272, 275, 278, 342, 343, 344, 346

2C. Pt/Silica: 32, 39a, 41, 54, 62, 126, 180, 340, 358, 364,

2D. Pt/Carbon: 37, 85

2E. Supported Nickel: 144, 163, 183, 187, 193, 222, 226, 230, 252, 361, 364

2F. Supported Pd: 183, 303, 345, 346, 351, 359

2G. Pt-Re/Alumina: 233, 234, 244, 245, 247, 248, 249

2H. Other Supported Metals: 218, 239, 241, 252, 363

3A. Reviews on Surface Area Measurements by Chemisorption: 27, 34, 65, 252, 331, 332

3B. Details of Chemisorption Apparatus: 57, 81, 252, 333, 334

3C. Moessabauer Spectroscopy (Mostly Reviews): 145, 147, 296, 299, 304, 307, 309, 348

3D. Auger Electron Spectroscopy: 145, 329, 336, 352, 354

3E. X-Ray Photoelectron Spectroscopy: 145, 218, 231, 301, 330, 339, 353, 355

3F. LEED: 134, 149, 177, 223, 349

3G. General Reviews on Experimental Techniques for Studies of Fundamental Phenomena in Catalysis: 145, 252, 300, 305, 319, 322, 326

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THE SINTERING AND REDISPERSION
OF SUPPORTED METAL CATALYSTS

by

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ABSTRACT

The experimental work and theoretical models for the sintering and redispersion of supported metal catalysts are reviewed and analyzed. The emphasis is on Pt/Alumina but other systems are also considered. Related topics in thin film phenomena and sintering of unsupported blacks are also discussed. Examination of the existing literature reveals that the mechanisms of sintering and redispersion are not well understood. Redispersion, in particular, is a complex phenomenon and has not been well characterized. The limitations of experimental techniques in these studies are discussed. Recommendations for further work in the fields of catalyst preparation, sintering, and redispersion are included.