

THE USE OF THERMAL ANALYSIS IN STUDYING CATALYSTS AND THE CHEMISORPTION PROCESS

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ABSTRACT

The term catalysis is examined closely and shown in application to a solid phase to be an approximation in that often not only the texture of the catalyst changes but also the composition. However, the action of catalysis still remains perfectly defined in that it opens up a new lower energy path for the reaction considered. The utilisation of thermal analysis techniques in conjunction with textural studies is shown to be a specially suitable method of investigating catalytic systems. An outline of the necessary thermodynamic and kinetic considerations in catalysis systems is given. Examples of studies on inert supports are given, namely alumina and silica. The occurrence of catalysis in the thermal decomposition of oxysalts is illustrated by reference to oxalates and permanganates. Finally, thermal analysis methods suitable for studying catalysis systems are outlined.

INTRODUCTION

A close examination of the term catalysis shows it to be generally inadequate to cover current usage. In typical text books [1] the term catalysis is applied to a system in which the rate of a chemical reaction is accelerated by the presence of a substance which is itself unchanged chemically in the process. This substance is called a catalyst. If such an added substance retards the rate of reaction this is referred to as negative catalysis or inhibition, and the material is termed an inhibitor.

There are certain characteristic features which serve to identify the criteria of catalysis under this traditional approach. These are:

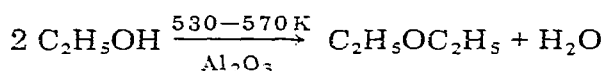
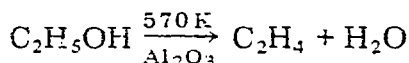
- (1) the catalyst is unchanged chemically at the end of the reaction;
- (2) a small quantity of catalyst only is sufficient to bring about the reaction;
- (3) the equilibrium position in a reversible reaction is unaffected;
- (4) the catalyst accelerates a reaction that is already possible.

Before considering the application of thermal analysis to the subject it is worthwhile judging whether the traditional features ascribed to catalysis are adequate in present usage. For a reaction to be possible the process must be accompanied by a decrease of free energy. The function of a catalyst (considered here as an accelerator of the process) is to make the overall process take place by an alternative path involving a smaller free energy of acti-

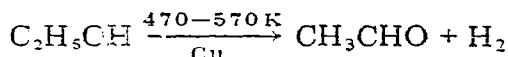
vation. If a reaction occurs in stages, then under the influence of a catalyst the free energy of activation of the slowest of these stages must be appreciably less than for the reaction in the absence of a catalyst.

The above thermodynamic reasoning implies in fact that more than one reaction may be possible, as the condition that the Gibbs free energy should be negative is not unique to a single reaction. It is therefore possible for different catalysts under different experimental conditions to produce different products.

The example commonly quoted is that of ethyl alcohol



and



The important fact is that the product depends on the catalyst, and in the operating temperature range the Gibbs free energy must be negative.

The fact that the equilibrium position for a reaction is unchanged may also be stated in terms of the Gibbs free energy. At any particular temperature the standard Gibbs free energy (ΔG^0) can have only one value, and by virtue of the relationship

$$-\Delta G^0 = RT \ln K_p$$

where K_p is the equilibrium constant in appropriate pressure units, there must also be a single value of K_p . The variation of ΔG^0 with temperature is usually stated in terms of the reaction isochore

$$\frac{d(\ln K_p)}{dT} = \frac{\Delta H^0}{RT^2}$$

where ΔH^0 is the standard enthalpy change at constant pressure. This is related to the entropy change (ΔS) by the equation

$$\Delta G = \Delta H - T\Delta S$$

The catalyst may be either of the same phase as the reactants, i.e. a homogeneous catalyst, or it may form a separate phase, i.e. a heterogeneous catalyst. In most systems investigated by thermal analysis the catalyst is generally present as a solid phase and most often the system involves a solid phase catalyst and a catalysed gas reaction involving the gaseous phase. Systems of this kind are often of industrial importance, e.g. the combination of nitrogen and hydrogen to form ammonia, the oxidation of ammonia, the oxidation of carbon monoxide in the presence of air, the Fischer—Tropsch reaction, and the Shift reaction.

The actual stage of catalysis takes place in such systems at the surface where the reactant gas phases are adsorbed, and react to form a new species

which is subsequently desorbed as a gaseous product. Such a reaction at the surface often incorporates surface atom or ion involvement. It is apparent therefore that such catalytic solid phases may undergo some alteration in chemical composition, particularly noticeable in any technique measuring surface composition. It must also be apparent that the surface properties of the catalyst system are very important. The basic process of such heterogeneous catalysis is simply one of adsorption, at adjacent positions on the surface, of reactant molecules with sufficient energy to form the adsorbed actuated complex. The reactants must not be too strongly adsorbed, for if a reactant is strongly adsorbed then the other reactant or reactants will not be able to have access to the surface, and the reaction is retarded. It is therefore essential that both gases will be adsorbed to an extent which allows an appreciable number to be adsorbed adjacent to the other gaseous species. In a catalysed unimolecular process of this kind the adsorbed species must acquire sufficient energy to form an activated species which is desorbed as a different species. The surface sites where catalysed adsorption and desorption can take place may form only a small fraction of the total available surface. These active sites may often be enhanced by the addition of promoters, or blocked off and reduced by the addition of catalytic poisons.

Therefore, for thermal analysis to find a use in investigating such systems, solid catalysts, in either a solid phase process or in a gaseous environment, would form the most suitable reactions for study.

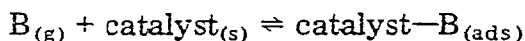
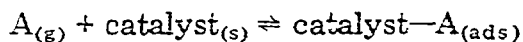
The thermogravimetric analysis techniques are an obvious choice for studying catalysis in the solid—solid system. This is because although the catalyst shows little detectable mass change, the solid state reaction which takes place can probably be followed by showing the mass change. However, in the solid—gas system, the catalyst is the solid phase and the catalysed reaction is a gaseous reaction with the catalysis occurring at the solid surface. The use of thermogravimetry on the catalyst is then not going to produce information about the catalysed reaction unless the product of gaseous interaction is itself a condensed phase and attached to the catalyst. The use of properly designed vacuum balances enables the accompanying processes of chemisorption and physical adsorption to be studied. It is then possible to tackle the problem in such cases by either studying the rate of adsorption or the adsorption isotherm (i.e. the equilibrium condition). In conventional studies these investigations were recorded as a series of isothermal experiments, but it is now economically more feasible to carry out thermal desorption experiments in which the adsorbed material is desorbed as the temperature is raised.

KINETIC CONSIDERATIONS IN CATALYTIC PROCESSES

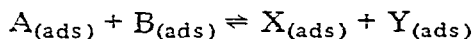
This is a wide subject and the reader is referred to other publications which deal with the subject in detail [2—9]. In heterogeneous catalysis several steps are involved and any one of these steps may be the rate-determining step. The following general steps may be involved:

- (i) transport of reactants to the catalyst;

(ii) adsorption of reactants on the catalyst, e.g.

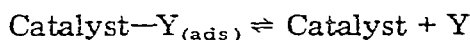
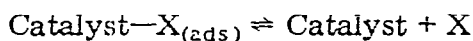


(iii) interaction of adsorbed reactants



[$A_{(ads)}$, $B_{(ads)}$, $X_{(ads)}$ and $Y_{(ads)}$ indicate that these species are all in the adsorbed state];

(iv) desorption of product from the catalyst



(v) transport of the products away from the surface.

The first and final steps involve no chemical change but, depending on the environment of the system under consideration, they can be rate-limiting. All the other steps involve chemical change and could be rate-limiting and be expected to obey an Arrhenius equation

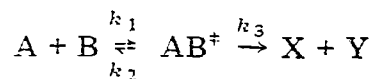
$$k = A \exp(-E/RT)$$

where k is the specific reaction rate, A is the exponential factor and E is the activation energy. This latter term is defined as a measure of the amount of energy which reactant molecules must have before they overcome the barrier between them and the product state. The exponential term in gas-phase reactions is supposed to specify the fraction of molecules having kinetic energy greater than E . If one is dealing with an order-type reaction, then the rate of reaction (r) at time t is given by

$$r = kP_A^m P_B^n$$

where P_A and P_B are the pressures of reactants A and B at time t , and m and n denote the order of reaction with respect to A and B. The term k is thus the rate when the reactants are at unit pressure.

A better approach is to use the transition state theory. In this the existence of a transition state is postulated, viz.



where AB^\ddagger indicates the transition state, and k_1 and k_2 are the specific reaction rates for the forward and reverse reaction, respectively. The transition complex AB^\ddagger is supposed to decompose so slowly that the equilibrium with reactants is not upset. It then follows

$$\frac{k_1}{k_2} = k_p^\ddagger = \frac{P_{AB^\ddagger}}{P_A P_B}$$

The overall forward reaction is given by

$$r_f = k_3 P_{AB^\ddagger}$$

However, the complex can be considered to decompose when a vibrational mode changes to a translational mode since this represents an irreversible vibration. The frequency of such a change is

$$\nu = \frac{\epsilon}{h}$$

where h is Planck's constant and ϵ is the average energy of the relevant vibration. For a thoroughly excited mode at temperature T

$$\epsilon = \frac{RT}{N}$$

and

$$\nu = \frac{RT}{Nh}$$

This is a simplified outline, the detailed and proper procedure is given by Laidler [10]. The end result is the same, and ν is identified with k_3 , so that

$$r_f = \frac{RT}{Nh} k_p^\ddagger P_A P_B$$

This can be compared with the formal equation

$$r_f = k P_A P_B$$

when

$$k = \frac{RT}{Nh} k_p^\ddagger$$

This can be put into thermodynamic parameters and thus

$$-\Delta G^\ddagger = RT \ln K_p^\ddagger$$

and

$$\Delta G^\ddagger = \Delta H^\ddagger - T \Delta S^\ddagger$$

where ΔG^\ddagger is the free energy of activation, ΔH^\ddagger is the standard enthalpy of activation, and ΔS^\ddagger is the standard entropy of activation. This gives

$$\begin{aligned} k &= \frac{RT}{Nh} \exp \frac{-\Delta G^\ddagger}{RT} \\ &= \frac{RT}{Nh} \exp \frac{\Delta S^\ddagger}{R} \exp \frac{-\Delta H^\ddagger}{RT} \end{aligned}$$

Comparison with the Arrhenius equation leads to the following identities

$$-\Delta H^\ddagger \equiv E$$

$$\frac{RT}{Nh} \exp \frac{\Delta S^\ddagger}{R} \equiv A$$

For any reaction to be catalysed the specific reaction rate must be

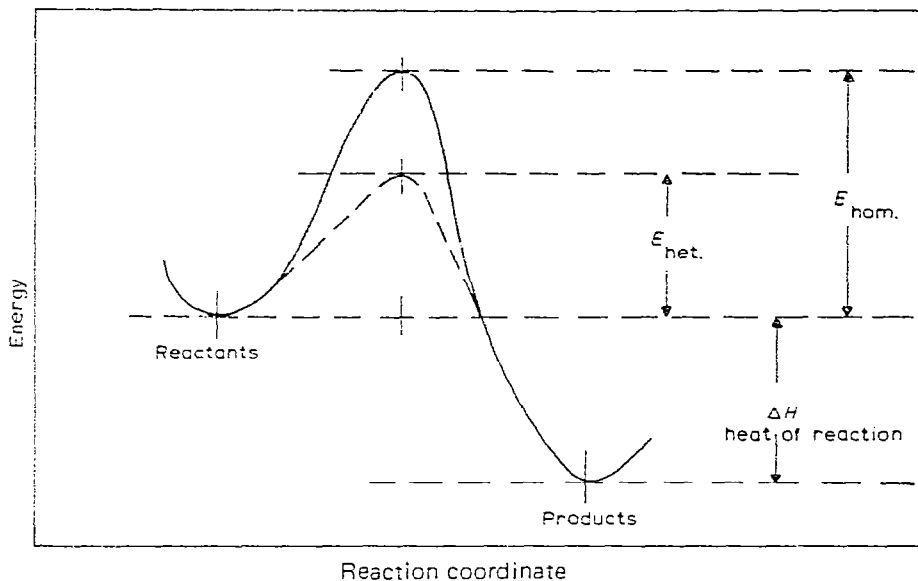


Fig. 1. The potential energy profile diagram for an exothermic catalysed reaction compared with the same homogeneous reaction.

increased and this means that there must be a decrease in the free energy of activation of the reaction (ΔG^\ddagger) given by

$$k = \frac{RT}{Nh} \exp \frac{-\Delta G^\ddagger}{RT}$$

caused by alterations in the value of the entropy (ΔS^\ddagger) or the enthalpy (ΔH^\ddagger). In heterogeneous catalysed reactions the entropy associated with the formation of the activated state will usually be less than that associated with the activated state in the uncatalysed reaction. This is because the

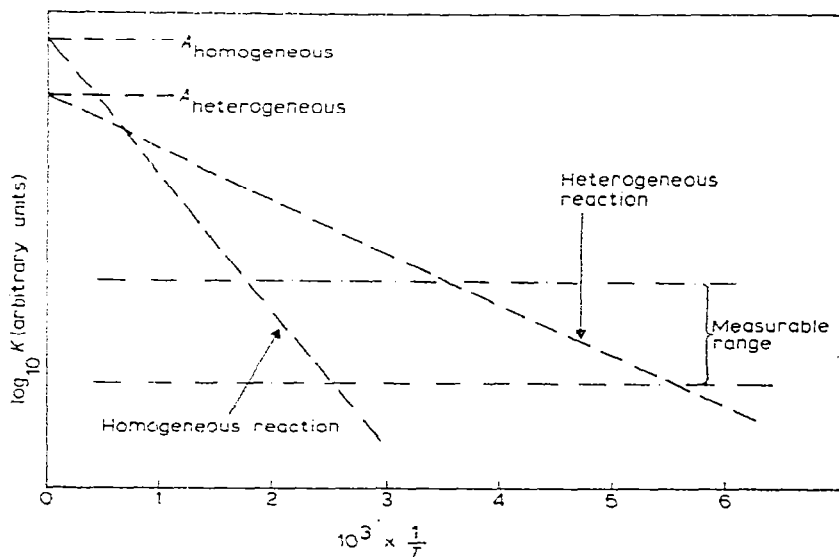


Fig. 2. The specific reaction rate and its dependence on temperature for equivalent homogeneous and heterogeneous reactions plotted according to the Arrhenius equation (schematic only).

transition complex will be sited on a catalyst surface, when there will be a consequent loss of transitional freedom. For good catalytic action the ΔH^\ddagger value must be decreased by an amount greater than the change in entropy. The potential energy profile diagram for an exothermic catalysed reaction compared with the same homogeneous reaction is shown in Fig. 1, and the temperature dependence of the rate for the corresponding homogeneous and heterogeneous reactions plotted using the Arrhenius parameters are shown in Fig. 2. It is then seen that the values of both A and E are lower for the heterogeneous reaction.

CHANGES IN CATALYST COMPOSITION IN CATALYSIS

The classical consideration of a catalyst remaining unchanged in composition would not seem to apply in heterogeneous catalysis. This is a reflection of the exchange process at the surface, where the rate of replacement of surface species may not match the rate at which these species are utilised during the catalysis process. This is not in accord with the classical definition of a catalyst, but would agree with the more basic definition that the catalyst allows the chemical reaction to proceed by a more energetically favourable reaction path.

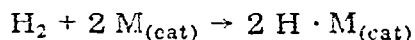
In most heterogeneous catalytic processes, the catalyst may be a metal, an oxide, or a sulphided oxide. These are the most common kind of catalyst in such systems. The metals are often supplied as oxides which have to be reduced in the catalytic reactor. The sulphide catalysts are sulphided in situ in the catalytic reactor so the starting material is once again an oxide [11]. Thermal analysis studies can be used to characterise the catalyst, to determine the chemistry of any preparative route by means of the mass changes involved and the endothermic or exothermic nature of these reactions. These show, especially in the oxide and sulphide systems, the non-stoichiometric nature of the prepared catalyst and the manner in which it depends on the nature of the experimental environment in the catalysis process. In the case of metal catalysis systems the question of non-stoichiometry does not arise, but in alloy systems or trace metal systems the surface phase may have a different composition to the bulk and this may vary from one surface position to another [12].

The TG technique may be used to note specifically the small changes in mass occurring at the catalyst during the reaction. Thus in the oxide catalyst systems the catalyst process occurs by a process of oxygen exchange. The oxygen may be present as a chemisorbed layer or incorporated in the lattice structure from which it may be abstracted during the catalysed process. An oxygen used during the catalyst process must be replaced from an available source such as atmospheric oxygen. In most cases the process of using up the oxygen available from the catalyst invariably exceeds the rate of replacement so the catalyst activity drops. The catalyst then has to be regenerated, usually in such cases by reheating in oxygen when desorption and gasification of things such as carbon residues occurs, followed by reincorporation of the oxygen in the catalyst usually at the surface [13].

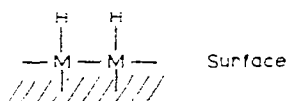
Such systems can obviously be studied using TG techniques.

Two points may be made regarding the catalyst action. The first is that an adsorption process of a gas or liquid species at the catalyst surface is involved. The second point is that the process is specific, and for each reaction there is one material, or a related group of solids that possess reasonable catalytic activity.

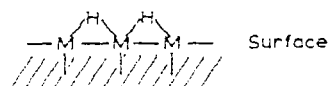
In the case of metal catalysts the catalysis step is often the addition to or removal from a molecule of hydrogen. The reason for this is that many metal surfaces can dissociate molecular hydrogen into hydrogen atoms. However, when heated in air, the semi-conductive oxide catalysts tend to either gain or lose oxygen from their surfaces and in some cases from the bulk lattice structure. They owe their semi-conductive properties to their non-stoichiometry. The lattice can usually accommodate a variable amount of oxygen and they tend to be good catalysts for reactions in which oxygen is added or removed from a molecule. Oxides such as Cr_2O_3 or copper chromite, CuCr_2O_4 , which are more difficult to reduce, can catalyse dehydrogenations and dehydrocyclizations which would otherwise only be thermodynamically possible above the decomposition temperature of the material concerned. The term stoichiometric oxides is applied to Al_2O_3 , SiO_2 and MgO although they do not always conform exactly to the stoichiometric formula. This group has a strong interaction with water and are usually good dehydration catalysts. It must be stressed, however, that although a distinction can be made between stoichiometric and non-stoichiometric oxides, these properties refer to bulk properties whereas the catalysis process takes place by adsorption at the surface. In the bulk lattice the atoms or ions are held in position by forces from the surrounding atoms or ions. However, at the surface these species cannot be held in such a perfectly balanced condition. Adsorption, both physical and chemisorption, represents a corrective process in which this balanced condition is partly restored. Although the definitions of physical adsorption and chemisorption are quite clear and distinct, on real surfaces it is possible to get forms of surface binding of an intermediate nature. Thus in water adsorption hydrogen bonding is a real possibility. There is also the fact that real surfaces are often heterogeneous and so on the same surface various forms of adsorption may be found. However, it should be noted that even with a uniform surface the specific process of chemisorption must always be accompanied by physical adsorption. There are two modes of catalytic adsorption on metal surfaces — dissociative and associative. Dissociative chemisorption is illustrated by hydrogen



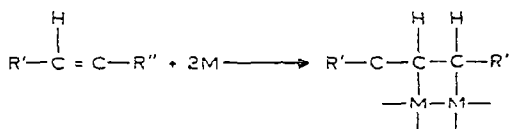
but this does not distinguish between various alternatives



or



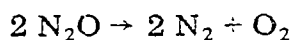
Associative adsorption can be illustrated by chemisorption of unsaturated organic molecules



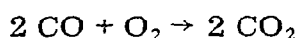
However, if the bonding forces in chemisorption are too strong then desorption of the products of catalysis becomes impossible. The generalisation must be that for catalysis to take place the adsorption bond must be strong enough to provide adequate coverage but not so strong that subsequent formation of a transition complex and the desorption of products is rendered impossible.

The non-stoichiometry of oxide catalysts and the fact that the extent of non-stoichiometry varies during the catalysis process makes TG experiments suitable for following catalysis processes when the behaviour of the solid catalyst phase is to be noted. This stoichiometry of the oxide can be altered when oxides are heated in various atmospheres and TG experiments of this nature can serve to characterise catalyst oxides. If such data are combined with measurements of the electrical conductivity of the sample during the heat treatment, then this information can be very valuable. The change in conductivity is the phenomenon to be followed, not the actual electrical conductivity of the material. This considerably simplifies the experimental design. However, it is not sufficient to say that *n*-type semi-conductor oxides lose oxygen on heating whilst *p*-type semi-conductor oxides gain oxygen on heating, as the experimental conditions need to be specified. Experiments of the above nature using normal TG equipment can provide a semi-conductor characterisation but can also provide an appropriate indication of catalytic mechanism. In most catalyst reactions involving oxides it is, as already stated, oxygen which is involved at reactant, transition or product stage. The oxide species can be attached to a surface metal ion either as $\text{O}_{(\text{ads})}^-$ or O^{2-} . In the latter case this may appear only in the adsorbed surface layer or incorporated via diffusion into the lattice structure. In some instances the oxide may incorporate both species but in two easily recognisable temperature regions.

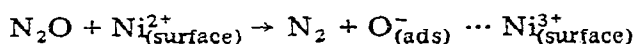
Two reactions [14,15] to which these comments especially apply are



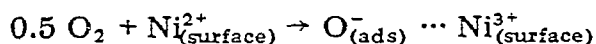
and



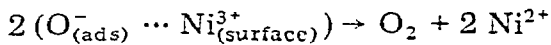
The use of nickel oxide as a catalyst in this first example may be represented as



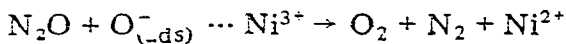
This may be compared with the chemisorption of oxygen on such surfaces



and the activity of *p*-type oxides in the decomposition of N_2O is in the same order as their ability to adsorb oxygen. Two mechanisms of desorption are available

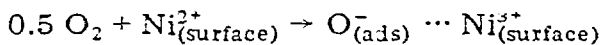


or

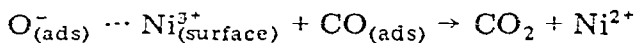


The above reaction pathways are not available for insulator and *n*-type oxides which are much less active.

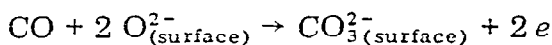
Two reaction pathways are available for the oxidation of carbon monoxide in the presence of oxygen [16,17]. For *p*-type oxides (NiO may be cited as an example, the oxygen first chemisorbed



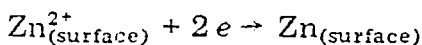
This is then followed by reaction with adsorbed carbon monoxide



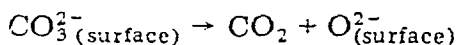
For *n*-type oxides the activity can lead to catalysis at a low temperature. The surface oxide ions can be reduced with CO to form a carbonate intermediate species. Zinc oxide is an example, and the probable reaction implied by the above supposition is



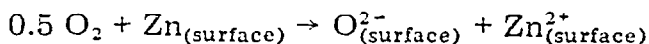
with



The decomposition of the CO_3^- intermediate species must then be considered, viz.



while the $Zn_{(surface)}$ species can be transformed into the ionic species by reaction with oxygen



The TG technique using vacuum microbalances would appear especially suitable as a method of investigating the unbalance between the rate of regenerating the oxygen and the rate at which it is used up to produce the product. The subsequent regeneration procedure, usually accomplished by heating in oxygen at a predetermined temperature, in order to replenish either the adsorbed surface oxygen or the surface lattice oxide ions, is also amenable to investigation by thermal analysis techniques.

Hopcalites and other double oxides, and compound oxides such as bismuth molybdate show a catalyst selectivity which is a reflection of the availability of lattice oxide ions [18,19]. The alumino silicates have a catalytic action which depends variously on their affinity for water, their acidic character or their molecular sieve properties [20].

CATALYST SUPPORT MATERIALS

To make a greater surface available it has become current practice to make use of inert support materials. Sometimes this affects the mode of preparation of the catalyst species which has to be deposited upon the inert support material. Inorganic solids such as nitrates, hydroxides, carbonates etc., are used as catalyst precursors and are converted to the oxide catalyst by thermal decomposition. In certain circumstances, e.g. with some oxalates in nitrogen [21], the metal may be the end product of the heat treatment, but this is rarely the practice in industry. In order to prepare metal catalysts the common industrial usage is to prepare the oxide first and then produce the metal catalyst by reduction in situ in a catalyst reactor. Sulphide catalysts are also produced by sulphiding processes carried out in situ on an oxide precursor. The thermal decomposition of many oxysalts produces an oxide with an extensive surface area available to the adsorption of vapours and gases [22]. Their surface texture characteristics are important properties of the catalyst oxide and this is influenced by the nature of the thermal pre-treatment [23]. The solid state chemistry of relevance is to be found in books by Galwey [24], Garner [25], Gregg [26] and Hedvall [27] and in various reviews [28,29]. The kinetics and associated mechanisms associated with the thermal decomposition have recently been reported in great detail [30].

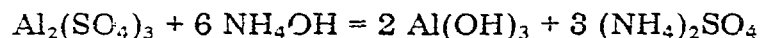
For supported catalysts the catalyst precursor must first be placed on the support surface. This involves two alternative processes, the first involving precipitation from solution onto an inert support, whilst the second requires the inert support to be soaked in a soluble salt solution of the metal species required as catalyst [31]. The salt normally chosen is the nitrate but this is not exclusively so. Aluminas, silicas or other insulator type oxides are typical support materials. In the method where soaking in a nitrate solution is employed the soaked material is dried to leave the nitrate on the support material surface. The layer of nitrate is then decomposed by further heat treatment to leave an oxide deposited and attached to the inert support surface. The thermal analysis techniques provide an excellent method for following the above preparative routes [32]. Individual materials used as either inert supports or as catalysts can readily be studied using thermal analysis techniques. Two examples are given here, selected largely from the present author's own range of studies and experience.

ALUMINA AS AN INERT SUPPORT

There is much literature on the use of alumina as a support material. The review by Lippens and Steggerda is especially detailed [33]. The aluminium hydroxide [$\text{Al}(\text{OH})_3$ or $\text{Al}_2\text{O}_3 \cdot 3 \text{H}_2\text{O}$] occurs as gibbsite [$\gamma\text{-Al}(\text{OH})_3$], bayerite [$\alpha\text{-Al}(\text{OH})_3$] and nordstrandite which can all be identified by X-ray diffraction methods. Two forms of the hydrate $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ can be found widely described, boehmite ($\gamma\text{-AlOOH}$) and diaspore ($\alpha\text{-AlOOH}$). The effect of heat treatment on these hydrate forms of alumina have been reviewed by

Mackenzie and Berggren [34], with special reference to differential thermal analysis studies.

The action of ammonia or other alkali on aluminium sulphate or chloride solutions produces a gelatinous precipitate of aluminium hydroxide. This is formally represented by



but the resultant "gel" has a great excess of water over the above formula. A freshly precipitated "gel" will dissolve in acids forming aluminium salts, but an "aged gel" dissolves with difficulty. The "gel" dissolves in caustic soda but not in ammonia to form the aluminate (NaAlO_2). The hydrated oxides or partially dehydrated oxides with a large surface area are termed active aluminas [35]. These are prepared by a variety of methods in industry, but heating to 800°C or above leads eventually to the formation of corundum ($\alpha\text{-Al}_2\text{O}_3$) with a greatly diminished surface area.

The preparation of pure gibbsite and bayerite from solutions of sodium aluminate neutralized with carbon dioxide has often been given in the literature [36–39]. Gibbsite is industrially important as it represents a stage in the production of aluminium from bauxite by the Bayer process. Hauschild [40] describes the preparation of nordstrandite by adding ammonia to a solution of aluminium nitrate suspended in a 70% ethylenediamine solution, keeping the mixture at 58°C for 60 days, filtering, washing with water and drying at 105°C . Aldcroft and Bye [41] prepared nordstrandite by the hydrolysis of aluminium butoxide with 20% aqueous ethylene glycol and ageing the product at 60°C in its mother liquor.

No simple preparation of diaspore ($\alpha\text{-AlOOH}$) has been described. It occurs in some clays and bauxite. It has been shown that between 275 and 425°C and a water vapour pressure above 140 atm and when seeded with small amounts of diaspores, all aluminium hydroxides and oxides are converted into diaspore [42–44].

Boehmite ($\gamma\text{-AlOOH}$) can be prepared in a crystallised form (termed "well-crystallised") and as a gelatinous material (called pseudo-boehmite). The well-crystallised boehmite is the end product of the ageing of aluminium hydroxide gel at $\text{pH} > 12$ and 80°C [36]. The gelatinous boehmite results if solutions of aluminium salts are neutralized with ammonia and the bulky amorphous precipitate left in contact with the mother liquor or with ammoniacal solutions [45,46]. The gelatinous boehmite prepared in this manner has a water content of 1.3 ~ 1.8 moles of H_2O per mole Al_2O_3 , determined by heat treatment sufficient to lose all the water and leave the Al_2O_3 , and noting the mass loss.

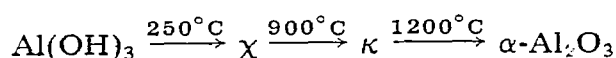
Apart from this overall observation the dehydration sequence is the subject of some controversy [47]. To portray the various possible sequences there is a need to classify the crystal structures of the active aluminas. The classification used [33,48] is based on the temperature at which the aluminas were obtained from the hydroxides. Two groups of active aluminas may be identified as follows:

(1) low temperature aluminas (γ -group): $\text{Al}_2\text{O}_3 \cdot n \text{H}_2\text{O}$, where n is given as $0 < n < 0.6$, obtained by dehydrating at temperatures up to 600°C .

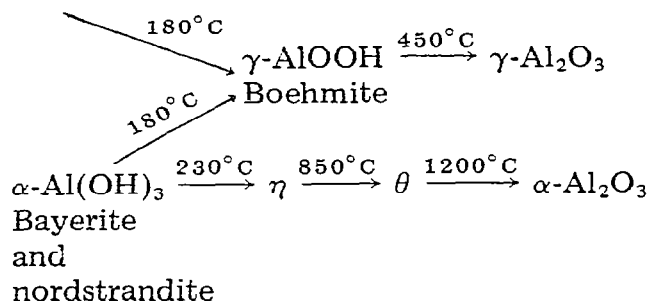
(2) high temperature aluminas (δ -group): nearly anhydrous Al_2O_3 obtained by heating between 900 and 1000°C.

There are various materials which can be identified in each group usually by X-ray diffraction methods. In group (1) are found ρ , χ , η and γ -alumina [33]. In group (2) are found κ , θ and δ -alumina. Corundum is the final form produced by heat treatment, is not an active alumina and is given the designation α . With these designations the schemes for dehydrations of hydrated aluminas can be outlined.

For $\text{Al}(\text{OH})_3$:
in air

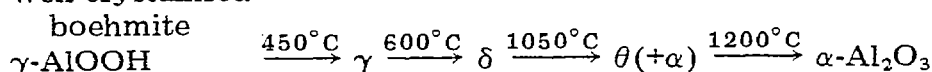


Gibbsite

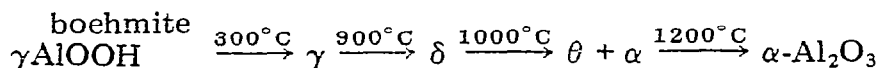


Boehmite is formed from coarser grained samples because intergranular conditions set up a hydrothermal environment and it is this situation which favours the formation of boehmite. The final product of heat treatment of boehmite is $\alpha\text{-Al}_2\text{O}_3$. Its dehydration reaction pathway is [33]

Well crystallised



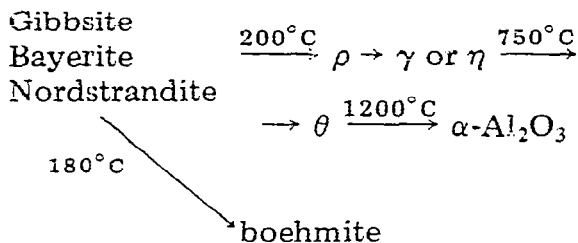
Pseudo-



It should be noted that due to the poor crystallinity of the pseudo-boehmite the opportunity for the formation of $\delta\text{-Al}_2\text{O}_3$ is very limited. In many bayerites the initial hydrothermal conditions lead to the formation of predominant amounts of boehmite. However, Mackenzie [49] does not believe that boehmite formation is related to the particle size or the amount of foreign ions present. In vacuum all three trihydrates dehydrate into an almost completely amorphous product (ρ -alumina) but the end product of heat treatment is again $\alpha\text{-Al}_2\text{O}_3$. Favourable hydrothermal conditions lead to the production of boehmite and this subsequently undergoes the changes already described. Under vacuum the reaction pathways can therefore be designated.

For $Al(OH)_3$:

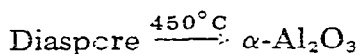
in vacuum



The ρ -alumina will react with water to form bayerite independent of the original trihydrate from which it was obtained [50].

Diaspore dehydrates directly into $\alpha\text{-Al}_2\text{O}_3$ [51]. The quoted temperature is 450°C , the product initially has a high surface area but this disappears due to growth of the crystal size.

The dehydration scheme is therefore simple



There is reasonable agreement on these transitions but alternative designations can be found. The TG technique should show the dehydrations, the transformations in the oxide should be detectable by DTA but in most cases X-ray diffraction methods are used.

SILICA AS AN INERT SUPPORT

The aluminas and silicas prepared with large surface areas available for gas adsorption are the most numerous cited catalyst supports. The silicas used as catalysts may generally be regarded as polycondensation products of orthosilicic acid. However, one must recognise that various forms of silica exist and these can easily be recognised by thermal analysis techniques. Three forms exist: tridymite, cristobalite and quartz. The phase change between these forms involves reasonably large molecular or ionic movements in the solid lattice and a finite time is required for the phase change to occur. Differential thermal analysis (DTA) proves to be an imperfect tool for these changes. However, there are more minor changes, "inversions", which involve far less movement in the lattice structure and can be seen on DTA traces. This enables the phases to be identified and used quantitatively to indicate the amount of each phase present. The classic studies of Fenner [52] are quoted in Table 1. The active silicas are quoted as being amorphous. Frondel [53] states that amorphous silica is not truly amorphous but consists of crystals of very small size which appear to have a cristobalite structure. However, from electron diffraction data Shingles [54] suggested a quartz structure was possible. It might seem that DTA could be used to identify the phase in such circumstances but although this has been claimed in some cases, the endothermic loss of water and possible changes from

TABLE 1

Transitions between quartz tridymite and cristobalite [52].

Temp. crystalline change ($^{\circ}\text{C}$)	Crystalline change
117	$\alpha\text{T} \rightleftharpoons \beta_1\text{T}$
163	$\beta_1\text{T} \rightleftharpoons \beta_2\text{T}$
198—241	$\beta\text{C} \rightarrow \alpha\text{C}$
220—275	$\alpha\text{C} \rightarrow \beta\text{C}$
570	$\beta\text{Q} \rightarrow \alpha\text{Q}$
575	$\alpha\text{Q} \rightarrow \beta\text{Q}$
870 ± 10	$\text{Q} \rightleftharpoons \text{T}$
1470 ± 10	$\text{T} \rightleftharpoons \text{C}$
1625	$\beta\text{C} \rightleftharpoons \text{silica glass}$

T = Tridymite, C = cristobalite, Q = quartz; α and β indicate high and low temperature forms, respectively.

regions of disorder to regions of order make these identifications difficult.

There are various terms used to refer to these amorphous and porous forms of silica. Silica gel is formed in a liquid medium and this is usually water but the pore structure may become filled with alcohol in some preparations. The term alcogel refers to a gel with the pores filled with alcohol, while aquagel refers to a gel with the pores filled with water (alternative name hydrogel). A xerogel is a gel from which the liquid has been removed from the pores but with some damage and collapse to the porous structure. The term aerogel refers to a gel in which the liquid medium in the pores is removed without a collapse or change in the porous structure. In spite of the above comments the term amorphous silica will be used here to cover all these forms.

The following methods of preparation are generally available:

- (1) precipitation from silicate solutions (generally by acid) [55—59];
- (2) hydrolysis of silicon derivatives such as silicon tetrachloride [60];
- (3) pyrogenic silica preparations (also called aerosils). This involves flame hydrolysis of silicon halides, or vaporisation of SiO_2 .

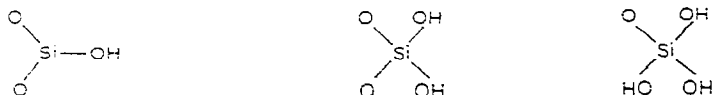
The water associated with the silica may actually be incorporated into the structure, especially at the surface and also simply fill up the porous structure. This makes the interpretation of TG data difficult.

The first product of the condensation of silicic acid is a hydrogel. The subsequent drying process produces the xerogel which is the usual form of the porous silica. The preparation, stability and adsorption properties of porous silicas have been reviewed by Okkerse [61] and the overall chemistry of silica has been described in detail by Iler [62].

The character, number and distribution of the silanol groups present determine the chemical nature of any particular silica. Experiments involving thermogravimetry, the adsorption of polar molecules, the reactions of various compounds with the hydroxyl groups, and IR spectroscopy studies all lead to an understanding of the arrangement of hydroxyl groups at the surface.

The adsorbed water may be physically adsorbed and chemisorbed. In this

case the chemisorbed or bound water refers to OH groups chemically bound to a silicon atom. These may be bound to the silicon in various ways



Further water may be hydrogen bonded to these silanol groups. It is generally agreed that if silica is heated to 200°C to constant mass on a thermobalance, then the mass loss can be ascribed to adsorbed water. The hydroxyl group content can be estimated from the further mass between 200°C and 1000°C [56,63–66]. The choice of 200°C is not accepted by all workers in the field. Figure 3 shows the behaviour pattern of water loss below and above 200°C. Disregarding the question concerning the temperature which differentiates between physisorbed and bound water, the utility of the TG balance in these studies is easily understood. The experiment usually involves programming the temperature up to the determined temperature for physically held water and then keeping it at this temperature until a constant mass is recorded. The temperature is then raised to 1000 or 1200°C, whichever of these higher temperatures is chosen, and then keeping it at this temperature until a constant mass is reached.

The temperature of 200°C is too high according to De Boer and Vleeskens [67,68], who conclude there is no easily distinguishing temperature that enables one to differentiate between physisorbed and hydroxyl surface groups. In this detailed study they conclude that a silica dried at 120°C in air would lose all its physisorbed water, but still retain all the surface hydroxyls. They claim that above this temperature there is a progressive loss

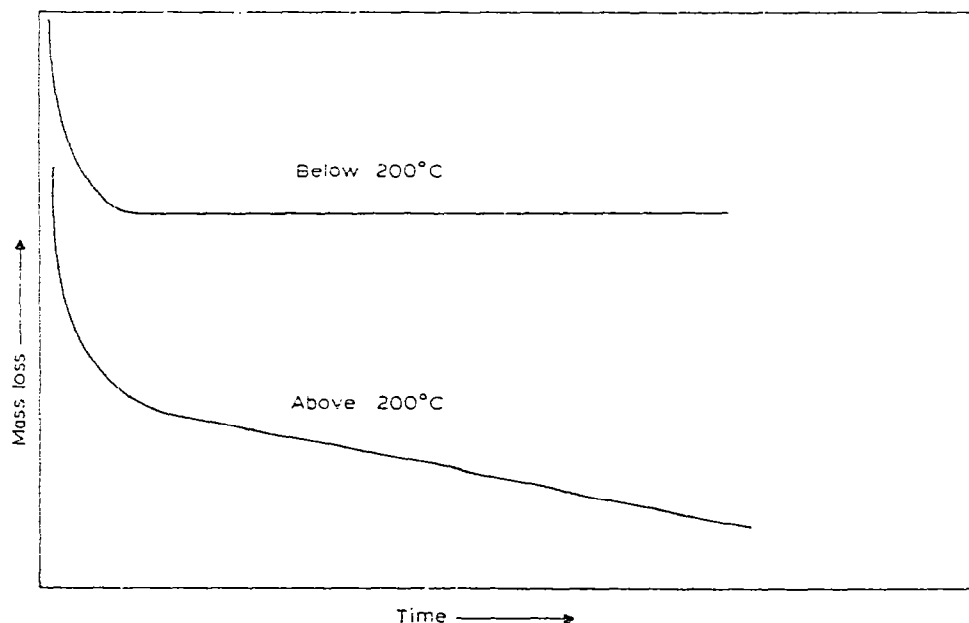


Fig. 3. The mass loss due to evolved water from silicas. Mass loss is plotted as % mass loss referred to mass loss on heating silica at 1200°C.

of hydroxyl groups. Their findings were based on the following:

(1) below 110°C the "residual" water content depends on the environmental water vapour pressure of the air in which the silica is dried;

(2) silica samples dried at 120°C under atmospheric conditions have the same water content (determined by heating to 1200°C) as when dried at 105°C and then stored over P_2O_5 , or when they are dried at 105°C and then pumped off under high vacuum at ambient temperature.

Dzisko et al. [69] came to a similar conclusion but added that above 600°C there is sintering with loss of surface together with simultaneous loss of water, but the number of remaining hydroxyl groups per unit area remains constant. Micropores are however present in some silicas and water may not be lost from such pores until a higher temperature is reached, when the higher temperature of 200°C may be preferred.

If the surface area is known, then the hydroxyl groups per square millimicron (N_{OH}) is given by Iler [62] as

$$N_{\text{OH}} = \frac{660W}{S}$$

where S is the surface area in $\text{m}^2 \text{g}^{-1}$, and W is % mass of bound water. The value of N_{OH} for full coverage is given by Iler as 8.

Dollimore and Heal [56] used a temperature of 200°C as the temperature that distinguishes between physically adsorbed water and surface hydroxyls for micro-porous silicas in this kind of test. They found that values of N_{OH} obtained by this method were very high in the region 20–30. These micro-porous silicas were prepared by an ion-exchange process, and gave Type 1 nitrogen adsorption isotherms in which the ratio of the monolayer capacity (V_m) to the volume adsorbed near saturation (V_s , the volume adsorbed at a relative pressure of 0.95) is greater than 0.9. The adsorption data for a variety of vapours shows that the majority of pores in these

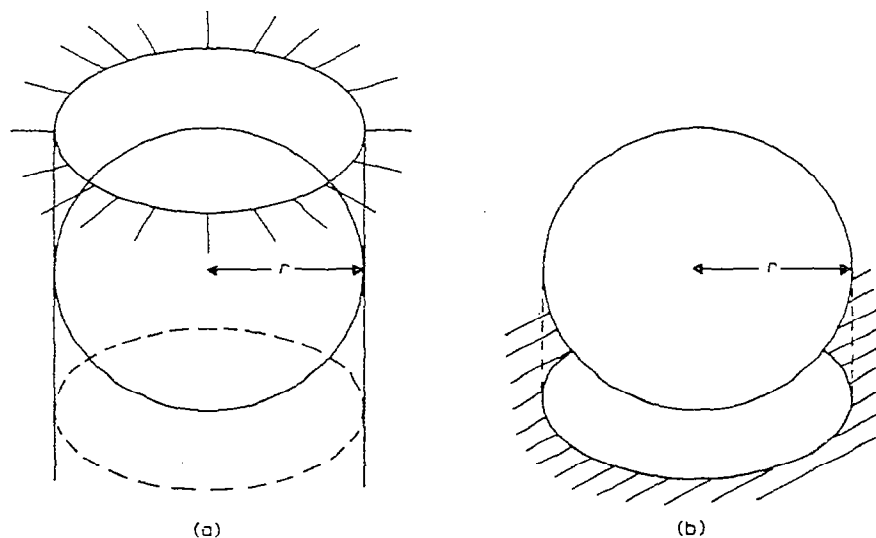


Fig. 4. Apparent and actual molecular coverage in molecular sized pores. (a) The molecule just fits into the pores; (b) the molecule on a planar surface.

samples are of diameters less than 3.9—4.8 Å. The high value for N_{OH} arises because the monolayer capacity was calculated from the BET equation and then using the accepted value of the cross-sectional area, the surface area could be calculated. Typical values of surface areas for these silicas calculated by the above method were around $200 \text{ m}^2 \text{ g}^{-1}$. Figure 4 demonstrates that the anomaly is due to the method of calculating the surface area. Thus in an extreme case the molecule of nitrogen just fits into the pore, and therefore one molecule covers the walls of a circumscribed cylinder. The area associated with the molecule is then $2r \times 2\pi r = 4\pi r^2$ (where r is the radius).

The BET value is that of the molecule covering a planar surface when the area is given by πr^2 . Then

$$\frac{\text{True area}}{\text{Apparent area}} = 4$$

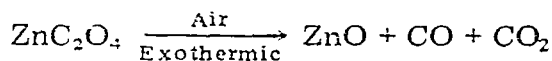
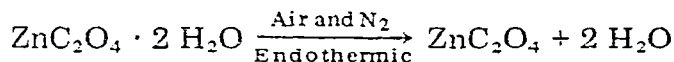
The apparent area is a little greater than the above value due to packing of the molecules, and the ratio is really 3.63.

In the case cited, the number of OH groups per nm^2 is between 20 and 30, and this is due to the apparent area being too small by a factor of 3—4. Making allowances for this would produce normal values for the OH population on a silica surface, namely $N_{OH} = 8$.

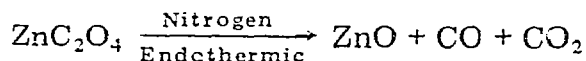
Other solids of importance as catalysts or as supports may also be studied in a similar fashion. Important among these solids is magnesia [70,71]. Carbon is another material; this is of importance in catalysis for a variety of reasons, as an adsorbent, as a deposit on catalysts causing deactivation, and as a support material [72—74].

CATALYSIS IN THERMAL DECOMPOSITION REACTIONS

The influence of catalysts in thermal decomposition can be readily ascertained. The decomposition of oxalates may be cited as an easily recognisable series of examples. These have been studied in various reports by Dollimore et al. [22,75,76]. The thermal decomposition of zinc oxalate hydrate in air or nitrogen can be represented schematically as follows

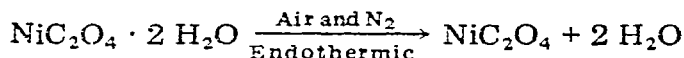


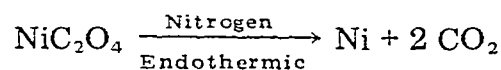
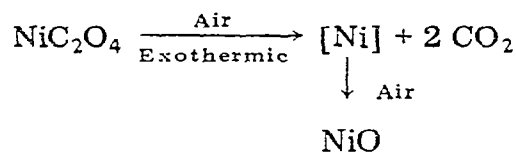
and



It is seen from this that an endothermic decomposition in nitrogen is seen as an exothermic decomposition in air.

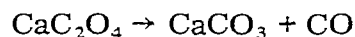
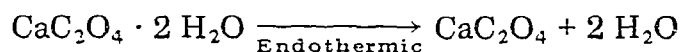
Nickel oxalate thermally decomposes in the manner set out





In a manner similar to the zinc oxalate decomposition, the decomposition of nickel oxalate in nitrogen is endothermic but becomes exothermic in air. It will be observed here, however, that the reaction pathway is now different.

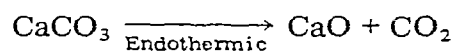
A further reaction sequence is shown by calcium oxalate. Schematically this sequence is



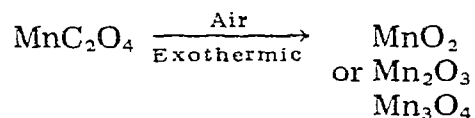
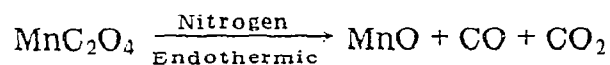
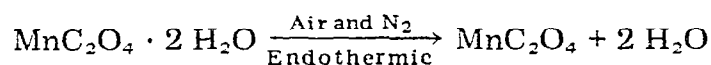
(i) endothermic in nitrogen

and

(ii) sometimes exothermic in air and then



Manganese oxalate dihydrate thermally decomposes in the following sequence which serves as an example of the thermal decomposition of variable valency metal oxalates



(depending on the temperature and conditions). The reaction pathways can be determined by a combination of experiments involving TG and DTA [75–78].

The overall observation is the change from an endothermic decomposition in nitrogen to an exothermic decomposition in air. The basic decomposition process is that occurring in nitrogen and is endothermic. The production of a high area nickel product which oxidises exothermally and spontaneously in air is the reason for the exothermic decomposition of nickel oxalate in air. However, the reaction pathway is the same for zinc oxalate decomposition in air and nitrogen, but the reaction is exothermic in air and endothermic in

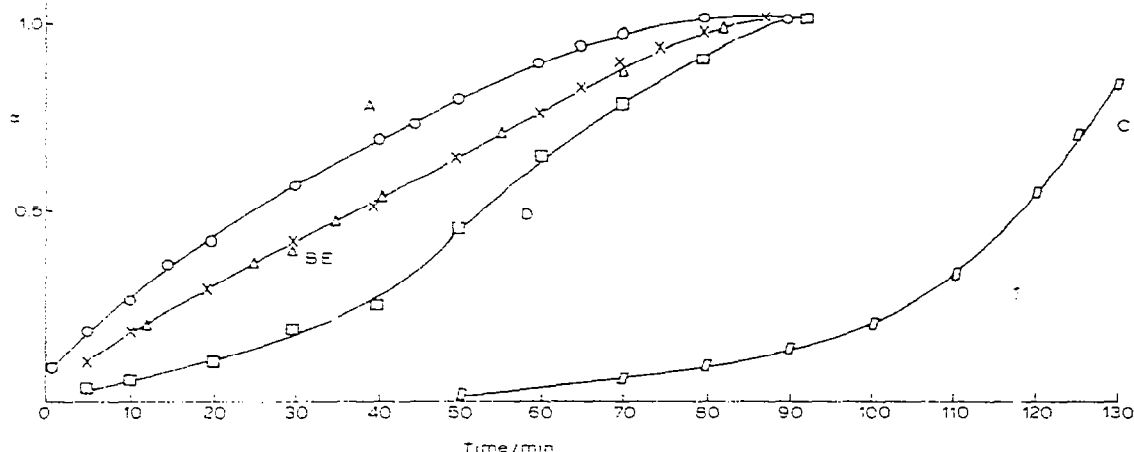


Fig. 5. $\alpha-t$ plots showing the catalytic effect of additives on the decomposition of KMnO_4 at 220°C . A, Powdered KMnO_4 crystals + 10% MnO_2 powder; B, powdered KMnO_4 crystals + 10% MnO_2 (mesh size 10–18); C, powdered KMnO_4 crystals + 10% of the “soluble portion” of the decomposition product of KMnO_4 thermal decomposition (up to 900°C); D, powdered KMnO_4 crystals only; E, as C with the exception that the “insoluble portion” is used.

nitrogen. The factor causing this change is the catalytic nature of the product zinc oxide surface which allows carbon monoxide to be oxidised to carbon dioxide in the presence of air. These two factors do not always coincide and this has produced very complex DTA signals [21]. The calcium oxalate decomposition to calcium carbonate is often found to be exothermic in air but endothermic in nitrogen. The exothermic nature of the decomposition in air is due to the catalyst action of container material. It would seem that both container material or the thermocouple material may act as a catalyst in these circumstances.

The catalytic effect of additions on the rate of thermal decomposition of potassium permanganate (KMnO_4) may be investigated using TG in an atmosphere of air [79]. The additives used were potassium manganate (K_2MnO_4), potassium hypomanganate (K_3MnO_4), the phase “ $\text{K}_4\text{Mn}_7\text{O}_{16}$ ”, manganese dioxide (MnO_2), zinc oxide (ZnO) and cuprous oxide (Cu_2O). The isothermal decomposition plots for KMnO_4 (fractional decomposition α plotted vs. time t) were found in the studies by Booth et al. [79] to produce an S-type $\alpha-t$ trace. This could be analysed using a Prout and Tompkins type equation with an initial acceleratory period being replaced by a deceleratory period over about half the decomposition. Typical data are shown in Fig. 5. These studies showed that the addition of MnO_2 caused the elimination of the acceleration period so that the rate was deceleratory throughout. The phase “ $\text{K}_4\text{Mn}_7\text{O}_{16}$ ” had a similar effect. The compounds K_2MnO_4 and K_3MnO_4 can be shown to have a negative catalytic effect upon the acceleratory period.

The introduction of a solid phase oxide to the potassium permanganate was shown to decrease the effect of the initial slow acceleratory reaction with an increase in the overall importance of the deceleratory process. These oxides do not eliminate the initial slow acceleratory period but all produce

their catalytic effect on the deceleratory rate process. It is considered that the excitation and transition of the electron is of importance in the thermal decomposition of potassium permanganate. KMnO_4 is known to be an *n*-type semi-conductor [80], and the additives accelerating the decomposition have a much greater work function compared with KMnO_4 [81–83]. In accelerating the decomposition the MnO_2 acts as an acceptor of electrons, whereas manganate and hypomanganate act as donors of electrons and thus inhibit the decomposition.

THE ADAPTATION OF THERMAL ANALYSIS METHODS TO STUDY CATALYSIS SYSTEMS AND PRECURSOR REACTIONS

In this concluding section the adaptation of thermal analysis methods to study catalysis are outlined so that the reader can make an appropriate choice of equipment and technique to study any particular system. In systems discussed so far the solids used as catalysts have been the object of study. However, the actual process of chemisorption and the catalytic reaction itself may also be investigated using thermal analysis.

The chemisorption of a gas on a catalyst surface may be measured using an automatic vacuum microbalance to determine the adsorption isotherm. There are many thousands of these isotherms reported in the literature and it is best to refer to the standard textbooks and reviews for examples [84–87]. In these adsorption isotherms the temperature is kept constant and the equilibrium amount adsorbed determined at various pressures of gas above the sample. It is possible, however, to allow chemisorption to take place up to saturation and follow how this saturation value alters as the temperature is altered. Further, on the assumption that hydrogen and carbon monoxide can chemisorb specifically on surface metal atoms, then the number of metal atoms at the surface can be ascertained from the uptake of these gases under suitable conditions [88]. The desorption can also be followed under vacuum by plotting the mass loss vs. temperature. Thus the gas can be chemisorbed to saturation and then progressively desorbed into vacuum as the temperature is raised. The differential plot (DTG) will then reveal peaks at characteristic temperatures as adsorption sites of a particular kind are desorbed. It is not of course necessary to restrict this technique to TG and the same peak effect may be achieved, for example, by desorbing hydrogen from Raney nickel catalysts and using mass spectroscopy to detect the desorption of hydrogen. In these experiments weakly bound hydrogen was desorbed at 102°C while more strongly bonded hydrogen was lost at 243°C [89].

Hydrogen is also utilised *in situ* in the catalytic reactor to reduce the catalyst precursor oxide to the catalyst metal or a lower oxide which is the active catalyst species. This process can be studied using TG equipment and examples can be found in the reduction of the oxides of uranium and nickel [90].

An alternative method of studying catalytic systems is the use of a pulsed system in which small quantities of reactive gas are injected at repeated time intervals into an inert carrier gas. Again, DTA equipment can be used in this

manner and an example can be found in the study by Richardson et al. [91] on the adsorption of ethylene onto a nickel catalyst.

The catalyst activity in pulsed techniques can be judged from the size of the exothermic peak on the DTA trace on a spent catalyst or catalysts regenerated several times. For a given amount of material the greater the area under the exotherm the greater the activity of the catalyst. This approach is not restricted to DTA provided an appropriate signal can be obtained. The activity of a range of catalysts for the oxidation of toluene has been studied by a technique of this kind [92].

Catalyst poisoning is related to the activity, and the above techniques can be utilised to follow the reduction of catalyst efficiency by the occupation of active sites on the catalyst. The deposited poison is most often a coke deposit and less often sulphur. The coke may be estimated and studied on TG equipment by burning off in air. The actual deposition of coke can be followed using TG methods. Thus Hughes and Zadeh [93] plotted the amount of carbon deposited vs. time for a system held at various temperatures comprising a silica-alumina catalyst exposed to *o*-xylene vapour in a nitrogen carrier gas. As the temperature was raised from 400°C to 500°C the amount of coke deposited after 240 min varied from about 0.5% mass gain at the lower temperature to about 2.5% mass gain at 500°C.

Water is a common source of poisoning in catalyst systems. It is, for example, essential to eliminate water in the oxidation of carbon monoxide to carbon dioxide over manganese oxides in the presence of air [18]. The effect of water is commonly to cause an alteration to active sites by allowing sintering to take place in lower temperature ranges. Sintering studies on magnesium oxide surfaces in the presence of water vapour serve as an illustration of the manner in which water vapour acts [71]. In another study Scheve and Heise [94] relate the catalyst efficiency to the mass loss due to dehydroxylation.

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