

THE PREPARATION AND INVESTIGATION OF
SUPPORTED HYDROCARBON OXIDATION CATALYSTS.

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A Submission For The Degree of M.Sc.

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DECLARATION

This thesis has not been submitted as an exercise for a degree of this or any other academic institution. The work described within this thesis is based on the authors own work.

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ABSTRACT

Alumina has been extensively used as a catalyst support material. It exists in several different phases namely γ , η , δ , θ and α .

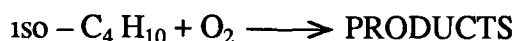
Phase transformations (e.g. $\gamma \rightarrow \delta \rightarrow \theta \rightarrow \alpha$) can occur at well defined temperatures. If transformations occur during catalyst use, then the activity of the catalyst can be reduced significantly.

In this project, the effect of addition of metals to η - Al_2O_3 was investigated in an effort to stabilise the high surface area phase at high temperatures. The following ions were added at 1 and 3wt% loadings: Ba^{2+} , Ca^{2+} , Ce^{3+} , Cs^+ , La^{3+} and Zr^{4+} .

In this investigation the order of the η - Al_2O_3 stabilisation at 1270K was found to be as follows

$$\text{La}^{3+} > \text{Ce}^{3+} \approx \text{Cs}^+ > \text{Zr}^{4+} \approx \text{Ba}^{2+} \approx \text{Ca}^{2+}$$

Chemisorption measurements on $\text{Pt}/\eta\text{-Al}_2\text{O}_3$ catalysts, showed that the maximum dispersion of platinum (Pt) was obtained at a 3wt% loading. Catalyst samples containing this loading of Pt on $\eta\text{-Al}_2\text{O}_3$ were then prepared with the incorporation of either of the ions, La^{3+} , Ce^{3+} , Cs^+ and Sn^{4+} . The method of preparation of these samples was varied by using either co-impregnation or step impregnation and the activity of the resulting catalysts was tested using the reaction,



the most active catalyst sample was found to be 1wt%Cs, 3wt%Pt/ $\eta\text{-Al}_2\text{O}_3$, having a catalytic activity of up to 10 times greater than a 3wt% Pt/ $\eta\text{-Al}_2\text{O}_3$.

CHAPTER 1

GENERAL INTRODUCTION TO
CATALYSIS

1.1. INTRODUCTION

Catalysis is an ever growing area, and plays a major role in producing goods worth in excess of £50 billion each year. It is becoming an ever increasing area of research where much time and effort is being devoted to developing new catalytic material for commercial exploitation(1).

Catalysis can be simply defined as substances that alter the rate of thermodynamically feasible reactions without being used up themselves. They are generally unchanged chemically at the end of the reaction, but they can be physically changed(2). A catalyst is usually specific in its action and if a reaction is reversible, both the forward and backward reactions are catalysed to the same extent. In other words the position of equilibrium of the reaction is unaffected(3).

Catalysts have made possible the manufacture of new chemicals and the maintenance of established chemicals both at home and in industry e.g. the production and manufacture of synthetic fibres which are used in everyday fabrics and household goods(1).

The petroleum industry illustrates the major importance that catalysts play in everyday life. Crude oil contains numerous different hydrocarbons. It is the naphtha fraction that is very important to the motorist. If that fraction were removed via fractional distillation, a very inferior gasoline fraction would result. However, with the introduction of a catalyst, the fractionation and hydrocarbon "cracking" process can be carried out far more efficiently and effectively resulting in a relatively substantial improvement in the gasoline fraction (3).

Catalysts have been used extensively within the automotive industry, in order to reduce the levels of carbon monoxide, nitrous oxides and unburnt hydrocarbons emitted as exhaust gases. They lower the amount of these materials in the car exhaust system by oxidising the CO and hydrocarbons to CO₂ and water and reducing the nitrous oxides to nitrogen and oxygen(3).

Jon Jakob Berzelius in 1836 is accredited with naming and defining catalysis. He proposed that the phenomenon involved the development of a force of affinity which came from the catalyst, and had an effect on the chemical activity of the reagents (3). At the end of the nineteenth century, catalysis was receiving more and more attention. Two of the most prominent chemists who have been accredited with the bringing together of catalytic science and technology were Paul Sabatier and Vladimir N Ipatieff. Sabatier found that, in the presence of nickel, some ethylene was converted to

its analogue, ethane. He then deliberately introduced hydrogen which resulted in a greater increase in the yield of ethane, with nickel acting as the catalyst (3)

By the year 1915 the physical chemist came to the forefront in the field of catalysis, which had been previously dominated by organic and inorganic chemists. The precise measurements by Irving Langmuir, of the absorption strength of various simple molecules on metals, gave rise to the concept of chemisorption (3)

The mechanism of a catalytic reaction may be explained as follows, the reactant molecules concerned must possess a minimum energy called an "activation energy", so that when the atoms or molecules collide they can react. A catalyst offers an alternative reaction route, whose activation energy is much reduced, relative to that of the uncatalysed reaction (2)

Catalytic reactions proceed via a set of one or several intermediates, if a substance is to act as a catalytic material it must provide alternative energy pathways to the required products, that are lower than standard gas phase reactions (4)

Catalytic reactions are normally categorised into three main types namely

- (a) heterogeneous,
- (b) homogeneous, and
- (c) enzymatic catalysis (3).

(a) *Heterogeneous Catalysis*

The reactants and products are in a different physical state than that of the catalytic material. Usually the catalytic material is a solid, e.g. the catalytic combustion of butane uses a platinum supported solid catalyst, while the reactants and products are both in the gas-phase (3, 5).

(b) *Homogeneous Catalysis*

These are processes in which the catalyst and reactants/products are dispersed in a one phase system, generally a liquid phase (3) e.g. the bromine catalysed decomposition of hydrogen peroxide, where all these materials are in the liquid phase

(c) *Enzymatic Catalysis*

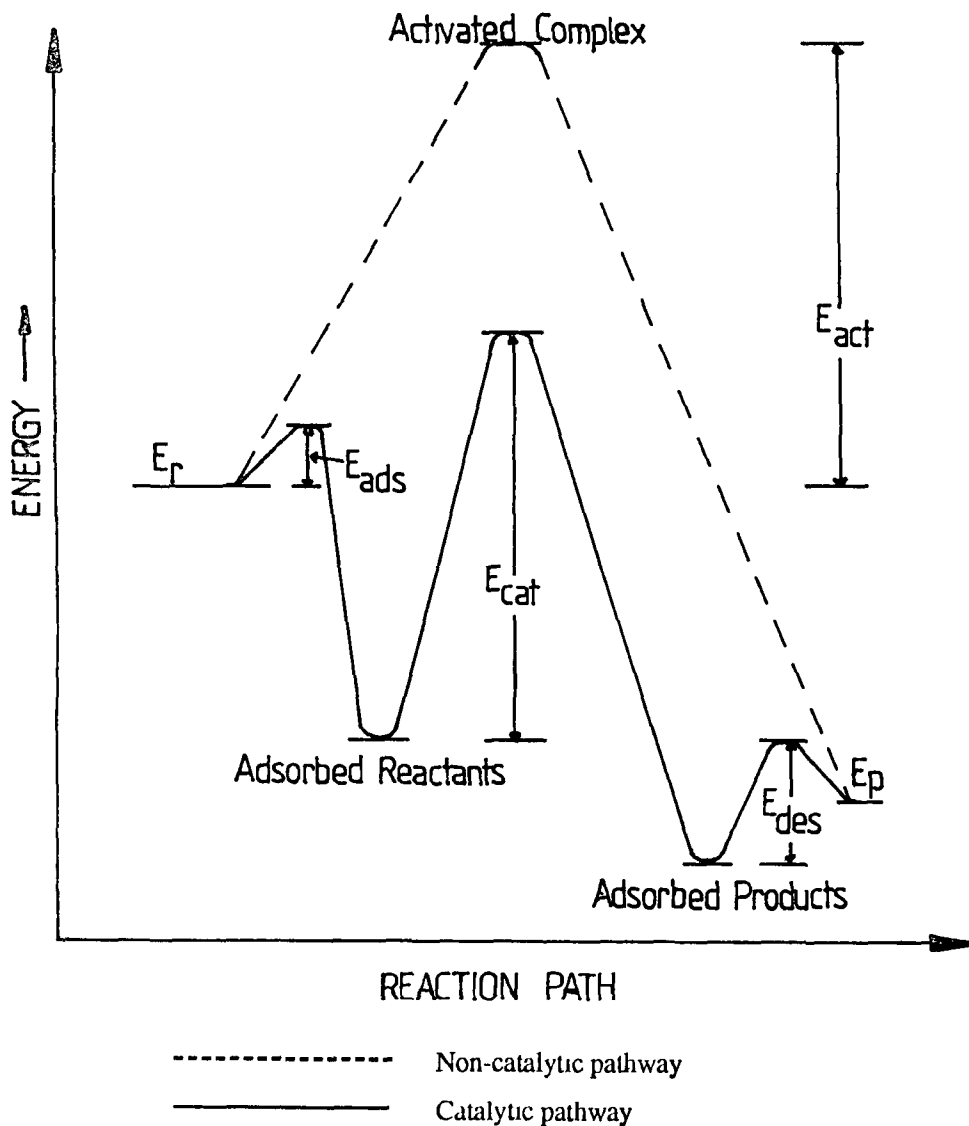
These processes are found in biological systems, where the catalyst is a complex protein molecule called an enzyme (3)

As this investigation is primarily concerned with a heterogeneous catalytic system, it will be more closely looked at

There are five main stages within a heterogeneous catalytic reaction process. They are as follows (3):

- (a) the diffusion of reactants to the surface of the catalyst,
- (b) the chemisorption of those reactants,
- (c) surface reaction occurring among those chemisorbed species,
- (d) the desorption of the resulting products, and
- (e) the diffusion of the resulting products from the catalyst's surface (Figure 1), note that the total energy change, ΔH , for the reaction is the same for both the catalysed and non-catalysed process, however, the activation energy is lower in the catalytic pathway

FIGURE 1
Energy changes associated with individual steps of a reaction
(adapted from Bond (6)).



One tries to ensure that steps (d) and (e) are relatively more rapid than the rest, but unfortunately this may not be achieved in many cases (3).

The adsorption process may be one of chemisorption or physisorption. A physisorbed species normally retains its original structure. Generally physisorption takes place first, paving the way for the chemisorption process to occur. The chemisorbed species can have substantial changes in their structure, especially between the adsorbed and desorbed compounds. In the majority of cases, the desorbed species may only be a fragment of the original molecule. At least one of the reactants must be chemisorbed before a reaction takes place (3).

Step (c) generally takes place via one or more elementary steps, during which the chemisorbed species react to produce new chemisorbed species. In step (d) the chemisorbed species desorbs, generally via associative desorption, to yield the final product.

In the majority of cases the mechanisms of homogeneous catalysis are far easier to elucidate than those of heterogeneous reactions. In homogeneous catalytic reactions, the reaction process proceeds via elementary steps involving simple intermediates. With heterogeneous catalytic processes, there is the contribution that the surface of the catalyst makes, and the intermediates formed can not be easily isolated. It is extremely difficult to isolate a surface intermediate, produced via a heterogeneous catalytic process and as a result these particular types of processes present special difficulties, in the elucidation of the mechanism(s) involved (3).

Many techniques, however are now available to the surface scientist, and physical chemist as aids to help in elucidating such mechanisms e.g. scanning electron microscopy, transmission electron microscopy and X-Ray diffraction line broadening spectroscopy.

Heterogeneous catalysts may be divided into three generalised classes; (a) metals, (b) non-metals (metal oxides and metal sulfides), and (c) salts and acids. The primary role of type (a) catalysts is in hydrogenation and dehydrogenation reactions (7).

Hydrogenation reactions within heterogeneous catalytic systems, are among many that have been extensively investigated and as a result their mechanisms have been thoroughly researched (3). Hydrogenation and dehydrogenation reactions generally occur at relatively reduced or moderate temperatures (7).

Metal oxide and noble metal catalysts, have been used to facilitate the oxidation of hydrocarbons e.g. CH_4 , C_4H_{10} , C_2H_6 , to CO_2 and H_2O . Solid acids and salts have been used to carry out the following types of reactions; polymerisation and isomerisation. However they are not used in oxidation reactions.

Extensive work has been undertaken in the past, to elucidate the characteristics of non-metallic catalysts, that govern their heterogeneous catalytic properties (7). One of the more accepted trends, is the role of d-shell electrons. Many notable scientists including Pauling (1948) and Wells (1968), have observed, that while the electronic levels of the cations of transition metal oxides of the fourth period are about the same, their catalytic activity varies through maxima and minima. These maxima are generally associated with three, six and eight d electrons, while the minima occur at zero, five and ten d electrons. The above observations ultimately led to the theory, that the observed variation in catalytic activity was due to differences in the catalyst's crystalline structure (7).

Blazowski et al (7) quote Dowden and Wells (1961) who explained the above relationship between catalytic activity and d-shell electrons by applying crystal field theory. The catalytic activity of metal oxides positioned in the lower periods of the periodic table, have been found to exhibit similar trends as those of the fourth period metal oxides. However, group VIII metal oxides, of the fifth and sixth periods are open to reduction reactions leading to the production of the metal itself. It was found that variation in catalytic activity with hydrocarbon type and operating temperature occurs with all metal oxides. Much work is still required to elucidate the relationship between the catalytic activity of metals and their electronic properties.

A generalised sequence of the catalytic activity of metals, for oxidation reaction involving hydrocarbons particularly CH_4 , has been given as, (7)



For oxidation reactions, it has been found only the noble metals such as platinum, palladium and silver are relatively highly active (7).

The majority of metals, operating in high temperature environments in the presence of oxygen are liable to either undergo bulk oxidation or form thick oxide layers on their surfaces. In the case of methane oxidation, supported noble metals were found to be active at lower temperatures than metal oxides (7).

The oxides of cobalt, chromium and manganese have been found to be among the most effective metal oxide catalysts for complete hydrocarbon oxidation. Platinum,

palladium and silver have been found to show activity at relatively lower temperatures than the metal oxides. However at temperatures in excess of 670K, metal oxides have been found to be slightly less active relative to platinum, for these reactions (7)

1.2 PREPARATION OF HETEROGENEOUS CATALYSTS

Heterogeneous catalysts are mainly produced via one of three general processes, namely;

- (a) impregnation,
- (b) mixing, or
- (c) precipitation.

All these methods involve the addition of a solution of the metal salt to the support material. This is followed by the removal of the excess solvent and the reduction/calcination of the catalytic material (8).

Catalysts prepared via impregnation involve the addition of a solution of the metal salt(s) to the support material, after which time the solvent is evaporated. The whole impregnation process may be repeated to increase the concentration of the catalytic agent(s). The procedures used during the impregnation of the salts, can control the radial concentration distribution of the metal in the catalyst. This is required for a number of reasons (8) e.g.

- (a) the concentration of the catalytically active components should be greatest near the support's surface. This facilitates a greater interaction between the catalytic active sites and the reactant(s)
- (b) the catalytic material should be uniformly distributed throughout the support material, leading to a greater number of active sites rather than the localisation of them.

In the precipitation method, the catalytic material is precipitated, with the support material. To facilitate the precipitation of the catalyst, two or more other solutions are mixed. Binders, activators, cements and other agents may also be added. However, the precipitation process can use much more of the catalytically active metal(s) than the impregnation process. This may be acceptable if the species is relatively inexpensive, but not if it is relatively expensive. The active metal can also be "caught" within the support material and as a result it will not be available for reaction, leading to wastage of the active metal (8)

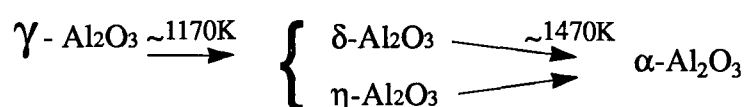
Once the support is impregnated, the resulting material must be dried to remove the excess solvent (8)

It has been found, that drying the prepared, catalytically active material at relatively lower temperatures and higher humidities, produce relatively better catalysts. Unfortunately these types of drying conditions require long drying times and quite expensive dryers. Thus a strategy for drying the catalyst(s) is needed (8).

Normally drying is conducted in stages, the initial drying stage being carried out to remove surface moisture (this can be conducted relatively rapidly but must be carefully controlled) with the final stage requiring relatively severe conditions to ensure that the catalytic material has reached the required dryness (8)

After drying the sample it is then calcined. The calcination step differs from the drying step only in the temperature at which it is conducted. However during calcination, differences in the equipment used and the transformations that can occur within the catalyst can alter the properties of the catalyst i.e., its activity, durability, mechanical strength and selectivity (8)

Drying normally occurs at temperatures slightly above 370K, but calcination takes place at temperatures in excess of 470K, in some cases even in excess of 1270K. Not only are the chemical properties of the catalysts affected but also are their physical properties e.g. alumina which is used as a catalyst support material, can undergo the following physical changes



The pore size and distribution can also be changed due to the temperature at which the calcination step is conducted, and thus can alter the performance and efficiency of the catalyst (8).

The thermal pretreatment primarily converts the compound(s) deposited into the active material. Stringent controls must be carried out during the manufacture of the catalyst to ensure that not only a suitable catalyst is produced, but that it will have the desired properties that it was initially designed to have

1.3 CATALYST POISONING

During the normal operation of a catalyst, it is prone to poisoning resulting from three main areas namely:

- (a) chemical,
- (b) thermal, and
- (c) mechanical (9).

Thermal deactivation of the catalyst is generally difficult to separate from chemical deactivation. This is due to the fact that many of the processes and/or phenomena that occur show a certain amount of dependence on the chemical environment of the catalytic material (9).

Thermal poisoning not only affects the support material e.g. by causing phase transformations to low surface area phases, but can also affect the catalytically active sites by encouraging particle nucleation and growth. This leads to a reduction in the specific catalytic surface area (due to the formation of larger particles) and ultimately a loss in catalytic activity (9).

During the operation of the catalyst, the catalytically active particles can become mobile at certain temperatures (depending on the components). These components then migrate over the surface and can form small metal clusters. As these clusters become larger they become increasingly able to attract more particles, thus leading to the growth of quasi-microscopic species, and an ever increasing reduction of the dispersion of these components resulting in nucleation and growth of these active metal particles. This overall phenomenon is usually referred to as sintering (10).

Chemical deactivation usually results from impurity or self poisoning mainly due (in hydrocarbon oxidation reactions) to the formation of carbonaceous species which is not desorbed off the catalysts surface (9,11).

Impurity poisoning results from the interaction of impurities (either from the feed stock or from the catalyst itself), which can adsorb onto the catalyst site and interact with the catalyst components, and support material. This adsorption process can be reversible or irreversible (9,12).

The adsorption of these poisonous species generally affects catalytic performance via competitive adsorption with the reactant species or by blockage of the catalytic active sites (9).

Mechanical deactivation can result from direct mechanical damage to the catalyst material e.g :

- (a) pelleted catalytic material in fluidized bed reactors can be damaged due to abrasion, and
- (b) the use of fibrous catalysts in applications where the fibre may be crushed.

1.4. OXIDATION CATALYSTS

Catalysts for total hydrocarbon oxidation generally consist of an active noble metal e.g. platinum, supported on an inert support material e.g. Al_2O_3 . As well as having to be active initially, the catalytic materials must remain active over relatively long periods of time. Initial activity is normally achieved by distributing the catalytically active metal (Pt) extensively over the support material in such a way as to achieve a high dispersion of small platinum particles

However with use at high temperatures, the catalyst may lose some or all of its activity due to a loss in platinum and/or support surface area. Generally it is desirable to inhibit such surface area losses in the support material, or at least to reduce its rate of change, so as to extend the life expectancy of such a catalytic material

It was due to such aims as trying to prevent catalyst support surface area losses during operation at relatively high temperatures (by the incorporation of certain metal salt additives) and to improve the catalyst's operating efficiency, that this research project was concerned with three main areas of investigation, namely.

- (a) the investigation of the effect of addition of metal salts in the thermal stabilisation of $\eta\text{-Al}_2\text{O}_3$,
- (b) the effect of these metal additives on the catalytic activity, and
- (c) to determine the activity of the resulting impregnated catalysts, in the oxidation of iso-butane.

This thesis consists of five main chapters, of which chapter one deals with a general discussion on catalysis with specific reference to heterogeneous catalytic oxidation of hydrocarbons

Chapter two is concerned with the thermal stabilisation of $\eta\text{-Al}_2\text{O}_3$. Chapter three deals with the determination of platinum metal dispersions at several loadings on the support material, and chapter four is concerned with the iso-butane activity measurements, obtained from several prepared catalysts. Finally chapter five gives the overall conclusions drawn from the results obtained in these investigations.

CHAPTER 2

THERMAL STABILISATION
OF $\eta\text{-Al}_2\text{O}_3$

2.1 INTRODUCTION

In this chapter, investigations into the use of metal salts to impart a thermal stabilising effect on η - Al_2O_3 were carried out. In our study η - Al_2O_3 was to be used throughout as the catalysts support material. This investigation's aim was to achieve a reduction of the rate of transformation of η - Al_2O_3 , being of relatively high surface area to α - Al_2O_3 which is a relatively low surface area material.

In a number of important industrial and commercial catalytic processes, temperatures as high as 1370K can be attained at the catalyst surface. This is particularly so in those processes employing catalysts for emission controls within the automotive industry (13).

It is at such temperatures, that catalyst deactivation processes can occur e.g. sintering of the catalyst's active components and restructuring of the support material.

These processes can lead to a loss in catalytic efficiency, activity and a reduction in the catalyst's life. The support material is not just used to provide a surface upon which the catalytic components may reside, but also a means by which they can be dispersed. It can also impart some thermal stabilising effect in order to delay/reduce the process of sintering (14).

Among the many oxide support materials used for catalytic processes, transition aluminas have been widely used and investigated, as well as other stable oxides such as TiO_2 and SiO_2 . The transition aluminas have been classified mainly into two groups. The first group containing the γ - and η -forms which contain hydroxyl species and secondly the δ - and θ - forms which are nearly dehydroxylated. They generally differ from one another in the ordering of the vacant sites in the cationic sublattice (13).

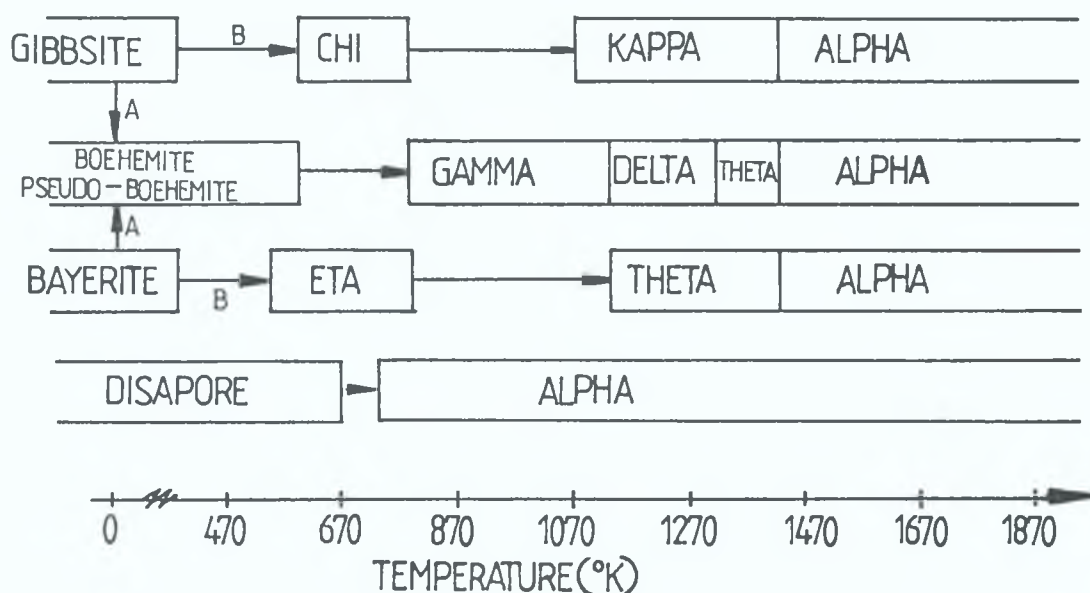
Several different phases of aluminas exist, i.e. γ , η , δ , θ and α (15), and they can change from one phase to another under certain temperatures, the order of transition being as follows:



The only thermodynamically stable phase of the transition aluminas is the α -phase. Alumina is a very good support material for oxidation catalysts due to its inherent characteristics namely; inertness, chemical stability, large surface area, control of pore volumes and pore size distributions, acidic and basic properties (16). However the thermal instability of alumina is a problem at high temperatures. Transformations can occur between the above phases by successive dehydroxylation via the removal of

water at high temperatures (Figure 2). The transformation from $\gamma\text{-Al}_2\text{O}_3$ to $\alpha\text{-Al}_2\text{O}_3$ is accompanied by a decrease in pore volume and also a decrease in surface area.

FIGURE 2
Phases of Alumina at Different Temperatures (17)



A = For $p > 1$ bar in wet air

B = For $p = 1$ bar in dry air

Factors such as particle size, heating rate, presence of impurities and ambient pressure have been known to effect the phase transformations of alumina (14).

The effect of cation additives as dopants has been investigated by some researchers (18,19,20) in an effort to stabilise the $\gamma\text{-Al}_2\text{O}_3$. These additives exert an influence on the kinetics of the transformations to low surface area aluminas. These dopants can accelerate or inhibit these phase transformations.

Generally it is of great benefit to minimise the rate of transformation, and to understand the mechanisms involved in such a process. It is the understanding of such processes, that ways of preventing them can be obtained (13,19,20).

A number of attempts have been made to develop mathematical expressions from postulated gaseous adsorption mechanisms in order to determine the surface area of a particular sample using the adsorption properties of a specific gaseous adsorbate. These mathematical expressions must fit the various experimental isotherm curves, when a gaseous adsorbate is adsorbed onto an adsorbent (21).

One of these mathematical isotherm equations which is most frequently used was due to Brunauer, Emmett and Teller (BET). The model proposed by BET is the most frequently used for surface area measurements employing N₂ gas as the adsorbate and helium as the carrier (21).

The theory of Brunauer, Emmett and Teller allows for multilayer adsorption on non-porous solid surfaces, that other models may not take into account, e.g. the Langmuir isotherm (21).

The BET equation is derived by balancing the rates of evaporation and condensation for the number of various adsorbed molecular layers. The theory assumes that a characteristic heat of adsorption, ΔH , applies to the first monolayer adsorbed while the heat of liquefaction ΔH_L of the gaseous adsorbate applies to adsorption in the second and subsequent layers (21).

The BET equation is usually written in the form;

$$\frac{P}{V(P_0 - P)} = \frac{1}{V_m C} + \frac{(C-1)P}{V_m C P_0} \quad (1)$$

where.

- (a) V is the volume (at standard temperature and pressure) of a gas adsorbed at a particular pressure P ,
- (b) P_0 is the saturation pressure, which is the vapour pressure of liquified gas at the adsorbing temperature,
- (c) V_m is the volume of gas (at STP) required to form an adsorbed monomolecular layer, and
- (d) C is a constant, which is related to the energy of adsorption.

Equation (1) can be rewritten in the form

$$(P/P_0)/V[1-(P/P_0)] = 1/(V_m C) + [(C-1)/(V_m C)] (P/P_0) \quad (11)$$

The surface area, S , of a sample knowing the monolayer adsorbed gaseous volume, V_m (at STP) can then be calculated from

$$S = V_m L X / Y \quad (iii)$$

Where:

- (a) L is Avogadro's number,
- (b) X is the area of one adsorbed gaseous molecule, and
- (c) Y the molar volume of the gas.

In single point surface area measurements, the constant C in equation (ii) is generally a relatively large number and as a result equation (ii) can be approximated closely to

$$(P/P_0)/V[1-(P/P_0)] = (1/V_m) [(1/C) + (P/P_0)] \quad (iv)$$

The term $1/(V_m C)$ of equation (iv) is also generally small, therefore equation (iv) can be further reduced to:

$$(P/P_0)/V[1-(P/P_0)] = (1/V_m) (P/P_0) \quad (v)$$

on simplifying equation (v), it becomes,

$$V_m = V[1-(P/P_0)] \quad (vi)$$

and on substituting equation (vi) into equation (iii) the following equation is obtained

$$S = V L X [1-(P/P_0)]/Y \quad (vii)$$

It is using equation (vii) that the surface area of a sample can be easily determined once the volume, V , of the gaseous adsorbate is measured and the appropriate values for the other variables are incorporated

The BET equation reduces to the Langmuir equation at low pressures and the model can also be applied to a system where porous solids are used as the adsorbent (21)

Thus for nitrogen gas adsorbed from a gaseous mixture of 30 mole% nitrogen and 70 mole % helium at liquid nitrogen temperatures the values in equation (vii) are arrived at as follows

The volume V of gaseous material (i.e. N_2) adsorbed is determined instrumentally at the prevailing atmospheric pressure. This volume, V , must be multiplied by the following ratios:

$$\frac{273.2^{\circ}\text{K}}{(\text{Room Temperature, }^{\circ}\text{K})} \times \frac{(\text{Atmospheric Pressure, mmHg})}{760\text{mmHg}}$$

in order to convert it to standard conditions (i.e. 0°C and 760 mmHg)

The equation for a 30mole%N₂/70mole%He gaseous mixture adsorbed at liquid nitrogen temperature is given by the following expression;

$$S = V \times \left[\frac{273.2}{R.T.} \right] \times \left[\frac{A.P.}{760} \right] \times \left[\frac{L \times X}{Y} \right] \times \left[\frac{1 - (\%N_2/100) \times A.P.}{SAT.P.} \right]$$

where

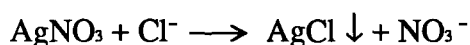
- (a) S = the surface area in (m²),
- (b) V = the volume of nitrogen adsorbed,
- (c) A.P. = the prevailing atmospheric pressure in mmHg,
- (d) R.T. = room temperature in degrees Kelvin,
- (e) SAT.P. = the saturation pressure of liquid nitrogen in mmHg,
- (f) L = 6.023 x 10²³ molecules/g - mole,
- (g) X = area of the solid surface occupied by one adsorbed nitrogen molecule, and
- (h) Y = is the molar volume of gas at standard temperature and pressure, (22414cm³/g-mole).

2.2 EXPERIMENTAL SECTION

PREPARATION OF ALUMINA

The form of alumina used, in this area of investigation was γ -alumina that used during dispersion measurements.

The fibre material in mat form was initially acid washed with 0.1M HCl at a rate of 25mls/g, and then it was washed with milli-Q water until no further chlorine was found in the wash. The presence/absence of chlorine was verified by AgNO_3 i.e.,



the AgCl produced if chlorine was present was a white precipitate

The support material was treated with HCl to remove any inorganic contaminants. The mat material was then dried in an oven, in air at 340K for 24 hours, after this time the material was ground to powder form using a mortar and pestle. Samples of this powder were then impregnated with various cations at 1 or 3wt% loadings. For each impregnation, 25mls of methanol solvent per gramme of alumina sample was used to dissolve the metal salt. This volume of solvent represented an excess of solution of the salts when added to the alumina powder. The metal salts were all of GPR grade and were as follows,

$\text{BaCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, CsCl , $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$, and $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$

The impregnated powder was then rotary evaporated at 340K for one hour to remove the methanol. Finally each sample was then air dried at 370K for 12 hours.

After drying all samples were calcined in a muffle furnace at 1270K for various lengths of time.

Approximately 1g of sample placed in a porcelain crucible, was heated in the furnace from room temperature to 1270K at a rate of 250K hr^{-1} and fired at 1270K for lengths of time varying from one to 42 hours. After firing, the samples were cooled to room temperature prior to surface area measurements. Specific details on the samples prepared are given in Table 1.

SURFACE AREA MEASUREMENTS^{28,3}

Surface area measurements were carried out using the Micromeritics Pulse chemisorb 2700 instrument. A sample of known weight was placed in a "U" tube. The sample was outgassed in argon at 370K for half an hour followed by 520K for one and a half hours prior to testing. For specific sample preparation steps refer to Table 2.

Surface area measurements were determined by B E T N₂ single point adsorptions at liquid N₂ temperatures from a 30mole%N₂/70mole% He mixture.

Quantities of N₂ adsorbed and desorbed by the sample were monitored using the thermal conductivity detector in the instrument.

After adsorption, each sample was heated to room temperature and the desorption peak was observed. Each sample was subjected to a minimum of three adsorption/desorption cycles, i.e. after the desorption peak was obtained, the sample would be cooled again to liquid nitrogen temperatures, and adsorption of the nitrogen monitored again. This was followed by heating to observe the desorption peak etc. The average results from the nitrogen adsorption measurements are reported in Table 3, the average results from desorption measurements in Table 4 and the overall average results between the adsorption and desorption measurements in Table 5. Differences of less than 6% were observed between adsorption and desorption peaks, whereas successive adsorption peaks agreed to within 3%. All adsorption/desorption measurements were corrected to S.T.P.

Table 6 gives a summary of the percentage decrease in the surface area of each of the samples after 20 and 40 hour heat treatments at 1270K.

Subsequent to this work, multipoint surface area determinations were carried out on samples of η -Al₂O₃, both acid washed and untreated (22). It was found from single point determinations on the untreated sample of η -Al₂O₃ that the surface area was 154m²/g. This value agreed closely to the value obtained for the same sample using multipoint determinations (i.e. S = 156m²/g). Samples of η -Al₂O₃ which had been previously treated by acid washing also gave similar values for surface area when measured. Thus it is assumed that by both single and multipoint techniques, single point determinations give reasonable accurate values for surface areas in comparison to the multipoint method.

2.3 RESULTS FROM SURFACE AREA MEASUREMENTS

The results obtained from surface area measurements are given in Tables 3 to 7 inclusive and illustrated graphically in Graphs 1-6.

It can be seen from the results that the surface area of the untreated alumina sample decreased rapidly over the initial 5 hour heat treatment and the rate of decrease is still significant after 42 hours. A 22% decrease in surface area occurred over the first five hours while over 42 hours a total decrease of 36% was observed – this corresponds to a final surface area of $113\text{m}^2\text{g}^{-1}$ compared to the initial reading of $178\text{m}^2\text{g}^{-1}$.

All of the samples tested suffered some loss in surface area with calcination and that loss was most significant over the first 5-7 hours of heating (see Table 7). The rate of surface area loss decreases sharply in all cases after this initial 5-7 hour period with La, Cs and Ce samples showing little change after this time.

All of the doped alumina samples have a lower surface area than the untreated alumina after equivalent heat treatment up to 20 hours. After that period of heating, the aluminas with 1wt%La, 1wt%Ce and 3wt%Ce have surface areas of equal or greater magnitude than the unmodified alumina. Clearly the presence of the cation initially decreased the surface area of the alumina. The rate of loss of surface areas is less for all of the doped aluminas compared to the untreated alumina sample, indicating some degree of thermal stabilisation of the alumina was achieved by the addition of dopant.

The rate of decrease in surface area varied depending on the dopant material. Generally the rate of decrease was greatest over the first 5 hours, and decreased up to 42 hours. In the case of 1wt%Ca, 3wt%La and 1wt%Ba additions, the rate of surface area loss increased with prolonged heating to 42 hours, while 3wt% Cs addition resulted in a constant rate of surface area loss over the complete time range.

After 20 hours at 1270K, a 23% loss in surface area was observed for 3wt%Ca and 1wt%Zr sample and these were not calcined any further. From the table of surface area loss, it is apparent that 1wt% additions of La, Cs and Ce greatly reduce the rate of loss of surface area giving the final surface areas of $128\text{m}^2\text{g}^{-1}$, $108\text{m}^2\text{g}^{-1}$ and $115\text{m}^2\text{g}^{-1}$ respectively after 42 hours, calcination. Untreated alumina had a final surface area of $113\text{m}^2\text{g}^{-1}$ after 42 hours calcination.

TABLE 1
SAMPLE PREPARATION

METAL/ η -Al ₂ O ₃	METAL SALT USED	WEIGHT OF METAL SALT USED	WEIGHT OF η -Al ₂ O ₃ USED	DURATION OF SAMPLES CALCINATION AT 1270K IN HOURS
1wt%Ba	BaCl ₂ .6H ₂ O	0.0208g	1.0300g	1,3,5,7,20,42
3wt%Ba	BaCl ₂ .6H ₂ O	0.0570g	1.0947g	1,3,5,7,20,42
1wt%Ca	CaCl ₂ .6H ₂ O	0.0544g	1.0015g	1,3,5,7,20,42
3wt%Ca	CaCl ₂ .6H ₂ O	0.1744g	1.0702g	1,3,5,7,20
1wt%Zr	ZrOCl ₂ .8H ₂ O	0.0368g	1.0288g	1,3,5,7,20
3wt%Zr	ZrOCl ₂ .8H ₂ O	0.1125g	1.0675g	1,3,5,7,20,42
1wt%La	LaCl ₃ .7H ₂ O	0.0269g	1.0191g	1,3,5,7,20,42
3wt%La	LaCl ₃ .7H ₂ O	0.0812g	1.0083g	1,3,5,7,20,42
1wt%Cs	CsCl	0.0139g	1.0152g	1,3,5,7,20,42
3wt%Cs	CsCl	0.0366g	1.0256g	1,3,5,7,20,42
1wt%Ce	Ce(NO ₃) ₃ .6H ₂ O	0.0318g	1.0320g	1,3,5,7,20,42
3wt%Ce	Ce(NO ₃) ₃ .6H ₂ O	0.1006g	1.0625g	1,3,5,7,20,42
η -Al ₂ O ₃	—	—	—	1,3,5,7,20,42

TABLE 2
SAMPLE PRETREATMENT PRIOR TO TESTING

OUTGASSING WITH ARGON: FLOW RATE: 30mls/min			OUTGASSING WITH 70mole%/30mole% He/N ₂ FLOW RATE: Helium: 10.5mls/min Nitrogen: 4.5mls/min		
STEP	DURATION	TEMPERATURE	STEP	DURATION	TEMPERATURE
1	30mins	290K	4	60mins	290K
2	90mins	520K			
3	30mins	290K			
NOTE: After step 4 samples were cooled to liquid N ₂ temperatures for N ₂ adsorption. After measurement, the sample was then heated to room temperature for N ₂ desorption.					

TABLE 3
N₂ ADSORPTION MEASUREMENTS
- SURFACE AREA DETERMINATIONS

SAMPLE ANALYSED % X on η -Al ₂ O ₃	SURFACE AREA (m ² /g) error ± 10 m²/g						
	CALCINATION TIME (Hr) AT 1270K						
	0 Hr	1Hr	3Hr	5Hr	7Hr	20Hr	42Hr
1wt%Ba	—	149	139	136	132	130	113
3wt%Ba	—	130	128	123	114	111	100
1wt%Ca	—	149	137	131	127	123	102
3wt%Ca	—	114	103	97	97	87	—
1wt%Zr	—	148	143	140	133	114	—
3wt%Zr	—	140	135	135	116	121	121
1wt%La	—	131	129	127	127	127	128
3wt%La	—	128	129	126	124	121	98
1wt%Cs	—	120	110	112	109	110	109
3wt%Cs	—	132	127	128	124	120	107
1wt%Ce	—	125	124	120	114	112	116
3wt%Ce	—	149	139	129	127	117	114
η -Al ₂ O ₃	178	161	153	139	137	130	113

TABLE 4
N₂ DESORPTION MEASUREMENTS
- SURFACE AREA DETERMINATIONS

SAMPLE ANALYSED % X on η -Al ₂ O ₃	SURFACE AREA (m ² /g) error ± 10 m²/g						
	CALCINATION TIME (Hr) AT 1270K						
	0 Hr	1Hr	3Hr	5Hr	7Hr	20Hr	42Hr
1wt%Ba	—	150	139	137	132	130	112
3wt%Ba	—	130	128	124	116	111	100
1wt%Ca	—	149	137	130	126	123	101
3wt%Ca	—	113	103	96	96	88	—
1wt%Zr	—	148	141	142	132	113	—
3wt%Zr	—	140	135	133	123	118	120
1wt%La	—	128	127	127	127	125	128
3wt%La	—	127	130	125	123	121	97
1wt%Cs	—	117	109	112	109	109	107
3wt%Cs	—	131	125	127	124	118	107
1wt%Ce	—	126	126	120	115	113	115
3wt%Ce	—	148	141	129	127	121	114
η -Al ₂ O ₃	177	160	152	138	137	128	113

TABLE 5
AVERAGE SURFACE AREA IN m²/g
BETWEEN ADSORPTION/DESORPTION MEASUREMENTS

SAMPLE % X on η -Al ₂ O ₃	AVERAGE SURFACE AREA (m ² /g) error ± 10 m ² /g						
	CALCINATION TIME (Hr) AT 1270K						
	0 Hr	1Hr	3Hr	5Hr	7Hr	20Hr	42Hr
1wt%Ba	—	149	139	136	132	130	113
3wt%Ba	—	130	128	123	115	111	100
1wt%Ca	—	149	137	130	127	125	102
3wt%Ca	—	114	103	97	97	87	—
1wt%Zr	—	148	142	141	132	114	—
3wt%Zr	—	140	135	134	120	120	121
1wt%La	—	129	128	127	127	126	128
3wt%La	—	127	130	126	123	121	97
1wt%Cs	—	119	110	112	109	109	108
3wt%Cs	—	131	126	128	124	119	107
1wt%Ce	—	126	125	120	115	112	115
3wt%Ce	—	149	140	129	127	119	114
η -Al ₂ O ₃	178	161	152	139	137	129	113

TABLE 6
DECREASE IN SURFACE AREAS

SAMPLE % X on η -Al ₂ O ₃	% DECREASE IN SURFACE AREA CALCINATION TIME (Hr) AT 1270K	
	After 20 Hr	After 42 Hr
1wt%Ba	13%	24%
3wt%Ba	14%	23%
1wt%Ca	17%	32%
3wt%Ca	23%	—
1wt%Zr	23%	—
3wt%Zr	15%	14%
1wt%La	3%	0%
3wt%La	5%	23%
1wt%Cs	8%	9%
3wt%Cs	9%	18%
1wt%Ce	10%	8%
3wt%Ce	20%	23%
η -Al ₂ O ₃	28%	36%

TABLE 7
SURFACE AREA LOSS

SAMPLE INVESTIGATED on η - Al_2O_3	INITIAL S A * m m^2g^{-1} $\pm 10\text{m}^2\text{g}^{-1}$ error	RATE S A LOSS*** 1-5 Hours $\text{m}^2\text{g}^{-1}\text{hr}^{-1}$	RATE S A LOSS*** 5-20 Hours $\text{m}^2\text{g}^{-1}\text{hr}^{-1}$	RATE S A LOSS *** 20-42 Hours $\text{m}^2\text{g}^{-1}\text{hr}^{-1}$
η - Al_2O_3	161**	5 52	0 65	0 76
1wt%La	130	0 73	0 05	0 00
1wt%Ce	126	1 45	0 50	0 00
1wt%Cs	119	1 72	0 18	0 06
1wt%Zr	148	1 69	1 83	N A †
1wt%Ba	150	3 21	0 40	0 81
1wt%Ca	149	4 61	0 50	1 02
3wt%La	128	0 46	0 30	1 08
3wt%Ce	149	4 93	0 67	0 22
3wt%Cs	132	0 93	0 56	0 55
3wt%Zr	141	1 60	0 95	0 00
3wt%Ba	130	1 64	0 81	0 52
3wt%Ca	114	4 23	0 63	N A †

NOTE

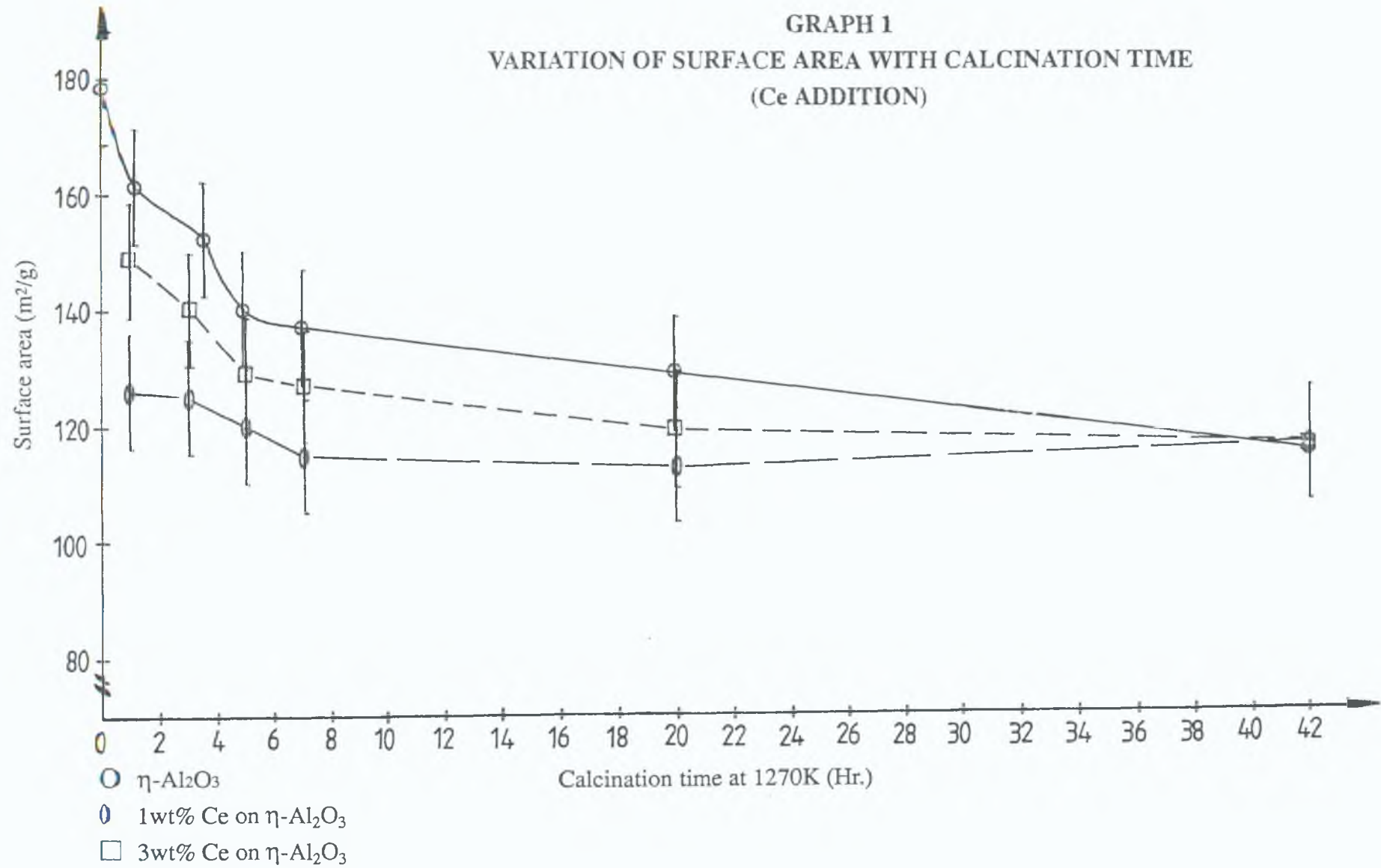
* Initial Surface area after 1 hour heating at 1270K

** The surface area of alumina prior to heating is $178\text{m}^2\text{g}^{-1}$, which gives a decrease in surface area over the first 5 hours of heating of $7.8\text{m}^2\text{g}^{-1}\text{hr}^{-1}$

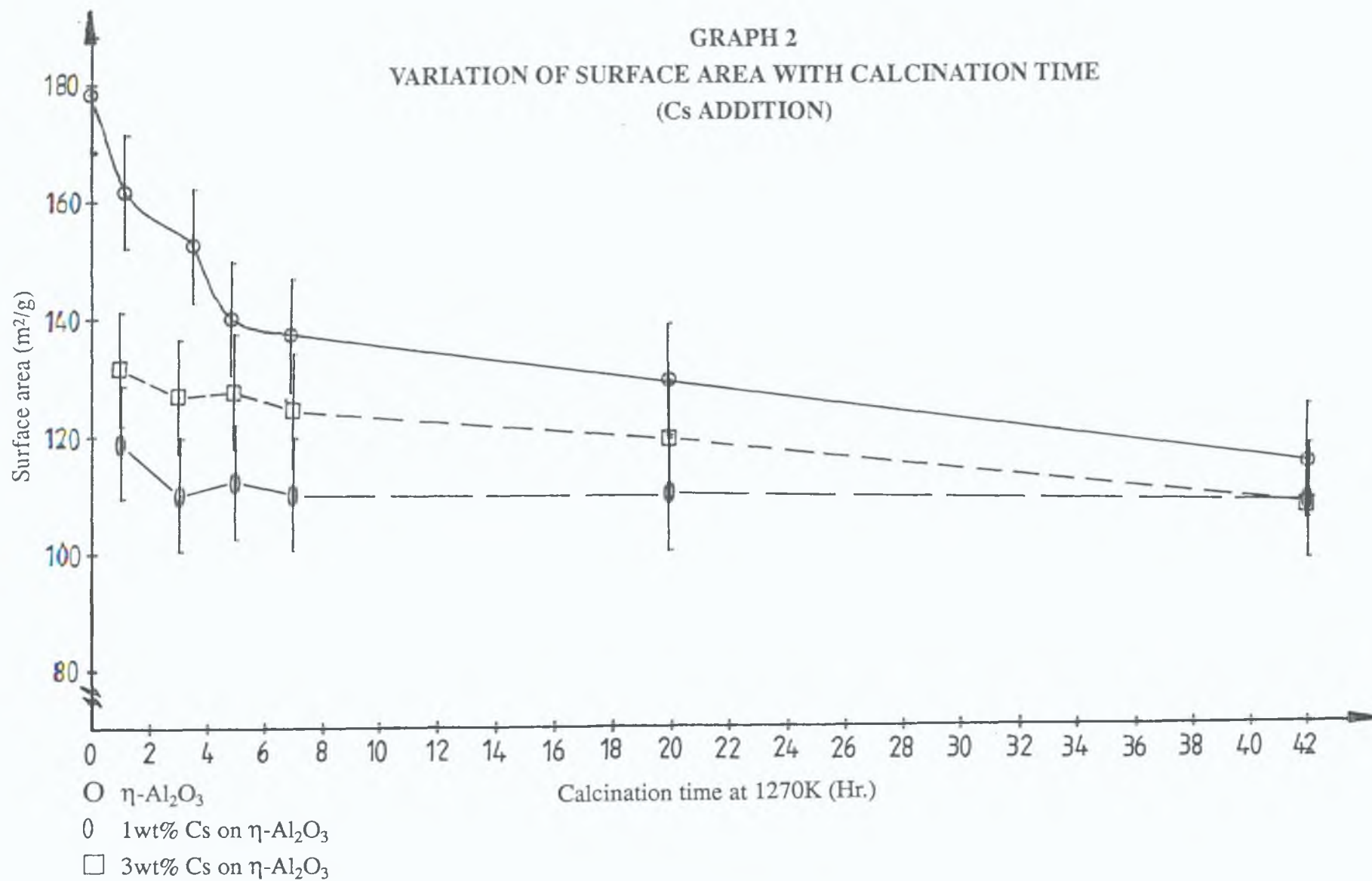
*** Rate loss of surface area between 1 and 5 hours heating, between 5 and 20 hours or 20 to 42 hours heating at 1270K

† Results not available

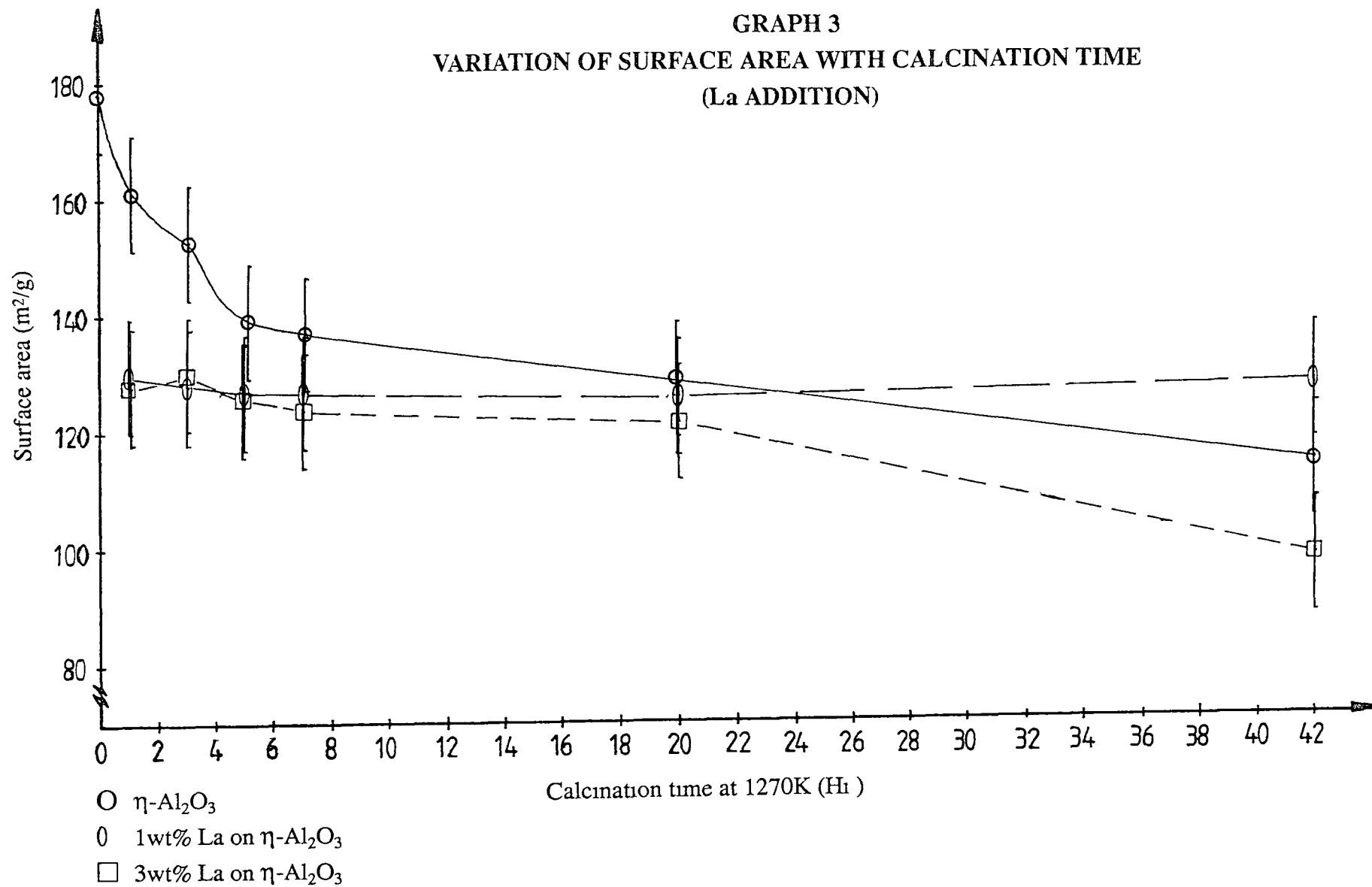
GRAPH 1
VARIATION OF SURFACE AREA WITH CALCINATION TIME
(Ce ADDITION)



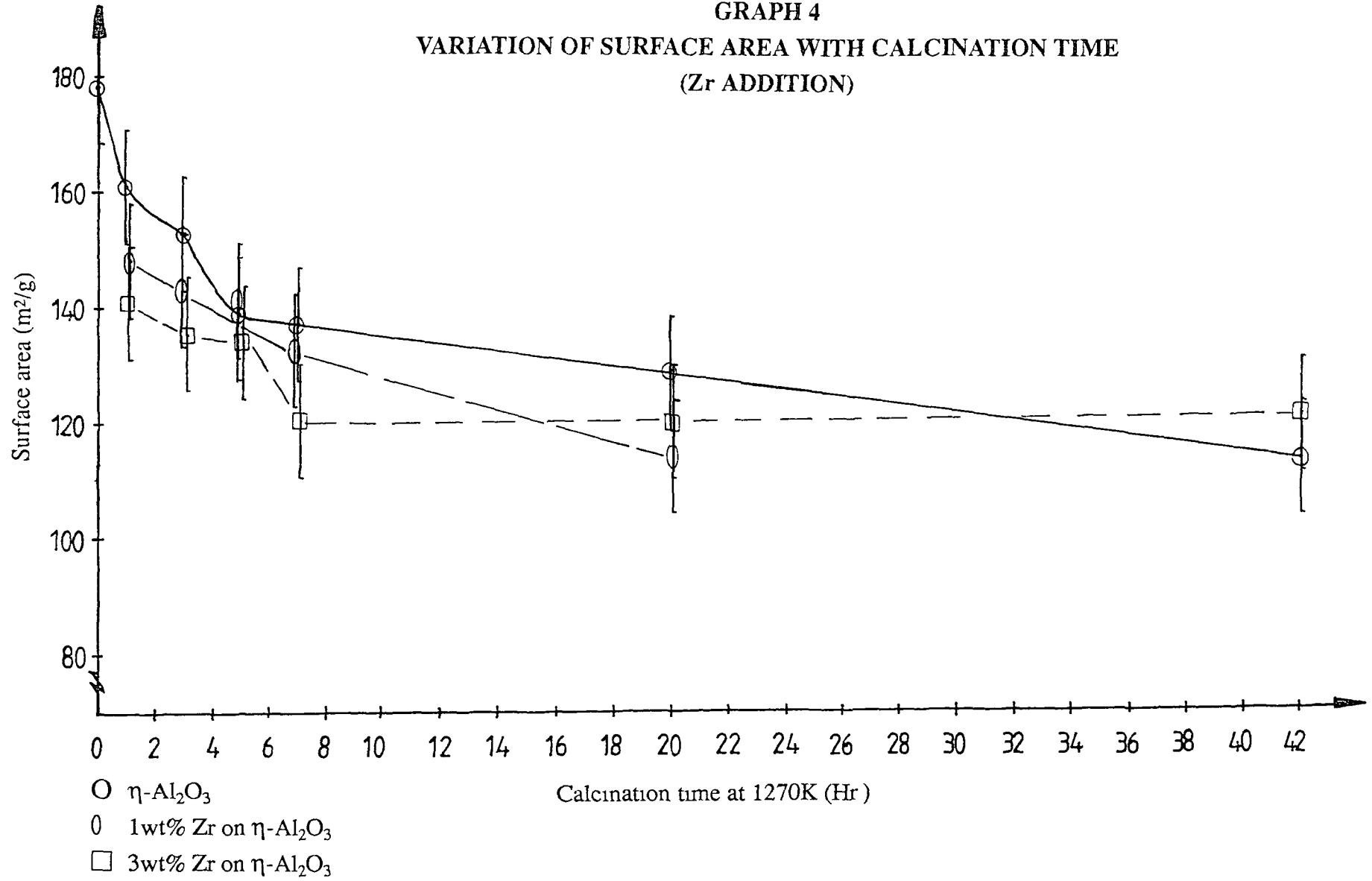
GRAPH 2
VARIATION OF SURFACE AREA WITH CALCINATION TIME
(Cs ADDITION)



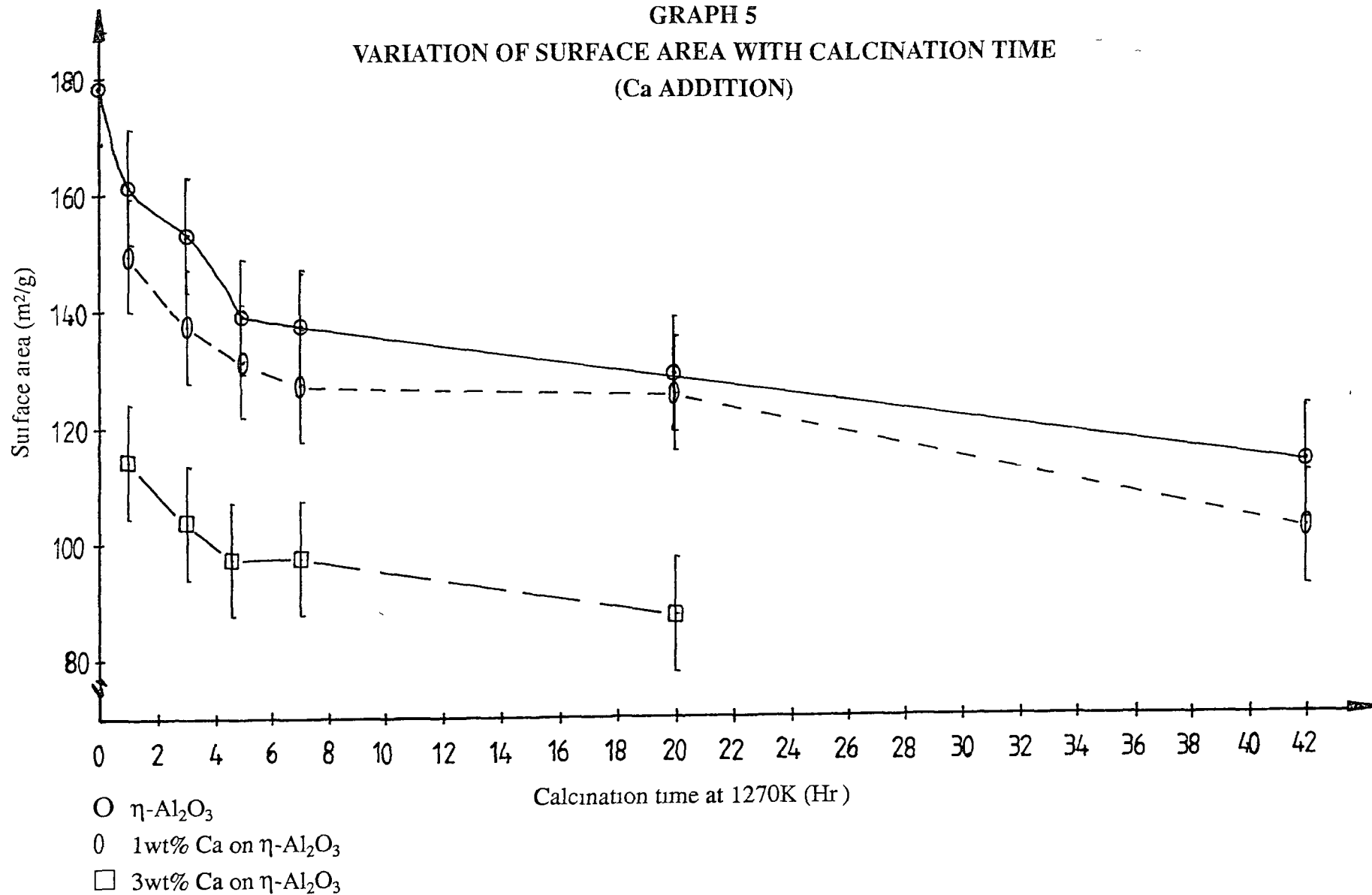
GRAPH 3
VARIATION OF SURFACE AREA WITH CALCINATION TIME
(La ADDITION)



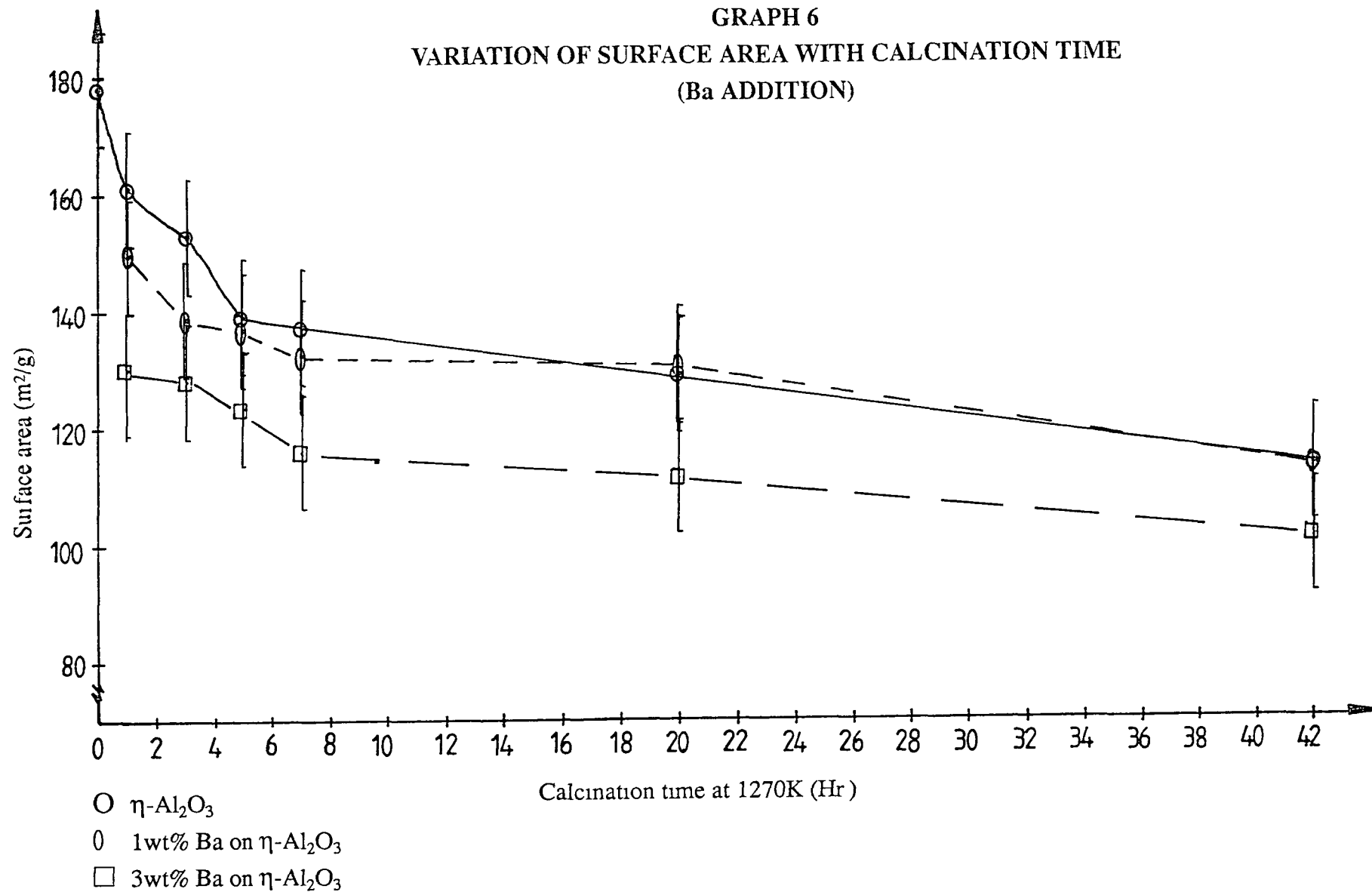
GRAPH 4
VARIATION OF SURFACE AREA WITH CALCINATION TIME
(Zr ADDITION)



GRAPH 5
VARIATION OF SURFACE AREA WITH CALCINATION TIME
(Ca ADDITION)

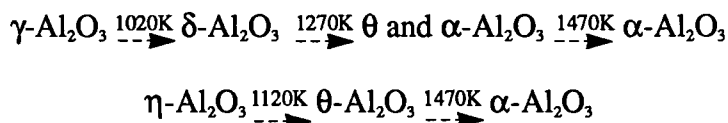


GRAPH 6
 VARIATION OF SURFACE AREA WITH CALCINATION TIME
 (Ba ADDITION)

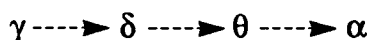


2.4 DISCUSSION OF RESULTS

Thermal dehydration of alumina to the stable α - Al_2O_3 form, results in the formation of the following transitional aluminas at the temperatures indicated (23).



The results presented here do not suggest that α - Al_2O_3 has been formed and it is more likely to be the transitional θ - Al_2O_3 phase that is present at the temperatures used. Detailed X-Ray analysis by Burtin et al (18) showed that the decrease in surface area of γ - Al_2O_3 corresponds to the sequence given below,



The θ - and α - Al_2O_3 phases are of markedly lower surface areas than γ -, η - or δ - Al_2O_3 (15). Gitzen (15) quotes results of Wakao and Hibino from 1962 which suggest that the transition temperature of γ - to α - Al_2O_3 could be reduced by up to 250K by the addition of metal oxides in quantities between 1 to 10%. They suggest that the larger the metal ion of the oxide, and the higher the vapor pressure of the oxide, at the transformation temperature of the alumina, the greater the reduction on the transition temperature.

The results show that the initial surface area (after one hour calcination at 1270K) of the doped aluminas is less than the undoped alumina sample. Schaper et al (24) showed that even heating to 723K causes a gradual decrease in surface area with increasing lanthanum oxide content; the greatest stability being achieved at 1mol% La_2O_3 addition. From the results obtained here, the addition of small amounts of dopant is more effective as a long term thermal stabilizer than larger amounts i.e. the rate of decrease in surface area for each dopant is less in the case of 1wt% additions than 3wt% addition after 5 hours heat treatment – except for Zr. However the opposite effect is seen for the initial five hour heating time i.e. 3wt% additions result in a slower decrease in surface area than 1wt% additions (except for Ce).

A study of Ni on γ - Al_2O_3 (25) shows that Ni delayed the transformation to α - Al_2O_3 at 1220K for 16 hours, but then a rapid transformation occurs. An explanation is advanced where the delay occurs until the diffusing Ni arrives at grain boundaries, nucleation sites are formed at the grain boundaries and a rapid transformation to the α -phase then occurs.

The loss of initial surface area after 1 hour calcination from these results, was independent of the concentration of the dopant added. The addition of 3wt%Ce and 3wt%Cs decreased the surface area less than 1wt% additions of the same cations, while the opposite was true for Ba²⁺, Ca²⁺ and Zr⁴⁺ ions. There was no significant difference between 1wt% and 3wt% La additions in initial surface area determinations.

Cations have been classified as accelerators or inhibitors for the thermal transformation into α -Al₂O₃. Lanthanum has been classified as an inhibitor (19, 24, 26, 27). In a survey of cation additives by Burtin et al (18), In³⁺, Ga³⁺, Al³⁺ and Mg²⁺ were found to be accelerators for the phase transformations, while Zr⁴⁺, Ca²⁺, Th⁴⁺ and La³⁺ were inhibitors. Nortier et al (20) suggest the same ions as inhibiting additives (Zr⁴⁺, Ca²⁺, Th⁴⁺ and La³⁺) and suggest that the larger the cation and the higher the cation charge, the more effective it will be for alumina stabilisation.

The present results indicate the order of inhibiting strength of the cations for η -Al₂O₃ surface area loss was as follows.

	La ³⁺	>	Ce ³⁺	=	Cs ⁺	>	Zr ⁴⁺	=	Ba ²⁺	=	Ca ²⁺
ionic radii	1.15		1.01		1.69		0.80		1.35		0.99 Å
VALENCY	+3		+3		+1		+4		+2		+2

Ionic radii and valency, as given above, indicate that these results are in general agreement with Nortier et al (20) that the higher the valency and the ionic radius, the greater the stabilising effect.

Calcination of γ -Al₂O₃ above 1270K converts it irreversibly to the more stable α -form ($\Delta H = -20 \text{ KJ mol}^{-1}$) (28). Several mechanisms for the transformation of transitional aluminas to α -phase have been proposed and discussed. α -Alumina has a rhombohedral crystal structure comprising a hexagonal close packed array of oxide ions (28), γ -Alumina consists of a defect spinel structure (tetragonal crystal system) with not all of the cation sites occupied, and of the general formula $\text{Al}_{8/3} \square_{1/3} \text{O}_4$ (29). θ -Alumina occupies an intermediate structure between the spinel lattice with cubic oxygen arrangement of γ -Al₂O₃ and the corundum lattice with the dense hexagonal oxygen arrangement and the alumina atoms exclusively in the octahedral positions of α -Al₂O₃ (15). η -Al₂O₃ is a cubic spinel structure of general formula $\text{Al}_8 [\text{Al}_{40/3} \square_{8/3}] \text{O}_{32}$ with the vacancies on the octahedral sites.

Oudet et al (27) proposes that the addition of a perovskite type oxide such as LaAlO₃ to the alumina surface inhibits the formation of low surface area alumina by

blocking the corundum nucleation sites. The LaAl_2O_3 , they suggest, is held at corners and/or edges i.e. high free co-ordination sites and these sites are the reactive areas that act as nucleation sites for the transformation reaction. The presence of lanthanum aluminate was confirmed by X-ray diffraction measurements on La stabilised alumina by Schaper et al (24)

Matsuda et al (19) gives evidence for $\text{La-}\beta\text{-Al}_2\text{O}_3$ formation. While evidence for an MgAl_2O_4 phase is given by Burtin et al (13), for Mg impregnated alumina, but found no evidence for lanthanum aluminate formation in equivalent La impregnated alumina

The general formula for $\gamma\text{-Al}_2\text{O}_3$ from Wells(29) was modified by Soled (30) to $\text{Al}_{2.5}\square_{0.5}\text{O}_{3.5}(\text{OH})_{0.5}$ to include OH species as a structural element. Burtin et al (18), suggested the general formula for transition states as $\text{Al}_2\square_{0.5}\text{O}_{3.5}(\text{OH})_{0.5}\diamond_{1.5}$ where $\square$ represents cationic vacancies in divalent states and $\diamond$, represents anionic vacancies of the spinel structure. When a foreign cation is introduced, it is incorporated into an Al^{3+} state or divalent vacancy.

The transformation reaction, involving dehydroxylation by removal of water followed by structural transformation, is described in terms of vacancy annihilation. The kinetic law discussed by Burtin et al (18) and Nortier (20) involves the annihilation of vacancies as the rate determining step in the transformation process.

It should be noted that the % decrease in surface area for these fibre samples of $\eta\text{-Al}_2\text{O}_3$ is less than $\gamma\text{-Al}_2\text{O}_3$ samples quoted, e.g. Nortier (20) gives results showing a fall off of 85% in surface area after 10 hours calcination at 1370K compared to a 35% decrease after 42 hours at 1270K in this study.

CHAPTER 3

DISPERSION MEASUREMENTS

3.1.1 INTRODUCTION

Heterogeneous catalysts are generally multicomponent systems in industrial applications, and the activity of such catalysts is now known to be a surface property (31). The activity of the catalyst is generally related to the dispersion of the active component(s) on the surface of the support material, and by using dispersion measurements the specific catalytic surface area of the metal, can be determined

By increasing the catalytic active component(s) surface to volume ratio, the quantity of that component can be reduced to effect the same catalytic efficiency. It is even more beneficial in catalysts containing costly active metals such as platinum and palladium (31).

It becomes evident that dispersion measurements can play a role in assessing the catalytic performance of a particular catalyst. It can also be used as a tool in understanding catalytic deactivation processes, e.g. coking and sintering (31).

The most common technique for determining the dispersion of a particular catalytically active component is the selective chemisorption of a relatively specific gaseous adsorbate for that component(s) of interest (31).

Generally, physisorption occurs prior to the chemisorption process. Physisorption results in a reduction in the activation energy required for chemisorption to occur, relative to that energy required if it were absent. The magnitude of this activation energy varies widely from system to system (20).

When a gas is brought into contact with a clean solid surface, some of it will be adsorbed onto the surface. The forces involved in such a process may be non-specific (i.e. weak, Van der Waals forces) or specific. The latter, results in a relatively stronger interaction than the former and such a process is referred to as chemisorption (20).

Only monolayer coverage is generally possible in chemisorption processes and an activation energy may be involved due to the attraction between the adsorbate and substrate. Because chemisorption processes involve the formation of chemical bonds, they are not readily reversible and are relatively slower than physisorption processes (20). A general comparison between physisorption and chemisorption processes are summarised in Table 8.

TABLE 8**COMPARISON OF PHYSISORPTION AND CHEMISORPTION (32).**

PHYSISORPTION	CHEMISORPTION
1. Attraction between the substrate and adsorbate usually involves weak Van der Waals forces	1. Attraction between the substrate and adsorbate involves the formation of chemical bonds.
2. Low heats of adsorption ranging from 20-40 kJ/mol.	2. Relatively high heats of adsorption ranging from 40 - 400kJ/mol.
3. Low activation energies	3. Relatively high activation energies.
4. Occurs at low temperatures, decreasing with increasing temperature.	4. Occurs at relatively higher temperatures.
5. Completely reversible.	5. Generally irreversible.
6. The extent of adsorption is approximately related to the ease of liquifaction of the gas.	6. No such correlation as physisorption
7. Not normally specific.	7. Often highly specific.
8. Multilayer adsorption.	8. Monolayer adsorption

There are several gaseous adsorbates available which are used in the elucidation of metal dispersions namely, CO, H₂ and O₂. Hydrogen is considered as the best choice of gaseous adsorbates for platinum. It also has a number of advantages associated with it. The principle advantage being, that it is only adsorbed to a relatively slight extent on the non-metallic part of the catalyst i.e. the support material (33).

Although physical adsorption of hydrogen may actually occur over both the non-metallic and metallic parts, it can be reduced to a negligible extent at ambient temperature and pressure. This fact is due to the very small adsorption enthalpy of hydrogen, which is less than 8kJ/mole (33).

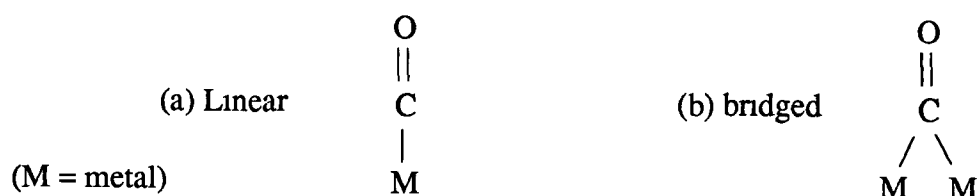
When hydrogen is used for chemisorption measurements to determine metallic dispersions, a knowledge of the chemisorption stoichiometry at monolayer coverage is required. This stoichiometric value is accepted as being one for hydrogen e.g. in platinum dispersion measurements, one hydrogen atom is adsorbed onto one platinum atom (33).

Anderson and his co-workers (34), concluded from their work that generally hydrogen chemisorption provides the best method for the determination of platinum dispersions. However due to hydrogen spillover on to the support material problems can be encountered in some systems e.g. for platinum supported on charcoal.

In addition to hydrogen spillover, there are other disadvantages associated with it namely.

- (a) after sample reduction, hydrogen coverage is not always zero, and
- (b) due to the temperature that certain samples are subjected to, either during sample pretreatment or sample evacuation, sintering of the metallic component may occur. This phenomenon can result in certain areas of the catalytic material deactivating during catalyst action (33).

Carbon monoxide has also been used by many investigators for determining metallic dispersions. One problem associated with this gaseous adsorbate is the translation of the amount of carbon monoxide chemisorbed to effect monolayer coverage, into free metal surface area. It has been found that CO can be chemisorbed in two main forms on metals, such as platinum, palladium and nickel (33) as follows:



Due to these various forms which have differing adsorption energies, and because the number of surface metal sites associated with the adsorption of one CO molecule can vary, then the relative proportions of those various forms can be temperature, pressure and metal particle size dependent (33)

Another associated difficulty with carbon monoxide as a gaseous adsorbate is that it can form volatile carbonyl compounds with those metallic species it adsorbs to. This is due to direct reaction between it and the metal of interest. Metal carbonyl formation may be quite extensive under conditions where the metal is finely divided (33)

There are several experimental techniques used to assess the particle size of metals, they include:

- (a) volumetric measurements,
- (b) gravimetric measurements,
- (c) continuous-flow techniques,
- (d) pulse technique,
- (e) X-Ray diffraction, and
- (f) electron microscopic techniques (33)

Volumetric measurements involve the monitoring of the loss of pressure in the system as the gas is adsorbed onto the surface and gravimetric measurements involve monitoring the change in weight of the sample as the gaseous adsorbate is adsorbed onto the sample's surface (33).

In our investigations into platinum dispersions on η -Al₂O₃ the pulsed gas technique was the method used to determine all our dispersion measurements. It utilises the fact that pulses of a known volume of a particular gaseous adsorbate (in our case hydrogen) once injected over the sample which had been previously treated are taken up by it. When the metal is totally saturated with the adsorbate, no further uptake of hydrogen occurs. The amount of hydrogen uptake can then be measured and related to the metal dispersion on the sample's surface (33).

Hydrogen chemisorption has been carried out with significant success on supported platinum catalysts. Freel (35) evaluated a hydrogen chemisorption method for platinum/ η -Al₂O₃ and platinum/SiO₂ supported catalysts, he found that constant reproducibility was obtained and the results corresponded well with results for hydrogen on platinum, employing a pulsed gas technique

Several other studies (34, 35, 36, 37) have also suggested that hydrogen chemisorption on platinum yields a reliable measure of specific catalytic surface area, provided it is assumed that each platinum atom adsorbs one hydrogen atom

Metallic dispersion, D_M , is defined as the state of subdivision of a particular metal in terms of the ratio of the total number of surface atoms to the total number of metal atoms present (33) i.e.

$$D_M = M_s/M_T \times 100$$

where M_s is the number of surface metal atoms per unit weight of catalyst, and M_T is the total number of metal atoms per unit catalyst weight.

As one hydrogen atom is assumed to be adsorbed on one platinum atom, therefore the number of strongly chemisorbed hydrogen atoms per unit catalyst weight, N_H , is equal to M_s and thus:

$$D_M = N_H/M_T \times 100 \quad (1)$$

M_T is determined as follows:

$$M_T = \frac{\text{WEIGHT OF SAMPLE}}{\text{MOLEC WEIGHT METAL}} \times \frac{6.02 \times 10^{23}}{1} \times \text{WEIGHT \% LOADING METAL}$$

and N_H is determined as follows:

$$N_H = \frac{V_{(\text{HYDROGEN ADSORBED})} \times 6.02 \times 10^{23} \times 2}{22414}$$

where:

- Weight % loading metal, is the percentage of Pt as weight, per unit weight of sample, and
- $V_{(\text{HYDROGEN ADSORBED})}$ is the total volume of hydrogen gas chemisorbed on the catalyst sample corrected to standard temperature and pressure, and it was determined as follows:

$$V_{(\text{HYDROGEN ADSORBED})} = V_{\text{ads}} \times (273/\text{ROOM TEMP}) \times (\text{ATMOSPHERIC PRESSURE}/\text{STANDARD PRESS})$$

where:

V_{ads} is the total volume of H_2 chemisorbed on the catalyst sample.

(c) 22414 cm³ / mole, is the volume, that one mole of gas occupies at standard temperature and pressure

6.02 x 10²³ is Avogadro's number, and is the number of particles of any substance contained in one mole of that substance

Hence on substitution into equation (1), the following expression, for the determination of the dispersion of platinum metal particles in the catalyst samples is obtained:

$$D_M = \frac{N_H}{M_T} = \frac{(V_{(\text{HYDROGEN ADSORBED})}) \times \text{Molar weight of metal} \times 2}{\text{WEIGHT OF SAMPLE} \times 22414 \times \text{WEIGHT \% METAL LOADING}} \times \frac{100}{1}$$

NOTE, WEIGHT OF SAMPLE is that weight of catalyst sample in grammes, which was used for dispersion measurements

For specific catalytic surface area measurements employing H₂ chemisorption, a knowledge of the chemisorption stoichiometry, X_m, at monolayer coverage, and a knowledge of the number of metal atoms per unit area of surface, M_s is required. If in relation to monolayer chemisorption, N_m^{*}, is the total adsorbate uptake expressed in molecules, then the total specific metallic surface area, S_H, is given by: (33)

$$S_H = N_m^* X_m M_s^{-1}$$

However, the number of surface atoms per unit area of polycrystalline metal surface, M_s, is not exactly known. In the case of platinum, M_s, is assumed to be 1.25 x 10¹⁹ surface atoms per m² of polycrystalline surface (33) assuming equal proportions of (111), (100) and (110) faces

Other distributions of the crystallographic surface planes have been put forward, namely, that for fcc metals of small crystallite size, the equilibrium shape corresponds to the exposition of 70% (111) planes, 25% (100) planes and 5% (110) planes

M_s for platinum, assuming the latter distribution is, 1.42 x 10¹⁹ surface atoms per m² of polycrystalline surface (33) This was the value that was used in further calculations.

Hence

$$S_H = N_m^* 2 M^{-1}$$

$$\Rightarrow S_H = N_m^* 2 (1.42 \times 10^{19} \text{ particles m}^{-2})^{-1}$$

where

$$N_m^* = \frac{V(\text{HYDROGEN ADSORBED}) \text{ cm}^3 \times 6.02 \times 10^{23} \text{ particles/mole}}{22414 \text{ cm}^3/\text{mole}}$$

therefore

$$S_H = \frac{V(\text{HYDROGEN ADSORBED}) \text{ cm}^3 \times 2 \times 6.02 \times 10^{23} \text{ PARTICLES MOLE}^{-1}}{22414 \text{ cm}^3 \text{ mole}^{-1} \times 1.42 \times 10^{19} \text{ PARTICLES m}^{-2}}$$

Determination of the mean platinum crystallite diameters from D_M is also possible, and can be derived as follows:

It is assumed that all particles (crystallites) of the metal are spherical and of radius r (meters).

$$\text{Surface area of particle (m}^2\text{)} = 4 \pi r^2$$

$$\text{and volume of particle (m}^3\text{)} = \frac{4}{3} \pi r^3$$

$$\frac{\text{Volume of sphere (m}^3\text{)}}{\text{Surface area of sphere (m}^2\text{)}} = \frac{\frac{4}{3} \pi r^3}{4 \pi r^2} = \frac{r}{3}$$

Therefore:

$$r = \frac{3 \text{ VOLUME OF SPHERE}}{\text{SURFACE AREA OF SPHERE}}$$

$$\text{therefore } 2r = d = \frac{6 \cdot \text{VOLUME OF SPHERE}}{\text{SURFACE AREA OF SPHERE}}$$

where d is the diameter of the sphere

Over the total sample:

$$\bar{d} = 6 \times \frac{\sum_i N_i V_i}{\sum_i N_i S_i} = \frac{\text{sum of volume of all particles}}{\text{sum of surface area of all part.}}$$

(where $\bar{d}$ is the average diameter of the metal particle in meters)

$$\Rightarrow \bar{d} = 6 \times \frac{1/\rho}{S_M}$$

where ρ is the density of the metal particles in the sample, and S_M is the total surface area of metal

$$\Rightarrow \bar{d} \text{ (meters)} = \frac{6 \times 1/\rho \times 10^{-6}}{S_M}$$

Hence the mean platinum crystallite diameter is calculated from:

$$\Rightarrow \bar{d}(\text{\AA}) = \frac{6 \times 1/\rho \times 10^4}{S_M}$$

3.1.2 X-RAY LINE BROADENING MEASUREMENTS

INTRODUCTION

X-ray line broadening measurements are very often used for estimations on the mean particle size of supported metal crystallites (38, 39)

The technique of X-ray line broadening for determining particle sizes relies on the fact that X-ray diffraction lines are broadened when the metal particles are smaller than about 100nm. The width of these broadened lines, can then be converted into an average particle diameter for particles larger than about 4nm, (smaller particles give diffraction lines too broad for an accurate analysis of particle size). However, the range of 4nm to 100nm includes many of the supported metals of interest. The X-ray measurements are also generally simple to make on a routine basis (40, 41)

It was decided to compare a measurement of particle size obtained via X-ray line broadening with that obtained via chemisorption measurements in this area of investigation.

The particle size from X-ray line broadening measurements was obtained, using the following formula (42):

$$\bar{d} = \frac{k \lambda}{B_d \cos \theta} \quad (1)$$

where

- (a) $\bar{d}$ is the average particle size of the analyte of interest,
- (b) k is a constant which is equal to 0.89,
- (c) B_d is the X-ray broadening term and is the angular width expressed in terms of 2θ radians,
- (d) θ is the diffraction angle of the x-ray radiation, and
- (e) λ is the radiation wavelength used (i.e. Cu, 1.5418 Å).

The X-ray broadening term, B_d , can be found from the following formula,

$$B_d = \sqrt{B_m^2 - B_o^2} \quad (b)$$

where:

- (f) B_m is the width at half height of the measured diffraction peak, and
- (g) B_o is the width at half height of the diffraction peak with large crystallites.

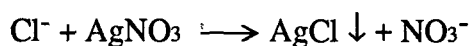
3.2 EXPERIMENTAL SECTION

This section deals with the preparation of the catalytic support material, the impregnation of this material with varying weight percent loadings of the platinum salt and the determination of the dispersion of the platinum particles.

PREPARATION OF THE CATALYST

The support material used throughout this work was Saffil fibre, manufactured by ICI (Runcorn). The composition of the fibre according to the manufacturers was > 95% Al₂O₃, < 5% SiO₂, with less than 2210ppm of the following impurities, Ca, Cl, Cr, Fe, Mg, Na and Ni. The alumina in Saffil was reported by ICI to be in the η -form. Typical fibre characteristics are as follows; surface area 150m²/g, mean fibre diameter 3 μ m, pore volume 0.2cm³/g.

Before impregnation with platinum, the fibre material was initially acid washed with 0.1M HCl (to clean the fibre) then washed with milli-Q water until no further traces of chlorine was detected in the wash. This was determined using AgNO₃ solution i.e.,



the AgCl produced was in the form of a fine white precipitate

The material was then air dried at 340K for at least 24 hours in an oven. It was then ground into a fine powder using a mortar and pestle.

Samples of this ground material were then impregnated with platinum. Impregnation solutions consisted of, chloroplatinic acid in excess methanol with sufficient salt to give the following loadings of platinum on the finished catalyst, 0.1, 2, 3, 5 and 10 weight percent loadings respectively.

The impregnated powder was then rotary evaporated at 340K for one hour to remove the methanol. The catalytic samples were then air dried at 310K for 24 hours in an oven. Finally the catalytic samples were then calcined at 900K for 15 minutes in a muffle furnace. Details of sample preparation are given in Table 9.

Once prepared, the samples were placed in a desiccator until required for analysis. Samples of acid washed and un-acid washed η -Al₂O₃ material were also analysed to determine whether or not hydrogen uptake occurred on the support material.

DISPERSION MEASUREMENTS

To determine the dispersion of the platinum particles on the support material, it was necessary to carry out chemisorption measurements employing a relatively specific gaseous adsorbate for the platinum metal particles

The gaseous adsorbate used was hydrogen, and chemisorption measurements were carried out using a pulsed gas technique

Platinum dispersion measurements were carried out using a Micromeritics Pulse Chemisorb 2700 instrument. A Schematic gas-flow diagram of which is given in Figure 3

Each sample was pretreated by outgassing with argon and then reduced with hydrogen. Sample pretreatment conditions are summarised in Table 10

After the reduction steps, each sample would be outgassed with argon (30mls/min) at 670K for at least 30 mins. The sample was then cooled to 310K under argon (30mls/min) prior to chemisorption

Platinum dispersions were determined by hydrogen chemisorption at 310K from a series of pulsed injections of 0.048cm³ of hydrogen

The above series of hydrogen pulses were injected over the sample. The quantity of hydrogen gas adsorbed on the sample's surface was monitored by the thermal conductivity detector within the instrument. Completion of hydrogen chemisorption by each sample was revealed by no further hydrogen uptake.

Desorption measurements were also carried out by heating the sample under investigation, from 310K to 520K and noting the detector response as the hydrogen was driven off from the sample.

Each sample was subjected to a minimum of two adsorption / desorption cycles

FIGURE 3
SCHEMATIC FLOW DIAGRAM OF THE PULSE CHEMISORB 2700 UNIT

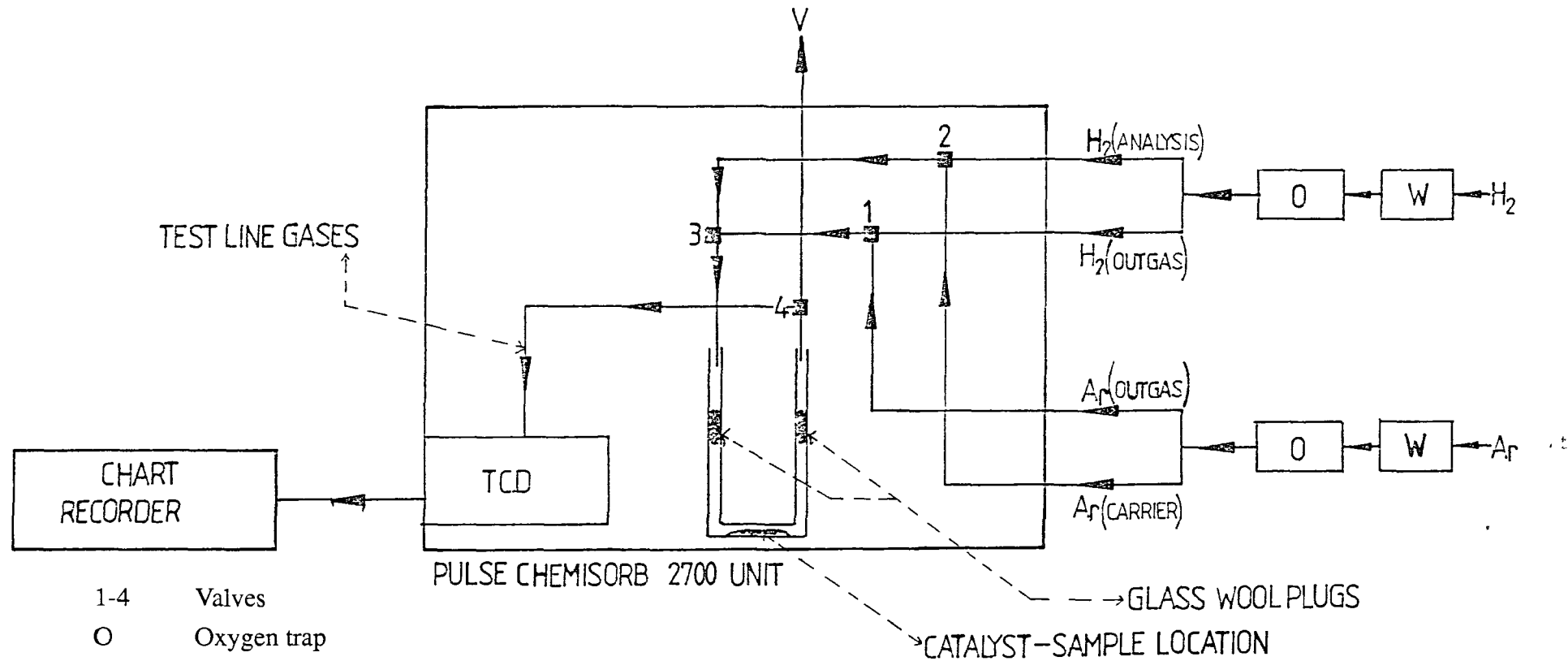


TABLE 9
SAMPLE PREPARATION

SAMPLE PREPARED Pt / η -Al ₂ O ₃	WEIGHT OF METAL SALT USED	WEIGHT OF η -Al ₂ O ₃ USED	VOLUME OF METHANOL SOLUTION
0.1 wt% Pt / η -Al ₂ O ₃	0.0042g	1.2222g	25mls/g of η -Al ₂ O ₃
2 wt% Pt / η -Al ₂ O ₃	0.0545g	1.0534g	25mls/g of η -Al ₂ O ₃
3 wt% Pt / η -Al ₂ O ₃	0.0881g	1.0972g	25mls/g of η -Al ₂ O ₃
5 wt% Pt / η -Al ₂ O ₃	0.3253g	2.5866g	25mls/g of η -Al ₂ O ₃
10 wt% Pt / η -Al ₂ O ₃	0.2875g	1.1363g	25mls/g of η -Al ₂ O ₃

TABLE 10
Pt / η -Al₂O₃ SAMPLE PRETREATMENT

OUTGASSING FLOW RATE OF ARGON 30mls/min			REDUCTION FLOW RATE OF HYDROGEN 30mls/min		
STEP	DURATION	TEMPERATURE	STEP	DURATION	TEMPERATURE
1	30 mins	290K	5	2 hours	470K
2	30 mins	320K	6*	5 hours (min)	670K
3	1 hour	370K			
4*	2 hours (min)	470K			

Note. Steps 4 and 6 were carried out for 2 hours and 5 hours respectively as minimum times. In Step 4, the length of time varied from 2 hours to 5 hours and in Step 6, the maximum length of time for reduction was 7 hours.

3.3 RESULTS FROM CHEMISORPTION AND X-RAY LINE BROADENING MEASUREMENTS

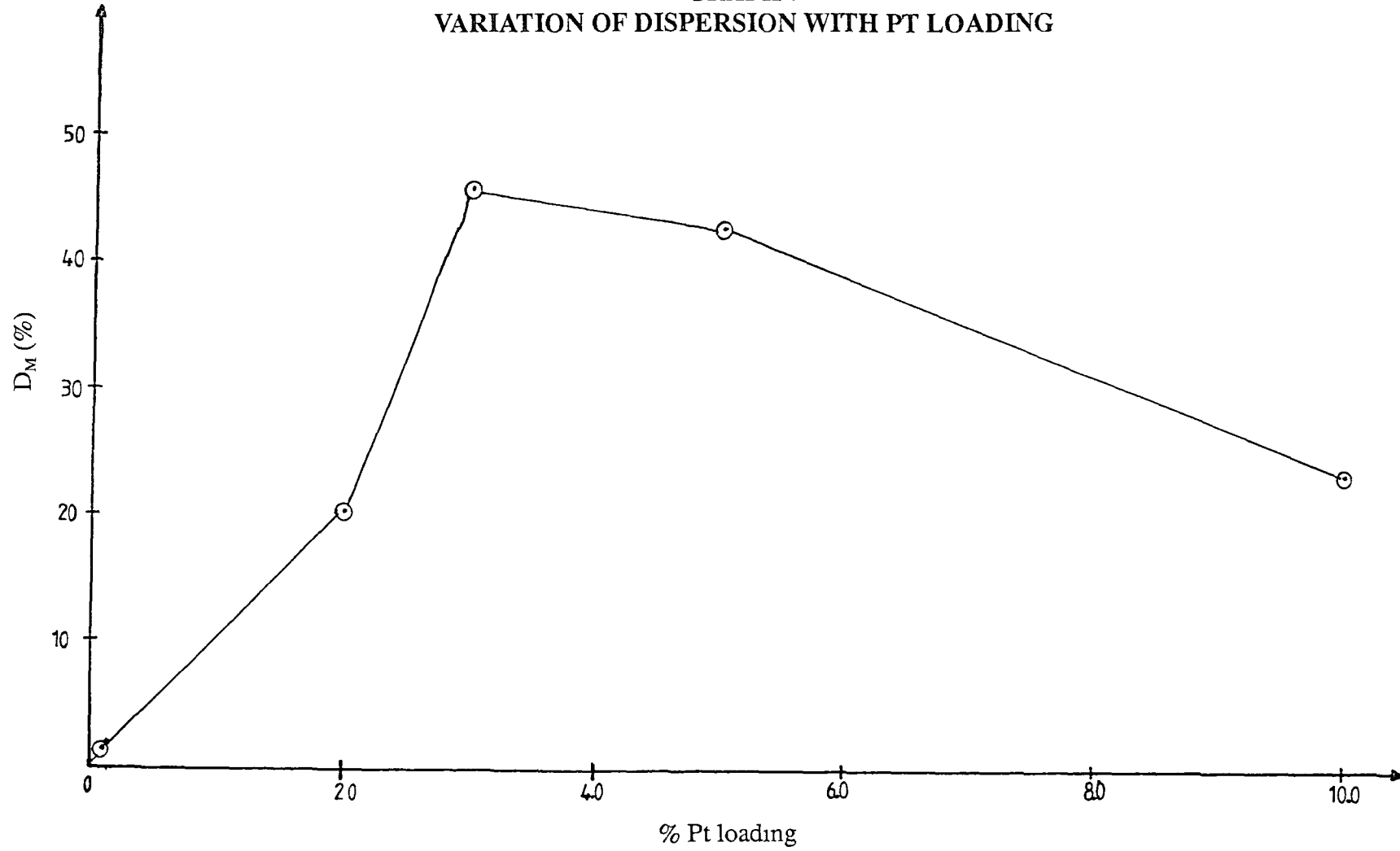
The dispersion measurements obtained via adsorption and desorption cycles were found to be in very close agreement within 2% and reproducible with a maximum discrepancy between them of 3%. The results are tabulated in table 11 and illustrated in Graphs 7 and 8

In the X-ray line broadening investigations the sample chosen, was a 3wt% Pt on η -Al₂O₃ , and was found to have a mean particle size of 91Å for the platinum particles, (the same sample had a mean particle size of 28Å obtained via chemisorption measurements).

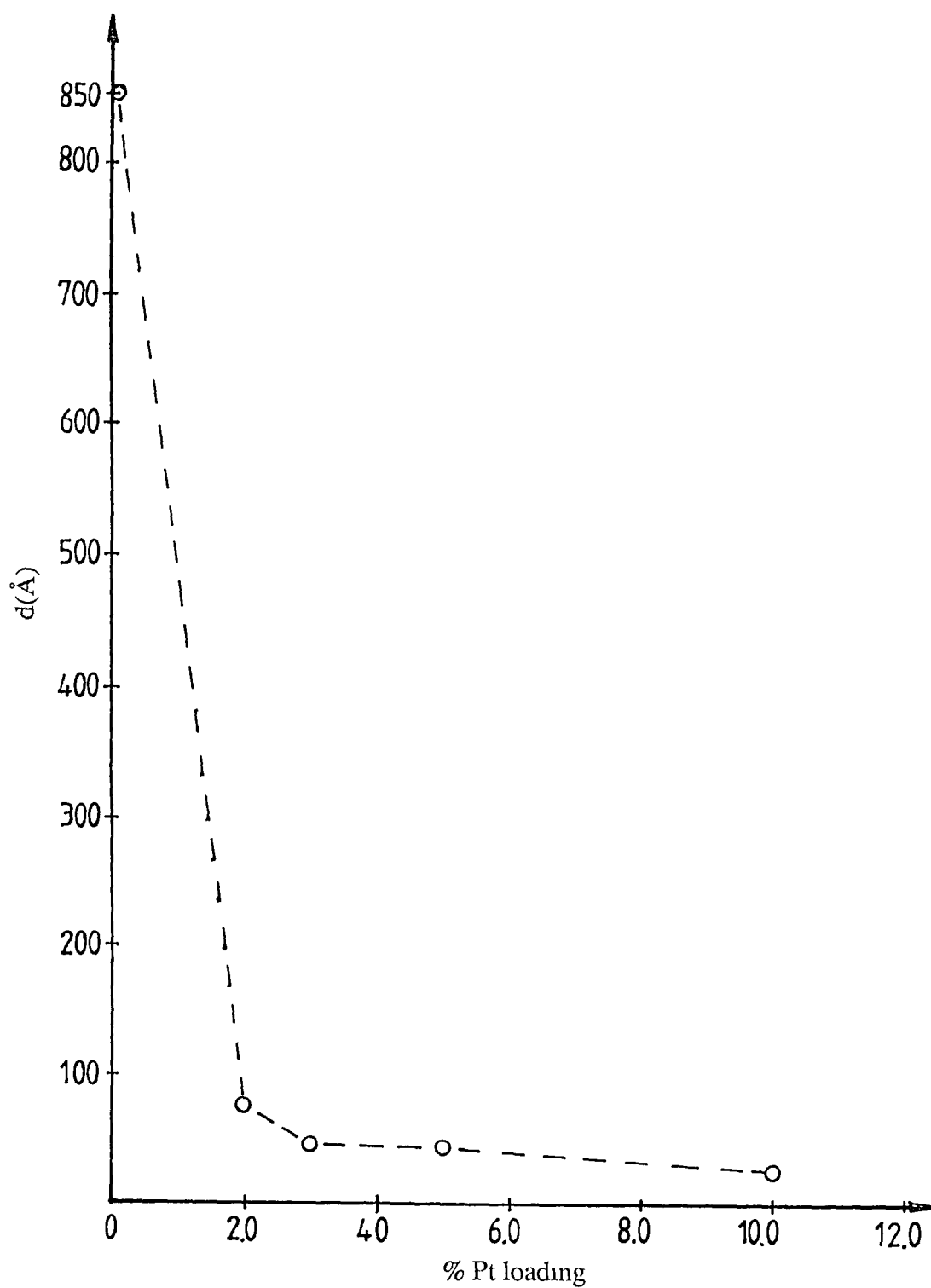
TABLE 11
RESULTS OF H₂ CHEMISORPTION MEASUREMENTS
AT VARIOUS Pt LOADINGS

wt% LOADING on η -Al ₂ O ₃	D _M	S _{Pt} (m ² /gPt)	$\bar{d}$ (Å)
10	24%	51m ² /g	77Å
5	43%	93m ² /g	30Å
3	46%	100m ² /g	28Å
2	20%	44m ² /g	76Å
0.1	2%	3m ² /g	850Å
ACID WASHED η -Al ₂ O ₃	0%	0m ² /g	0Å
UN-ACID WASHED η -Al ₂ O ₃	0%	0m ² /g	0Å
NOTE D _M Platinum (Pt) dispersion S _{Pt} : Platinum Surface area $\bar{d}$ Average Platinum particle size			

GRAPH 7
VARIATION OF DISPERSION WITH PT LOADING



GRAPH 8
VARIATION OF PARTICLE SIZE WITH Pt LOADING



3.4 DISCUSSION OF CHEMISORPTION AND X-RAY RESULTS

From the chemisorption results it was observed that as platinum loadings increased from 0.1 wt% to 10 wt%, the dispersion values reached a maximum at 3 wt% and decreased thereafter. A 10 wt% loading of platinum gave a dispersion measurement of 23.6%. This measurement was comparable to that measurement obtained on a sample containing 2 wt% Pt which had a 20.3% dispersion. This indicates that once a certain loading of platinum was achieved, (e.g. 3 wt%), the platinum particles influence the further uptake of the metal by “forcing” the new metal into the bulk.

It was noticed that at a 5 wt% Pt loading, a 43% dispersion was obtained. This value was relatively similar to that obtained for a 3 wt% Pt sample. It is worth noting that the lowest loading tested i.e. 0.1 wt%, gave a very low dispersion of 2% with a corresponding particle size of 830 Å. This indicates that a large amount of the platinum was not available on the surface for chemisorption.

It was also found that acid and un-acid washed η -Al₂O₃ did not take up any hydrogen. This indicated that no hydrogen chemisorption was taking place on the support material, and as such the hydrogen chemisorption measurements obtained for the platinum impregnated η -Al₂O₃ samples, were representative of platinum only.

From the X-ray line broadening measurements a particle size of 91 Å was obtained, whereas the same sample yielded a particle size of 28 Å from chemisorption measurements. A possible reason for the substantial difference in the results from the two methods, was the non-uniformity of particle size of platinum throughout the sample.

Freel (5) on studying the particle size of platinum on SiO₂ found in his study that for a 2.8 wt% loading of platinum on SiO₂ an average particle size of 31 Å was obtained, (for 3 wt% Pt on η -Al₂O₃, 28 Å particle size was found in this study). He also determined a particle size of 81 Å for a 1.83 wt% Pt on η -Al₂O₃. This result compares favourably to the particle size obtained in this investigation for 2 wt% Pt on η -Al₂O₃ i.e. 76 Å.

However, the particle size and dispersion measurements made on any catalyst sample can vary if the sample preparation and pretreatment is altered in any way (33).

Dorling et al (43) also carried out investigations into platinum dispersions on silica and they determined the mean particle sizes for platinum as follows:

wt %Pt loading	particle size (43)	particle size from Graph 8
0.15 wt%Pt	39Å	820Å
3.10 wt% Pt	36Å	44Å
4.9 wt% Pt	40Å	43Å
10.2wt%Pt	54Å	25Å

It can be seen from the table that there is little agreement between the results of the two laboratories

CHAPTER 4

CATALYTIC ACTIVITY MEASUREMENTS

4.1 • INTRODUCTION

The aim of this area of investigation was to study the activity properties of specifically prepared catalytic materials, for the conversion of iso-butane.

With the ever increasing demands placed on our decreasing reserves of fossil fuels, coupled with the associated air pollution problems, much time and energy is now devoted to developing a means of reducing the levels of pollutants and using the finite reserves of fossile fuels more efficiently (4).

Emissions of nitrous oxides (NO_x) and sulphur oxides (SO_x), have caused increasing concern about serious damage to health and the environment. It is because of this that some catalytic processes have come to the forefront to try to solve some of the above problems, generally in the form of catalytic combustors (4).

Catalytic combustors provide a means of not only increasing the efficiency of the combustion process, but in also reducing the levels of NO_x that can result. Catalytic combustion processes are also more controllable. They can operate at reduced temperatures and are more efficient for combustion than normal flame combustion.

Substantial work has already been devoted to catalytic combustion since the early 1970's(4). The oxidation of methane (CH_4) over platinum which was discovered by H. Davy in 1817(44), was one of the first known heterogeneously catalysed processes.

Production of energy by combustion has always been desired, but has some degree of difficulty associated with it. Combustion can be hard to control, as it will only occur efficiently within well defined air:fuel ratios, and it can lead to the production of pollutants at these specific ratios. With the introduction of a heterogeneous catalyst, the combustion process can be easier to control over wider air:fuel ratios, and the process can be more efficient in the reduction of the levels of pollutants (45).

Catalysts used in the oxidation process act by reducing the temperature at which combustion occurs, hence removing some of the processes by which pollutant emissions can occur at higher temperatures (45). e.g.



With a suitable combustion catalyst, efficient combustion processes can be achieved. Reducing the temperature at which normal flame combustion takes place can however, result in an increase in emissions of CO and hydrocarbons without the

presence of a catalyst, e.g. in the oxidation of CO to CO₂, the rate of the major reaction responsible for the oxidation of CO to CO₂ (i.e. $\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}$) is reduced, as the temperature is decreased (4). However with the introduction of a suitable metal oxide or a number of such metal oxides, an increase in the rate at which CO is converted to CO₂ is attained (46, 47)

Yung-fang Yu Yoa (46, 47) is one of many researchers that have studied the oxidation processes of CO and hydrocarbons to CO₂ and H₂O, employing perovskite type oxides, Co₃O₄ and Cr₂O₃ metal oxides. He found that the cobaltites of perovskite structure (e.g. LaCoO₃, BaCoO₃) showed lower reaction rates for C₂H₄ oxidation than Co₃O₄, but higher rates than manganite type perovskites (i.e. La_{0.7}Pb_{0.3}MnO₃, La_xSr_{1-x}MnO₃ with x = 0 to 1). The activity for all catalysts studied increased significantly with the introduction of 100ppm Pt. With the use of Cr₂O₃ it was found that the order of oxidation activity was as follows, (for the series of hydrocarbons and CO investigated), C₃H₆ > C₃H₈ > CO = C₂H₄ > C₂H₆.

It has also been found that in the oxidation of methane and its homologues, only in rare cases can partial oxidation products be detected. Generally their oxidation results in the formation of CO₂ and H₂O when using metal oxide catalysts, e.g. Co₃O₄, MnO₂, Cr₂O₃ and NiO, with Co₃O₄ exhibiting the greatest effects (48)

Unfortunately, during catalytic oxidation processes, the catalytically active material may sinter, poison and can even melt under certain operating conditions. However if these processes are prevented or even reduced to within acceptable limits, then the life span of the catalyst can be extended (4)

Catalysts used for catalytic combustion usually consist of the catalytically active component(s) deposited onto a suitable support material of sufficiently high thermal stability and surface area (4, 45)

The choice of catalyst system (i.e. the active components and support material) has a major influence on the production of a successful combustion catalyst. Prasad et al (4) have suggested that the catalyst system used in oxidation processes should possess the following properties:

- (a) the catalyst should be capable of igniting a fuel/air mixture at the lowest possible temperature,
- (b) the activity of the catalyst should be sufficiently high to maintain complete combustion at the lowest levels of air pre-heat and the highest values of mass through-put,

- (c) the support should have a large geometric surface, a low pressure drop, an excellent thermal shock resistance, and also a high working temperature,
- (d) the support should be capable of maintaining a high surface area under high temperature combustion conditions ($\approx 1370\text{K}$), and
- (e) the catalyst system should maintain a high activity even after prolonged use at elevated temperatures (1270-1770K).

Noble metal catalysts and metal oxide catalysts have been used for hydrocarbon and/or CO oxidation, and Blazowski et al (7) recommended them for the complete oxidation of an organic compound.

The general sequence of activity of the noble metals for oxidation has been found to be(4):



However due to high volatility and limited supply, the use of these metals has been limited to Pt and Pd(4).

The use of Pd and Pt in oxidation catalysts has been widely reported and they are among the most active metals for the oxidation of a number of different hydrocarbons (44). The high activity of the above metals is due to their inherent ability to activate O-H₁, O₂, C-H and H₂ bonds (4).

On comparing the catalytic activity of Pd with Pt it has been found (4):

- (a) for the oxidation of CO, olefins and methane, the activity of Pd is reported to be higher than that for Pt,
- (b) for aromatic compounds, Pd and Pt, have been found to be similar in activity, and
- (c) for the oxidation of paraffinic hydrocarbons (C₃ and greater), Pt, was found to be more active than Pd.

On comparison of Pt and Pd with base metal oxides, it has been established (4) that the noble metals have certain advantages, namely:

- (a) higher specific activity for hydrocarbon oxidation,
- (b) greater resistance to the loss of low temperature activity,
- (c) less deactivation by sulphur at temperatures below 770K, and
- (d) relative ease of preparation in a highly dispersed form on several different support materials.

It is for these reasons that relatively small quantities of these noble metals are only normally required for combustion catalysts

Generally, high oxidation activity, demands that metal ions can assume more than one valence state and can take part in reduction-oxidation reactions. It has also been established that many transition metal oxides have more than one valence state. The catalytic activity of these oxides is determined by their d-shell electronic configuration. Maximum activity has been found for three, six and eight d-electron configurations, whereas minimum activity has been found for zero, five and ten d-electrons (7)

As with noble metal catalysts, the combustion of hydrocarbons has been studied with metal oxides also (44,45). In general it has been found that for CO and hydrocarbon oxidation, Co_3O_4 is the most active metal oxide catalyst. However oxides of La and Ce for example, have also been used for CO oxidation (46, 47, 48). However under normal combustion conditions, their activities have been comparable to those of noble metals (4)

Although Pt has been used for complete oxidation of hydrocarbons, it has also been used to catalyse other reactions e.g. for partial oxidation reactions (48), in reforming processes (50, 51, 52) and in dehydrogenation processes (53, 54)

It is insufficient for a hydrocarbon catalyst just to possess a suitable noble metal and/or metal oxide(s) to catalyse the reaction of interest, because a suitable support material is also generally required, upon which these catalytically active components can be dispersed

This support material has three main functions namely.

- (a) to provide a relatively thermally inert support,
- (b) to increase the surface area of the catalytically active component(s) by providing a support onto which these active components can be dispersed as small particles, and
- (c) to reduce the mechanism of sintering (4)

The most commonly used support material is alumina. It is relatively inexpensive, it can operate at temperatures greater than 1750K and is reasonably resistant to thermal shock. Although alumina is commonly used, SiO_2 and TiO_2 support materials have also been used (40, 41).

In chapter two of this thesis the thermal properties of the support material (η - Al_2O_3), was investigated. Several metal salts were investigated in an effort to stabilise the support. The effect of the metal salts on the activity of the Pt/ η - Al_2O_3 catalyst are now investigated.

From the chemisorption results, the best dispersion obtained was with 3wt%Pt loading, therefore it was decided to use this particular metal loading, and also to introduce the following ions

(a) La^{2+} , (b) Cs^+ , (c) Ce^{3+} , and (d) Sn^{4+} .

The above salts of these metal ions were introduced onto alumina at either of two loadings i.e. 1 or 3 wt% Table 12 summarises the catalysts prepared.

4.2 EXPERIMENTAL SECTION

Initially the weight of metal salt required to yield the desired percentage loading on the support material was dissolved in a specific quantity of solvent. The quantity of solvent was calculated on the basis that 25mls/g was required to totally saturate the $\eta\text{-Al}_2\text{O}_3$. The solvent used was 100% methanol GPR grade.

This solution was then added to a ground sample of $\eta\text{-Al}_2\text{O}_3$ of known weight to form a slurry. This mixture was then placed in a round bottomed flask. The solvent was then removed via rotary evaporation at 340K for approximately one hour.

The material was then dried in an oven at 370K for ten hours, and finally the sample was calcined (to form the oxides of the metal salts) in a muffle furnace at a temperature and time indicated in Table 13.

A list of samples prepared is given in Table 12 and a summary of the preparation conditions used in Table 13.

Two variations in the sample preparation process were carried out, namely co-impregnation and step impregnation.

(a) *Co-impregnation*

In this particular type of impregnation procedure both metal salts are impregnated onto the support material ($\eta\text{-Al}_2\text{O}_3$) in one single impregnation step, i.e. both metal salts are initially dissolved and applied to the support in one solution.

(b) *Step-impregnation:*

Step-impregnation involves the use of two separate impregnation steps. Initially one of the salts is dissolved and then impregnated onto the support followed by the dissolution and impregnation of the second metal salt. In between these impregnation steps further processing can occur (as did in this investigation i.e. drying and calcination, followed by the secondary impregnation of the second metal salt, which was then proceeded by a drying and calcination).

TABLE 12
CATALYST SAMPLES PREPARED

SAMPLE	METAL SALTS USED	LOADING (wt%)	ORDER OF METAL* SALT IMPREGNATION	METHOD OF IMPREGNATION
Pt3	H ₂ PtCl ₆ 7H ₂ O	3wt%	—	ONE STEP
** La1Pt3	H ₂ PtCl ₆ 7H ₂ O LaCl ₃ 7H ₂ O	3wt% 1wt%	2 1	STEP
La3Pt3	H ₂ PtCl ₆ 7H ₂ O LaCl ₃ 7H ₂ O	3wt% 3wt%	2 1	STEP
Cs1Pt3	H ₂ PtCl ₆ 7H ₂ O CsCl	3wt% 1wt%	2 1	STEP
*** Cs1Pt3(co)	H ₂ PtCl ₆ 7H ₂ O CsCl	3wt% 1wt%	—	CO- IMPREGNATION
Pt3 Cs1	H ₂ PtCl ₆ 7H ₂ O CsCl	3wt% 1wt%	1 2	STEP
Cs3Pt3	H ₂ PtCl ₆ 7H ₂ O CsCl	3wt% 3wt%	2 1	STEP
Ce1Pt3	H ₂ PtCl ₆ 7H ₂ O Ce(NO ₃) ₃ 6H ₂ O	3wt% 1wt%	2 1	STEP
*** Ce1Pt3(co)	H ₂ PtCl ₆ 7H ₂ O Ce(NO ₃) ₃ 6H ₂ O	3wt% 1wt%	—	CO- IMPREGNATION
*** Sn3Pt3(co)	H ₂ PtCl ₆ 7H ₂ O SnCl ₄ 5H ₂ O	3wt% 3wt%	—	CO- IMPREGNATION

* Refers to the order of salt addition to the support in step impregnation e g catalyst La1Pt3 was prepared by the addition of 1wt% LaCl₃ 7H₂O followed by 3wt% H₂PtCl₆ 7H₂O.

** La1Pt3 refers to the sample prepared with 1wt%La and 3wt%Pt, with the lanthanum salt being impregnated 1st and the platinum salt 2nd

*** (co) refers to the co-impregnation of the metal salts used in the catalyst sample

TABLE 13: CATALYST PRODUCTION AND PRETREATMENT:

CATALYST SAMPLE	METAL SALT	WEIGHT OF SALT USED (g)	WEIGHT OF GROUND η -AL ₂ O ₃ USED (g)	VOLUME OF CH ₃ OH USED (mls)	TEMPERATURE AND DURATION OF ROTARY EVAPORATION	CALCINATION TEMPERATURE AND TIME
Pt3	H ₂ PtCl ₆ 7H ₂ O	0 0988g	1 2098g	30mls	(a) 340K for 1 hour (b) 370K for 10 hours	900K, 15 mins
La1Pt3	H ₂ PtCl ₆ 7H ₂ O LaCl ₃ 7H ₂ O	0 0832g 0 0293g	1 0829g	25mls 25mls	(a) 340K for 1 hour (b) 370K for 10 hours	900K, 15 mins 900K, 15 mins
La3Pt3	H ₂ PtCl ₆ 7H ₂ O LaCl ₃ 7H ₂ O	0 0795g 0 0834g	1 0603g	25mls 25mls	(a) 340K for 1 hour (b) 370K for 10 hours	900K, 15 mins 900K, 15 mins
Cs1Pt3	H ₂ PtCl ₆ 7H ₂ O CsCl	0 0928g 0 0111g	1 1116g	28mls 28mls	(a) 340K for 1 hour (b) 370K for 10 hours	900K, 15 mins 900K, 15 mins
Cs1Pt3(co)	H ₂ PtCl ₆ 7H ₂ O CsCl	0 0839g 0 0114g	1 0049g	25mls	(a) 340K for 1 hour (b) 370K for 10 hours	(a) 900K, 15 mins (b) 1270K, 3 hours
Pt3Cs1	H ₂ PtCl ₆ 7H ₂ O CsCl	0 0868g 0 0128g	1 0351g	25mls 25mls	(a) 340K for 1 hour (b) 370K for 10 hours	900K, 15 mins 1270K, 3 hours
Cs3Pt3	H ₂ PtCl ₆ 7H ₂ O CsCl	0 0954g 0 0432g	1 1440g	28mls 45mls	(a) 340K for 1 hour (b) 370K for 10 hours	1270K, 3 hours
Ce1Pt3	H ₂ PtCl ₆ 7H ₂ O Ce(NO ₃) ₃ 6H ₂ O	0 0920g 0 0338g	1 1039g	25 mls 25mls	(a) 340K for 1 hour (b) 370K for 10 hours	900K, 15 mins 1290K, 7 hours
Ce1Pt3(co)	H ₂ PtCl ₆ 7H ₂ O Ce(NO ₃) ₃ 6H ₂ O	0 0842g 0 0308g	1 0069g	25mls	(a) 340K for 1 hour (b) 370K for 10 hours	(a) 900K, 15 mins (b) 1270K, 7 hours
Sn3Pt3(co)	H ₂ PtCl ₆ 7H ₂ O SnCl ₄ 5H ₂ O	0 1064g 0 1171g	1 2763g	32mls 32mls	(a) 340K for 1 hour (b) 370K for 10 hours	900K, 15 mins 900K, 15 mins

4 2 2 CATALYST SAMPLE PRETREATMENT PRIOR TO ACTIVITY MEASUREMENTS

The sample (of approx 0.015g) was placed in a reactor tube and then placed in the activity unit as shown schematically in Fig 4. The activity unit was designed so as to have the facility of passing a mixture of pure gases over the heated sample and of bypassing it. At all times, a flow of gas could be maintained over the catalyst. The analysis was carried out using an in-situ Pye Unicam 4550 G.C. with F.I.D. detector. For the G.C. parameters used during this study refer to Table 14.

Once the catalyst samples were produced, each sample was treated prior to activity measurement, as outlined in Table 15

In all activity measurements, the catalyst sample was heated using a heating mantle which enveloped the U tube containing the sample. The temperature of the heater was controlled using a thermocouple located at the inner base of the mantle. Therefore all the temperatures given in this work are those of the heating mantle and do not necessarily represent the temperature of the catalyst.

As the catalytic oxidation of butane is an exothermic reaction, the temperature of the catalyst would be expected to increase sharply once the reaction commenced. However, in subsequent studies in this laboratory (22), a reactor tube with an indentation above the sample was used which enabled a thermocouple to be placed within 2mm of the catalyst bed. Even using this type of reactor tube for butane reactions, no significant difference between the temperature of the catalyst and the temperature of the heater was observed (22).

TABLE 14
CHROMATOGRAPHIC INSTRUMENTATION AND PARAMETERS

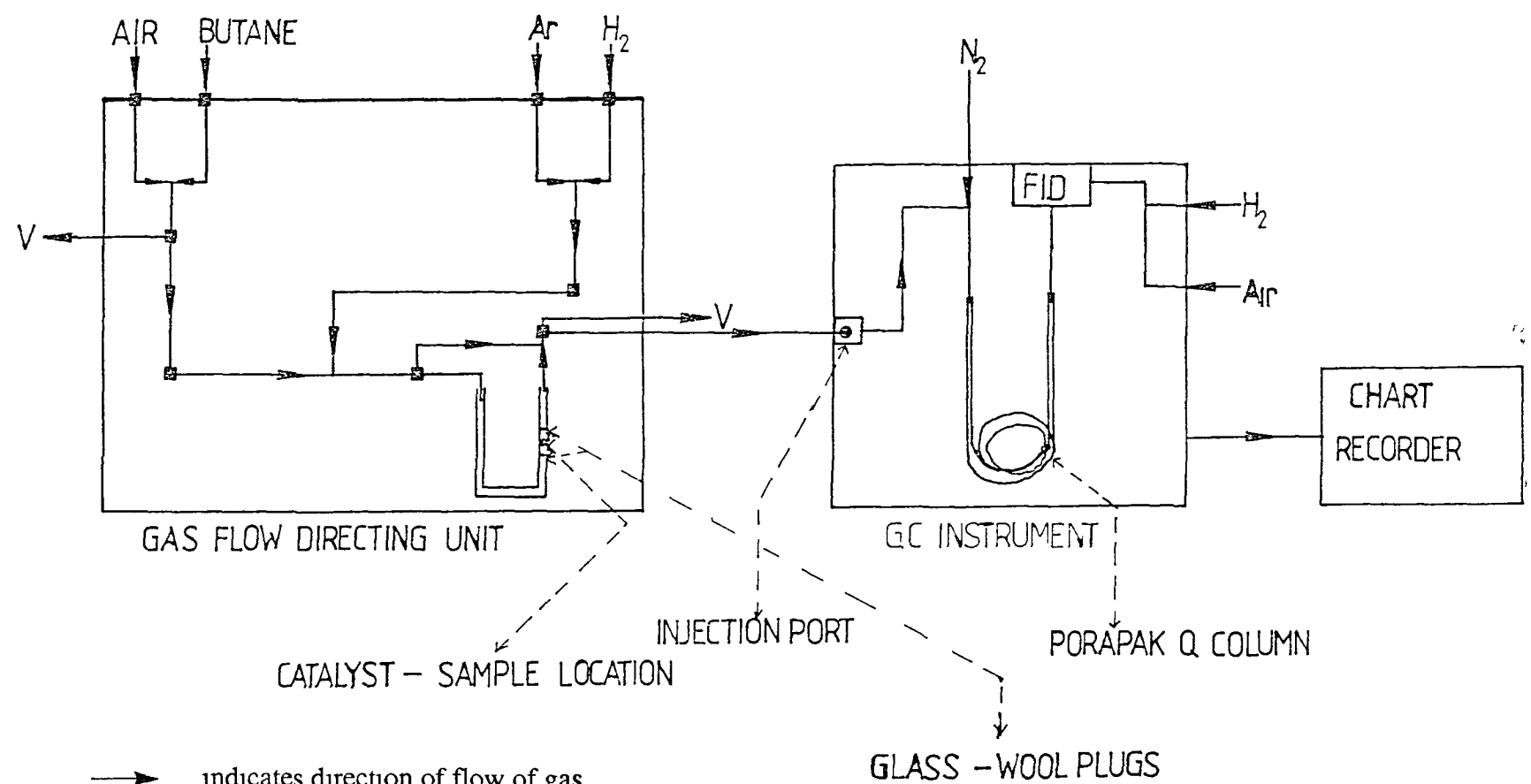
GAS CHROMATOGRAPHIC INSTRUMENT USED: PYE UNICAM 4550	
DETECTOR:	FLAME IONISATION
RECORDER:	OMNISCRIBE STRIP CHART RECORDER
CHROMATOGRAPHIC COLUMN PACKING MATERIAL: PORAPAK Q, 50-80 MESH	
COLUMN DIMENSIONS:	1 METER X 4mm PACKED
COLUMN TEMPERATURE:	420K
DETECTOR TEMPERATURE:	470K
INJECTOR TEMPERATURE:	460K
FUEL GASES:	HYDROGEN - FLOW RATE: 30mls/min
	AIR - FLOW RATE: 300mls/min
CARRIER GAS:	NITROGEN - FLOW RATE: 30mls/min

TABLE 15
CATALYST SAMPLE PRETREATMENT

OUTGASSING: FLOW RATE OF ARGON-30mls/min			REDUCTION: FLOW RATE OF HYDROGEN-30mls/min		
STEP	DURATION	TEMPERATURE	STEP	DURATION	TEMPERATURE
1	30mins	290K	5	2Hours	470K
2	30mins	320K	6*	5 Hours (Minimum)	670K
3	1 Hour	370K			
4*	2 Hours (Minimum)	470K			

Note: Steps 4 and 6 were carried out for 2 hrs and 5 hrs respectively as minimum times. In step 4, the length of time varied from 2 hrs to 5 hrs and in Step 6, the maximum length of time for reduction was 7 hrs.

FIGURE 4
SCHEMATIC DIAGRAM OF ACTIVITY UNIT



4.2.3 ACTIVITY MEASUREMENTS

The reaction which was to be studied was as follows



The iso-butane conversion activity of each of the catalyst samples was determined in-situ after outgassing and reduction pretreatments as described. The activity measurements were carried out as follows; after the sample was reduced with hydrogen at 670K it was then cooled to 370K under a stream of argon flowing at 30mls/min. A gaseous mixture containing the following gaseous component flow rates

- (a) Argon - 30mls/min,
- (b) Air - 70 mls/min, and
- (c) iso - butane 0.6mls/min.

was then passed through the catalyst sample at which time the G C chart recorder was switched on (to indicate time-zero). The hydrocarbon mixture as it was passing through the sample reacted over the surface of the catalyst, and then the gaseous products leaving the sample were injected into the G C column (via a 6-port gas sampling valve) in 1cm³ quantities for analysis.

The peak(s) due to iso-butane recorded on the chart recorder after each series of injections, represented the un-reacted iso-butane. It was these peaks that were compared to the average peak area obtained when no iso-butane had reacted (i.e. when samples of the gaseous feed stock to the catalyst sample were injected into the G C to determine the peak area of iso-butane when the catalyst was absent) to yield the activity measurement for iso-butane conversion for each catalyst studied.

The catalysts during each activity measurement were heated at 50K intervals from 370K to a final temperature of 670K. At each temperature interval, several injections were made of the gaseous effluent from the catalyst into the G C. When a steady state had been achieved (i.e. no observed increase or decrease in the iso-butane recorded peak), the sample was then heated to the next temperature interval and the whole process of injecting the gaseous effluent repeated, until the maximum temperature of 670K was achieved. The catalyst sample was then cooled to a relatively lower temperature and its activity re-investigated.

Once the catalytic iso-butane conversion investigations for the sample had been completed, the hydrocarbon gaseous feed stock to the catalyst was redirected, so that it could by-pass the sample. Injections of this gaseous mixture were then made into the G C. The subsequent peaks obtained indicated the level of hydrocarbon present prior to contact with the catalyst (i.e. 100% iso-butane). Thus an assessment of the sample's conversion properties for iso-butane could then be determined by a direct comparison between the 100% iso-butane peaks and the unreacted iso-butane (after contact with the catalyst).

4.3.1 RESULTS FROM ACTIVITY MEASUREMENTS

All catalysts employed in the activity measurements contained a three weight percent (3wt%) loading of platinum on η -Al₂O₃ and also contained differing levels of a secondary metal salt.

For a summary of the results obtained refer to Tables 16, 17 and the graphical representations in Graphs 9-15.

TABLE 16: STEADY STATE ACTIVITY MEASUREMENTS

Catalyst Sample Analysed	% Iso Butane Reacted at Temperature Indicated							
	300K %Reacted	370K %Reacted	420K %Reacted	470K %Reacted	520K %Reacted	570K %Reacted	620K %Reacted	670K %Reacted
* Pt3(a)	-	40%	12%	6%	3%	91%	95%	97%
Pt3 (b)	-	5%	6%	5%	51%	77%	91%	95%
Pt3(c)	-	36%	4%	4%	99%	98%	99%	99%
La1Pt3	-	4%	4%	5%	5%	11%	94%	96%
La3Pt3	-	10%	11%	6%	3%	96%	97%	99%
** Cs1Pt3(a)	-	61%	61%	60%	58%	95%	63%	99%
Cs1Pt3(b)	-	22%	7%	7%	18%	52%	67%	77%
Cs1Pt3(co)	-	17%	12%	12%	13%	55%	67%	79%
Pt3Cs1	-	10%	9%	8%	7%	43%	67%	94%
Cs3Pt3	-	4%	3%	8%	2%	1%	78%	86%
Ce1Pt3	14%	14%	14%	22%	53%	70%	85%	96%
CePt3(co)	-	15%	15%	12%	92%	95%	96%	97%
Sn3Pt3(co)	-	24%	6%	4%	10%	93%	96%	98%

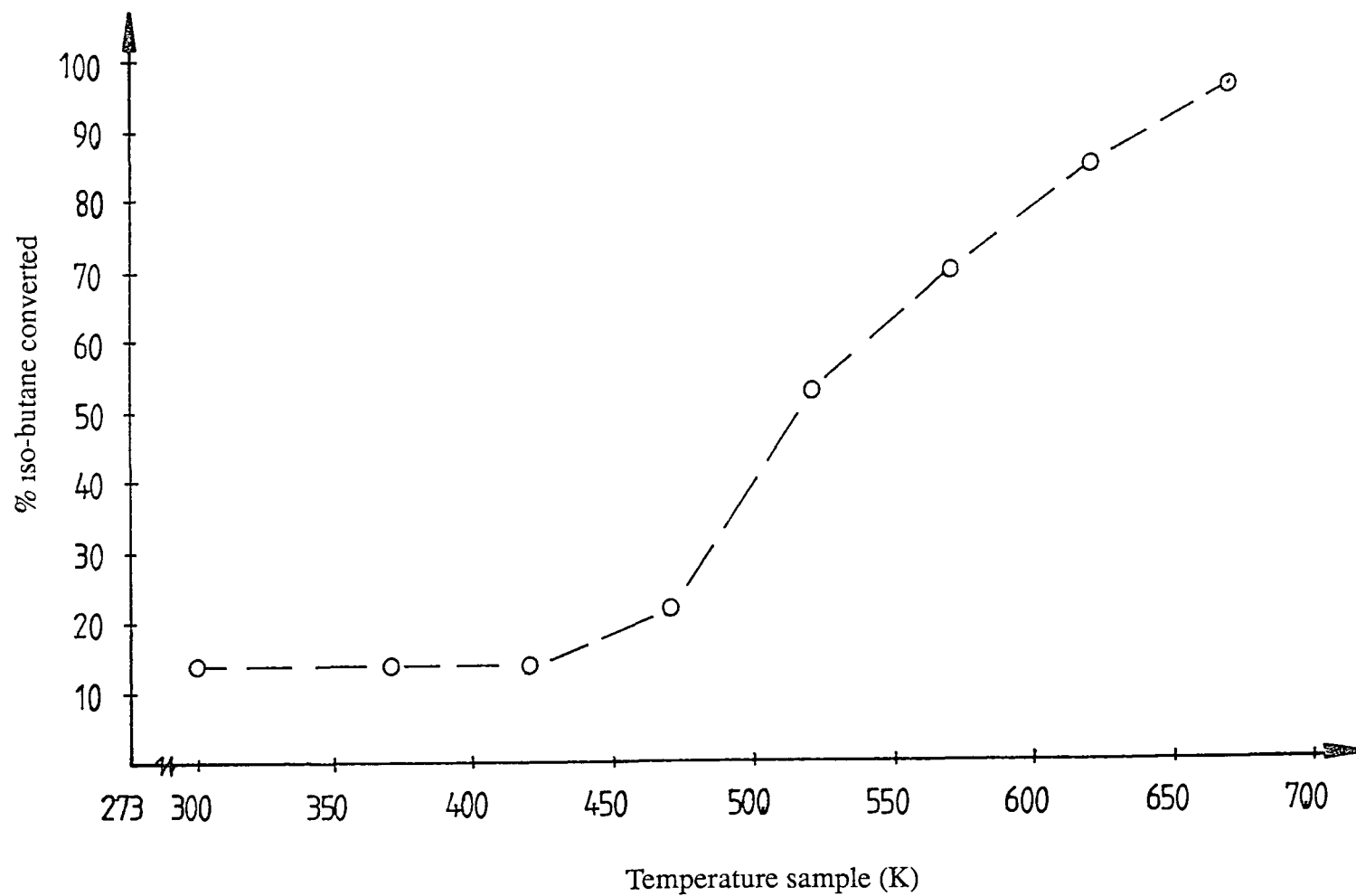
*Pt3(a), (b) and (c) were repeat measurements made on fresh samples of Pt3

** Cs1Pt3(a) and (b) were repeat measurements made on fresh samples of Cs1Pt3.

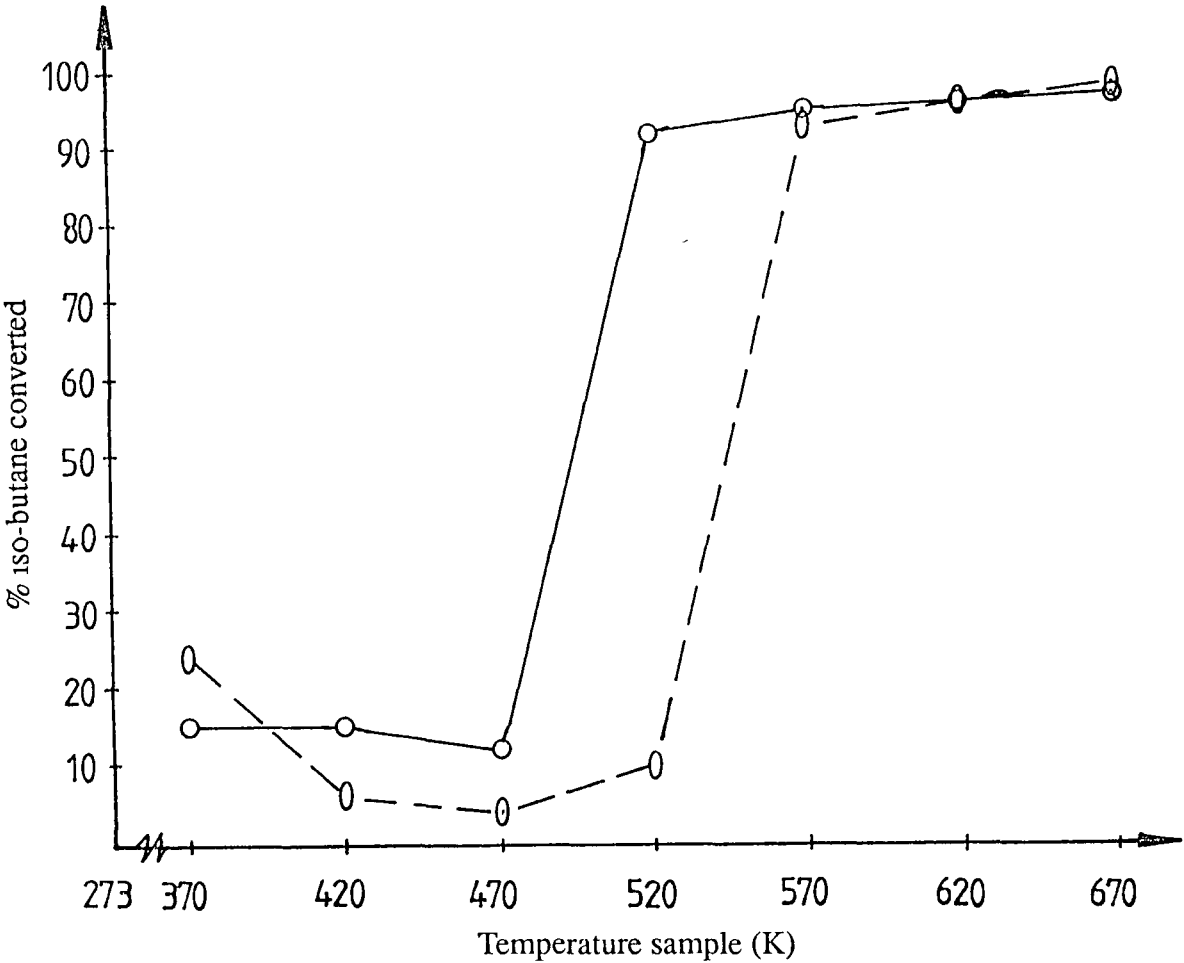
TABLE 17: REPEAT ACTIVITY MEASUREMENTS (AT STEADY STATE)

Temperature at which catalyst activity was assessed	%ISO-BUTANE REACTED							
	SAMPLE							
	Ce1Pt3	Ce1Pt3(co)	Sn3Pt3(co)	Pt3(b)	Pt3(c)	Cs1Pt3(a)	Cs1Pt3(b)	Cs1Pt3(co)
520K	53%	92%	10%	51%	99%	18%	13%	7%
670K cools to 520K	-	94%	80%	53%	97%	8%	7%	4%
Sample oxidised in Air at 770K, cooled to 520K	-	-	-	-	97%	6%	30%	-
	14%							
370K	14%							
470K	22%							
570K	70%							
670K	96%							
670K cooled to 570K	70%							
570K cooled to 470K	23%							
470K cooled to 270K	3%							
370K cooled to 300K	0%							

GRAPH 9
ACTIVITY MEASUREMENTS FOR ISO-BUTANE CONVERSION FOR
Ce1Pt3 CATALYST

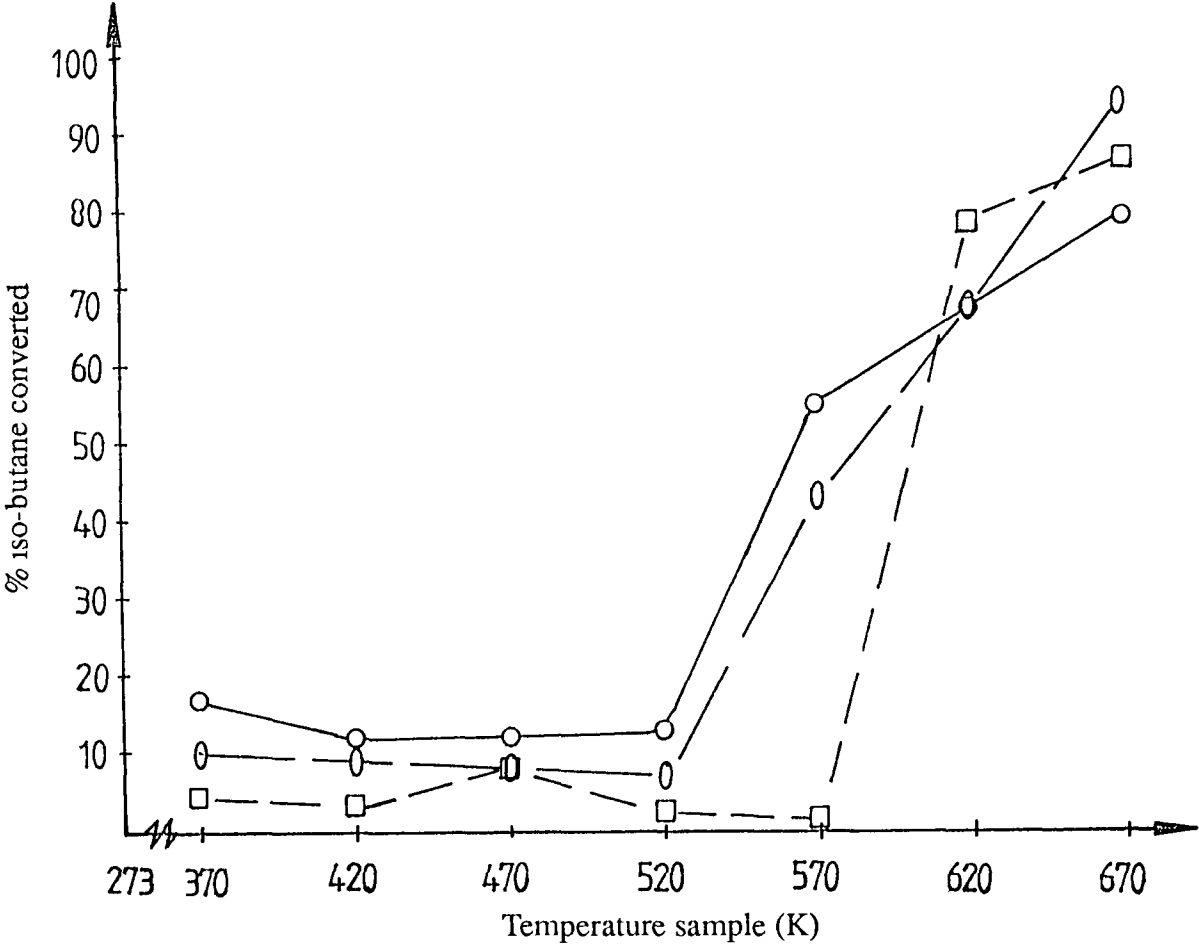


GRAPH 10
ACTIVITY MEASUREMENTS FOR ISO-BUTANE CONVERSION FOR
Ce1Pt3(CO) and Sn3Pt3(CO) CATALYSTS



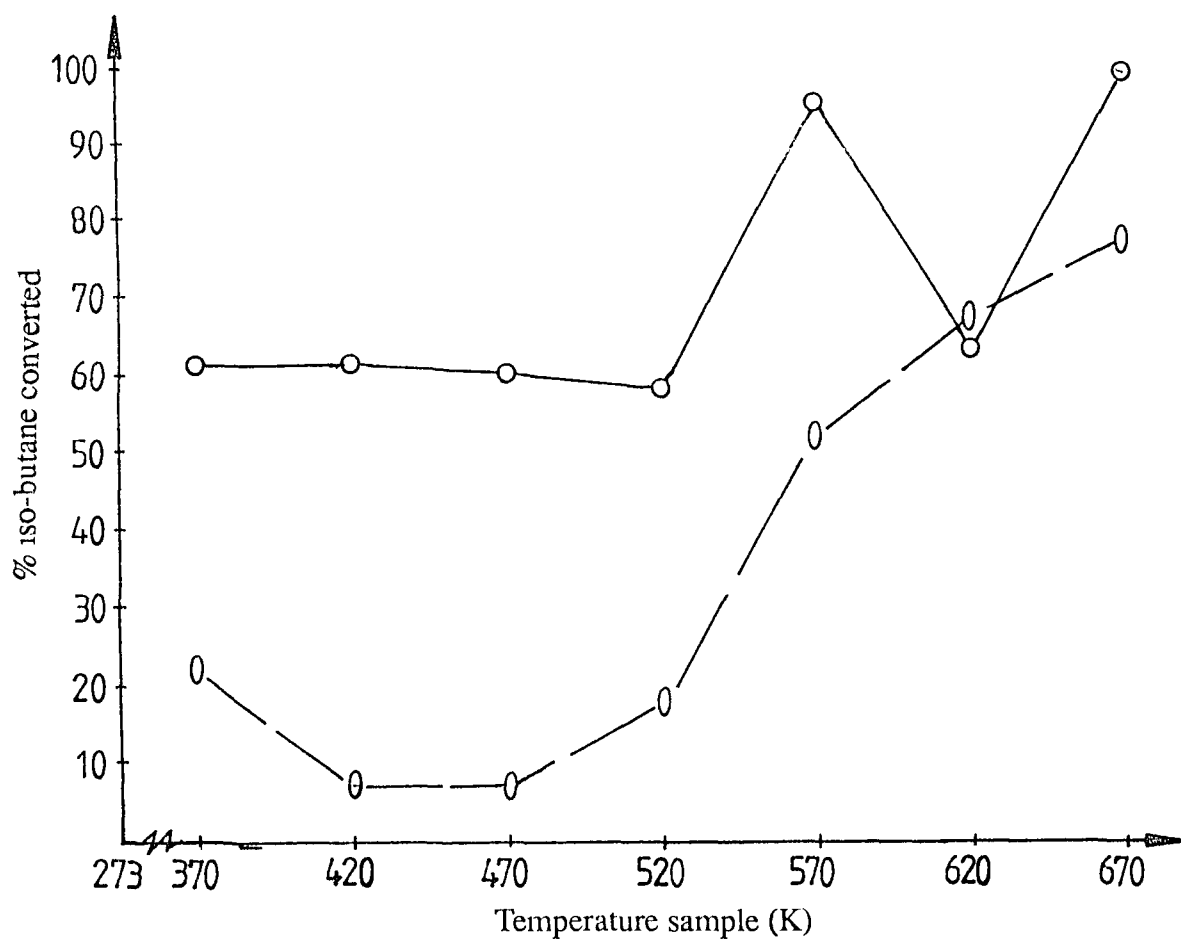
○ Ce1Pt3(CO)
 ○ Sn3Pt3(CO)

GRAPH 11
ACTIVITY MEASUREMENTS FOR ISO-BUTANE CONVERSION FOR
Cs1Pt3(CO), Pt3Cs1 AND Cs3Pt3 CATALYSTS.



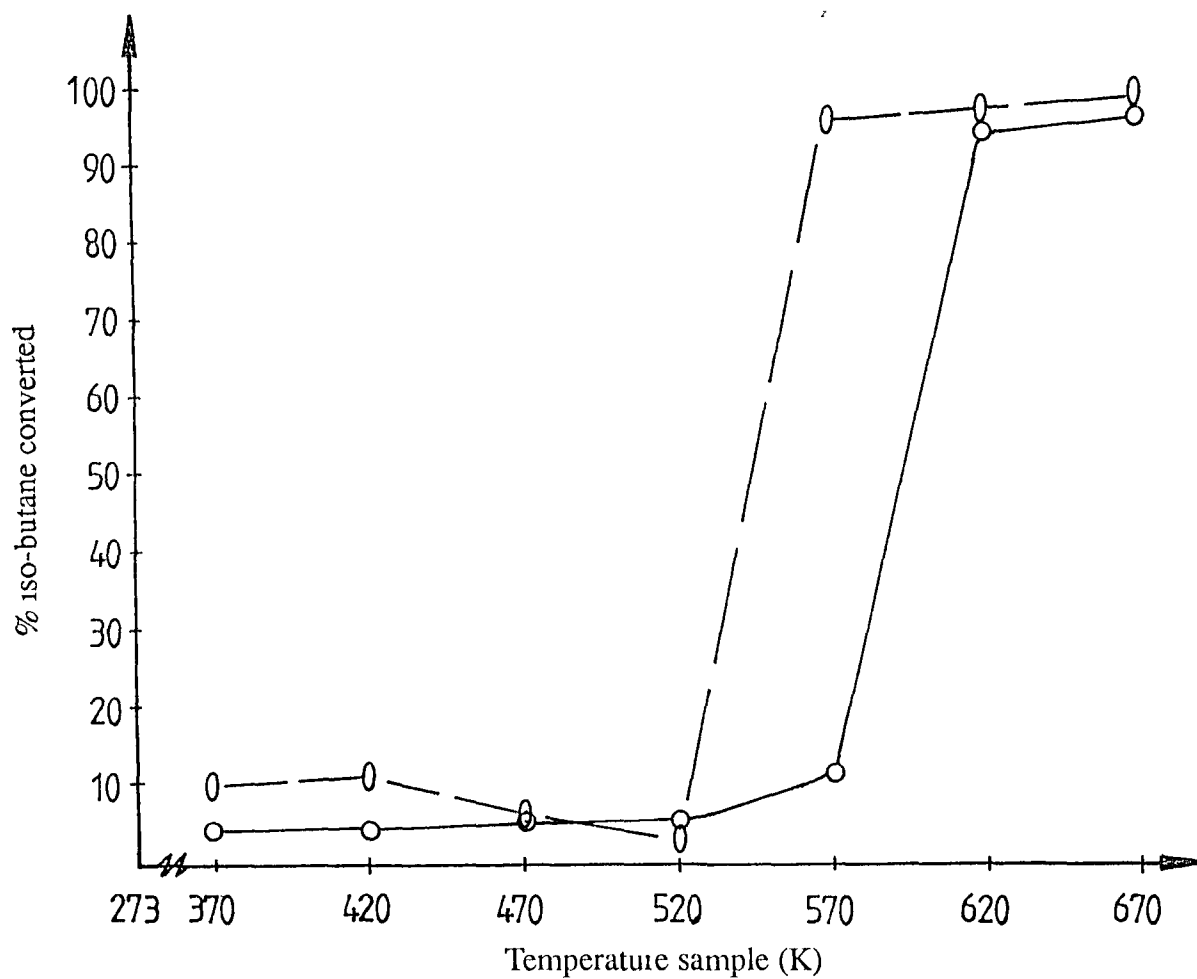
○ Cs1Pt3(CO)
○ Pt3Cs1
□ Cs3Pt3

GRÁPH 12
ACTIVITY MEASUREMENTS FOR ISO-BUTANE CONVERSION FOR
Cs1Pt3(a) and Cs1Pt3(b) CATALYSTS.



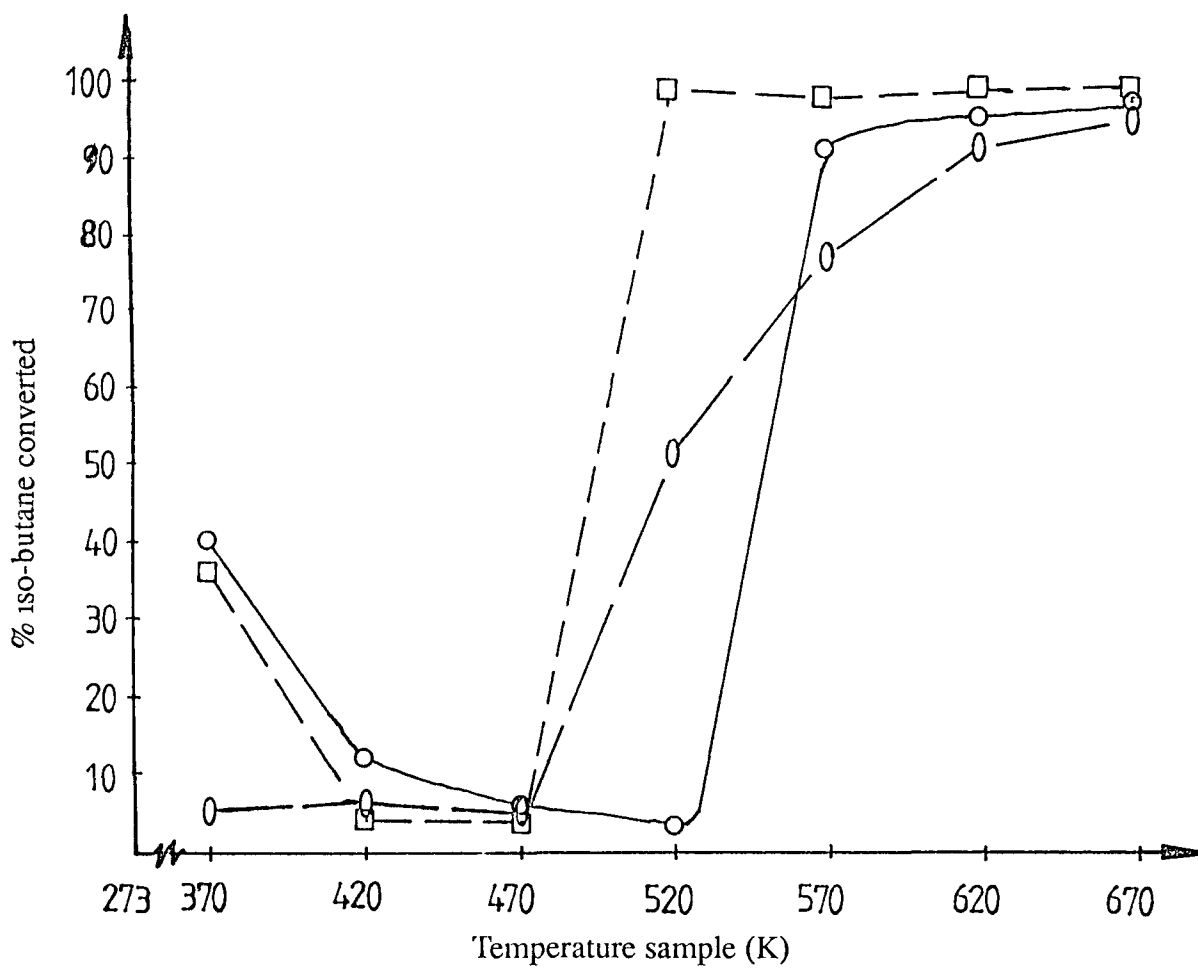
○ Cs1Pt3(a)
 ○ Cs1Pt3(b)

GRAPH 13
ACTIVITY MEASUREMENTS FOR ISO-BUTANE CONVERSION FOR
La1Pt3 and La3Pt3 CATALYSTS.



O La1Pt3
 0 La3Pt3

GRAPH 14
ACTIVITY MEASUREMENTS FOR ISO-BUTANE CONVERSION FOR
Pt3(A), Pt3(b), Pt3(c) CATALYSTS



- O Pt3(a)
- Pt(b)
- Pt(c)

Table 17 indicates repeat analyses conducted at the temperatures indicated during the normal determination of iso-butane reactivity for each catalyst indicated. It involved successive heat ups and cool downs, to specific temperatures at which the catalytic sample of interest was to be reassessed for iso-butane reactivity, e.g. catalyst Cs1Pt3(co), which had 94% iso-butane conversion at 520K after being cooled from 670K to 520K (after its preliminary testing at 670K).

From the results obtained, the percentage of iso-butane converted generally increased with increasing temperature for all samples. At 670K all samples were found to have a greater than 77% conversion for iso-butane.

In general, all samples studied increased their activity on cooling i.e. they gave lower conversions on initial testing at that temperature e.g. for catalyst Sn3Pt3(co) it had an activity of 10% at 520K on initial heating, but on cooling from 670K to 520K the activity increased to 80%. This may be due to a thermal equilibrium effect.

The cesium/platinum system (i.e. samples Cs1Pt3(a) and Cs1Pt3(b)) were found to be the most active for iso-butane reaction, relative to the rest of the catalysts studied. Cs1Pt3(a) was found to have a relatively high level of conversion of 61% at 370K, compared to the other samples studied which all had activities less than 24%. The catalyst sample Cs1Pt3(a), showed constant activity at all temperatures up to 570K where there was a sharp increase of activity to 95% conversion. At 670K it was found to be 99%.

However, using a fresh sample of the same catalytic material, the results were different, in that catalyst Cs1Pt3(b) had a lower activity over the entire temperature range than Cs1Pt3(a) e.g. at 470K the reactivity for catalyst Cs1Pt3(a) was 60%, whereas for Cs1Pt3(b) the reactivity for iso-butane at the same temperature was 7%.

Lanthanum was found previously to enhance the thermal stability of η -Al₂O₃. However lanthanum in conjunction with platinum (i.e. for La1Pt3) was found to be the least active of the catalysts studied for iso-butane conversion.

The effect of variation in the order of metal salt impregnation on the η -Al₂O₃ support material was also investigated. Thus three catalyst samples were prepared namely Cs1Pt3(a), Cs1Pt3(co) and Pt3Cs1.

Catalyst samples Cs1Pt3(co) and Pt3Cs1 were found to be less efficient than Cs1Pt3(a) in the conversion of iso-butane. However they were found to be of similar activity on comparison with an analysis on Cs1Pt3(b), except at 670K where Cs1Pt3(co) and Pt3Cs1 were less active.

At 670K catalyst Cs1Pt3(co) had an increased activity of 94% on comparison to Pt3Cs1 which was only 79% Catalyst Cs1Pt3(a) was found to be more active than either Cs1Pt3(co) or Pt3Cs1, hence the order of catalyst activity for iso-butane conversion is.

$$\text{Cs1Pt3(a)} > \text{Cs1Pt3(co)} > \text{Pt3Cs1}$$

On comparison of catalyst Cs1Pt3(a) for iso-butane conversion with catalyst Cs3Pt3, it was found that Cs1Pt3 had an increased ability to convert iso-butane This indicates that an increased loading of cesium reduced the ability of the catalyst sample to convert iso-butane.

4.3.2. CATALYST DEACTIVATION INVESTIGATIONS

Specific catalytic samples were calcined at 1370K for 12 hours and their activity assessed, to determine whether or not these catalysts retained their conversion properties for iso-butane. A platinum supported $\eta\text{-Al}_2\text{O}_3$ catalyst was used as the standard

The catalyst samples that were investigated were as follows

- (a) Catalyst Pt3(a); 3wt% Pt/ $\eta\text{-Al}_2\text{O}_3$
- (b) Catalyst Cs1Pt3 (a); 1wt%Cs, 3wt% Pt/ $\eta\text{-Al}_2\text{O}_3$
- (c) Catalyst Ce1Pt3, 1wt%Ce, 3wt%Pt/ $\eta\text{-Al}_2\text{O}_3$

The catalysts Pt3(a), Cs1Pt3(a) and Ce1Pt3 have been previously investigated for iso-butane conversion, a summary of the results of which are summarised in table 16

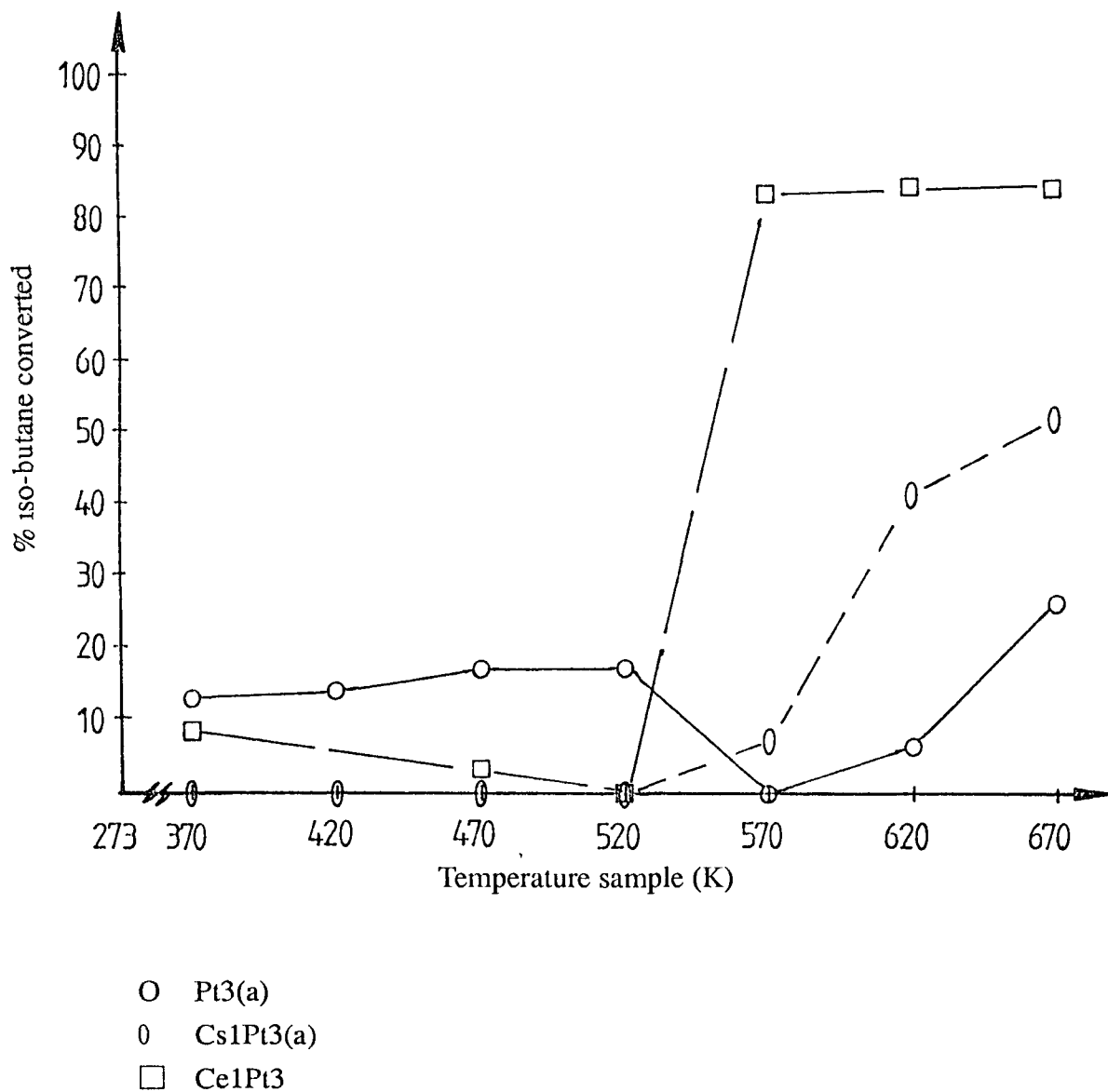
The above samples were placed in a porcelain crucible and then calcined in a muffle furnace at 1370K for 12 hours in air. Activity measurements were carried out as previously described

These catalytic samples were also cooled to various temperatures and their activities redetermined. Refer to table 18, for the activities obtained for each of the samples for iso-butane conversion The results are also represented graphically in Graph 15

TABLE 18
ACTIVITIES OF CALCINED SAMPLES:

CATALYST SAMPLE ANALYSED	%ISO-BUTANE REACTED						
	370K	420K	470K	520K	570K	620K	670K
Pt3(a)	13% COOLED FROM 470K 1%	14% —	17% COOLED FROM 570K 1%	17% —	0% COOLED FROM 670K 16%	6% —	26% —
Cs1Pt3(a)	0% COOLED FROM 470K 13%	0% —	0% COOLED FROM 570K 13%	0% —	7% COOLED FROM 670K 15%	41% —	52% —
Ce1Pt3	8% COOLED FROM 470K 78%	— —	3% COOLED FROM 570K 82%	0% —	83% COOLED FROM 670K 82%	84% —	84% —

GRAPH 15
ACTIVITY MEASUREMENTS FOR ISO-BUTANE CONVERSION FOR
Cs1Pt3(a), Ce1Pt3 AND Pt3(a) CATALYSTS.



4.4 DISCUSSION OF ACTIVITY MEASUREMENTS

It is apparent that generally in all the catalysts studied, the activity of each increased with increasing temperature e.g. La1Pt3 had an initial activity of 4% at 370K which gradually increased until a temperature of 620K had been achieved, where there was a significant increase in activity to 94% conversion

However at lower temperatures i.e. from 300K to 520K, there was no significant increases in catalytic activity until a specific temperature had been reached e.g. Pt3(a) had a maximum activity of 6% between 370K and 470K, until 520K where there was a sharp increase to 51% conversion.

The platinum/ η -Al₂O₃ system was found to be similar in activity relative to the other catalysts studied over the temperature range 370K to 670K. However at 670K it was found to have a relatively greater activity for iso-butane conversion than the majority of the catalysts studied e.g. Cs1Pt3(co) and Cs3Pt3 both had activities of 79% and 86% respectively compared to platinum/ η -Al₂O₃ which had an activity of 99%.

The rate of increase in catalytic activity with temperature for all catalysts was generally found to be dissimilar and varied significantly from catalyst to catalyst.

In the majority of the catalysts studied, their activities were generally found to be less than that of platinum/ η -Al₂O₃ e.g. La1Pt3 had an activity of 11% at 570K where as Pt/ η -Al₂O₃ had an activity of 98% at the same temperature. However Cs1Pt3 was found to be significantly more active for iso-butane conversion at the lower temperature range i.e. from 370K to 520K, relative to the other catalysts studied and in fact was the most active of the catalysts investigated.

Reproducibility of iso-butane conversion measurements for specific catalyst samples were also investigated, i.e. for Pt/ η -Al₂O₃ and Cs1Pt3

For platinum/ η -Al₂O₃, three fresh samples of were taken from the same bulk material and investigated. It was found that reproducibility could generally, only be attained between 570K and 670K and not at relatively lower temperatures, e.g. at 670K the three samples showed a maximum difference in iso-butane conversion properties of 4% where as at 370K the maximum difference was found to be as much as 35%. However for Cs1Pt3 no reproducibility could be attained over the entire temperature range relative to Pt/ η -Al₂O₃, for fresh samples of the same bulk material.

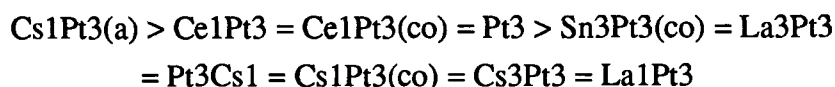
Investigations into the effect that catalyst preparation has on iso-butane conversion was studied using both the cesium/platinum and cerium/platinum systems. It was found in both cases, that the co-impregnation of the metal salts on $\eta\text{-Al}_2\text{O}_3$ resulted in an increase in catalytic activity relative to the step-impregnation of the salts, at the lower temperature ranges i.e. from 300K to 570K e.g. Ce1Pt3(co) had an activity of 92% at 520K compared to Ce1Pt3 which had an activity of 53%. However for the cesium/platinum system, the order in which the metal salts were step-impregnated also caused an effect on the resulting catalysts iso-butane conversion properties, e.g. for forward step impregnation i.e. Cs1Pt3(a), its activity was significantly increased relative to reverse step-impregnation i.e. Pt3Cs1 over the temperature range 370K to 670K, e.g. Pt3Cs1 had an activity of 8% at 470K compared to Cs1Pt3(a) which had an activity of 60%.

Thus in these cases, the order in which the metal salts were impregnated onto the support material can affect the relevant catalysts conversion properties for iso-butane, but the degree to which their conversion properties are affected varies between the different salts.

The results obtained for the catalysts La1Pt3 and La3Pt3 indicate that on increasing the wt% loading of lanthanum from a 1wt% to a 2wt% loading, caused an increase in catalytic activity over the entire temperature range e.g. La1Pt3 had an activity of 11% at 570K where as La3Pt3 had a conversion of 96%. However this difference in catalytic activity was less pronounced between 620K and 670K. Comparisons between Cs1Pt3(a) and Cs3Pt3 indicate the opposite effect for an increase in wt% loading of cesium for iso-butane conversion relative to lanthanum, e.g. Cs1Pt3(a) conversion properties significantly increased between 370K and 670K relative to Cs3Pt3. The catalyst Cs1Pt3(a) was found to have an activity of 61% compared to Cs3Pt3 which had an activity of 4% at 370K. From the above results it is evident that the effect of increasing the wt% loading of the secondary metal salt (i.e. for La and Cs) on the resulting catalyst for iso-butane conversion, varies significantly between these metals and is dependant on the metal salt used.

The activities of all the catalyst studied were redetermined after initial testing, at the higher temperature range, (refer to Table 18). It was found that generally, the activity of each catalyst varied significantly relative to its redetermined value at the same temperature. In some cases the catalyst activity, was found to increase on secondary testing e.g. Sn3Pt3(co) had an initial activity of 10% at 520K, but on secondary testing it rose to 80%. For Ce1Pt3 some of its repeat measurements were similar to its initial activity e.g. at 570K it was originally 70%, and on a repeat investigation it was also found to be 70% indicating some degree of catalyst activity retention.

Hence from the results obtained in the determination of each catalysts activity for iso-butane conversion, the order of increasing activity is as follows:



In order to determine whether or not the most active catalysts (i.e. Cs1Pt3(a) and Ce1Pt3) retained their activity for iso-butane conversion after prolonged calcination, the catalysts Cs1Pt3(a), and Ce1Pt3 were calcined at 1370K for 12 hours in air and their activities were then determined and compared to the catalyst Pt3(a), (which had also been treated in a similar fashion).

It was found that all three calcined catalysts had decreased in activity at all temperatures on comparison with the results with the uncalcined samples. Cs1Pt3(a) had an activity of 58% at 520K but after prolonged calcination it was found to be inactive for conversion of iso-butane at this temperature. It was also found to be inactive between 370K and 520K, whereas catalyst Pt3(a) and Ce1Pt3 showed some degree of activity.

Generally, for Cs1Pt3(a), Ce1Pt3 and Pt3(a), it was found that it was not until these catalysts had been heated to relatively higher temperatures that their relative activities increased significantly.

The cerium / platinum system i.e. Ce1Pt3 was found to have a significantly higher activity than the other two (i.e. Cs1Pt3(a) and Pt3(a)), in the temperature range 570K to 670K. However the same catalyst had a relatively lower activity than the calcined Pt3(a) catalyst, in the temperature range 370K and 520K.

With the catalyst Ce1Pt3, both the uncalcined and calcined samples showed similar conversion properties between 570K and 670K, however this was not the case for Cs1Pt3(a) and Pt3(a). Overall the results clearly indicate, that catalyst deactivation had occurred with Cs1Pt3(a), Ce1Pt3 and Pt3(a), but to varying extents.

It was also found that when each of the above catalysts had been cooled and retested at certain temperatures they were found to have increased their activity; e.g. Ce1Pt3 during initial investigation was found to be 8% active at 370K but when it had been cooled from 470K to 370K and retested, its activity had increased to 78%. This phenomenon could possibly be attributed to coking on the catalyst at the lower temperatures, but after heating to higher temperatures this coke deposit was possibly combusted, so that when the catalyst was retested the activity was found to have increased.

Therefore from the results obtained Ce1Pt3 retained some of its activity relative to its uncalcined counter-part for iso-butane conversion even after prolonged calcination at 1370K and to a greater extent relative to the other catalysts studied, i.e. Cs1Pt3(a) and Pt3(a). Hence, not only is cesium able to impart a relatively high thermal stabilising effect on η -Al₂O₃, it was also found to be one of the most active co-catalysts with platinum for iso-butane conversion even after prolonged calcination at 1370K

The order of catalyst activity for the conversion of iso-butane after prolonged calcination at 1370K was found to be as follows



For a summary of the results obtained during the catalytic activity investigations refer to Table 19.

Cerium has been used in previous studies by other researchers (55, 56) for hydrocarbon oxidation studies in association with noble metals. It has also been previously found to stabilise Al₂O₃ against thermally induced surface area loss and to increase the dispersion of the noble metals used (56, 57, 58, 59)

Cerium oxide has been used as a major base metal additive for commercial three-way catalysts, used for the simultaneous conversion of carbon monoxide, hydrocarbons, and nitrogen oxides (55).

Summers and Ausen (60), have observed that the steady state CO oxidation activity of a Pt/Al₂O₃ catalyst was enhanced upon the addition of small quantities of cerium i.e. 0.6-1.3 wt%. They found that any further increases in the cerium content of the catalyst deteriorated the CO oxidation activity.

From the investigations conducted into the effect of increasing the wt% loading of cerium from 1wt% to 3wt% for iso-butane conversion, there was also a decrease in catalytic activity. However at a relatively lower wt%, loading i.e. 1wt% a relatively higher catalyst activity was observed

Le Normand et al (56), also found in their studies, the same effect reported by Summers and Ausen (60) for low and high cerium loadings on γ -Al₂O₃ supported palladium catalyst

Drozдов et al (61), investigated the effect of cerium, lanthanum and zirconium oxides on the thermal stability of Pt/Al₂O₃ catalysts. They found that the platinum in the

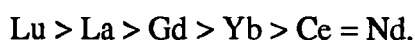
catalysts had a higher degree of dispersion and a lower tendency to aggregate, relative to the unmodified Pt/Al₂O₃ catalyst, if the above oxides were incorporated. In fact the platinum dispersion in a sample with added cerium was significantly higher than with any of the other metal oxides present, and the order of increasing thermal stabilisation effect was found to be (61),



The catalytic activity for complete oxidation of methane over the cerium, platinum/Al₂O₃ catalyst was retained for longer periods of time than the unmodified Pt/Al₂O₃ catalyst and for the catalyst incorporating lanthanum or zirconium. The same effect due to cerium and lanthanum incorporation was seen in the complete oxidation of butane. While the addition of both cerium and lanthanum to the Pt/ η -Al₂O₃ catalyst significantly increased the platinum dispersion, the thermal stability of the catalyst and the activity for oxidation of butane, cerium addition however was found to be more effective. This agrees with the present work, where cerium addition was found to be more beneficial for catalytic combustion of iso-butane than lanthanum and that both the cerium and lanthanum additions increased the activity of the Pt/ η -Al₂O₃ catalyst. Drozdov et al (62) employed catalysts containing 2.53wt% loadings of platinum and the additives were introduced to give a 5:1 atomic ratio of the metal to platinum. In this study, a 3wt% loading of platinum was used and the most effective ratio of cerium to platinum for iso-butane conversion was 0.5:1.

Galas and Wrzyszczyk (63) also investigated the effect of rare-earth elements (namely, La, Ce, Nd, Gd, Yb and Lu oxides) on the platinum dispersion in platinum/ γ -Al₂O₃ catalysts. In their studies the atomic ratio of Pt oxide was 1:1. They found in their studies that the platinum in the catalysts sinter at 1020K yielding catalysts of small platinum surface area. However on the introduction of the rare earth oxides, large platinum surface areas were obtained even after calcination at 1020K for 5 hours.

In further work, Galas and Wrzyszczyk (64) studied the effect of the rare earth oxides on the activity of Pt/ γ -Al₂O₃ catalysts for the complete oxidation of iso-butene. The catalyst they employed contained a 0.5wt% Pt and a 1:1 atomic ratio of Pt:rare earth oxide. They found, that the activity of Pt/ γ -Al₂O₃ modified by rare earth oxides and calcined at temperatures up to 1020K were greater than that of the unmodified catalysts. The activity decreased in the following order (64),



The above result is in contrast to the results obtained in the present work and also with those obtained by Drozdov et al (62), in that lanthanum addition has a greater effect for increased activity than cerium addition. Note however that the ratio of platinum to additive was different (Drozdov et al (62) used an atomic ration of 5:1 for additive Pt, Galas and Wrzyszc (64) used a ratio of 1:1 and this present work used a ratio of 0.5:1).

Gelsthrope et al (65) studied the effect of lanthanum and cerium on the catalytic activity of Ni/Al₂O₃ catalysts, for the methanation of carbon monoxide. They found that both lanthanum and cerium additions resulted in a slight increase in activity. This increase in activity was explained by the fact that the Ni dispersion had increased with cerium or lanthanum addition.

Therefore, from the present work and other studies, the addition of metals such as Ce, La, Cs, and zirconium have significant effects on the activity and thermal properties of the total oxidation catalysts. It was found that there is general agreement with the fact that cerium is the most effective agent for the stabilisation of the support and to increase the catalyst's activity. Also, it helps to maintain the activity of the catalyst even after treatment at relatively high temperatures. The reason for cerium stabilisation is not completely understood. Possible explanations are as follows.

- (a) the prevention of phase transformations in Al₂O₃,
- (b) increased platinum dispersions, and
- (c) the prevention of platinum sintering at high temperatures

Refer to Table 19 for a summary of the results obtained in this area of investigation (combining also the results obtained in Chapter 2)

TABLE 19
INTERPRETATION OF ACTIVITY MEASUREMENTS
(Employing steady state results)

CATALYST SAMPLE	LOWEST TEMPERATURE AT WHICH % ISO-BUTANE CONVERTED > 50%	ORDER OF ACTIVITY	ORDER OF IMPORTANCE FOR THERMAL STABILITY AFTER 42 HRS AT 1270K
			ORDER OF STABILISATION of η -Al ₂ O ₃
Pt3(a)	570K	3	Not Applicable
Pt3(b) and Pt3(c)	520K	2	Not Applicable
La1Pt3	620K	4	1
La3Pt3	570K	3	5
Cs1Pt3(a)	370K	1	3 VERY SIMILAR TO CERIUM IN THERMAL STABIL- ISING ABILITY FOR η -Al ₂ O ₃
Cs1Pt3(b)	570K	3	3
Cs1Pt3(co)	570K	3	3
Pt3Cs1	570K	3	3
Cs3Pt3	620K	4	4
Ce1Pt3	520K	2	2
Ce1Pt3(co)	520K	2	2
Sn3Pt3(co)	570K	3	Not Applicable

CHAPTER 5

CONCLUSION

Alumina is extensively used as a support material for oxidation catalysts, due to its inherent characteristics of inertness, chemical stability, large surface area, control of pore volumes and pore size distributions, acidic and basic properties. However several phases of alumina exist and irreversible phase transformations from the relatively high surface area phases to the relatively low surface area phases can occur at high temperatures. The addition of several metal cations namely, Ba^{2+} , Ca^{2+} , Ce^{3+} , Cs^+ , La^{3+} and Zr^{4+} were investigated in an effort to stabilise the high surface area alumina ($\eta\text{-Al}_2\text{O}_3$) and prevent transformation to low surface area phases ($\alpha\text{-Al}_2\text{O}_3$). The order of effectiveness as phase transfer inhibitors for the above cations was found to be as follows:

$$\text{La}^{3+} > \text{Ce}^{3+} = \text{Cs}^+ > \text{Zr}^{4+} = \text{Ba}^{2+} = \text{Ca}^{2+}$$

While the addition of the cations decreased the initial surface area relative to the untreated $\eta\text{-Al}_2\text{O}_3$, the rate of decrease in surface area with time was less in all cases than the untreated alumina.

Small additions (1wt%) of La, Ce and Cs were found to be the more effective inhibitors of the transformation reaction of $\eta\text{-}$ to higher or $\alpha\text{-Al}_2\text{O}_3$, with La being the most effective. This stabilisation by La is in agreement with previous work quoted for $\gamma\text{-Al}_2\text{O}_3$ transitions.

The order of metal cation stabilisation generally agrees with the order of atomic radii and metal ion charge. The concentration of the metal salts of the above cations also affected the stabilisation processes, in most cases a 1wt% loading was found to be the optimum.

A range of $\text{Pt}/\eta\text{-Al}_2\text{O}_3$ samples were investigated in an effort to determine the relationship between platinum dispersion and platinum metal loading. Up to a 2wt% Pt loading the dispersion of platinum increased, reaching its maximum dispersion of 46% for a 3wt% loading, and thereafter the dispersion decreased. Therefore a 3wt% loading of platinum was chosen for activity measurements.

The effect of the metal stabilising cations on the activity of $\text{Pt}/\eta\text{-Al}_2\text{O}_3$ catalysts was investigated. The reaction chosen for catalyst activity measurements was the oxidation of iso-butane, and the rate of loss of iso-butane was determined.

The addition of the metal salts $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and CsCl at 1wt% loadings to $\text{Pt}/\eta\text{-Al}_2\text{O}_3$ increased the activity for iso-butane conversion relative to $\text{Pt}/\eta\text{-Al}_2\text{O}_3$, while the addition of the metal salts $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ and $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ had little or no effect on increasing the activity of the $\text{Pt}/\eta\text{-Al}_2\text{O}_3$ catalyst relative to the unmodified sample

The effect of step and co-impregnation of the metal salts $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and CsCl with platinum (supported on $\eta\text{-Al}_2\text{O}_3$) for iso-butane conversion were also investigated. The results indicate that the relative activities between step and co-impregnated catalyst samples vary between the salts. Generally the co-impregnation of 1wt% cesium with platinum indicated a reduction in activity relative to its step impregnated counterpart over the entire temperature range studied, whereas the co-impregnation of 1wt% cesium with platinum showed similar catalytic activities for iso-butane conversion, at specific temperatures

From all the catalysts studied, the order of initial activity for iso-butane conversion can be summarised as follows,

$$\text{Cs1Pt3(a)} > \text{Ce1Pt3} = \text{Ce1Pt3(co)} = \text{Pt}/\eta\text{-Al}_2\text{O}_3 > \text{Sn3Pt3(co)} = \text{La3Pt3} \\ = \text{Pt3Cs1} = \text{Cs1Pt3(co)} = \text{Cs3Pt3} = \text{La1Pt3}$$

With the sample Cs1Pt3(a) showing a maximum increase in catalytic activity of 55% over the $\text{Pt}/\eta\text{-Al}_2\text{O}_3$ unmodified catalyst.

High temperature calcination at 1370K for 12 hours, decreased the activity of $\text{Pt}/\eta\text{-Al}_2\text{O}_3$, by as much as 91%, however, the activity of cerium treated $\text{Pt}/\eta\text{-Al}_2\text{O}_3$ was only lowered in activity by a maximum of 52%. Therefore, while Ce and La are among the most effective metal salts studied for the thermal stabilisation of $\eta\text{-Al}_2\text{O}_3$, the addition of Ce is more effective than La addition for stabilisation of the catalyst activity at relatively high temperatures for iso-butane conversion

REFERENCES

- 1 Bylinsky, G , Fortune 56, 56 (1985)
- 2 Atkins, P.W., Physical Chemistry, Oxford Student Addition, Oxford, 2nd Edition (1984)
- 3 Haensel, V , and Burwell, R.L., Scien. Amer. 225(6), 46 (1971).
- 4 Prasad, Kennedy and Ruckenstein, Catal. Rev Scien. and Eng 26(1), 2 (1984)
- 5 Freel, J , J Catal. 25, 149 (1972)
- 6 Bond, G., Heterogeneous Catalysis, Clarendon Press, Oxford (1987)
- 7 Blazowski, W S and Walsh, D.E., Comb Scien. and Tech. 10 233 (1975)
8. Foulton, J.W , Chem. Eng 93 (13) 59 (1986).
- 9 Hegedus, L L and McCabe, R W. in Delmon, B , and Fromert, G F , (Eds), Catalyst Deactivation, Studies in Surface Science and Catalysis, Vol. 6, Elsevier, Amersterdam, 471 (1980).
- 10 Wynblatt, P in Bourdon, J , (Ed), Growth and Properties of Metal Clusters, Studies in Surface Science and Catalysis, Vol. 4, Elsevier, Amsterdam, 15(1980).
- 11 Leiske, H., Sárkány, A , and Volter, J., Appl Catal., 30 69 (1987)
- 12 Cullis, C F , and Willatt, B M , J Catal 86 187 (1984).
- 13 Burtin, P , Brunelle, J P., Pijolat, M., and Soustelle, M., Appl Catal 34 225 (1987)
- 14 Geus, J W in Poncelet, G , Grange, P. and Jacobs, P A , (Eds), Preparation of Catalysts III, Studies in Surface Science and Catalysis, Vol 3, Elsevier, Amsterdam, 1 (1983)
- 15 Gitzen, W H , Alumina as a Ceramic Material, The American Ceramic Society, Inc , Columbus (1970).

16. Knözinger, H. in Imelik, B., Naccache, C., Coudurier, G., Ben Taarit, V., Vedrine, J.C., (Eds.), *Catalysis by Acids and Bases, Studies in Surface Science and Catalysis*, Vol. 20, Elsevier, Amsterdam 111 (1985).
17. Trimm, D.L. and Staruslaus, A., *Appl. Catal.*, 21 215 (1986).
18. Burtin, P., Brunelle, J.P., Pijolat, M. and Soustelle, M., *Appl. Catal.*, 34 239 (1987).
19. Matsuda, S., Kato, A., Mizumoto, M. and Yamashita, *Proceedings of the Eighth International Congress on Catalysis, Berlin, 1983, Dechema, Frankfurt am Main* 4 879 (1984).
20. Nortier, P. and Soustelle, M., in Crucq, A. and Frennet, A., (Eds.), *Catalysis and Automotive Pollution Control, Studies in Surface Science and Catalysis*, Vol. 30, Elsevier, Amsterdam, 275 (1987).
21. Shaw, J.D., *Introduction to Colloid and Surface Chemistry*, Butterworths, London 3rd Edition (1985).
22. Finlayson, O. and Curley, J., Private Communication (1989).
23. Lippens, B.C., de Boer, J.H., *Acta. Cryst.* 17, 1312 (1964).
24. Schaper, H., Doesburg, E.B.M. and Van Reijen, L.J., *Appl. Catal.* 7 211 (1983).
25. Young, D.J., Udaja, P. and Trimm, D.L. in Delmon, B. and Froment, G.F., (Eds.), *Catalyst Deactivation, Studies in Surface Science and Catalysis*, Vol. 6, Elsevier, Amsterdam, 331 (1980).
26. Oudet, F., Bordes E., Courtine, P., Maxant, G., Lambert, C. and Guerlet, J.P. in Crucq, A. and Frennet, A., (Eds.), *Catalysis and Automotive Pollution Control, Studies in Surface Science and Catalysis*, Vol. 30, Elsevier, Amsterdam, 313 (1987).
27. Oudet, F., Courtine, P. and Vejax, A., *J. Catal.*, 114 112 (1988).
28. Greenwood, N.N. and Earnshaw, A. *Chemistry of the Elements*, Pergamon Press, Oxford 275 (1986).

- 29 Wells, A F. Structural Inorganic Chemistry, Oxford Press, London (1962)
- 30 Soled, S , J. Catal , 81 252 (1983).
- 31 Shustorovich, E , Acc Chem Res 21 5 (1988)
32. Gross, J M. and Wiseall, B , Principles of Physical Chemistry, McDonald and Evans Hand Book Series, McDonald and Evans Ltd , Plymouth (1979)
- 33 Scholten, J J F , Pijpes, A P. and Hustings, A.M L., Catal. Rev. Scien Eng , 27 (1), 151 (1985).
- 34 Anderson, J.R , Structure of Metallic Catalysts, Academic Press, London (1975)
- 35 Freel, J , J Catal 25, 139 (1972).
- 36 Dorling, T A., Burlace, C J. and Moss, R L , J. Catal , 12 207 (1968)
- 37 Welson, G R and Hall, W K , J. Catal 17 190 (1986)
- 38 Le Bail, A. and Louer D., J Appl. Crystallog 11 50 (1978)
39. Schlatter, J.C Mater Sci. Res 10 141 (1975)
- 40 Huizinga, T , Grondelle, J.V. and Pruis, R Appl Catal. 10 199 (1984)
- 41 Duivervoorden, F B M., Kip, B.J., Koningsberger, D C. and Prins, R , J. Phys Colloq Vol. 1, 227 (1986).
42. Klug, H P and Alexander, L.E , X-Ray Diffraction Procedures, Wiley, New York (1954).
- 43 Dorling, T A., Lynch, B.W J. and Moss, R.L.J , J. Catal 20 190 (1971).
- 44 Golodets, G I , (Ed), Heterogeneous Catalytic Reactions Involving Molecular Oxygen, Studies in Surface Science and Catalysis, Vol 15, Elsevier, Amsterdam, 280 (1983)
- 45 Trimm D.L., Appl. Catal 7 249 (1983)

- 46 Yu-Yao, Y Y., J Catal. 28 139 (1973)
47. Yu-Yao, Y Y., J Catal 36 266 (1975)
48. Golodets, G I. (Ed), Heterogeneous Catalytic Reactions Involving Molecular Oxygen, Studies in Surface Science and Catalysis, Vol 15 , Elsevier, Amsterdam, 437 (1983)
- 49 Kern-Tálas, E , Hegedus, M., Gobolos, S., Szedlacsek, P. and Margitfalvi, J in Delmon, B , Grange, P , Jacobs, P.A. and Poncelet, G. (Eds.), Preparation of Catalysts IV, Studies in Surface Science and Catalysis, Vol. 31, Elsevier, Amsterdam, 689 (1987).
50. Schay, L , Matusek, K. and Gucci, L , Appl. Catal. 10 173 (1984)
- 51 Baronetti, G T , de-Miguel, S R , Scelza, O A., Fritzler, M A. and Castro, A A , Appl Catal 19 77 (1985).
- 52 Lieske, H , Sárkány, A and Volter, J Appl. Catal 30 69 (1987).
- 53 Barbier, J , Marecot, P., Martin, N , Ellassal, L. and Maurel, R. in Delmon, B and Froment, G F , (Eds), Catalyst Deactivation Studies in Surface Science and Catalysis, Vol 6, Elsevier, Amsterdam, 53 (1980).
- 54 Baronetti, G T., de-Miguel, S R , Scelza, O A and Castro, A A , Appl. Catal , 24 109 (1986)
- 55 Se, H OH and Eickel, C C , J Catal 112 543 (1988)
- 56 Le Normand, F , Hilaire, L , Kılı, K., Krill, G. and Maire, G., J Phys. Chem 92 2561 (1988)
- 57 Hindin, S G, Englehard Mineral and Chemical Company, U S Patent 3, 870, 455 (1973)
- 58 Maselli, J , Ernest, M. and Graham, J.W.R , Grace Company, German Patent 2,362, 601 (1974).
- 59 Kummer, J T., Yao, Y Y and McKee, D S.A.E. Paper No. 760143 (1976)

- 60 Summers, J.C. and Ausen, S A J., J Catal 58 131 (1979).
- 61 Drozdov, V A., Tsyrl'mikov, P G , Popovski, V V., Pankrat'ev, D. Yu., Davydor, A A and Moroz, E M., Kinet and Katal , 27 3, 623 (1986)
- 62 Drozdov, V.A Tsyrl'nikov, P.G., Pestryakov, A.N., Davydov, A A and Popovski, V V , Kinet and Katal , 29, 2, 420 (1988)
- 63 Galas, J.W and Wrzyszc, J React. Kinet. Catal. Lett., 19 (1), 23 (1982)
- 64 Galas, J W. and Wrzyszc, J. React. Kinet Catal Lett , 19 (1), 27. (1982)
65. Gelsthorpe, R.M , Kam Bun Mok and Ross, R H J , J. Molec. Catal , 25 253 (1984)

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PUBLICATION

THERMAL STABILISATION OF ALUMINA FIBRES

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ABSTRACT

As an industrially important catalytic support material, a form of fibrous alumina, η - Al_2O_3 , was investigated for its thermal stability. Cation addition was used as a means of improving the stability at elevated temperatures. The following cations were investigated: Ba^{2+} , Ca^{2+} , Ce^{3+} , Cs^+ , La^{3+} , Zr^{4+} ; the order of effectiveness as phase transfer inhibitors was found to be

$$\text{La}^{3+} > \text{Ce}^{3+} = \text{Cs}^+ > \text{Zr}^{4+} = \text{Ba}^{2+} = \text{Ca}^{2+}.$$

These results are compared to known methods of γ - Al_2O_3 thermal stabilisation.

Introduction

The catalytic combustion of hydrocarbons has received much attention recently, for example in automotive control systems, energy recovery systems and flameless heaters (Trimm 1983). An advantage of catalytic oxidation is that NO_x is not generally produced in the products. These oxidation catalysts usually consist of an active metal (Pt, Pd, Rh) on an inert support material (alumina, silica). Hydrocarbon oxidation, such as butane oxidation



is an exothermic reaction and the catalyst must be stable to high temperatures. In some applications, the temperature of the catalyst may rise to 1270K or greater during use.

Alumina is a good support material for oxidation catalysts owing to its inherent characteristics, i.e. inertness, chemical stability, large surface area, control of pore volumes and pore size distributions, acidic and basic properties (Knozinger 1985). However, the thermal instability of alumina is a problem at high temperatures.

Alumina exists in many phases— γ , η , θ , δ , α (Gitzen 1970)—and transformations can occur between the phases by successive dehydroxylation by removal of water at high temperatures. Transformation from γ - Al_2O_3 to α - Al_2O_3 is accompanied by a decrease in surface area and a decrease in pore volume. Such transformations in a catalyst material can lead to entrapment of the active metal and so loss in catalytic activity. Factors such as particle size, heating rate, presence of impurities and ambient pressure have been known to affect the phase

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transformations (Gitzen 1970). The effect of cation additives as dopants has been investigated by several researchers in an effort to stabilise the $\gamma\text{-Al}_2\text{O}_3$, minimise the transformation to low surface area aluminas, and understand the mechanism of the transformation (Burtin *et al.* 1987a; Matsuda *et al.* 1984; Nortier and Soustelle 1987).

In this study, the thermal stability of an alumina fibre is investigated by monitoring changes in surface area with heat treatment at 1270K. Cation dopants that have been shown in the literature to stabilise $\gamma\text{-Al}_2\text{O}_3$ powders were added to the fibrous $\eta\text{-Al}_2\text{O}_3$ material and the surface areas monitored with calcination. The cations chosen were Ba^{2+} , Ca^{2+} , Ce^{3+} , Cs^+ , La^{3+} and Zr^{4+} .

Experimental

Preparation of alumina

The form of alumina fibre used was Saffil, manufactured by ICI (Runcorn). The composition of this fibre according to the manufacturers is $>95\%$ Al_2O_3 , $<5\%$ SiO_2 with less than 2210 p.p.m. of the following impurities: Fe, Cr, Ni, Na, Mg, Ca and Cl. The alumina in saffil is quoted as being in the η -form. Typical fibre characteristics are as follows: surface areas $150\text{m}^2\text{g}^{-1}$, mean fibre diameter $3\mu\text{m}$, pore volume $0.2\text{cm}^3\text{g}^{-1}$.

The fibre material was ground into a powder using a mortar and pestle and various cations were introduced in either 1 or 3wt% loadings. An excess of the solution of the salts prepared in methanol was added to the alumina powder. The salts used were $\text{BaCl}_2\cdot 6\text{H}_2\text{O}$, $\text{CaCl}_2\cdot 6\text{H}_2\text{O}$, $\text{Ce}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$, CsCl , $\text{LaCl}_3\cdot 7\text{H}_2\text{O}$ and $\text{ZrOCl}_2\cdot 8\text{H}_2\text{O}$. The samples were then dried using a rotary evaporator and finally air-dried in an oven at 70°C overnight.

Calcination

All samples were calcined in air for various intervals of time in a muffle furnace at 1270K. Approximately 1g of sample contained in a porcelain crucible was heated in the furnace from room temperature at a rate of 250K h^{-1} and the samples were fired at 1270K for lengths of time varying from 1 to 42 hours. After firing, the samples were cooled to room temperature before testing.

Surface area measurement

Surface area measurements were carried out using the Micromeritics Chemisorb 2700 instrument. Each sample was outgassed in Ar at 370K for half an hour followed by 520K for one and a half hours prior to testing.

Surface areas were determined by N_2 adsorption at liquid N_2 temperature from a 30% $\text{N}_2/70\%$ He mixture, i.e. single point determination. Quantities of N_2 adsorbed and desorbed were monitored using the thermal conductivity detector in the instrument. After adsorption, each sample was heated to room temperature to observe the desorption peak. Each sample was subjected to a minimum of three adsorption/desorption cycles. Differences of less than 6% were observed between adsorption and desorption peaks and successive adsorption peaks agreed within 3%.

All adsorption/desorption measurements were corrected to STP.

Results

The results are summarised in Table 1, giving the changes in surface area determined with both 1 and 3% additions of various cations. It is clear that the surface area of the untreated alumina sample decreases rapidly over the initial 5-hour heat treatment and the rate of decrease is still significant after 42 hours. A 22% decrease in surface area occurred over the first 5 hours, while over 42 hours a total decrease of 36% was observed—this corresponds to a final surface area of $113\text{m}^2\text{g}^{-1}$ compared to the initial reading of $178\text{m}^2\text{g}^{-1}$.

TABLE 1—Surface area measurements

Sample	Initial SA* m^2g^{-1}	Rate SA loss***	Rate SA loss***	Rate SA loss***
		1–5h $\text{m}^2\text{g}^{-1}\text{h}^{-1}$	5–20h $\text{m}^2\text{g}^{-1}\text{h}^{-1}$	20–42h $\text{m}^2\text{g}^{-1}\text{h}^{-1}$
Al_2O_3	161**	5.52	0.65	0.76
1% La	130	0.73	0.05	0.00
1% Ce	126	1.45	0.50	0.00
1% Cs	119	1.72	0.18	0.06
1% Zr	148	1.69	1.83	NA [⊕]
1% Ba	150	3.21	0.40	0.81
1% Ca	149	4.61	0.50	1.02
3% La	128	0.46	0.30	1.08
3% Ce	149	4.93	0.67	0.22
3% Cs	132	0.93	0.56	0.55
3% Zr	141	1.60	0.95	0.00
3% Ba	130	1.64	0.81	0.52
3% Ca	114	4.23	0.63	NA [⊕]

* Initial surface area after 1h of heating to 1270K

** The surface area of alumina prior to heating is $178\text{m}^2\text{g}^{-1}$, which gives a decrease in surface area over the first 5h of heating of $7.80\text{m}^2\text{g}^{-1}\text{h}^{-1}$

*** Rate loss of surface area between 1h and 5h of heating, between 5h and 20h or 20h to 42h of heating at 1270K

⊕ Results not available

All of the samples tested suffered some loss in surface area with heating and the loss was most significant over the first 5–7 hours of heating (see Table 1). The rate of surface area loss decreases sharply in all cases after this initial 5–7 hour period with La, Cs and Ce samples showing little change after this time.

All of the doped alumina samples have a lower surface area than the untreated alumina after equivalent heat treatment up to 20 hours. After that period of heating, the aluminas with 1% La, 1% Ce and 3% Ce have surface areas of equal or greater magnitude than alumina. Clearly the presence of the cation initially decreases the surface area of the alumina. The rate of loss of surface areas is less for all of the doped aluminas compared to the untreated alumina sample, indicating some thermal stabilisation of the alumina by the addition of dopant.

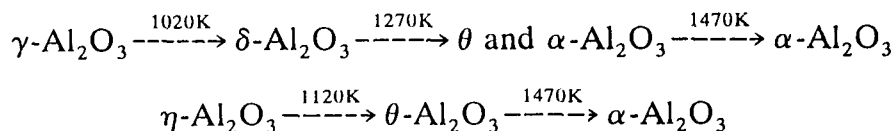
The rate of decrease in surface area varied depending on the dopant material. Generally the rate of decrease was greatest over the first 5 hours and decreased up to 42 hours. In the case of 1% Ca, 3% La and 1% Ba additions the rate of surface area loss increased with prolonged heating to 42 hours, while 3% Cs addition resulted in a constant rate of surface area loss over the complete time range.

After 20 hours at 1270K, a 23% loss in surface area was observed for 3% Ca and 1% Zr samples and these were not calcined any further. From Table 1 it is clear that 1% additions of La, Cs and Ce greatly reduce the rate of loss of surface area, giving the final surface areas of $128\text{m}^2\text{g}^{-1}$, $108\text{m}^2\text{g}^{-1}$ and $115\text{m}^2\text{g}^{-1}$ respectively after 42 hours of calcination. Untreated alumina had a final surface area of $113\text{m}^2\text{g}^{-1}$ after 42 hours of calcination.

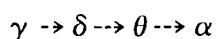
(25)

Discussion

Thermal dehydration of alumina to stable α - Al_2O_3 results in the formation of the following transitional aluminas at the temperatures indicated (Lippens and de Boer 1964)



The results presented here do not suggest that α - Al_2O_3 has been formed and it is more likely to be the transitional θ - Al_2O_3 phase that is present at the temperatures used. Detailed X-ray analysis by Burtin *et al* (1987a) showed that the decrease in surface area of γ - Al_2O_3 corresponds to the sequence given above



The θ - and α - Al_2O_3 phases are of markedly lower surface areas than γ -, η - or δ - Al_2O_3 (Gitzen 1970). Gitzen (1970) quotes results of Wakao and Hibino from 1962 which suggest that the transition temperature of γ - to α - Al_2O_3 could be reduced to up to 250K by addition of metal oxides in quantities between 1% and 10%. They suggest that the larger the metal ion of the oxide, and the higher the vapour pressure of the oxide at the transformation temperature of the alumina, the greater the reduction on the transition temperature.

These results show that the initial surface area (after one hour of calcination at 1273K) of doped aluminas is less than the undoped alumina sample. Schaper *et al*. (1983) showed that even heating to 723K causes a gradual decrease in surface area with increasing lanthanum oxide content, the greatest stability being achieved at 1mol% La_2O_3 addition. From the results in this paper, addition of small amounts of dopant is more effective as a long-term thermal stabiliser than larger amounts, i.e. the rate of decrease in surface area for each dopant is less in the case of 1% additions than 3% additions after 5 hours of heat treatment (except for Zr). However, the opposite effect is seen for the initial 5-hour heating time, i.e. 3% additions result in a slower decrease in surface area than 1% additions (except for Ce).

A study of Ni on γ - Al_2O_3 (Young *et al* 1980) shows that Ni can delay the transformation to α - Al_2O_3 at 1220K for 16 hours, but then a rapid transformation occurs. An explanation is advanced where the delay occurs until the diffusing Ni arrives at grain boundaries, nucleation sites are formed at the grain boundaries and a rapid transformation to the α -phase then occurs.

The loss of initial surface area after 1 hour of calcination from these results was independent of the concentration of the dopant added. The addition of 3% Ce and 3% Cs decreased the surface area less than 1% additions of the same cations, while the opposite was true for Ba^{2+} , Ca^{2+} and Zr^{4+} ions. There was no significant difference between 1% and 3% La additions in initial surface area.

Cations have been classified as accelerators or inhibitors for the thermal transformation into α - Al_2O_3 . Lanthanum has been classified as an inhibitor

(Matsuda *et al* 1984, Oudet *et al* 1987, Oudet *et al* 1988, Schaper *et al* 1983) In a survey of cation additives by Burtin *et al* (1987a), In^{3+} , Ga^{3+} , Al^{3+} and Mg^{2+} were found to be accelerators for the phase transformation while Zr^{4+} , Ca^{2+} , Th^{4+} and La^{3+} were inhibitors. Nortier and Soustelle (1987) suggest the same ions as inhibiting additives (Zr^{4+} , Ca^{2+} , Th^{4+} and La^{3+}) and suggest that the larger the cation and the higher the cation charge, the more effective it will be for alumina stabilisation.

The present results indicate the order of inhibiting strength of the cations as follows

	$\text{La}^{3+} > \text{Ce}^{3+} = \text{Cs}^+ > \text{Zr}^{4+} = \text{Ba}^{2+} = \text{Ca}^{2+}$					
Ionic radii	1.15	1.01	1.69	0.80	1.35	0.99 Å
Valency	+3	+3	+1	+4	+2	+2

Ionic radii and valency, as given above, indicate that these results are in general agreement with Nortier and Soustelle (1987), that the higher the valency and the ionic radius the greater the stabilising effect.

Calcination of $\gamma\text{-Al}_2\text{O}_3$ above 1270K converts it irreversibly to the more stable α -form ($\Delta H = -20\text{kJ mol}^{-1}$) (Greenwood and Earnshaw 1986). Several mechanisms of the transformation of transitional aluminas to α -phase have been proposed and discussed. α -Alumina has a rhombohedral crystal structure comprising a hexagonal close-packed array of oxide ions (Greenwood and Earnshaw 1986). γ -Alumina consists of a defect spinel structure (tetragonal crystal system) with not all of the cation sites occupied, of general formula $\text{Al}_{8/3}\square_{1/3}\text{O}_4$ (Wells 1962). θ -Alumina occupies an intermediate structural transition between the spinel lattice with cubic oxygen arrangement of $\gamma\text{-Al}_2\text{O}_3$ and the corundum lattice with the dense hexagonal oxygen arrangement and the aluminium atoms exclusively in the octahedral positions of $\alpha\text{-Al}_2\text{O}_3$ (Gitzen 1970). $\eta\text{-Al}_2\text{O}_3$ is a cubic spinel structure of general formula $\text{Al}_8[\text{A}_{40/3}\square_{8/3}]\text{O}_{32}$ with the vacancies on octahedral sites.

Oudet *et al* (1988) propose that the addition of a perovskite-type oxide such as LaAlO_3 to the alumina surface inhibits the formation of low surface area alumina by blocking the corundum nucleation sites. The LaAlO_3 , they suggest, is held at corners and/or edges, i.e. high free coordination sites, and these sites are the reactive areas that act as nucleation sites for the transformation reaction. The presence of lanthanum aluminate was confirmed by X-ray diffraction measurements on La-stabilised alumina by Schaper *et al* (1983).

Matsuda *et al* (1984) give evidence for $\text{La-}\beta\text{-Al}_2\text{O}_3$ formation. While evidence for an MgAl_2O_4 phase is given by Burtin *et al* (1987a) for Mg-impregnated alumina, they found no evidence for lanthanum aluminate formation in equivalent La-impregnated alumina.

The general formula for $\gamma\text{-Al}_2\text{O}_3$ from Wells (1962) was modified by Soled (1983) to $\text{Al}_{2.5}\square_{0.5}\text{O}_{3.5}(\text{OH})_{0.5}$ to include OH species as a structural element. Burtin *et al* (1987b) suggest the general formula for transition states as $\text{Al}_2\square_{3-u/2}(\text{OH})_u\diamond_{1-u/2}$, where $\square$ represents cationic vacancies in divalent states and $\diamond$ represents anionic vacancies of the spinel structure. When a foreign

cation is introduced, it is incorporated into an Al^{3+} site or divalent vacancy. The transformation reaction, involving dehydroxylation by removal of water followed by structural transformation, is described in terms of vacancy annihilation. The kinetic law discussed by Burtin *et al* (1987b) and Nortier and Soustelle (1987) involves the annihilation of vacancies as the rate-determining step in the transformation process.

It should be noted that the % decrease in surface area for these fibre samples of $\eta\text{-Al}_2\text{O}_3$ is less than $\gamma\text{-Al}_2\text{O}_3$ samples quoted, e.g. Nortier and Soustelle (1987) give results showing a fall off of 85% in surface area after 10 hours of calcination at 1370K compared to a 35% decrease after 42 hours at 1270K in this study.

Conclusion

The fibrous alumina, $\eta\text{-Al}_2\text{O}_3$, is relatively more stable at elevated temperatures (1270K) than other forms of $\gamma\text{-Al}_2\text{O}_3$ quoted in the literature. The loss in surface area is greatest over the first 5 to 7 hours of calcination in all alumina samples, doped and undoped.

The addition of the cations decreases the initial surface area relative to untreated alumina and the rate of decrease in surface area with time is less in all cases than the untreated alumina.

Small additions (1wt%) of La, Ce and Cs were the more effective inhibitors of the transformation reaction of η - to higher or $\alpha\text{-Al}_2\text{O}_3$, with La being the most effective. This stabilisation by La is in agreement with previous work quoted for $\gamma\text{-Al}_2\text{O}_3$ transitions.

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REFERENCES

- BURTIN, P., BRUNETTI, J. P., PUOLAT, M. and SOUSSTELLE, M. 1987a Influence of surface area and additives on the thermal stability of transition alumina catalyst supports. I. Kinetic data *Appl. Catal.* **34**, 225–38.
- BURTIN, P., BRUNETTE, J. P., PUOLAT, M. and SOUSSTELLE, M. 1987b Influence of surface area and additives on the thermal stability of transition alumina catalyst supports. II. Kinetic model and interpretation *Appl. Catal.* **34**, 239–54.
- GIJZEN, W. H. 1970 *Alumina as a ceramic material*. Columbus: The American Ceramic Society, Inc.
- GREENWOOD, N. N. and EARNSHAW, A. 1986 *Chemistry of the elements*. Oxford: Pergamon Press.
- KNOZINGER, H. 1985 Acidic and basic properties of aluminas in relation to their properties as catalysts and supports *Studies in Surface Science and Catalysis* **20**, 111–25.
- LIPPENS, B. C. and DE BOER, J. H. 1964 Study of phase transformations during calcination of aluminium hydroxides by selected area electron diffraction *Acta Cryst.* **17**, 1312–21.
- MATSUDA, S., KATO, A., MIZUMOTO, M. and YAMASHITA, H. 1984 A new support material for catalytic combustion above 1000°C *Proc. 8th Int. Cong. Catal.*, Berlin 1984, **4**, 879–89. Weinheim: Verlag Chemie.
- NORTIER, P. and SOUSSTELLE, M. 1987 Alumina carriers for automotive pollution control *Studies in Surface Science and Catalysis* **30**, 275–300.
- OUDELI, F., BORDES, E., COURRIOL, P., MAXANI, G., LAMBERT, C. and GUERLET, J. P. 1987 Structural consideration with respect to the thermal stability of a new platinum supported lanthanum-alumina catalyst *Studies in Surface Science and Catalysis* **30**, 313–21.

- ODULI, F., COURRIEL, P. and VIJAY, A. 1988 Thermal stabilization of transition alumina by structural coherence with LnAlO_3 ($\text{Ln} = \text{La, Pr, Nd}$) *J Catal* **114**, 112–20
- SCHAPLER, H., DOESBURG, E. B. M. and VAN RIJSEN, L. L. 1983 The influence of lanthanum oxide on the thermal stability of gamma alumina catalyst supports *Appl Catal* **7**, 211–20
- SOLLID, S. 1983 $\gamma\text{-Al}_2\text{O}_3$ viewed as a defect oxyhydroxide *J Catal* **81**, 252–7
- TRIMM, D. H. 1983 Catalytic combustion review *Appl Catal* **7**, 249–82
- WELLS, A. F. 1962 *Structural inorganic chemistry* London: Oxford University Press
- YOUNG, D. J., UDAJA, P. and TRIMM, D. L. 1980 Deactivation due to metal-catalysed phase transformations in $\gamma\text{-Al}_2\text{O}_3$ supports *Studies in Surface Science and Catalysis* **6**, 331–40