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INHIBITION OF HYDROCARBON
OXIDATION OVER SUPPORTED PRECIOUS METAL CATALYSTS.

by

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degree of Doctor of Philosophy
of the City University.

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ABSTRACT.

This investigation involves a study of the processes that cause deactivation of supported precious metal catalysts during the oxidation of methane. Of particular interest were the causes of loss in activity observed for catalytic beads which are used for the detection and estimation of hydrocarbons. Initially, the kinetics and mechanism of methane oxidation were studied using a pulse-flow microreactor in the presence and in the absence of gaseous oxygen. The orders of reaction and activation energies are in good agreement with those obtained by other investigators. A Langmuir-Hinshelwood mechanism with reaction between adsorbed methane and adsorbed oxygen is proposed.

The effects of thermal deactivation and self-poisoning on the oxidation of methane were shown to be severe only under extreme conditions. Although water vapour had no lasting effect on powder catalysts in the microreactor, it could cause loss of activity for catalytic beads in a static reactor. Deactivation by carbon deposition was unlikely to affect the catalyst as long as contact times remained short and oxygen was present in excess. Both the support and the precious metal underwent some physical changes at higher temperatures but, although severe agglomeration of catalyst particles occurred, methane oxidation remained substantially unaffected.

Addition of small amounts of inhibitors such as halocarbons and organosiloxanes to the reactants caused some loss in activity for hydrocarbon oxidation. The support played a significant role in the degree of deactivation observed for the precious metal and the ability of the catalyst to recover from inhibition depended to some extent on the support used. Supports for which strong precious metal-support interactions were present tended to affect beneficially the ability of the catalyst to recover. Surface analysis techniques such as transmission electron microscopy, Auger electron spectroscopy and X-ray photoelectron spectroscopy were applied to provide information as to the effect of the inhibitor on the precious metal and support as well as the fate of the inhibitor, both during and after inhibition. The possible mechanisms by which inhibition occurred are discussed.

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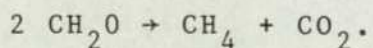
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1:1 General background.

Methane is by far the most abundant hydrocarbon in the atmosphere. While a large number of other simple organic compounds are found at concentrations in the parts per billion range, methane is present at concentrations in the order of one part per million (Graedel, 1978). It has been suggested (Oparin, 1957) that in the pre-archeozoic world, before life on earth, the atmosphere was composed mostly of hydrogen, water, ammonia and methane. Non-biological synthesis of amino acids from these compounds has been achieved by the use of ultra-violet radiation or electronic discharge.

Most methane in the atmosphere is of recent biological origin (Ehhalt, 1974). Fermentative decay of vegetable remains in swamps and paddy fields and enteric fermentation in animals are the major land-based sources, while organic marine sediments provide methane from under the sea. At the most, only 20% of atmospheric methane is obtained from fossil fuels and leakage from oil and gas wells. Roughly 0.7 to 2% of all photosynthetically produced organic matter decays to produce methane; the rest is converted to carbon dioxide (Holland, 1978). Decomposition of formaldehyde by fermentation in decaying organic matter is thought to be the dominant process,



Modern sewage treatment by anaerobic fermentation produces methane in large quantities and this technique can

be applied to animal and plant crop wastes. It is even proposed to harvest marine sediments of high organic content obtained from enclosed areas such as the Black Sea and the Great Lakes of America by raising these sediments from the sea bed and obtaining methane by heating.

Geothermal activity is the major cause of methane production underground where it is usually found in the presence of petroleum. Associated gas is the volatile portion of crude oil which probably has its origins in marine material (The World Energy Book, 1978). Non-associated gas is apparently unrelated to liquid oil accumulations and may be derived from vegetable matter. Natural gas is the term generally given to a mixture of predominantly hydrocarbon gases found in subsurface rock reservoirs. The main constituent gas is methane (often consisting of 85-95 per cent of the total), together with ethane, propane and butane. As a premium fuel, the use of natural gas is widespread with the advantage that, being gaseous, it may be transported either by pipeline or pressurised in tanks and cylinders. It has the disadvantage, however, of forming an explosive mixture when present at concentrations of between 5 per cent (lower explosive limit or LEL) and 32 per cent (upper explosive limit or UEL) by volume in air (Firth, Jones and Jones, 1973). This necessitates its detection in enclosed spaces where it presents a serious explosion hazard.

The earliest application for gas detection arose in mines where naturally occurring methane in conjunction with

air is readily ignited by sparks from miners' tools or any unprotected flame. (Firedamp is the name given to the gas in coal mines, which contains, at times, about 96% methane). The first catalytic transducer which converted heat evolved at its surface by catalytic oxidation of a flammable gas into an electrical signal was a platinum wire filament introduced in 1880. Due to difficulty in maintaining electrical stability caused by evaporation of platinum over a long period of operation at high temperatures (1175-1273K) (Bussiere et al, 1956), a catalytic gas sensing bead was developed by Baker (Baker and Firth, 1969). This bead comprises a platinum wire coil, which acts both as a heater and a sensor, embedded in a refractory oxide impregnated with a precious metal catalyst, usually palladium. An electric current is passed through the coil to heat the catalyst to its operating temperature. Exposure to a flammable gas causes an exothermic reaction at the bead surface with accompanying rise in the temperature of the sensor and hence in the resistance of the coil. This increase in resistance results in a change in the voltage across the sensor element which is used as a measure of the gas concentration.

A major drawback in the use of catalytic gas detectors is their susceptibility to poisoning by a number of compounds which may be present in the atmosphere (Firth, Jones and Jones, 1972). Particularly hostile conditions are encountered on offshore oil production and drilling platforms in the North Sea (Denney, 1979). Silicone oils are thought to be the major poisons on these platforms

but welding fumes, salt spray, halogenated hydrocarbons and sulphur compounds, as well as lead products from engine exhausts, also present a hazard. Gas detection in car parks is hampered by high levels of lead, while hydrogen sulphide is often encountered in sewers along with flammable gases. The presence of these poisons in concentrations as low as a few parts per million may cause the failure of catalytic gas detectors by preferential adsorption of the poison and subsequent loss of signal. This particular type of failure is not fail-safe and only testing with a calibration gas can confirm satisfactory performance.

Despite their limitations, catalytic gas detectors are more widely used than other types of gas detector such as infra-red, thermal conductivity or semiconductor devices (Fire Surveyor, 1977). Although infra-red detectors are specific to a particular flammable gas, they are expensive and intrinsic safety is difficult to achieve for such a device. The signal obtained from thermal conductivity beads at low concentrations is too small to be of use, but these beads may be used to measure methane levels at the upper explosive limit and above, while semiconductor devices are often non-selective and problems may arise if a number of gases with different explosive limits are present simultaneously.

The widespread use of methane as a fuel, and increasingly as a feedstock for ammonia and hence fertilizer production, has meant that the requirements for its detection are

rapidly increasing. The development of catalysts capable of operating under hostile conditions in which methane may be present is essential. An improved understanding of the mechanisms involved in both the catalytic oxidation of methane and the poisoning of this reaction is the main purpose of this research.

1:2 The physics and chemistry of catalysis.

1:2:1 General.

Methane is the most difficult of the simple hydrocarbons to oxidise requiring high temperatures and very active catalysts (Ahuja and Mathur, 1967). The heterogeneous catalytic oxidation of methane rarely leads to the formation of significant amounts of partial oxidation products; carbon dioxide and water being invariably the predominant compounds produced. Small amounts of formaldehyde and formic acid have been isolated but the yields of these compounds are significant only when catalysts of low activity are used (Margolis, 1963). The reason for the low selectivity of most catalysts is the ease of further oxidation of the oxygen-containing intermediates formed initially. Nevertheless, total oxidation of methane is of industrial importance, although the products of the reaction have no application that is economically significant. Catalysts responsible for the removal of unburnt hydrocarbons from the exhausts of internal combustion engines rely on the conversion of these compounds to carbon dioxide and water to reduce atmospheric

pollution (Wei, 1975) while enclosed vessels such as submarines and spacecraft use catalytic scrubbers for hydrocarbon removal.

Many studies have been made of the catalytic oxidation of methane over transition metals, the first being that by Davy (1817). The requirement for high activity led to an investigation by Anderson et al (1961) who found the order of effectiveness for methane oxidation by a number of metals supported on γ -aluminium (III) oxide to be:

$\text{Pd} > \text{Pt} > \text{Cr} > \text{Mn} > \text{Cu} > \text{Ce} > \text{Co} > \text{Fe} > \text{Ni} > \text{Ag}.$

Cobalt (VI) oxide was the most effective of the unsupported catalysts tried. Mezaki (1963) also found that palladium was the most effective catalyst for methane oxidation when compared with vanadium (V) oxide, cobalt (III) oxide, aluminium (III) oxide, copper-chromite and hopcalite (a mixture of manganese (IV) oxide, copper (II) oxide, cobalt (III) oxide and silver (I) oxide). Highly active oxidation catalysts almost invariably contain transition metals with partially filled inner electron shells (d-shells). Either metals (palladium, platinum, etc.) or metal oxides (semiconductors such as vanadium (V) oxide, molybdenum (VI) oxide, tungsten (VI) oxide, copper (I) oxide etc., and complex semiconductors such as spinels) are the catalysts most widely used for hydrocarbon oxidation.

1:2:2 Theories of catalysis by metals.

A complete understanding of the factors that contribute towards the catalytic activity of a particular metal or

metal oxide has not yet been fully realised. The primary function of the catalyst is to increase the rate at which the chemical reaction proceeds. This is achieved by lowering the energy barrier required for the reaction. The heterogeneous catalytic process may be represented as a series of steps (Sabatier, 1912) involving:

- a) Diffusion of reactants from the gas phase to the surface.
- b) Chemisorption of the reactants and their migration to active sites.
- c) Chemical reaction of the adsorbed species to form adsorbed products (often via a series of reaction intermediates).
- d) Desorption of the products from the catalyst surface.
- e) Diffusion of the products into the gas phase.

The first and last steps involve the making and breaking of chemical bonds with the surface atoms of the catalyst. Bond creation will depend both on the electronic properties of the surface and, to a lesser extent, on the electronic properties of the bulk catalyst. In addition, a geometric factor has to be considered. Not only will lattice dimensions vary between different catalysts but in catalysts of the same elemental composition different planes, steps and surface defects (such as screw and edge dislocations) will be present. These geometric and electronic factors cannot be studied independently. Pauling (1960) has shown that the lattice spacing of metals is directly related to their electronic properties and that considerable

rearrangement of surface atoms occurs during the course of a surface reaction. It would appear, therefore, that both electronic and geometric factors play an interrelated role in heterogeneous catalysis.

Several theories have been introduced to explain the behaviour of a metallic catalyst in purely quantum mechanical terms, the most significant being the band theory and the valence bond theory. These have produced some correlation of catalytic activity with the properties of the metals. It is the transition metals which show catalytic activity and some trends in physical properties are observed on moving across the transition series in the periodic table. Those properties related to cohesive energy (melting point, boiling point and interatomic distance) show maxima around Groups VA and VIA, while the surface energy and density show maxima and the interatomic distance exhibits a minimum in the region of Group VIII.

1:2:3 The band theory of metals.

The band theory (Mott and Jones, 1936) suggests that the atomic orbitals of individual atoms must be coalesced in the solid to form discrete energy bands separated by energy gaps. The electrons then fill these bands to provide the lowest energy level. The Fermi level in a partially filled band is the energy level with an electron occupation probability of one half.

The band widths in metals are such that overlap of bands

may occur; in particular s- and d-band overlap occurs in transition metals. This will affect the degree of occupancy of the d-band. For example, ten electrons per atom are required to fill the 3d-band. In the case of nickel there are ten 3d- and 4s-electrons but because of band overlap some electrons go into the 3d-band and some into the 4s-band. With nickel, palladium and platinum, there are about 0.4-0.6 electron holes in the d-band per atom; with cobalt the value is 0.75 and with iron it is 0.95. With copper and silver the holes are completely filled but the s-band remains half filled (Figure 1:1). As the d-band is narrow, the density of states is high and, where the d-band is partly filled as in the transition metals, the density of states at the Fermi level is also high. As electrons are progressively added, they go first into the s-band and this increases the cohesive strength. Thereafter they go into both bands and the cohesive strength diminishes, possibly due to repulsion between s-electrons (Bond, 1962). The magnetic properties of the transition metals can be accounted for when the presence of unpaired electrons in the incompletely filled d-band is considered. Copper with a filled d-shell is diamagnetic as expected. Hence, the band theory provides a qualitative explanation of the physical properties of transition metals of Group VIII and beyond in the Periodic Table.

1:2:4 The valence bond theory of metals.

The valence bond approach to metallic bonding was

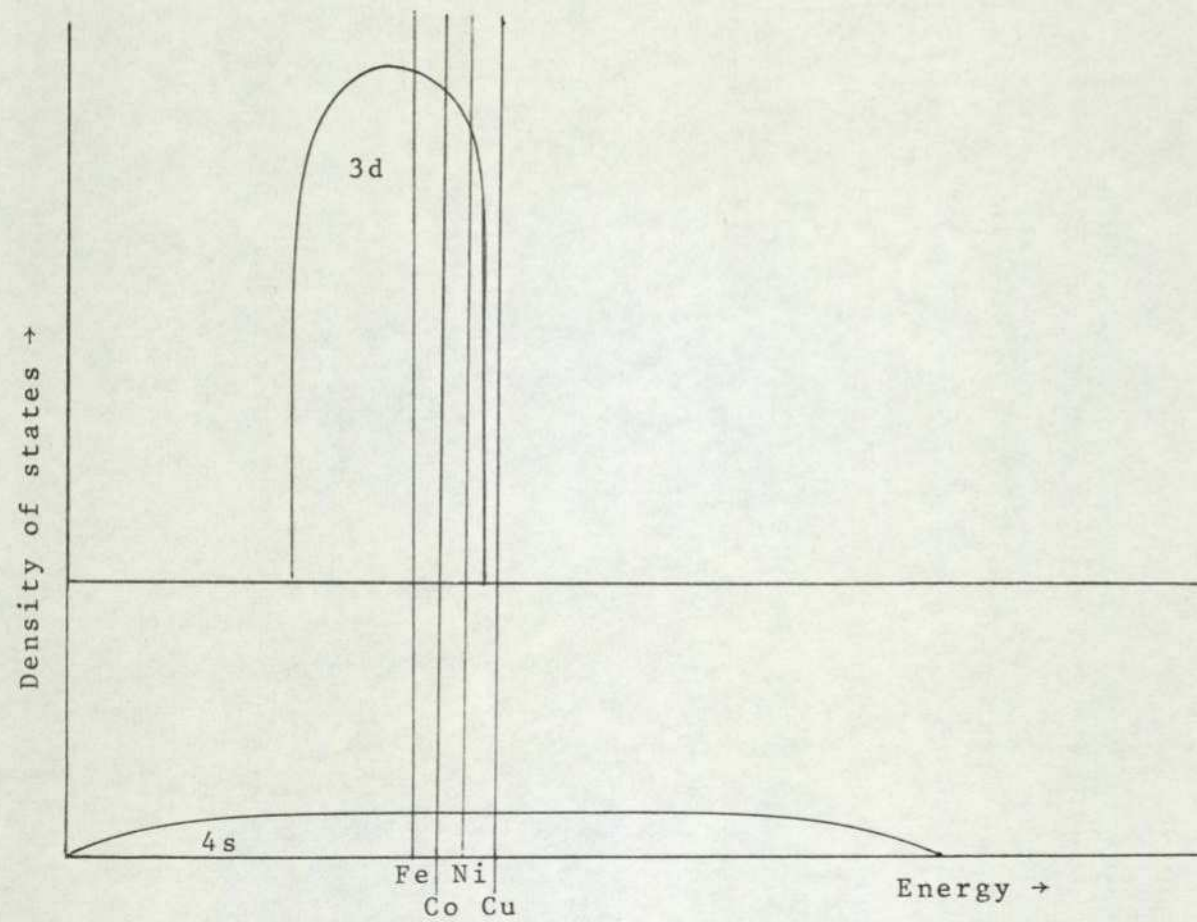


FIGURE 1:1 FILLING OF 3d AND 4s BANDS BY IRON, COBALT, NICKEL AND COPPER.

suggested by Pauling (1960). In his model each metal atom provides dsp-hybrid orbitals, overlap between which leads to metallic bonding. It is assumed that the actual electronic configuration in the metal arises from resonance between all possible bonding arrangements, the number of orbitals in use exceeding the number of electrons. Each atom is assigned two types of d-orbital, those that are involved in bonding which form dsp-hybrids and those that remain as atomic d-orbitals. There are nine orbitals per atom and it is assumed that the magnetic properties of iron, cobalt and nickel are due to the unpaired electrons in the atomic d-orbitals. The contribution that the d-orbitals make to the dsp-hybrids may be calculated. This percentage d-character has a value of 40% in Ni, Mn and Co, 46% in Pt and 50% in Ru and Rh (Anderson, 1975).

A ligand field modification to the band theory was introduced by Trost (1959) and Goodenough (1963), in which the effect of the crystal field is to direct valence electrons into the regions between the nearest and the next nearest neighbour atoms. This theory falls between band theory and a valence bond approach. In an isolated atom in a cubic field, the five-fold degenerate d-level splits into three-fold (t_{2g}) and two-fold (e_g) degenerate levels. The former contains d_{xy} , d_{zy} and d_{zx} orbitals and the latter contains the $d_{(x^2-y^2)}$ and d_{z^2} orbitals. In the metal, the d-band is split, the t_{2g} and e_g levels have orientations similar to those of the atomic orbitals. Bonds formed in the metal occur by overlap of

the twelve lobes of the t_{2g} orbitals. In the case of a face-centered cubic metal structure there are twelve nearest neighbours linked by t_{2g} orbitals; and the six next nearest neighbours are bonded using the e_g orbitals.

1:3 Chemisorption of gases on metals.

1:3:1 Theories of chemisorption.

Chemisorption at a metal surface will occur when the energy of the atomic valence states of the atom to be adsorbed lies within the energy of the valence band of the metal. The chemisorption bond is a covalent bond between electrons from the adsorbate and unpaired electrons in atomic d-orbitals (Trapnell, 1955). The wave functions of the metal surface will mix with those of the atom undergoing adsorption, forming bonding orbitals whose character represents the orbitals of the nearest atoms. In other words, close to the adatom the wave functions have the character of the free atom valence states and on moving towards the metal they represent more closely the orbitals of the metal. The electrons then fill these orbitals, leaving the corresponding antibonding orbitals unfilled.

The valence bond theory assumes that the dsp-orbitals which are at the surface and so unbound, will be orientated towards the positions that would be occupied by metal atoms in the next layer. The d-orbitals are also available for bonding. On the Goodenough model, the t_{2g} orbitals point towards the position of the nearest neighbours (like the dsp-orbitals in Pauling's model) while the e_g orbitals point

towards the next nearest missing neighbours.

Transition metals vary in their ability to chemisorb gases. Dissociative chemisorption of hydrogen, oxygen, nitrogen and alkanes occurs on these metals. Non-dissociative adsorption of alkenes and aromatics takes place by interaction between the surface metal atoms and the π -electrons of the molecule. There is also weak molecular chemisorption of hydrogen and nitrogen at low temperatures and coverages. The type of bonding by which non-metallic atoms such as H, O, S and N interact with the surface also varies. In the case of oxygen, there is evidence that, in certain circumstances, the oxygen carries a substantial negative charge (Anderson, 1975).

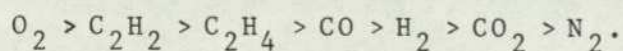
The geometric relationship between an adatom and the surface metal atoms in most cases remains unresolved. Use of low energy electron diffraction (LEED) to study the surface symmetry of the adatom does not show its position relative to the surface metal atoms. Nevertheless, use of ion-neutralisation spectroscopy on oxygen and sulphur adsorbed on a nickel (100) surface (Hagstrum and Becker, 1969) has revealed the possibility of co-ordination of the adatom to more than one surface atom. Adsorption of carbon monoxide has been shown by infra-red spectroscopy (Little, 1971) to occur in two forms, bridged and linear, the former involving bonding to two metal surface atoms, the latter involving bonding to only one. The use of electron spectroscopy for surface studies is providing much useful information

on the surface states of adsorbed species and the results are reviewed in a later section.

1:3:2 Adsorption and catalysis.

The adsorption of one or more of the reactants may play a major role in the overall catalytic reaction. The catalyst increases the rate of reaction by providing a surface on which the reactant is adsorbed and activated, thus lowering the potential energy barrier between the reactants and the transition state. Hence it would be expected that the strength of the bond joining the metal atom to the adatom would need to have an optimum value. If it is too weak the reactant will be insufficiently activated; if it is too strong, the reactant will be too stable. With the transition metals, the chemical reactivity tends to decrease from left to right across the Periodic Table. The Group IB and IIB metals (Cu, Zn, Au, Ag, etc.) have full d-shells and undergo chemisorption less readily. A compromise in terms of activity is reached in Group VIII which contains many of the active metal catalysts.

The strength of the adsorbate-metal bond depends on the gas undergoing adsorption as well as on the metal. It is possible to place the strengths of the bonds in some common gases in the following order for any transition metal (Trapnell, 1953),



The heat of formation of metal-adsorbate bonds may

also be related to the catalytic activity of the metal concerned. For example, a relationship exists between the heat of formation of metal formates and the catalysed decomposition of formic acid over those metals (Sachtler and Fahrenfort, 1961). On moving across the transition metal series in the periodic table a peak in activity is obtained at Group VIII. This may be explained by the fact that a low heat of formation as in the case of silver and gold provides a low concentration of the active species. When the heat of formation is high, as with iron, the adsorbed intermediates are too strongly held. This theory may be applied to other reactions, for example the hydrogenation of ethylene, where the rate of hydrogenation increases as the rate of adsorption of hydrogen or ethylene decreases (Beeck, 1950a). In most cases, however, the situation is more complex especially when more than one reactant is present either because a number of adsorbed species with different coverages and strengths of adsorption are competing with one another or because the geometric relationships between the adsorbed species and the surface need to be considered. The decomposition of ammonia over transition metals shows little correlation between heats of activity and rate of reaction (Bond, 1962). Fundamental information about the factors that control catalytic activity are rarely obtained at a molecular level from this approach.

1:3:3 The study of catalyst surfaces.

The use of techniques for studying the surfaces of

catalysts and the species adsorbed on them has increased markedly over the past few years. The application of ultra-violet and X-ray photoelectron spectroscopy, infra-red reflection and adsorbance spectroscopy and Auger electron spectroscopy has provided a physical contribution to the understanding of chemisorption and catalysis which provides information on the electronic and geometric properties of simple adsorbed species at a surface.

The surfaces studied are, of necessity, either those of clean single metal crystals or of clean polycrystalline materials at a very low pressure (10^{-8} - 10^{-12} Torr), this situation being far removed from that for catalysts operating under normal conditions. Furthermore, the strongly bound intermediates normally studied are usually those of high sticking probability under steady state conditions. Such adspecies may take little part in the kinetic processes that determine rates and catalytic activity. Nevertheless, alteration of the electronic environment in the immediate vicinity of the surface may promote the formation of an active intermediate.

Sensitive photoelectron spectroscopic techniques have been developed for investigating the surface properties of metals and alloys as well as of chemisorbed species. X-ray photoelectron spectroscopy (XPS) involves exciting the specimen with X-rays while in ultra-violet photoelectron spectroscopy (UPS), the exciting source is ultra-violet radiation. Photoelectrons ejected from the surface atoms

are then detected. The energy of the absorbed X-ray or ultra-violet photon is partially lost in overcoming the energy which binds the electron to the atom and the rest is converted to kinetic energy of the ejected electron. This kinetic energy is then analysed in a high resolution energy analyser and a plot is obtained of kinetic energy versus the number of electrons. The binding energy of the ejected electrons may be found from a consideration of the energy of the incident X-rays. This binding energy is a function of the chemical environment and shifts of several electron volts are common for different oxidation states. Hence information concerning the oxidation state and elemental composition can be obtained.

Energy level shifts that accompany chemisorption may also be measured using photoelectron spectroscopy to obtain an understanding of the bonding of adsorbed species. Kinetic energy peaks for electrons ejected from the surface of solids on which chemisorption has occurred correspond to ionisation of electrons initially in the orbitals of the surface complexes. The orbital energies depend on hybridisation, nature of bonding, image and relaxation effects. Thus energy level changes between free and adsorbed molecules provide basic information on bonding.

XPS is relatively easy to quantify and chemical bonding information can often be obtained from peak shapes and positions. On account of the impossibility of focussing

the intense X-ray beam, however, XPS yields poor spatial resolution. It will give no information on the arrangement of molecules adsorbed on the surface so that their orientation with respect to the surface cannot be found. UPS will give geometric information on the adspecies and is particularly sensitive to the chemical states at the surface, yielding information on the electronic structure of the adsorbate.

The use of Auger electron spectroscopy (AES) is becoming more widespread due especially to its suitability for the analysis of surface composition and the provision of surface mapping of elements. Auger electrons are ejected from the atoms with energies uniquely related to the energy levels of the atoms from which they emanate. Hence, peaks in the electron energy distribution may be used to identify elements present at the surface. AES is an insensitive method for exploring the density states of valence electrons but is most effective for the detection and identification of foreign atoms at the surface and so finds a use in studies of catalyst poisoning.

A great advantage of all these techniques is that the examination is confined to the outer atomic layers of the surface. The kinetic energy of the electrons released by irradiation is rapidly dissipated by inelastic scattering and only those electrons that are found within the escape depth (two or three atomic layers, 0.5 - 3 nm) are photo-emitted despite the deeper penetration of the incident beam.

Turning briefly to work on specific adspecies, carbon monoxide is among the most widely studied adsorbates on metals. The two main spectral bands, with an energy difference of about 3 eV (Conrad, Ertl, Küppers and Latta, 1974) have roughly the same peak energies suggesting that its bonding is similar on all metals. It appears that the same two bonding orbitals are always involved despite the different electronic configurations of the adsorbent. However, the catalytic activity of metals for the oxidation of carbon monoxide is markedly different even though the peak energy values are the same. This suggests that there are two states of adsorbed carbon monoxide, only one of which is active in the catalytic process. These two different adsorbed states have been observed by Winterbottom (1973) on a platinum catalyst using a thermal desorption technique and are usually known as α - and β -CO. In the presence of low concentrations of oxygen, α -carbon monoxide was desorbed but oxygen was not adsorbed on the α -carbon monoxide sites and no carbon dioxide was observed. Above the α -carbon monoxide desorption temperature, β -carbon monoxide was desorbed, oxygen was adsorbed on the β -carbon monoxide sites and carbon dioxide was evolved. Similar results were obtained over a nickel catalyst (Horgan and King, 1971). Hence the β -carbon monoxide species is active in catalysis and spectral lines obtained by electron spectroscopy refer to α -carbon monoxide which probably obscures β -carbon monoxide in the spectrum. At present, however, UPS results do not provide sufficient information to predict the relative activity of metal catalysts for the oxidation of carbon monoxide.

The study of intermediates and adradicals formed at the surface during a catalytic reaction and identification of the electron orbitals of the adsorbates used in forming the chemisorption bond are essential for an understanding of the catalytic process. The surface interactions of larger adsorbed species are being increasingly investigated in order to provide orbital identification of the new surface energy levels created by chemisorption. The adsorption of benzene and ethylene on nickel has been studied (Demuth and Eastman, 1974) while the different chemisorption behaviour associated with different crystal planes is being examined (Clarke, Gay, Law and Mason, 1975).

Surface techniques have provided information on the electronic distribution of the outermost layer of atoms on which reaction proceeds. The influence of the bulk metal on this layer or the depth to which penetration of the reactants into the bulk of the catalyst occurs may be assessed by use of argon ion bombardment to etch away surface layers. A depth profile of the elemental composition up to at least 100 nm may be obtained by this technique and the contribution of these layers to the reaction may be appraised.

1:4 Supported precious metal catalysts.

1:4:1 The function of the catalyst support.

A catalyst support acts as a base on which the precious metal is dispersed (Innes, 1954). Its desirable properties

may include its ability to:

- a) Increase the active surface area of the precious metal by increasing its dispersal over the support. This will provide a greater active area than would be achieved by an equivalent amount of unsupported catalyst - an important consideration when expensive precious metals are used. Greater poison resistance may also be achieved by the use of greater surface areas.
- b) Increase the stability of the precious metal by keeping the well-dispersed metal crystallites apart and preventing sintering.
- c) Improve the catalytic activity of the precious metal by increasing the accessibility of the active surface. Conversely, to prevent inhibitors from reaching the catalyst, the precious metal may be dispersed down pores in the support surface which allow only the passage of reactants to the catalyst.
- d) Dissipate heat and prevent local overheating by transfer of heat away from the precious metal, thus preventing sintering.
- e) Interact with the precious metal catalyst to produce enhanced catalytic effects.

The precious metal may be incorporated into the support either by adsorption or by ion exchange of the precious metal salt (usually the chloride or nitrate). The salt is then dried and subjected to thermal decomposition. The provision of a reducing atmosphere (e.g. hydrogen) during decomposition should leave the precious metal in the metallic state (Betizeau et al, 1976). Alternative methods

may involve precipitation (Innes, 1954), mechanical mixing (Fallows and Mellers, 1926), spraying (Innes, 1954), chemical vapour deposition (Giraitis and Whaley, 1964) or vapour phase adsorption (Russell and Stokes, 1946). Sputtering of the precious metal on to supports such as silicon (IV) oxide and aluminium (III) oxide provides another method of catalyst preparation (Tyerman, 1975).

After impregnation of the support with the precious metal salt, drying and calcination provides dispersed metal particles. The requirement for the calcination temperature is that it should be low enough to prevent agglomeration of particles but high enough to cause total decomposition of the salt so that only the metal or its oxide remains on the surface. In practice, catalysts prepared from chlorine-containing salts of the precious metal (e.g. H_2PtCl_6 or PdCl_2) retain some chlorine on their surfaces (Bozon-Verduraz et al, 1978). Decomposition of the metal salt may be carried out in hydrogen, air, an inert gas or in a vacuum.

With all supported catalysts there is a tendency towards larger metal particle size as the concentration of the metal on the support increases. This agglomeration of metal particles or sintering may lead to catalyst deactivation. These factors will, however, be affected by the nature of the support both in its surface structure and its interaction with the precious metal itself. High surface area supports may undergo loss of porosity and surface area, which may leave some of the dispersed metal inaccessible to reactants

as well as providing a reduced surface for the remaining precious metal. If the reaction is site-selective (e.g. the preferred reaction site may be one particular crystal plane), catalytic activity may decrease with no change in metal dispersion due to changes in the surface topography of the dispersed metal. If the deactivation is due to adsorption of a poison at the metal surface, there will not necessarily be any correlation between the decline in activity and any change in metal dispersion.

In general, the greater the dispersion of the precious metal, the greater its susceptibility to deactivation by agglomeration. The effect of poisons will be less severe at high dispersions; for the fraction of surface area covered will be smaller the greater the degree of dispersion. Clearly, an investigation of the activity of supported metal catalysts requires an understanding of the support and its effect on the precious metal.

The final dispersions and metal particle sizes may be measured by a number of techniques. Factors controlling metal particle diameter are the temperature and gas atmosphere during calcining and the nature of the support and of the precious metal. The degree of impregnation of the precious metal into the support may also be studied (Summers and Ausen, 1978). The rate of precious metal uptake is partly controlled by pore diffusion and partly by the rate of chemical interaction between the metal complex and the support which results in impregnation profiles of different shapes. The depth of penetration into

the support may affect the catalytic activity of the final product (Summers and Hegedus, 1978).

A number of workers, (van Hardeveld and van Montfoort, 1966a; Aben, 1968; Scholten and van Montfoort, 1962) have measured the average palladium particle size for palladium on aluminium (III) oxide catalysts and obtained values in the region 1.0 - 4.5 nm. Heating in a vacuum in the range 370 - 670K did not have much influence on palladium particle size but at 770K it resulted in an increase by a factor of 3 - 4. On the other hand, the palladium dispersion was more sensitive to the temperature of hydrogen reduction; an increase in the reduction temperature increased the average palladium particle size by a factor of nearly two. There is a trend to larger average particle sizes with increased palladium loadings. For instance, an average diameter of 3.7 nm for 5 weight per cent palladium prepared by impregnation may be compared with a value of 2.2 nm for 2 weight per cent (Scholten and van Montfoort, 1962). Changes in the support will not always bring about changes in particle size; the dispersions of platinum on γ - and ϵ -aluminium (III) oxide were found to be similar, other factors being the same (Swift, Lutinski and Tobin, 1966). Differences have been found in sintering behaviour between palladium and platinum when on the same support and under the same conditions (Dodgson and Webster, 1976).

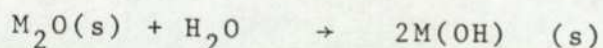
In the field of automobile catalysts, Lester et al (1975) found that the most stable binary palladium-platinum

catalysts for hydrocarbon oxidation were those with a Pd:Pt ratio of 4:1.

1:4:2 Properties of catalyst supports.

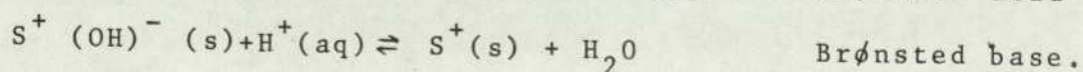
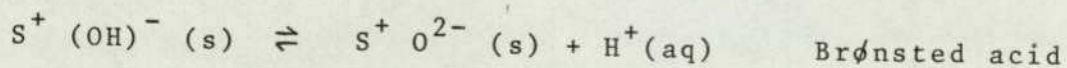
There is a wide range of support materials available on which precious metal salts may be dispersed. Those most commonly used are either refractory metal oxides (e.g. silicon (IV) oxide or aluminium (III) oxide) or carbon. Features common to most of these supports are their high surface area, their porous or microporous structure and the ability to adsorb water dissociatively on their surfaces.

Much of the surface chemistry of oxides is dominated by the extent to which adsorption of water occurs. The subsequent reactivity of the surface hydroxyl groups formed by the reaction:



is of interest as is the Brønsted acid/base behaviour and the extent to which metal atoms are exposed at the surface so as to generate Lewis acid sites.

The hydrated surface of an oxide may exhibit ion-exchange properties. The net surface charge carried by the oxide may be negative (Brønsted acid) or positive (Brønsted base) as shown by:



These surface effects are important in understanding the

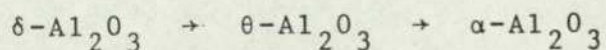
phenomenon of adsorption of precious metal ions on the surface of the support. Adsorption will take place to a greater or lesser degree depending on the surface charge on the support as well as on the precious metal used.

The initial process which the support undergoes on being heated is loss of water. For aluminium (III) oxide and silicon (IV) oxide loss of physically adsorbed water occurs if temperatures up to 390K are achieved (de Boer and Vleeskens, 1958). Heating above this temperature will result in the progressive loss of hydroxyl groups. However, even at high temperatures, hydroxyl groups are still present. For silicon (IV) oxide, the proportion of surface to internal hydroxyl groups increases with increasing dehydration temperature. The internal component is still significant at temperatures as high as 870K (Fripiat and Uytterhoeven, 1962).

High temperatures may also have a detrimental effect on the surface area of the support. A major requirement for the catalyst support is that of a high surface area that is stable at temperatures to which the catalyst is subjected. In addition, phase transformations and sintering of the support may alter considerably the behaviour of the catalyst, while attack by inhibitors may chemically erode the support as well as reducing the activity of the precious metal.

Supports which are commonly used to carry dispersed metallic particles are usually porous. This pore structure influences the way in which the metallic particles are deposited as well as reactant access when the catalyst is in use. It may also provide resistance to inhibition or poisoning if the inhibitor molecule is larger than the reactant molecules by preventing the inhibitor reaching the precious metal deposited in the pores. This pore structure, too, may be altered by heating.

Stabilisation of metal oxides to thermal degradation may be achieved by the addition of stabilisers. Gauguin et al (1975) studied the phase changes that occurred when γ -aluminium (III) oxide was heated and found that the stability of the alumina (surface area and crushing strength) was dependent on the phase transformations. Addition of certain oxides, however, resulted in the formation of stable compounds formed with the aluminium (III) oxide. Rare earth oxides favoured the formation of a theta-type structure stable at high temperatures. A surface area of $30 \text{ m}^2 \text{ g}^{-1}$ was retained at 1473K for aluminium (III) oxide "doped" with cerium (IV) oxide. The rare earth oxides prevented the phase change,



which occurs above 1323K, by stabilising the δ -phase formed from the γ -phase at ca. 1273K.

Interactions between the metal and support may take place which, if strong, may be responsible for degradation

of the support and loss of precious metal by the formation of alloys or mixed oxides with the support. Tauster and Fung (1978) studied the behaviour of iridium supported on metal oxides from Groups IIA, IIIB, IVB and VB, and measured hydrogen chemisorption following reduction at 473K. If supported on MgO , Sc_2O_3 , Y_2O_3 , ZrO_2 or HfO_2 , hydrogen chemisorption is not affected by reduction temperatures as high as 973K. If the carrier is TiO_2 , U_2O_3 or Nb_2O_5 , however, the hydrogen/metal ratio is decreased nearly to zero by reduction at 773K, while Ta_2O_5 requires a temperature of 973K for the ratio to decrease.

This strong metal-support interaction is not confined to supported indium. A titanium (IV) oxide/aluminium (III) oxide mixture was heated to 623K and 773K with and without 0.3% palladium added (Kravchuk et al, 1977). The presence of palladium facilitated reduction of the titanium (IV) oxide. A "spill-over" mechanism of hydrogen from the palladium onto the titanium (IV) oxide was proposed. Tauster, Fung and Garten (1978) postulated the formation of intermetallic compounds of the type TiPd_3 when palladium on titanium (IV) oxide catalysts were heated in hydrogen. The formation of these alloys explains the drop in hydrogen or carbon monoxide sorption after reduction of these catalysts in hydrogen at 773K. The catalytic activity of supported precious metal catalysts may be expected to depend on the temperature of reduction if strong support-precious metal interactions occur. The calcining temperature should be kept low in such cases and prolonged operation at high temperatures should be avoided.

1:4:3 Surface area determination

1:4:3:1 Supports.

Determination of the surface area of metal oxides used as supports is important for an understanding of the behaviour of the supported catalysts under operating conditions. Measurement of the total surface area may involve a number of techniques, either static or dynamic, based on physical adsorption of a gas at temperatures around its boiling point. Nitrogen is the gas most commonly used but other non-polar gases such as argon and krypton are also suitable. Static methods involve pressure-volume measurements. Dynamic techniques are less frequently used but involve the adsorption of a gas in a continuous flow system.

Static surface area measurement may be achieved by use of either gravimetric or volumetric measurements (Gregg, 1961). The gas or vapour is admitted to an evacuated space containing the adsorbent and the amount of gas taken up is found either by measuring the space occupied by the gas before adsorption (volumetric) or by weighing the adsorbent and the gas adsorbed on its surface (gravimetric). The balance introduced by McBain and Baker (1926) and developed by Rhodin (1950) is universally used for gravimetric measurements.

Dynamic surface area measurement by means of nitrogen adsorption may be carried out using a flow system introduced by Nelsen and Eggertsen (1958). This technique

differs from static methods in that the amount of gas adsorbed is determined by concentration measurements in a continuous flow system.

Adsorption measurements provide an adsorption isotherm from which the quantity of gas adsorbed, n_g , can be obtained using the BET equation (Brunauer, Emmett and Teller, 1938) where,

$$n_g = \frac{n_m^s c P}{(P_o - P) \left(1 + (c-1) \frac{P}{P_o} \right)}$$

$$\text{or } \frac{P}{n_g (P_o - P)} = \frac{(c-1)}{n_m^s} \cdot \frac{P}{P_o} + \frac{1}{n_m^s c}$$

n_m^s = quantity of adsorbed gas needed to form a monolayer.

P = equilibrium pressure.

P_o = vapour pressure of adsorbate in the condensed state at the adsorption temperature.

c = constant.

The slope of a plot of $\frac{P}{(P_o - P)n_g}$ versus $\frac{P}{P_o}$ gives a value for n_m^s . Hence the surface area, A , can be obtained from the equation:

$$A = a_m n_m^s,$$

where a_m = the area per molecule for a monolayer.

When nitrogen is the adsorbent, the value of a_m is taken as 0.16 nm^2 (Gregg, 1961).

Evidence of pore structure may also be obtained from adsorption isotherms using static gas adsorption measurements.

1:4:3:2 Active surface area measurement.

Techniques commonly used for measurement of the dispersion of precious metals over a support are electron microscopy or chemisorption of a gas on the exposed metal surface. Electron microscopy reveals the range of precious metal particle diameters as well as the average particle size. Chemisorption of a gas will provide the "active" surface area of the precious metal.

Estimation of metal surface area by gas chemisorption is achieved by measuring the uptake of a gas on the metal surface only. Chemisorption on the support should be negligible. Hydrogen, carbon monoxide and oxygen are gases regularly used for the measurement of surface areas of dispersed palladium and platinum catalysts. The average number of surface metal atoms associated with the adsorption of each adsorbate molecule as well as the number of metal atoms per unit area of surface must be known. Also, clean metal surfaces must be present before adsorption takes place.

Hydrogen is the gas most commonly used for metal surface area measurement. It does, however, have some disadvantages. Its adsorption on platinum may be slow, especially on certain crystal planes (Gruber, 1962). The hydrogen may

"spill over" from the platinum onto the support (Boudart, Vannice and Benson, 1969) or be taken up into the bulk of the metal (this is especially so in the case of palladium (Spenadel and Boudart, 1960)). Low temperature adsorption encourages hydrogen adsorption on the support as well as on the precious metal and the presence of contaminants, especially oxygen, can influence adsorption measurements.

Chemisorption of oxygen or carbon monoxide is generally less satisfactory than that of hydrogen for "active" surface area measurement, because monolayer formation and the chemisorption stoichiometry are less easily controlled. Carbon monoxide has been shown (Stephens, 1959) to undergo adsorption on two sites, bridged sites requiring a palladium: carbon monoxide ratio of 2:1 or linear sites where the ratio is 1:1. The ratio of bridged to linear sites has to be estimated.

The most favourable technique for gas adsorption studies for the measurement of the surface areas of palladium metal catalysts involved oxygen adsorption at 298K followed by hydrogen titration at 393K (Paryjczak and Jozwiak, 1975).

The electron microscope may be used to observe and measure the precious metal particle size directly. Modern transmission electron microscopes will resolve precious metal particles as small as 0.5 nm and are to be preferred to scanning electron microscopes which can be used only for particles bigger than about 100 nm. A statistically

large number of particles from much of the sample should be measured for accurate representation of particle size (a histogram or diameter distribution curve can be obtained for the sample). Flynn, Wanke and Turner (1974) have reviewed the difficulties arising in the use of transmission electron microscopy to measure particle size. A particular problem arises from the different contrast obtained for different particles, especially small particles (< 2 nm in diameter) due possibly to different electron beam orientation or to the orientation of the particle on the support. Furthermore apparent size is a sensitive function of "defocus"; identical particles in separate micrographs could appear to have differing sizes because of different settings of the objective focus.

A comparison between electron microscopy and gas adsorption methods of metal surface area and dispersion measurement was made by Paryjczak and Szymura (1979). Good agreement was obtained for well dispersed palladium on silicon (IV) oxide and aluminium (III) oxide for both methods of measurement of metal crystallite sizes below 6 nm diameter. Above this size, the hydrogen chemisorption and the electron microscopy results were in good agreement but for oxygen adsorption, the oxygen:palladium (surface) ratio was reduced from 1:1 to 0.66:1.

1:5 Kinetics and mechanisms of heterogeneous catalysis.

1:5:1 Introduction.

For a reaction over a solid catalyst, the physical steps are the transfer of the reactants to the catalyst surface, diffusion of the reactants into the interior of the pellet, diffusion of products back to the surface and transfer of the products from the exterior surface to the main stream. To simplify the kinetic interpretation of the experimental data, these physical steps have to be minimised. The chemical steps involve activated adsorption of reactants with or without dissociation, surface reaction on active sites and activated desorption of products. At least one of the reactants must be adsorbed for true heterogeneous catalysis to occur.

When the rate of the chemical reaction is lower than that of the physical steps, then true chemical kinetics are observed. When it is higher, diffusion kinetics are observed and the results will not be dependent on the chemical reactivity of the system.

1:5:2 Diffusion kinetics.

At high temperatures and conversions, diffusion may become the rate-limiting process. If only the external surface of a catalyst particle is accessible to the reactants, the overall rate of reaction becomes limited by the rate of mass-transfer to the surface. If the catalyst is microporous (as many refractory oxide-supported

palladium and platinum catalysts used for total oxidation are (Weisz, 1959)), then pore-diffusion or Knudsen diffusion may become rate-limiting. Operation of a catalyst in a region of diffusion control means that the reaction rate, the selectivity and the activation energy will vary compared with operation in a region of chemical control (Table 1:1).

The rate of molecular diffusion is not very sensitive to temperature and some transport limitation of the rate is most probable when the rate is high. This phenomenon is usually revealed as a fairly sharp fall in the apparent activation energy above a certain temperature. The rate of a chemical reaction increases exponentially with temperature, T , while the diffusion coefficient is proportional to $T^{\frac{1}{2}}$ for Knudsen diffusion and to $T^{\frac{3}{2}}$ for bulk diffusion.

Pore diffusion during hydrocarbon oxidation over copper (II) oxide/aluminium (III) oxide pellets was studied by Thomas and Nobe (1968), who found that larger diameter pellets were prone to diffusion effects. Smaller pellets prepared by dissecting the larger ones did not undergo pore diffusion at similar temperatures.

An alternative method of studying diffusion control in continuous and pulse-flow microreactors is to vary the flow through the catalyst bed while keeping the contact time constant by varying the bed length. For a pulse-flow microreactor, the pulse volume should be kept constant.

	True chemical control	Diffusion control	
		Knudsen diffusion	Bulk diffusion
Rate dependence on temperature.	$\text{Rate} \propto e^{-\frac{1}{T}}$	$\text{Rate} \propto T^{\frac{1}{2}}$	$\text{Rate} \propto T^{\frac{3}{2}}$
Activation energy.	E	$\frac{E}{2}$	Approaching zero.
Order of reaction.	n	$\frac{n+1}{2}$	$\frac{n}{2}$
Effect of particle size on conversion efficiency (fixed catalyst area).	Conversion independent of particle size.	Conversion increases with reduced particle size.	Conversion independent of particle size.
Effect of flow rate on conversion efficiency (fixed contact time).	Conversion independent of flow rate.	Conversion increases with flow rate.	Conversion increases with flow rate.

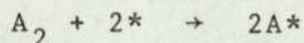
Table 1:1 The effect of diffusion on the observed kinetic relationships.

If bulk diffusion is rate controlling, then an increase in the flow rate will increase the turbulence, decreasing the boundary layer width and increasing the reaction rate. If bulk diffusion is absent, the conversion will be independent of flow rate.

1:5:3 Rate control by rates of adsorption and desorption.

If the rate of the surface reaction is rapid, the rate of adsorption or desorption becomes rate-controlling. This is, however, rare and adsorption is usually extremely rapid and its measurement is correspondingly difficult. There are some exceptions such as hydrogen adsorption on transition metals and carbon monoxide adsorption on palladium, platinum and nickel, where adsorption is rate-controlling.

The rate of adsorption or desorption can be expressed in terms of the number of particles adsorbed per unit time. For the process,



where * represents an adsorption site, the rate of adsorption will be:

$$r_a = - \frac{dP_{A_2}}{dt} = [**] \sigma Z' \exp \left(-\frac{E_a}{RT} \right) \quad \dots (1)$$

where P_{A_2} = pressure of A_2 in the gas phase.

** = concentration of pairs of empty sites.

σ = chance of a collision of a molecule with

pair of empty sites which results in adsorption.

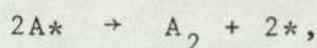
Z' = number of collisions of A_2 with total surface per cm^2 per second.

Z' may be replaced by $P_{A_2} (2\pi mkt)^{-\frac{1}{2}}$,

where m = mass of A_2 molecule.

k = Boltzmann constant.

For desorption,



the rate of desorption,

$$r_d = + \frac{P_{A_2}}{dt} = k_d \theta^2 \exp \left(- \frac{E_d}{RT} \right) \quad \dots (2)$$

where θ = fraction of sites covered by atom A.

E_d = activation energy for desorption.

k_d = velocity constant for desorption.

As rates of desorption are high, E_d is usually small and the exponential term may often be ignored. However, desorption requires activation and E_d is equal to the heat of adsorption ($-\Delta H_a$), when E_a is zero. The activation energy for adsorption, initially zero, becomes positive and progressively larger as the coverage increases. The activation energy of adsorption cannot exceed that of desorption; otherwise adsorption would be endothermic. Initially rapid "non-activated" adsorption is often followed by slower uptake of gas, the rate of which is readily measured. The slow chemisorption of oxygen on palladium, nickel and iron (Beeck, 1950b; Oda, 1954) may be ascribed to diffusion of oxygen from the surface to the

bulk leading to the formation of bulk oxide. Slow chemisorption of methane on nickel (Elovich and Zhabrova, 1939) has been found to obey the Elovich equation.

The rate of reaction for an adsorption or desorption process may be related to the surface coverage. When desorption is rate-controlling, the surface will be completely covered with reactants and products and the reaction will therefore be of zero order with respect to the reactants. If the reactants can be adsorbed by displacement of the product molecules, then there will be a definite dependence of rate on reactant concentrations.

The number of occupied sites θ and the number of vacant sites $(1-\theta)$ will vary but E_a and E_d will be dependent on the values of θ . If the dependence is linear then

$$E_a = (E_a)_o + \alpha\theta$$

$$\text{and } E_d = (E_d)_o + \beta\theta$$

Substituting in equations 1 and 2,

$$-\frac{dP_{A_2}}{dt} \propto (1-\theta)^2 \exp\left(-\frac{\alpha\theta}{RT}\right)$$

$$+\frac{dP_{A_2}}{dt} \propto \theta^2 \exp\left(-\frac{\beta\theta}{RT}\right)$$

For even coverage, variations in the fraction of sites occupied are only important in the exponential term and so:

$$-\frac{dP_{A_2}}{dt} = \frac{d\theta}{dt} = a \exp\left(-\frac{\alpha\theta}{RT}\right)$$

$$+\frac{dP_{A_2}}{dt} = -\frac{d\theta}{dt} = b \exp\left(-\frac{\beta\theta}{RT}\right)$$

On integration, the more commonly used forms are obtained,

$$\theta = \frac{RT}{\alpha} \log \frac{t + \frac{RT}{\alpha A}}{\frac{RT}{\alpha A}} \quad \text{and} \quad \theta = \frac{RT}{\beta} \log \frac{\frac{RT}{\beta b}}{t + \frac{RT}{\beta b}}$$

These equations are called Elovich equations and many adsorption reactions obey this form of relationship.

1:5:4 Kinetics of surface reactions.

The mechanism of a bimolecular reaction may be described by one of two different theories. One is that of Langmuir and Hinshelwood, whose mechanism involved adsorption of the two reacting species on adjacent sites followed by their interaction and the desorption of products. Alternatively Rideal and Eley suggested that adsorption of only one of the reactants may be necessary, reaction occurring by collision of molecules of the other reactant in the gas phase with the adspecies, forming products which were then desorbed. Establishment of the mechanism from the kinetics of the reaction alone is rarely possible. Conversely, however, the kinetics may be used to provide support for a particular mechanism.

The most fundamental method of expressing the rate of a reaction is to define that rate as the number of moles

or molecules of reactants disappearing per unit time. If n is the number of moles of reactant present at time t , the rate is $-\frac{dn}{dt}$ moles per second.

For a bimolecular reaction, the rate of disappearance of reactants is governed by the fraction of sites occupied by them and this is related to their pressure in the gas phase by the Langmuir Isotherm. For a reaction of the type



if the rate of reaction is determined by the adsorption of reactants on sites on the catalyst surface, then the rate of loss of A is given by:

$$-\frac{dP_A}{dt} = k\theta_A\theta_B \quad \dots\dots (i)$$

where P_A = partial pressure of reactant A.

θ_A = fraction of sites occupied by A.

θ_B = fraction of sites occupied by B.

k = rate constant.

The fraction of surface covered by each of the reacting species can be described by an extension of the Langmuir Isotherm. When the rate of adsorption equals the rate of desorption, the fraction of sites occupied by reactant A,

$$\theta_A = \frac{b_A P_A}{1 + b_A P_A + b_B P_B}$$

where b_A = Langmuir constant for reactant A.

b_B = Langmuir constant for reactant B.

and for reactant B,

$$\theta_B = \frac{b_B P_B}{1 + b_A P_A + b_B P_B}$$

$$\text{or } \frac{\theta_A}{\theta_B} = \frac{b_A P_A}{b_B P_B}$$

Substituting in equation (i),

$$-\frac{dP_A}{dt} = k \theta_A \theta_B = \frac{k b_A P_A b_B P_B}{(1 + b_A P_A + b_B P_B)^2}.$$

If both A and B are weakly adsorbed, this becomes:

$$-\frac{dP_A}{dt} = k b_A b_B P_A P_B$$

and the reaction is first order with respect to each reactant and second order overall.

If only A is weakly adsorbed and B is strongly adsorbed, then

$$-\frac{dP_A}{dt} = \frac{k b_A b_B P_A P_B}{(1 + b_B P_B)^2}.$$

However,

$$b_B P_B \gg 1$$

so that,

$$-\frac{dP_A}{dt} = \frac{k b_A P_A}{b_B P_B}.$$

If one reactant, say B, is not adsorbed (Eley-Rideal mechanism),

$$-\frac{dP_A}{dt} = \frac{k b_A P_A P_B}{1 + b_A P_A}$$

If $b_A P_A \gg 1$ the reaction is first order in B and zero order in A.

If $b_A P_A \ll 1$ the reaction is first order in A and zero order in B.

With slow desorption of products, the concentration of available active sites for reactant adsorption will decrease as the reaction proceeds. The rate of desorption may then become rate-controlling and the surface will at all times be covered with reactants and products. The rate will then be zero order with respect to the reactants.

For the heterogeneous catalytic oxidation of methane, reaction may take place via adsorption of both methane and oxygen followed by their interaction. In this case, the rate of reaction may be represented as:

$$-\frac{d[\text{CH}_4]}{dt} = k \theta_{\text{CH}_4} \theta_{\text{O}_2}.$$

If gaseous methane reacts with adsorbed oxygen, the rate may be:

$$-\frac{d[\text{CH}_4]}{dt} = k' \theta_{\text{O}_2} P_{\text{CH}_4}.$$

Substitution of values of θ derived from the Langmuir adsorption isotherms should provide a rate equation that is in reasonable agreement with the proposed reaction mechanism. Thus theoretical rate equations may be developed to describe all reasonable reaction mechanisms dependent on the strength of adsorption of each species and the number of sites occupied by each reactant, product or intermediate.

These models may then be compared with the rate dependence on concentration found experimentally. In practice, however, similar behaviour is predicted by a large number of theoretical reaction models precluding a choice of mechanism on kinetic grounds alone.

The variation in the rate of a heterogeneous reaction with temperature is normally expressed by the Arrhenius equation:

$$\frac{d \log_e k}{dT} = \frac{E_a}{RT^2}$$

where k = rate constant,

E_a = activation energy,

T = temperature, (K),

R = gas constant.

If E_a , the activation energy, is independent of temperature, integration gives:

$$\log_e k = -\frac{E_a}{RT} + \text{const.}$$

$$\text{or } k = A \exp\left(-\frac{E_a}{RT}\right)$$

where A = pre-exponential or frequency factor.

1:6 Catalytic reactor systems.

1:6:1 Pulse-flow microreactor.

For studies involving highly active catalysts, a flow reactor is generally preferable to a static reactor. Thus, for example, the pulse-flow reactor allows pre-equilibrium

times and states to be investigated and may reduce inhibition by the products of the reaction. Other advantages are that:

- a) Chromatographic analysis of the reaction products may be achieved for each pulse because the microreactor is inserted in the carrier gas line to the chromatograph.
- b) Small catalyst beds requiring small pulse volumes may be used allowing short contact times.
- c) Measurement of gas adsorption and hence catalyst surface area may be achieved "in situ".
- d) Diffusion effects may be minimised by careful temperature and flow control.

The catalyst is usually in the form of a powder or granules in a cylindrical bed which may be similar to that found in a continuous reactor. For thin film or wire filament catalysts longer contact times are required, as the "active" surface area and hence conversion of reactants are low. A static or possibly a continuous flow reactor is more suitable for these catalysts.

A major problem caused by the diversity of catalytic reactors is that comparison between the kinetic results obtained by each technique is not always possible. Hattori and Murakami (1968) compared the pulse-flow reactor with the continuous-flow reactor and found that there was good agreement of results if the reaction was first order and linear. Complications arose, however, if chromatographic separation of the reactants occurred due to different strengths of adsorption of the gaseous components on the

catalyst. This may be avoided by use of a rectangular pulse to prevent separation and the kinetics of the reaction may be compared directly with those of a continuous reactor.

Operation of a pulsed-flow reactor in which chromatographic separation of reactants and products takes place may be used to increase the product yield by moving the equilibrium favourably towards the products (Matsen, Harding and Magee, 1965). This is achieved by reducing the interactions between the products, thus allowing the reaction to proceed to completion. Equilibrium-limited reactions with small equilibrium constants are especially suitable for this method. Despite these advantages, the kinetics and thermodynamics are deliberately modified, thus providing little knowledge as to the true features of the reaction, and the results cannot be compared with those provided by other reactors.

To ensure that the catalyst bed is operating in a non-chromatographic regime, the length of the pulse is chosen such that it is far greater than the length of the bed and peak spreading is avoided by minimising mixing of the carrier gas and the reactants (Petsev and Dimitrov, 1966). The use of porous, high surface area supports for metal catalysts is undesirable when water is a product of the reaction as it may be retained on such supports unless the temperature is high.

For a simple first order reaction

A → products,

mixing of the carrier gas and reactant pulse in the pulse reactor will not affect the conversion (Bassett and Habgood, 1960). The rate of reaction may be written as:

$$-\frac{dA}{dt} = k[A]_0$$

and the conversion equals $k[A]_0 t$, where t is the time of reaction. Dilution of the reactant pulse by a factor Y means that:

$$[A]_0 \rightarrow \frac{[A]_0}{Y}$$

and $t \rightarrow tY$.

If the reaction is not first order, then the conversion will be dependent on $[A]_0^n$ and Gaziev et al (1963) have calculated some conversion dependencies for various values of n on the conversion factor x (e.g. when $n = 0$, conversion $\propto x$; $n = 0.5$, conversion $\propto x^{0.5}$ and when $n = 1.5$ conversion $\propto x^{-0.5}$).

The contact time or the time during which the reactant pulse is in contact with the catalyst bed is dependent on the flow rate and the pulse volume as well as the temperature of the catalyst bed. The relationship

$$t = \frac{V}{F} \cdot \frac{T}{T_0}$$

where t = contact time.

V = catalyst volume.

T = temperature of catalyst bed.

T_0 = room temperature.

will provide a value of the contact time at temperature T. Measurement of the variation of conversion with contact time may be achieved by varying the length of the bed and hence its volume while maintaining a constant flow rate and temperature. Only the use of a rectangular pulse will provide a contact time that is described by the above equation. Murakami, Hattori and Hattori (1968) observed that the conversion increased with decreasing pulse width and hence shorter contact time for cracking of cumene on a silica-alumina catalyst.

1:6:2 Catalytic bead reactor.

The use of a platinum filament or a calorimetric bead for investigating the catalytic oxidation of hydrocarbons is well documented (Hiam, Wise and Chaikin, 1968; Sieger, 1963; Baker and Firth, 1969). The bead calorimeter consists of a temperature-sensing device surrounded by a catalyst which measures the change in temperature produced by the reaction at the catalyst surface. The catalyst bed is in the form of a single pellet or bead on to which the catalyst is deposited while heating and temperature-sensing is provided by the platinum coil. In contrast to conventional catalytic systems where the conversion of reactants to products is studied, the heat evolved during catalytic combustion is measured.

The bead calorimeter can be operated either isothermally (Jones, Firth and Jones, 1975; Firth, 1971) or non-isothermally (Firth, 1966; Firth and Holland, 1969; Cullis, Nevell

and Trimm, 1973). During isothermal operation, the temperature is maintained constant during the catalytic reaction and the rate is obtained in terms of the difference in power dissipation of the calorimeter under reacting and non-reacting conditions. The non-isothermal method involves allowing the temperature of the bead to rise due to the catalytic reaction on exposure to the combustible gas and relating the rate of reaction to the increase in temperature.

1:6:3 The non-isothermal bead method.

The calorimetric bead is powered to its reaction temperature by passage of a current that is maintained constant through the platinum coil. As the reaction proceeds at the catalyst surface, heat passes through the bead to the coil which raises its temperature and hence the voltage across the coil. The theoretical considerations leading to a relationship for the voltage output:

$$V = \left[K \alpha \Delta H \left(\frac{dW}{dT} \right)^{-1} \left(\frac{dR}{dT} \right) \right] \frac{dn}{dt}$$

where K = constant.

α = fraction of heat which is measured by the calorimeter.

ΔH = heat of reaction.

$\frac{dW}{dT}$ = change in power difference with temperature.

$\frac{dR}{dT}$ = change in resistance with temperature.

$$\frac{dn}{dt} = \text{rate of reaction.}$$

are covered in the papers by Cullis et al (1973) and Jones et al (1975). The output is related to the rate of reaction if the values in the square brackets remain constant over the range of conditions used. The values of α , ΔH and $\frac{dR}{dT}$ are largely independent of temperature and K is a constant. The function $\frac{dW}{dT}$ will vary, however, with gas composition and temperature. Problems associated with changing gas composition may be avoided either by one reactant or a diluent being present in large excess. Temperature variation may be corrected by determining values of $\frac{dW}{dT}$ over a range of temperatures. (Cullis et al (1973) have shown that $\frac{dW}{dT}$ can vary by as much as 2.7% for a 10K rise in temperature). The presence of an inactive bead in one arm of the Wheatstone bridge acts as a compensator correcting variations in the output caused by temperature changes following differences in heat loss characteristics of changing gas mixture composition.

1:6:4 The isothermal bead method.

The requirement that the bead temperature is kept constant necessitates the use of a constant resistance power supply. The bead is inserted in a Wheatstone bridge system and the voltage output compared with that of a compensating bead in the presence and absence of a reacting gas mixture. As the reaction proceeds, heat is passed to the coil reducing the power required to maintain the coil at a constant resistance. Measurements are taken of the rate of the reduction in electrical power necessary to maintain

the bead at the same temperature in the presence as in the absence of reacting gas. The reaction rate is related to the power generated from the reaction by the equation:

$$-\frac{dn}{dt} = \frac{\Delta P}{\alpha \Delta H}$$

where P = power difference $(P - P_0)$.

For methane oxidation this can be written as:

$$-\frac{d[CH_4]}{dt} = \frac{\Delta P}{\alpha \Delta H} = k \times f(P_{O_2}) f(P_{CH_4})$$

where k = rate constant.

x = surface area of catalyst.

$f(P_{O_2})$, $f(P_{CH_4})$ = functions of oxygen and methane pressures respectively.

Kinetic information, such as the variation in rate constant with temperature and the order of reaction with respect to oxygen and methane, may then be obtained from the power output. Operation of a calorimetric bead under isothermal conditions in a region of diffusion control will ensure that the output is almost independent of temperature.

The isothermal method is to be preferred under most conditions, especially when the power generated by the catalytic reaction is significant compared with that required to maintain the bead at the reaction temperature. When the power generated by the reaction is small, however, the isothermal method is required to measure small differences in heat output and hence voltage change, so that the non-isothermal method may be preferable.

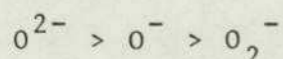
The advantage of the calorimetric bead over more con-

ventional catalytic reactors is that it provides a small reactor requiring small amounts of materials whose performance can be easily and quickly assessed by changes in its temperature. In order that a measurable output may be obtained, however, catalytic reactions suitable for investigation require large heats of reaction. In addition, complex reactions involving intermediates or a number of products cannot be studied as different values of ΔH will apply. Accurate estimation of the temperature at the bead surface is not easily achieved, only a part of the heat generated at the catalyst surface is transmitted to the coil and the operating temperature of the bead needs to be higher than that in more conventional reactors due to its small surface area. Both Firth and Holland (1969) and Nevell (1968) used a bead temperature of 673K to study the oxidation of methane. The reaction temperature will also depend on the nature and composition of the catalyst.

1:7 The adsorption of oxygen and methane on precious metals and their subsequent reaction.

1:7:1 Adsorption of oxygen.

Initial chemisorption of oxygen on precious metals is rapid and involves dissociation of oxygen molecules over the metal surface forming adradicals or negative ions. The order of stability of these is:

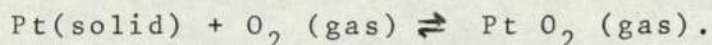


and these species may undergo homonuclear oxygen exchange at temperatures above 473K only over a small part of the precious metal surface (3% in the case of platinum, 2% in the case of

palladium) (Boreskov, 1966). The surface coverage by oxygen depends on the oxygen pressure and temperature as well as on the precious metal. Brennan, Hayward and Trapnell (1960) measured the oxygen uptake at room temperature and found the surface coverage by oxygen to be 63%, 74% and 97% in the case of platinum, palladium and rhodium respectively. At high oxygen pressures, Mummey and Schmidt (1980) using Auger electron spectroscopy observed multilayer formation of oxygen on platinum. True oxygen chemisorption rather than oxide formation is probably observed at these low temperatures.

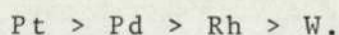
Palladium, unlike platinum and rhodium, adsorbs oxygen away from its surface into its bulk at temperatures above 523K. Campbell, Foyt and White (1977) found the rate of oxygen uptake to be independent of pressure, indicating that oxygen penetration into the bulk of the palladium occurred from an oxygen saturated surface and that the rate-determining step was limited by the process in which chemisorbed oxygen moved out of the surface layer towards the interior of the palladium. The oxygen in the bulk is initially in the form of a solid solution of oxygen in palladium rather than of stoichiometric palladium (II) oxide. This solid solution was expected to be a precursor to bulk oxide formation which occurs at >770K (Paryjczak, Jozwiak and Goralski, 1978). At temperatures above ca. 1173K, palladium (II) oxide dissociates into its constituent elements. Rapid cooling to room temperature retains palladium as the metal, slow cooling in an oxygen atmosphere provides the oxide.

Platinum forms only a thin oxide layer which is resistant both to diffusion outwards of platinum or inwards of oxygen (Betteridge and Rhys, 1962). This layer cannot be detected by weight change nor is it visible. At higher temperatures (above ca. 1273K), platinum forms a volatile oxide (Alcock and Hooper, 1960):



The formation of volatile oxides is also observed with palladium and rhodium, although loss of these metals by volatilization occurs to a smaller extent than with platinum.

A relationship between the strength of the metal-oxygen bond or the heat of formation of the metal oxide and the catalytic activity for hydrocarbon oxidation has been observed by a number of workers (Boreskov, 1966; Morooka and Ozaki, 1966; Trost, 1959). The order of activity for oxidation of olefins was found to be (Patterson and Kemball, 1963):

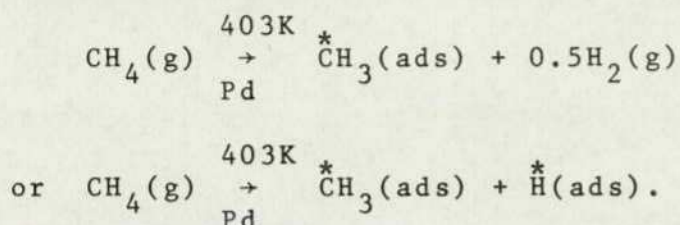


The heats of adsorption of oxygen were 277 kJ mol^{-1} for palladium and platinum, 319 kJ mol^{-1} for rhodium and 756 kJ mol^{-1} for tungsten. The highest catalytic activity for olefin oxidation was observed for metals that adsorbed oxygen least strongly.

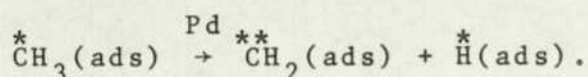
1:7:2 Adsorption of methane.

Studies of the adsorption of simple hydrocarbons by metal surfaces have shown that rapid dissociative adsorption can

occur at room temperature and below (Trapnell, 1956; Roberts, 1963). For methane over palladium, however, chemisorption is observed only at 373K or above (Ross, Roberts and Kemball, 1972). There are two possible adsorption mechanisms:

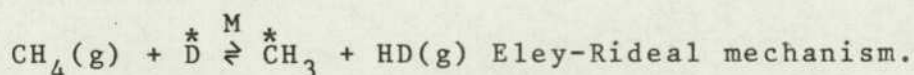


Further hydrogen abstraction at these temperatures may lead to adsorbed methylene fragments,



Cullis, Keene and Trimm (1971) considered the formation of such adradicals to be an essential step in methane oxidation. Higher temperatures (above 523K over palladium) may lead to further dehydrogenation, leaving carbon on the catalyst (Egloff, 1937).

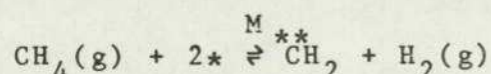
The exchange reaction between methane and deuterium on the surface of precious metal films (Kemball, 1951) has provided some insight into the mechanism of methane adsorption. Two mechanisms may be involved, one producing monodeuteromethane,

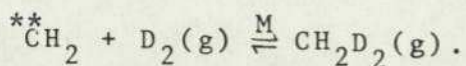


The order of catalytic activity for this reaction was:

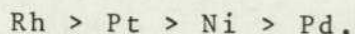


The second mechanism produced di, tri, and tetradeuteromethane:





The order of activity for this reaction was:



McKee and Norton (1964) obtained an order of activity at 423K for both hydrogen and deuterium exchange and the cracking reaction of $\text{Pt} > \text{Rh} > \text{Pd}$. Alloys of these precious metals showed intermediate activity.

Under conditions where the catalysts operate, oxygen is present on the precious metal surface. The surface coverage by hydrocarbons is quite small, far short of a monolayer (Trapnell, 1956). Since the heat of chemisorption of oxygen is greater than that of methane, preferential adsorption of oxygen would be expected to occur. Some competition between methane and oxygen for adsorption sites may occur and adsorption of hydrocarbon on a layer of adsorbed oxygen cannot be ruled out. This adsorption on oxygen rather than on the metal is not likely to predominate, however. Roberts (1963) added a monolayer of oxygen to a clean rhodium film and found that this inhibited the adsorption of ethane. This rate of disappearance of ethane in the presence of adsorbed oxygen decreased a hundred-fold and water was formed as a product. Difficulties arose during adsorption of hydrocarbons on metal oxides due to side reactions (Turkevich and Taylor, 1934).

The adsorption of higher hydrocarbons occurs more readily than adsorption of methane on palladium and platinum as the hydrogen is more readily abstracted. The order of ease of retention of hydrocarbons over an alumina-supported palladium

catalyst was found to be:

alkanes < cyclopropane < alkenes < alkynes

(Taylor, Thomson and Webb, 1968). Carbon-carbon bond rupture was unimportant below 473K.

1:7:3 Catalytic oxidation of methane over palladium and platinum.

Methane has been chosen as a suitable hydrocarbon for total oxidation studies over precious metal catalysts by a number of investigators (Table 1:2). Different techniques provided results with limited agreement. However, a zero order in oxygen due to rapid adsorption of this gas on the palladium surface has been universally observed but there is less agreement about the behaviour with respect to methane. The difference in activation energy between static beds and flow reactors may be due to the operation of the beds in a region of diffusion control where the activation energy is half that obtained for a region involving chemical control.

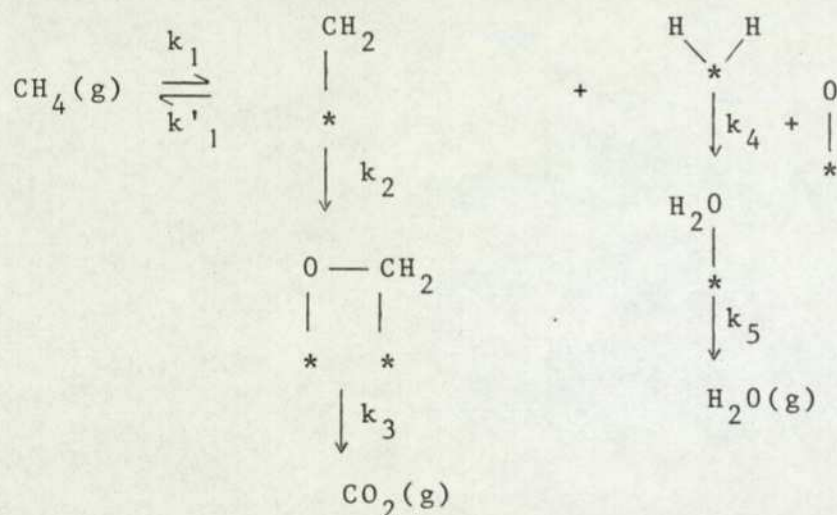
Despite evidence by Mezaki and Watson (1966), most investigators consider that methane as well as oxygen is adsorbed on the catalyst before reaction. Oxygen adsorption is strong, involving dissociation of oxygen molecules. Methane adsorption is also dissociative occurring by hydrogen abstraction and is probably the rate-determining step. Surface reaction between these two dissociatively adsorbed species then occurs.

The nature of the reaction products may be affected by

Catalyst/ support	Temp.range (K)	Reactant mixture composition	Method	E_A (kJ mol ⁻¹)	Reaction order in		Ref.
					CH ₄	O ₂	
Pd/SiO ₂	473-673	-	Integral flow.	-	-	Small negative.	Reyerson and Swearin- gen, 1928.
Pd/Al ₂ O ₃	473-723	CH ₄ pulse in O ₂ .	Integral pulse-flow.	88 and 92.	-	-	Anderson, Stein, Feenan and Hofer, 1961.
Pd/Al ₂ O ₃	573-613	6-30% CH ₄ in O ₂ .	Different- ial flow.	ca.70-101	-	-	Schwab and Watson, 1965.
Pd/Al ₂ O ₃	593-653	not given.	Integral flow.	-	1.0	0	Mezaki and Watson, 1966.
Pd/Al ₂ O ₃	623-773	0.5-2% CH ₄ in O ₂ + N ₂ .	Static bead.	139 and 52.	-	0	Firth, 1969.
Pd/ThO ₂ on Al ₂ O ₃	673-873	0.5-5% CH ₄ in O ₂ .	Static bead.	42-59.	0.8	0	Nevell, 1968.
Pd/13X molecular sieve.	573-673	CH ₄ in O ₂ / N ₂ .	Static bead.	88.	1.0	0.05	Firth and Holland, 1968.
Pd sponge.	568	CH ₄ :O ₂ (2:1)	Pulse-flow microreac- tor.	80-90.	0.5	0	Cullis, Keene and Trimm, 1971.
Pd-Pt/ Al ₂ O ₃	523-793	3.3% CH ₄ .	Flow circul- ator techni- que.	13-63	-	-	Zozulya, 1976.

Table 1:2 A survey of previous studies involving the oxidation of methane over palladium.

temperature. Carbon dioxide and water are universally observed, the water content increasing at high $[\text{CH}_4]:[\text{O}_2]$ ratios due to the formation of carbon on the catalyst surface (Cullis, Keene and Trimm, 1971). Carbon monoxide and hydrogen are produced at temperatures above 673K, especially when the gas mixtures are methane-rich. Traces of formic acid were detected by Campbell (1929) and small quantities of formaldehyde were detected at low temperatures (<673K) by Cullis, Keene and Trimm (1971). Indeed, it was postulated by the latter investigators that the reaction proceeded via a formaldehyde-type adsorbed intermediate, the mechanism being:



Ahuja and Mathur (1967), believe, however, that oxygen is not dissociated but adsorbed molecularly, while Firth and Holland (1969) showed that the adsorbed oxygen is similar in form to that found in palladium (II) oxide. Cullis and Nevell (1976) have shown that the catalyst should be partially oxidised or reduced rather than totally oxidised or totally reduced for optimum catalytic activity.

There has been little investigation of the physicochemical properties of the palladium catalyst and support and the effect of these properties on methane oxidation. Cullis, Nevell and Trimm (1972) studied the role of the catalyst support on methane oxidation over palladium using a catalytic bead. The support was found to have negligible influence on catalytic activity but affected the long-term stability of the system.

Platinum, too, is considered to be an effective catalyst for methane oxidation (Anderson, Stein, Feenan and Hofer, 1961; Pechanec, 1973). Loboiko et al (1978) obtained reaction products of water, carbon dioxide and formaldehyde from methane oxidation at temperatures of 373-1273K. Other workers (Davies, 1936; Lintz, Pentenero and Le Goff, 1962) using platinum wire catalysts at high temperatures (ca.1273K) postulated that chemisorption of both oxygen and methane occurred before reaction. Their results were obtained, however, in a temperature region in which Knudsen diffusion control was operating. Pechanec (1973) found that rhodium (III), iridium (IV), platinum (IV) and palladium (II) oxides were active for methane oxidation. Firth and Holland (1969) studied methane oxidation over catalytic beads coated with palladium, platinum, rhodium and iridium, obtaining values for the activation energies of 139, 200, 113 and 71 kJ mol⁻¹ respectively. Finally, a palladium-gold alloy present on the surface of a catalytic bead gave activation energies that varied between 40 and 53 kJ mol⁻¹ depending on the gold content (Firth, 1966).

Methane is the most oxidation-resistant of the simple hydrocarbons as it contains hydrogen atoms in a primary configuration only. These primary carbon-hydrogen bonds are stronger than secondary or tertiary carbon-hydrogen bonds and this is reflected in the high temperatures required for methane oxidation. Catalytic oxidation of higher hydrocarbons by Group VIII noble metals has received some attention especially in the field of catalysts used for the removal of atmospheric pollutants from automobile exhausts.

A review of catalytic oxidation of hydrocarbons written by L. Ya. Margolis appeared in 1963. In this article, the importance of oxide formation by the metal catalyst was stressed. The proposed mechanism of catalytic hydrocarbon oxidation was that of dissociative adsorption of hydrocarbons followed by reaction of oxygen in the form of the oxide. The adsorption of the hydrocarbon was complicated due to previously adsorbed oxygen on the surface. These suggestions are supported by Hiam, Wise and Chaikin (1968) who studied the oxidation of hydrocarbons on a platinum filament. It proved difficult to distinguish whether the hydrocarbon was adsorbed on an oxygen-free portion of the surface or on top of already adsorbed oxygen prior to reaction. Hydrogen abstracted from the $-CH_2-$ group occurred more readily than from the primary carbon atom and this abstraction step was rate-determining. The difference in activation energies for different hydrocarbons reflected the ease with which hydrogen could be abstracted from the hydrocarbon. Co-adsorbed oxygen on the surface led to rapid oxidation as an oxygen-lean surface could

be readily poisoned by hydrocarbon residues. The need for fractional surface coverage by both reactants, hydrocarbon and oxygen was felt to be the major cause for the observed difference in the catalytic properties of palladium and platinum. Variation in catalytic activity may be associated with the degree of oxygen coverage exhibited by the two metals (Schwartz, Holbrook and Wise, 1971).

Evidence for the different catalytic activities of precious metals was obtained by Patterson and Kemball (1963) for ethylene oxidation over palladium and platinum films in a static reactor. Approximately first order dependence on olefin pressure was observed over palladium but different kinetics were found with platinum, for which there was a zero order dependence on olefin. Experiments carried out with other metal films (rhodium, gold and tungsten) indicated that the strength of the metal-oxygen bond is an important factor governing the relative activity of these metals as catalysts. As with other hydrocarbons, it was difficult to decide whether the adsorption of olefin required in the rate-determining step took place on top of an oxygen-covered surface or was chemisorbed directly on to the metal. No evidence of inhibition by oxygen meant that the former mechanism is more likely but not certain. Platinum was found to be more effective for olefin oxidation than palladium.

1:8 Deactivation of catalysts.

1:8:1 General.

A prime requirement of a catalyst is the maintenance of a steady activity for as long as possible. Processes causing

deterioration in activity include thermal degradation, poisoning by reactants or products (self-poisoning) or by strong adsorption of a foreign chemical which excludes the reactants from the surface. Since these processes all involve active sites, an understanding of their function, nature and concentration on the catalyst surface is essential for an understanding of the mechanisms involved in deactivation.

1:8:2 Active sites in catalysis.

Modern theories of catalysis attribute catalytic activity to co-ordinative unsaturation at the catalyst surface rather than to the collective properties of the solid. As early as 1925, Taylor (1925, 1926) introduced the concept of geometric and energetic heterogeneity of catalyst surfaces. This heterogeneity gives rise to catalytically active sites whose presence is now universally accepted, although in most cases their chemical nature is unknown and there are only a few instances in which their concentration on the surface has been determined satisfactorily.

The co-ordination numbers of surface atoms may be expected to vary with the involvement of different crystallographic faces, edges, intersecting planes and steps as well as dislocations and point defects present to some degree on all surfaces. It is to be expected that some surface atoms or sites will be more active than others. Atoms of low co-ordination number and high valence unsaturation may be present as sites of highest activity. A particle size effect will be one consequence. This has been observed by Boudart

et al (1968) for the isomerisation and hydrogenolysis of neopentane over platinum and by Maurel et al (1975) for hydrogenolysis of cyclopentane over platinum. These reactions are classified as "demanding" or "structure sensitive" reactions where the activity is proportional to metal surface area.

The rates of most catalytic reactions do not, however, show large differences when different crystal faces are involved and particle size effects are usually small. Ertl and Koch (1973) observed identical catalytic activities for the oxidation of carbon monoxide on different palladium single crystal planes and on polycrystalline palladium wire. These reactions were insensitive to orientation of the exposed crystal planes and to particle size and are therefore called "facile" or "structure insensitive". The surface atoms in these cases would be expected to have the same activity, irrespective of the volume unsaturation, per surface atom. The activity per unit area of surface is independent of particle size and the nature of the support material. Boudart et al (1966) showed that the specific activity for the hydrogenation of cyclopropane over various platinum catalysts was independent of platinum content on two different forms of alumina, independent of the nature of the support, viz. alumina or silica gel, and almost the same for highly dispersed samples in which nearly every platinum atom was a surface atom as for a platinum foil. The latter observation bridges the gap between very small particles (<5 nm) and bulk metal, as deviations from normal behaviour characteristic of the bulk metal were predicted by Poltorak and Boronin (1966)

and van Hardeveld and van Montfoort (1966b) for particles smaller than about 5 nm.

The reason for the low selectivity despite valence unsaturation of active sites undergoing facile reaction is still not completely understood. Furthermore, it is frequently not known whether only single atoms or a number of surface atoms are necessary for a given catalytic process. The effects of interactions between neighbouring atoms and interactions between atoms of the catalyst and the support are of fundamental interest. Information on the support-catalyst interactions may be obtained by comparison of a support which is inert towards the catalyst under the conditions operating during catalysis and the support actually used.

For facile reactions on metals, the entire catalyst surface may be presumed to be active. Multicentre sites of the current configuration (composed of identical atoms) may thus be accessible for reactant molecules to form di- or tri-adsorbed intermediates. Multisite processes will, therefore, occur quite frequently on metals undergoing structure-insensitive reaction. Oxides, on the other hand, expose cations, oxygen ions and hydroxyl groups often in unusual co-ordination numbers (Boehm, 1966). Thus surface co-ordinative unsaturation may be considered as the cause of activity of the various surface sites (Burwell, Haller, Taylor and Read, 1969). Multisite processes on equivalent surface ions or groups is less probable as the packing of equivalent sites is less dense and homolytic bond cleavage

is certainly less common on oxides than on metals. Only a few sites in a given distribution can probably be considered as catalytically active. The surface properties of many oxides can be described in terms of surface acidic and basic sites which may exist in different configurations and hence different strengths. Of these acid-base sites, it is probable that only a few are catalytically active and the co-ordination of these active sites may be assumed to be unusual.

Surface sites which react specifically with the reactant allowing adsorption to occur are termed adsorption sites. If, after adsorption, the site possesses the ability to activate the adsorbed molecule and form an intermediate, then it may be classified as an active site. However, initial activities are often observed to be high and to fall to lower values of final stable activity. Catalytic surfaces may expose sites that are "too active", so that fragmentation of the reactant may occur or surface reaction may lead to blocking of these extremely active sites (self-poisoning). These sites will not contribute to the catalytic conversion under conditions of stable activity.

1:8:3 Thermal deactivation.

Precious metal catalysts operating in the absence of poisons may still show a loss in activity induced by thermal effects. This loss of activity is normally due to sintering of either the catalyst or the support. Surface area losses result in both cases, and these are caused by crystallite growth from agglomeration of smaller into larger particles.

Heating may also cause formation of compounds between the catalyst and the support with resultant loss of active precious metal. Furthermore, an active metal catalyst may be converted into an inactive oxide or vice versa. In the case of supported palladium (II) oxide, temperatures above ca. 1173K will result in palladium metal formation which may not be as suitable for oxidation reactions as the oxide. Some precious metals such as platinum become volatile at high temperatures in the presence of oxygen and will evaporate reducing the amount of precious metal available for reaction (see section 1:7:1).

For a structure-insensitive or facile reaction, thermal deactivation would not be expected to inhibit greatly the rate of reaction (Boudart, Aldag, Benson, Dougharty and Harkins, 1966). Hence, in the absence of mass transfer effects, loss in surface area due to heating would cause loss of catalytic activity for a demanding reaction only.

Separation of thermal and chemical deactivation may normally be achieved by operating identical catalysts in the presence and absence of inhibitors and identifying changes in the physicochemical properties of the catalysts. A technique used by Dalla Betta and co-workers (1976) for supported noble metal catalysts involved measurement of metal particle size by transmission electron microscopy. A parallel measurement of accessible or active surface area by carbon monoxide chemisorption afforded a means of separating the chemical and thermal effects on the active area and hence on activity.

A comparison between the thermal stabilities of palladium and platinum catalysts by Klimisch et al (1975) revealed that palladium catalysts maintained their activity at high temperatures under oxidising conditions much better than their platinum counterparts. At 923K, sintering of platinum was far greater than that of palladium in oxygen atmospheres. In reducing atmospheres the opposite was observed, the palladium surface area being greatly reduced for example by the action of hydrogen at 923K. These results were reflected in the abilities of the different catalysts to oxidise carbon monoxide.

1:8:4 Self-poisoning.

Retardation of a catalytic reaction by competitive adsorption of reactants and reaction products or by a strong adsorption on the active sites by the reactant may occur. The latter process is called self-poisoning or coking and is caused by chemical transformations of the reactants, which leads to stable surface species that cannot be desorbed or displaced by further reactants.

Deposition of carbonaceous products on precious metal surfaces caused by dehydrogenation of hydrocarbons and leading to a decrease in catalytic activity is well documented (Beeck, 1950a). The process involved is probably a stepwise one, adsorption of the hydrocarbon followed by loss of hydrogen. Carbon species thus formed may then combine into larger molecules as has been shown to occur in the case of ethylene, where C_4 and C_6 species have been

detected on the surface after ethylene has been retained on precious metals (McCarroll and Thomson, 1970). The presence of reducing or oxidising atmospheres reduces the carbon build-up on the catalyst surface by forming volatile products. In the case of methane oxidation over palladium, some conversion of methane to carbonaceous residues was observed by Cullis, Keene and Trimm (1971) especially under oxygen-lean conditions when up to 20% of the active metal surface area was lost. This carbonisation was observed to be reversible on passage of hydrogen through the catalyst bed to give methane.

Use of a porous support over which the precious metal is evenly distributed may lead to pore-mouth poisoning by deposition of carbon at the mouths of pores. The precious metal dispersed down those pores will be unable to take part in the reaction and subsequent loss of catalytic activity may occur (Wheeler, 1951). If mass transfer (usually by diffusion) of the reactants through the pores is rate-controlling, the reaction rate becomes slower as carbon builds up at the pore-mouth. Pore-mouth poisoning is not limited to carbon deposition. Acres et al (1975) attributed the poisoning of precious metal catalysts by phosphorus to pore-mouth poisoning and Klimisch et al (1975) observed the same for lead poisoning.

A study of the stability of a porous catalyst subjected to carbon deposition was undertaken by Firth and Holland (1971) for a catalytic bead system. The effect of the interaction of carbon with α -aluminium (III) oxide was to reduce

the mechanical strength of the bead. The stability was directly proportional to the mechanical strength. The crushing strength of the bead was greatly reduced after operation in methane atmospheres over long periods.

Retardation of methane oxidation over supported precious metal catalysts may also be caused by the products of reaction other than carbon. These may include carbon monoxide, carbon dioxide, hydrogen and water.

Carbon dioxide is not adsorbed on palladium to any extent (Collins and Trapnell, 1957). Carbon monoxide will undergo chemisorption on palladium at room temperature. The rate and heat of chemisorption of carbon monoxide on transition metals approaches those of oxygen (Bond, 1962). The desorption of carbon monoxide occurs only at high temperatures and its presence as a product is observed only above 723K, when palladium catalysts are used for hydrocarbon oxidation. Adsorption of carbon monoxide on palladium (II) oxide may occur with the formation of carbon dioxide which is readily desorbed. In the absence of available oxygen or at low temperatures, carbon monoxide may thus act as an inhibitor. The formation of a carbon film on the surface of precious metal catalysts has been observed during oxidation of carbon monoxide (Hori and Schmidt, 1975).

Hydrogen, like carbon monoxide, can be reversibly adsorbed on precious metal surfaces. Adsorption on palladium surfaces is complicated by hydrogen dissolving into the bulk

of the metal. Platinum too may dissolve hydrogen below its surface, though to a lesser extent than palladium. Heating to temperatures of 393K for 2 hours was sufficient to remove the reversibly bound hydrogen from a palladium on γ -aluminium (III) oxide catalyst (Paryjczak and Jozwiak, 1975). Shorter desorption times can be achieved only at higher temperatures. "Spillover" of hydrogen from the precious metal on to the γ -aluminium (III) oxide support may occur forming dissociatively adsorbed hydrogen which requires high temperatures of desorption (ca. 750K) (Kramer and Andre, 1979). The hydrogen is adsorbed dissociatively on the precious metal and this atomic hydrogen spills over on to the support. In the presence of palladium, the effect of the support is, presumably, to retain the water which may then react with the palladium to form the hydroxide. Appreciable deactivation by water vapour was, however, observed only when the water vapour concentration was greater than that being produced by the reaction.

1:8:5 Deactivation by poisoning.

1:8:5:1 General.

The poisoning of a metallic catalyst was defined by Maxted (1951) as a preferential adsorption effect dependent on abnormally strong adsorptive bonds between a catalyst and certain types of adsorbed species involved in the catalytic process. Adsorption takes place on active sites which possess the ability to activate the adsorbed molecules and form intermediates. Hence only small amounts of poisons

are required, sufficient to block only these active sites; total surface coverage is unnecessary.

There is some confusion in the literature as to the correct definition of the terms, inhibitor and poison. Innes (1954) defined an inhibitor as a substance which when added during catalyst preparation, reduced the catalytic activity (i.e. the opposite of a promoter), whereas a poison was present in the gas stream and had an adverse effect on catalytic activity. Kemball (1973) stated that the two terms have similar meanings, the only difference being that inhibition had a less drastic effect on the reaction rate. Removal of the impurity causing deactivation from the gas stream may often result in a return to the activity obtained before deactivation; inhibition may thus be reversed. Pore-mouth blocking is not poisoning in the strictest sense as the deposits formed impede the use of all sites rather than individual ones.

Two types of poisoning may be observed, selective and non-selective (sometimes called specific and non-specific). A non-selective poison is adsorbed indiscriminately on all sites, whereas a selective poison is adsorbed only on specific sites. Selective poisoning cannot, therefore, occur on catalysts with uniform sites. Those catalysts with a variety of active sites may, however, be selectively poisoned so that one particular pathway is more favoured than another. For example, hydrogenation and hydrogenolysis over aluminium (III) oxide-supported platinum catalysts was studied by Maurel et al (1975). Hydrogen sulphide and sulphur

dioxide, which together produce atomic sulphur on the platinum surface, reduce the rate of hydrogenolysis of cyclopentane more than the rate of hydrogenation of benzene. Hence selective poisoning is observed, as the hydrogenation is a facile reaction and the hydrogenolysis is a demanding reaction. Hydrogen sulphide or sulphur dioxide alone are non-selective and have the same result on both reactions.

Selective poisoning is of great value in industrial catalytic processes. The yield and purity of the reaction product is increased by poisoning the sites responsible for undesirable side reactions. Catalysts possessing a variety of sites are probably much more common than those with uniform sites hence the possibility of achieving selective poisoning is correspondingly greater (Kemball, 1973).

1:8:5:2 Types of catalyst poison.

Precious metals are normally deactivated by adsorption of foreign species which prevent access of the reactants to the surface. These poisons may operate or may deactivate either by converting the active sites to inactive ones or by adversely affecting the number of free electrons, unpaired electrons or "holes" needed for catalysis. Alternatively, attack on the support may cause precious metal-support interactions that did not occur in the absence of the poison. The latter effect is not as common as the former but may occur over a longer time scale.

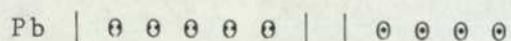
Typical poisons or inhibitors of hydrocarbon oxidation

by precious metals include sulphur and phosphorus compounds, heavy metals such as lead and mercury, halogenated hydrocarbons and organosiloxanes.

1:8:5:3 Toxic metals.

Metals which poison palladium and platinum are found either in Groups IVB and IIIB or in the transition series of the Periodic Table (Maxted and Marsden, 1940). Maxted (1949) has attributed this toxicity to a strong adsorptive bond formed only by those metals in which all five orbitals of a d-shell, immediately preceding s- or p-valency orbitals, are occupied by electron pairs or by single d-electrons (Cu^+ , Zn^{2+} , Cu^{2+} , Ag^+ , Au^+ , Hg^{2+} , Pb^{2+} , Ba^{2+}). Hence these toxic metals differ from the non-metallic poisons of Groups VB and VIB, for which strong bonds to precious metal catalysts can be formed using s- or p-valency electrons.

This theory may be extended to derivatives of metals (Maxted and Moon, 1949). Tetramethyl lead, highly toxic to precious metals, has four of its s- and p-orbitals taken up in bond formation with carbon,



5d hybridised 6sp^3 levels bonded to
carbon.

Lead is the major contaminant in the exhaust gases from internal combustion engines burning leaded petrol causing deactivation of catalytic exhaust gas purifiers and catalytic gas detectors sited in or near exhaust gas outlets. There have been many studies (Shelef, Otto and Otto, 1978) of the effects of lead on supported precious metal catalysts. Oxid-

ation of hydrocarbons has been found to be more vulnerable than oxidation of carbon monoxide to lead poisoning (Shelef, Dalla Betta, Larson, Otto and Yao, 1973; Weaver, 1969; Holt, Wigg and Neal, 1974). The least reactive hydrocarbon, methane, was the most susceptible to poisoning. The effect of lead on the catalyst was determined by the concentration of lead in the gas stream, the temperature and the retention of lead by the catalyst.

Williams and Baron (1975) exposed palladium and platinum films to lead from an automobile exhaust at 830K and examined the surface using Auger electron spectroscopy. At low exposures, lead was present on the platinum surface but not on that of palladium. This was explained by the diffusion of lead into the bulk of the palladium, the high solubility of lead (II) oxide in palladium (II) oxide making this possible. The lead is normally carried to the catalyst as lead halide, its interaction with the precious metal forming strong lead-catalyst bonding with desorption of the halogen. With base metal catalysts, lead will similarly cause poisoning, especially at high temperatures. The mechanism of poisoning is different for base metals with the lead forming monolayer coverage as was observed with nickel (II) oxide and manganese (IV) oxide (Bucknell, Cullis and Hucknall, 1978). The affinity of lead for precious metals is demonstrated by studies on supported catalysts. For aluminium (III) oxide-supported precious metal catalysts, most of the lead is present on the precious metal, although some may diffuse through onto the alumina. For aluminium (III) oxide-supported base metal catalysts (copper (II) oxide or nickel (II) oxide) lead halide

was preferentially adsorbed on the alumina.

1:8:5:4 Poisons containing non-metallic elements of
Groups VB and VIB.

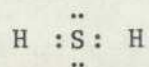
Compounds which contain elements of Groups VB and VIB may be considered as catalyst poisons provided that the elements remain unsaturated or unshielded. The non-metallic members of Groups VB and VIB include:

Group VB	Group VIB
N	O
P	S
As	Se
Sb	Te

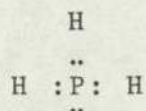
Not all compounds containing these elements are toxic, the ability to cause poisoning depending on the electronic configuration and the element in question. If the element is electronically shielded, it may not deactivate the catalyst (Table 1:3).

The toxicity of a particular compound may be reduced if the conditions in which it is operating remove its poisoning effect. For example, hydrogen sulphide is particularly toxic towards hydrogenation reactions over platinum catalysts where reducing conditions are present. Under oxidising conditions, hydrogen sulphide is a less severe poison and total oxidation of hydrocarbons over precious metal catalysts is poisoned by sulphur only at temperatures below 760K (Hunter, 1972), presumably due to its oxidation to a shielded non-toxic species.

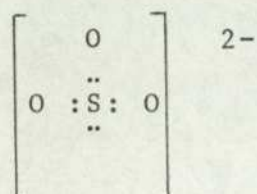
Toxic species
(non-shielded)



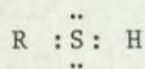
Hydrogen sulphide



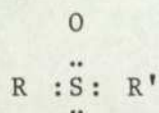
Phosphine



Sulphite ion

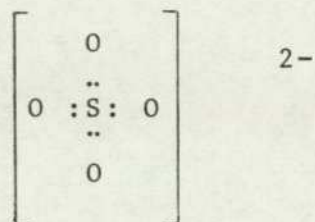


Organo-thiol

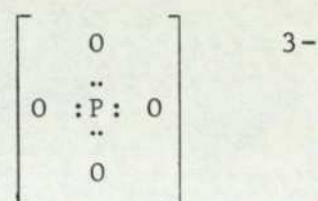


Sulphoxide

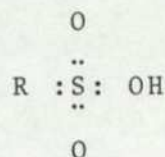
Non-toxic species
(shielded)



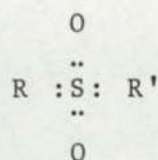
Sulphite ion



Phosphate ion



Sulphonic acid



Sulphone

Table 1:3 The influence of electronic configuration on toxicity for Groups VB and VIB compounds
(Maxted, 1951).

The reason for including the first elements of Groups VB and VIB, nitrogen and oxygen, as poisons is not so evident. As with the other members of these Groups, however, the rate of catalytic hydrogenation of hydrocarbons over platinum is considerably reduced in the presence of unshielded nitrogen-containing substances such as pyridine. Furthermore, oxygen and water chemisorbed on metal surfaces may inhibit reactions involving hydrogen such as the synthesis of ammonia over iron.

Adsorption of hydrogen sulphide on palladium is dissociative with desorption of hydrogen and formation of bulk sulphide occurring at temperatures above 350K (Saleh, 1970). Sulphur dioxide, too, is adsorbed on palladium but coverage does not exceed 80% even when high temperatures (523K) are reached. The presence of oxygen in the gas streams allows oxidation of adsorbed sulphur dioxide to sulphur trioxide, which may then form a stable sulphate. For some base metal catalysts, such as CuCr_2O_4 , adsorption of sulphur dioxide or sulphur trioxide may be the deactivation mechanism while for cobalt or copper, sulphate formation is responsible for loss of activity (Farrauto and Wedding, 1974). Hence, the thermal stability of the sulphate may decide the degree of toxicity.

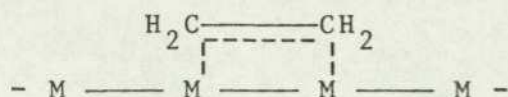
Supported precious metal catalysts show a greater retention of sulphur under oxidising conditions, normally in the form of the sulphate, by the support rather than by the precious metal, even when high temperatures are used.

A study of the mechanism of the poisoning of platinum catalysts by sulphur (Somorjai, 1972) revealed that the surface reactions that are inhibited by sulphur are sensitive to changes in the surface structure of platinum, i.e. are structure-sensitive. The sulphur will catalyse the recrystallisation of platinum (111) planes with the sixfold symmetry of a face centered cubic structure to (100) crystal planes with fourfold rotational symmetry.

1:8:5:5 Poisons containing multiple bonds.

Unsaturated hydrocarbons, carbon monoxide and derivatives of cyanogen can all prove poisonous to precious metal catalysts especially for hydrogenation-type reactions. A strong chemisorption bond between the metal and the poison is responsible for the toxicity of these compounds. On nickel, catalytic hydrogenation of ethylene occurs by interaction of chemisorbed ethylene with physically adsorbed hydrogen (Twigg and Rideal, 1939). Ethylene prevents the chemisorption of hydrogen on nickel, no hydrogen atoms being present on the surface. Likewise, benzene, even in small amounts, retards the hydrogenation of cyclohexene over palladium and platinum by suppressing chemisorption of hydrogen.

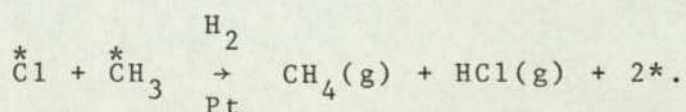
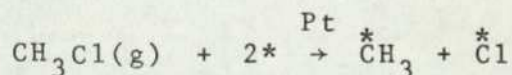
The strong chemisorptive bond formed between these unsaturated compounds and transition metals is attributed to a resonance system between the π -electrons of the adsorbent and the d-electrons of the adsorbate, i.e. for ethylene,



Removal of the toxic effect of these unsaturated poisons may be achieved by conversion to saturated compounds. Carbon monoxide may be oxidised to carbon dioxide or reduced to methane, both of which are non-toxic. Hence its presence in the feed gas in small amounts under strongly oxidising or reducing conditions may not cause deactivation as it is detoxicated by the catalyst (Bredig and Ikeda, 1901).

1:8:5:6 Halogenated hydrocarbons.

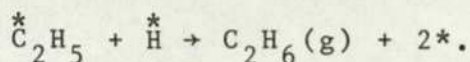
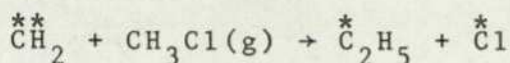
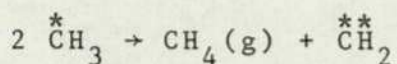
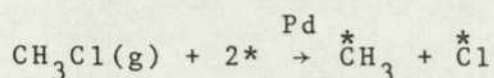
Adsorption of chloroalkanes on a number of metal films (Ni, W, Cu, Pt, Co, Mn, Al, Ag, Pd and Ti) resulted initially in carbon-chlorine bond rupture before any carbon-hydrogen bonds were broken (Anderson and McConkey, 1968). By use of ^{13}C and ^{38}Cl , it was shown that after adsorption of monochloromethane on titanium, the carbon-chlorine bond rupture was totally irreversible. Over platinum and aluminium, methane was the only hydrocarbon product when hydrogen was added.



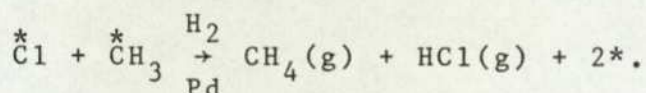
With palladium and titanium, higher hydrocarbons were formed; dichloromethane and hydrogen produced polymers, and olefins were the main C_2 and C_3 products over titanium.

The mechanism of the reaction of monochloromethane with

a palladium surface appears to involve dissociative adsorption followed by dehydrogenation of the hydrocarbon residue. This dehydrogenation increases with increasing temperature, and the methylene residues so formed can then react with hydrogen to give methane and higher hydrocarbons. Chemisorbed hydrogen was directly involved in product desorption. Hence,



At higher hydrogen pressures, the behaviour is similar to that observed for platinum, i.e.,



Over titanium, inter-residue hydrogen transfer was responsible for desorption.

Confirmation of these findings was obtained by Arkharova et al (1978), who also observed dehalogenation followed by dehydration for di-, tri- and tetra-chloro-methanes over a platinum electrode. The species formed were analogous to those formed during methane adsorption.

Work on aluminium (III) oxide-supported platinum catalysts by Noelke and Rase (1979) and Weiss, Gambhir and Leon (1971) has suggested that the support plays an active

role in the dechlorination of trichloromethane. In the presence of water and hydrogen, dichloromethane was formed at 468K. The water had the function of replacing chlorine adsorbed on the aluminium (III) oxide surface with hydroxyl groups and so regenerating the alumina. Without water the reaction was slower, presumably because the support rapidly became inert and the reaction depended on the platinum alone to remove the chlorine.

The order of effectiveness for the inhibition of methane oxidation over palladium sponge was found (Keene, 1969) to be:

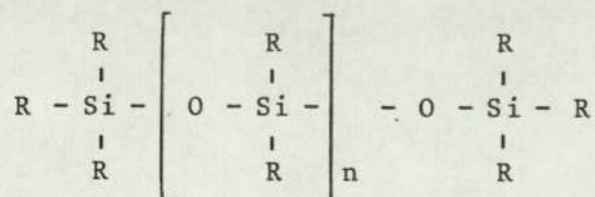


Furthermore, an increase in the number of chlorine atoms in the molecule caused a corresponding increase in the effectiveness of the inhibitor, i.e. dichloromethane was more effective than monochloromethane.

1:8:5:7 Organosiloxanes.

The poisoning effect of organosiloxanes on precious metal catalyst systems has been little studied except in the case of catalytic beads. Under the conditions in which the beads operate, the atmosphere sampled may contain silicone vapours arising from lubricating oils and greases or industrial polishes.

The most common organic siloxanes are of the type:



where R is either $-\text{CH}_3$ or $-\text{C}_6\text{H}_5$ or a mixture of both. The value of n may vary from one to many thousands.

These silicone fluids are thermally stable to temperatures of over 473K and remain liquid over a wide range (223 to 373K for the monomer hexamethyldisiloxane) and have a high surface wettability.

The mechanism by which these compounds poison precious metal catalysts during hydrocarbon oxidation is uncertain. Firth and Holland (1968) have suggested that non-volatile silicon oxides are produced at the surface, hindering further activity. The ability of organosiloxanes to poison oxidation catalysts at very low concentrations suggests that they are selectively adsorbed on sites that are active in the oxidation process. Clearly, they are powerful deactivators of catalytic beads used for hydrocarbon oxidation.

1:8:5:8 The effect of poisons on the reaction rate and the activity.

The most common method of representing catalyst poisoning is by means of a poisoning curve of activity versus poison concentration. Maxted and Evans (1937a) studied the effect of sulphur compounds on platinum catalysts, obtaining a linear decay in activity with poison concentration (curve 1 in Figure 1:2). This line may be represented by the equation:

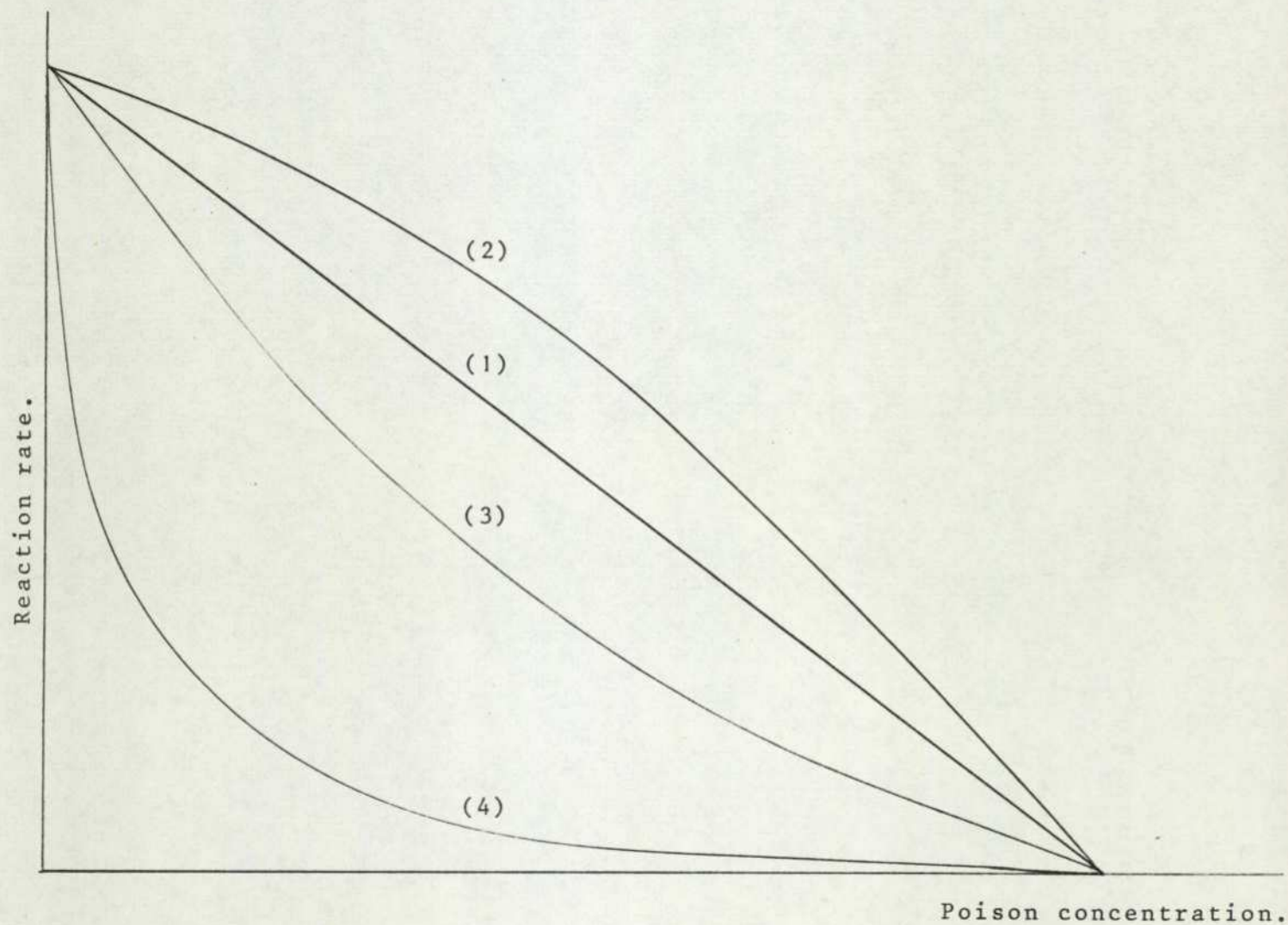


FIGURE 1:2 A SERIES OF CURVES SHOWING THE POSSIBLE EFFECTS OF POISON CONCENTRATION ON THE REACTION RATE.

$$k_c = k_o (1 - \alpha c)$$

where k_c = catalyst activity in the presence of poison
of concentration c ,

k_o = original unpoisoned activity,

α = poisoning coefficient,

c = concentration of poison.

The surface is fully covered when $c = 1/\alpha$ and the number of active sites may be calculated by extrapolation of the poison curve if the number of poison molecules required per active site is known. Bulky poison molecules may inhibit large areas of the surface, excluding more than one active site from the reactants (Maxted and Evans, 1937b).

Other forms of poisoning curve may be obtained (Figure 1:2). Provided that diffusion is not involved in the poisoning process (see section 1:8:5:1), these curves may be labelled:

- (1) Equal, i.e. non-selective poisoning of all sites.
- (2) Preferential poisoning of least active sites.
- (3) Preferential poisoning of most active sites.
- (4) Preferential poisoning of one type of active site, when two types of site are present.

It is unwise, however, to assume that selective poisoning can always be interpreted by assigning different active sites to different reactions. For example, poisoning by hydrogen of a platinum catalyst for the decomposition of ammonia without inhibiting the decomposition of hydrogen iodide has been quoted (Hinshelwood, 1940) as an example of selective poisoning and interpreted as an indication

that the two reactions proceed on different sites. In the decomposition of ammonia, nitrogen atoms may be hindered from attaching themselves to the surface by strong adsorption of hydrogen. Decomposition of hydrogen iodide may occur, however, by reaction of chemisorbed hydrogen atoms with gas-phase hydrogen iodide or with molecules in the van der Waals layer. Free hydrogen atoms will attack hydrogen iodide more readily than ammonia and it is likely that the surface atoms have the same relative rates of attack.

1:8:5:9 Uniform and pore-mouth poisoning.

A porous catalyst may undergo diffusion poisoning at high temperatures. There are two types, uniform (homogeneous) and pore-mouth poisoning. In the first case, the sites rendered inactive by the poison are considered to be uniformly distributed around the pore (for complete kinetic control, the fractional activity of the poisoned catalyst is inversely proportional to the fraction of sites poisoned). As the surface reaction rates increase, the fractional activity decreases less than linearly with the fraction of sites poisoned, because the poisoned portion in the inner pore is not used due to diffusion limitations. For complete external control, the rate in the unpoisoned part of the pore would be the same for the unpoisoned catalyst.

During pore-mouth poisoning, the poison is assumed to concentrate selectively in the region of the pore entrance (Wheeler, 1951). Thus a pore of length, l , with fractional

poisoning, α , is considered to be made up of a completely inactive region of length αl followed by an active portion of length $(1-\alpha)l$. As in the case of the uniform model, fractional activity decreases directly with the fraction poisoned for kinetic control. As pore-diffusion effects become important, however, the activity relative to the unpoisoned catalyst decreases markedly. Diffusion limitations have made the active inner portion of the pore less accessible, while the outer portion is completely inactive. Thus the pore-mouth presents no active surface for the reaction but instead represents an additional mass-transfer resistance.

The effect of temperature on a catalyst undergoing diffusion poisoning would be expected to be small, as the diffusion rate varies only as $T^{\frac{1}{2}}$. Poison entrainment, decomposition, etc. is, however, often markedly affected by temperature, so that this type of poisoning would be similarly affected. Catalysts undergoing pore-mouth poisoning will show apparent activation energies characteristic of a diffusion process (essentially zero activation energy) in regions where the unpoisoned or uniformly poisoned catalyst would have values somewhere between zero and the intrinsic activation energy (Rajadhyaksha and Doraiswamy, 1976). Activation energies for kinetically controlled poisoning may be higher than those obtained in the absence of a poison.

Before a particular poisoning curve can be assigned to a particular type of poisoning, the presence or absence of

diffusion must be ascertained.

1:8:5:10 Examination of poisoned catalysts.

The use of surface techniques for studying poisons adsorbed on catalyst surfaces has provided much information on the mechanism of poisoning. In particular, Auger electron spectroscopy has proved to be of great value in identifying small amounts of poisons adsorbed on the surface. X-ray fluorescence and electron microprobe techniques will provide information on the retention of the poison throughout the support, while the nature of the adsorbed species may be studied by XPS, UPS or infra-red spectroscopy. Since poisoning is normally an adsorption effect, similar treatments will apply to those discussed in section 1:3:3.

1:8:6 Catalyst regeneration.

It may be possible to regenerate the activity of a catalyst after deactivation but only if poisoning or coking has been responsible for its loss of activity. Sintering is scarcely ever reversible, as regeneration of structure is rarely possible. Treatment with chlorine and carbon monoxide is, however, believed to redisperse platinum and nickel.

A catalyst poisoned by an adsorptive mechanism can usually be regenerated by desorption or decomposition of the poison. Often high temperatures and the passage of air, hydrogen or steam through the catalyst will remove coke and hydrogen residues as well as many poisons (Rideal and Taylor, 1926;

Hart, Hoog and Weeda, 1950). Lead-poisoned supported precious metal catalysts may be partly recovered by leaching out the lead using nitric acid or an acetate solution (Houdry and Calvert, 1959) or by reaction with halides forming a volatile lead salt which can be removed at relatively low temperatures (Lester, 1963).

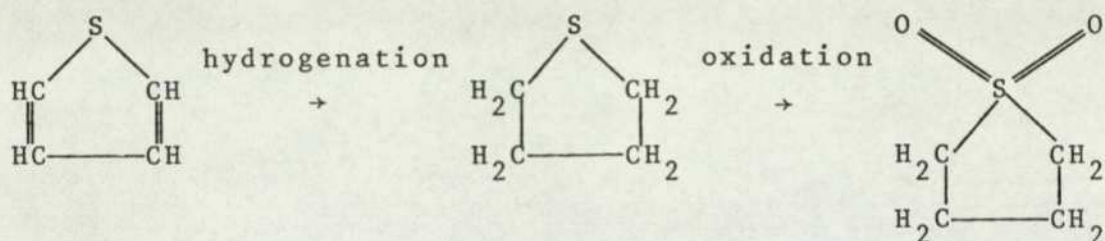
The effect of the rejuvenation process on the catalyst may not always be desirable. High temperatures and oxidising atmospheres may cause sintering of the active component and deterioration of the support. Regeneration of an aluminium (III) oxide-supported palladium catalyst poisoned by lead, sulphur and phosphorus involved oxidation and reduction cycles at 1273K (Hori, Kinoshita and Uchida, 1976). Rejuvenation was short-lived as massive loss in surface area occurred, reducing the service life and poison-resistance of the catalyst.

Mild regeneration is normally more effective. A silver catalyst used for olefin oxidation was reactivated by West and West, (1949) by treatment first with a stream of gas containing a halogen followed by ammonia and water at 443 to 600K with little loss of surface area.

1:8:7 Prevention of deactivation.

Whenever possible, poisons are removed from the gas stream before reaching the catalyst or converted to non-toxic compounds. The latter process, called detoxication (Maxted, 1951), may be applied to compounds containing unshielded elements from Groups VB and VIB. For example,

thiophene (Maxted, 1947), which acts as a poison for the hydrogenation of benzene over platinum, may be detoxicated by oxidation to thiophane sulphone in which sulphur is shielded.



Its removal from the gas stream then becomes unnecessary.

Coking is harder to control but water vapour or hydrogen can be added to the gas stream to reduce coke formation (Kearby, 1950). Fouling of the catalyst by dust particles can be avoided by the use of a filter.

If it is impossible to remove the poison before it reaches the catalyst, a suitable temperature can be chosen, which may prevent poisoning. Poisons that operate by adsorption will often be desorbed at higher temperatures. Other compounds may become poisons only at high temperatures and are non-toxic if the temperature is kept low. Chlorinated hydrocarbons will poison palladium catalysts at low temperatures but these are desorbed at high temperatures (Otto and Montreuil, 1976).

Sintering plays an important role in catalyst deactivation at high temperatures. Structure stabilizers may be added to the catalyst; these include aluminium (III) oxide, which is added to iron (III) oxide in ammonia synthesis catalysts. Metal oxide supports, too, may be stabilised either by

addition of other oxides or by choice of a stable phase of the metal oxide.

1:9 The present work.

It is most desirable that catalytic systems containing precious metals remain in stable operation for as long as possible. To achieve this aim, an understanding of the factors that cause catalyst deactivation is necessary. In the case of catalytic gas detectors, their performance in the presence of poisons or inhibitors is of crucial importance.

The mechanism of inhibition of precious metal catalysts is, in many cases, not fully understood and it is the intention of the work described to elucidate some of the processes involved. A comparison between powder catalysts with variable precious metal loadings and catalytic beads with high loadings of precious metals has provided a useful correlation between two catalytic systems. Furthermore, support-precious metal interactions, precious metal dispersions, surface adsorption, etc., were studied for different supports and precious metals and related to catalytic activity. With an understanding of the mechanism of methane oxidation and the performance of the catalysts used, studies were made of the deactivation of these catalysts in the presence of halogenated hydrocarbons and organosiloxanes.

Section 2. EXPERIMENTAL.

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2:1 Materials.

2:1:1 Catalyst supports.

γ -aluminium (III) oxide (Brockmann grade II, "for chromatographic purposes") was supplied by B.D.H. Limited. The material was shown by X-ray diffraction to contain, in addition to γ - Al_2O_3 , small amounts of κ - and ϵ - with traces of α -, θ - and χ - Al_2O_3 .

Silicon (IV) oxide ("silica gel for carbon monoxide determination", 60-120 mesh) was supplied by Hopkin and Williams Limited as was titanium (IV) oxide ("pigment grade") which consisted mainly of anatase with 11% of rutile present. A sample of pure rutile was obtained from Tioxide Limited.

Thorium (IV) oxide was prepared by decomposition of 'AnalaR' thorium (IV) nitrate hexahydrate (B.D.H. Limited) by heating it for 0.5 hours at 783K followed by 6 hours at 1523K.

Tin (IV) oxide ("Specpure") was obtained from Johnson Matthey Limited. A mixed tin-aluminium oxide support was prepared by allowing ammonium hydroxide to react with a mixture of hydrated tin (IV) chloride ($\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$) and anhydrous aluminium (III) chloride (both supplied by B.D.H. Limited). The resultant gel was filtered, washed to remove NH_4^+ and Cl^- ions and then dried at 395K. Calcination in air at 800K produced an off-white powder, analysis of which, using EDAX, indicated that there was less than 1% chlorine in the sample.

The refractory oxide supports required for the catalytic beads were obtained by thermal decomposition of aluminium (III) nitrate nonahydrate, thorium (IV) nitrate pentahydrate (both 'AnalaR' grade) and hydrated tin (IV) chloride ("laboratory reagent" grade) all supplied by B.D.H. Limited.

2:1:2 Precious metals and their salts.

Hydrated platinum (IV) oxide ($\text{PtO}_2 \cdot x\text{H}_2\text{O}$; Adams' catalyst), palladium (II) oxide ($\text{PdO} \cdot x\text{H}_2\text{O}$) tetraammine palladium (II) chloride ("Specpure"), tetraammine platinum (II) chloride ("Specpure") and rhodium (III) chloride ("laboratory chemical") were supplied by Johnson Matthey Limited. Palladium (II) chloride, palladium (II) nitrate and hydrogen hexachloroplatinate (IV) hydrate (all "laboratory reagent" grade) were obtained from B.D.H. Limited.

2:1:3 Catalyst preparation.

Precious metal catalysts supported on powdered refractory oxides were prepared with metal loadings from 0.5 - 40% w/w using one of the following techniques:

(i) Refluxing, for ca. 3 hours, an aqueous solution of the precious metal salt to which the required amount of support had been added. The water was removed at its boiling point.

(ii) Mixing the precious metal salt with the support, then adding enough water to produce a slurry followed by evaporation of the water at its boiling point.

(iii) (For palladium (II) oxide catalysts only). Mixing the support and palladium (II) oxide as a slurry in methanol and allowing the volatile component to evaporate.

Further treatment was unnecessary for catalysts prepared by method (iii) while those obtained by methods (i) and (ii) were dried at 400K for several hours, crushed and sieved, the 100-200 mesh (75-150 μm) fraction being retained for use. Catalyst preparation using palladium (II) chloride required the addition of a few drops of 0.880 ammonia solution to dissolve the chloride in water while palladium (II) nitrate required a few drops of concentrated nitric acid for its dissolution.

All catalysts expressed in future as X% precious metal on support refer to X% (w/w) precious metal on support.

2:1:4 Construction of catalytic beads.

The catalytic beads were constructed around a platinum wire coil which provided both a means of heating and of sensing the heat produced by catalytic action at the surface of the bead (Firth, 1966). Platinum was used due to its high temperature coefficient of resistance, its ability to withstand oxidation or corrosion and its mechanical strength. A coil with five and a half turns of 0.025 mm diameter platinum wire (Johnson Matthey, minimum purity 99.99%) was used with coil diameter 0.46 mm and pitch 0.15 mm. Each coil was coated with aluminium (III) oxide as the catalyst support by dipping 17 times in a saturated aqueous solution of aluminium (III) nitrate and decomposed to the oxide by

heating, using the coil as the heater. A coat of thorium (IV) oxide followed, prepared in a similar manner except that only four dips in a saturated aqueous solution of thorium (IV) nitrate were needed. Six dips in a solution of tetraammine palladium (II) chloride (3% (w/w) in water) provided the final catalyst coat. Careful heating to dry and decompose the precious metal salt to the metal and metal oxide was carried out in air. The diameter of the resulting bead was ca. 1 mm and it was dark brown in colour. Analysis using a scanning electron microscope fitted with EDAX revealed that the thorium:palladium ratio was in the region 1:0.05 and that the palladium was evenly distributed over the surface of the bead. A drawing of the bead construction is shown in Figure 2:1.

The platinum trail wires from the bead were spot-welded to gold-coated nickel posts embedded in a resin plug.

2:1:5 Reactants.

Methane (Air Products "C.P." grade; quoted minimum purity 99.5%) was further purified by condensation at 78K followed by distillation. This was repeated at least twice, the middle fraction being collected each time.

Oxygen (Air Products "high purity" grade, quoted minimum purity 99.6%) was condensed at 78K and distilled and the middle fraction was retained for use.

Nitrogen (Air Products "high purity" grade, minimum quoted purity 99.999%) and hydrogen (Air Products "high

MICROCALORIMETRIC BEAD

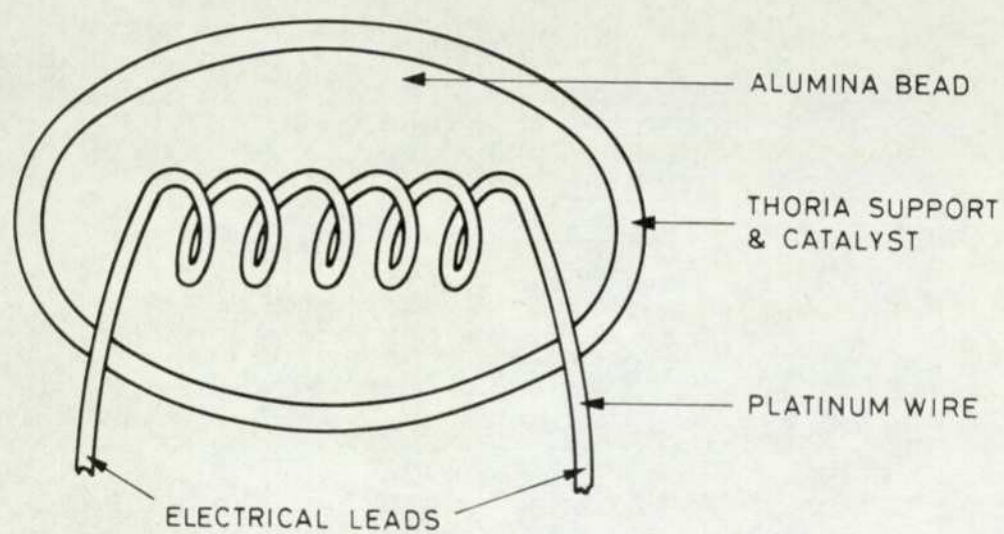


FIG. 2.1 CATALYTIC GAS DETECTION ELEMENT

purity" grade, minimum quoted purity 99.99%) were passed through liquid nitrogen traps before use.

2:1:6 Reaction products.

Carbon dioxide (P.K. Morgan Limited, quoted minimum purity 99.995%) was condensed at 78K and sublimed from trap to trap, the middle fraction being retained for use.

Water was distilled and deionised. It was degassed before use.

Carbon monoxide (P.K. Morgan Limited, quoted minimum purity 99.5%) was used without further purification.

Ethane (P.K. Morgan Limited, quoted minimum purity 99%) was condensed at 78K and distilled from trap to trap and the middle fraction was retained for use.

2:1:7 Inhibitors.

Trichloromethane and tetrachloromethane were of "aristar" grade from B.D.H. Limited. Dichloromethane (AnalaR), dibromomethane (L.R. grade) and 1,2-dichloromethane (L.R. grade) were obtained from B.D.H. Limited. They were degassed and used without further purification.

Hexamethyldisiloxane $\{(\text{CH}_3)_3\text{Si}-\text{O}-\text{Si}(\text{CH}_3)_3\}$ and polydimethylsiloxane $\{\text{viscosity} = 1 \text{ cs.}, (\text{H}_3\text{C})_3\text{Si}-(\text{OSi}(\text{CH}_3)_2)_n-\text{OSi}(\text{CH}_3)_3 \text{ where } n = 2 \text{ to } 3\}$ were obtained from Hopkin and Williams Limited. They were frozen at 78K and distilled under vacuum twice, the middle fraction only being retained.

2:1:8 Purification of carrier gas.

The helium supplied by Air Products Limited for use as a carrier gas was "ultrapure" grade with certified minimum purity of 99.995% containing levels of oxygen less than 1 ppm and nitrogen less than 10 ppm. Further purification was carried out by passing the carrier gas through the following three stages:

- (1) A Matheson gas purifier containing 13X molecular sieve to remove oil and water vapour.
- (2) A Supelco gas purifier consisting of a heated tube (30 cm long by 1.3 cm diameter) containing granules for the removal of oxygen and water.
- (3) A liquid nitrogen trap to remove condensable gases.

By these means, only inert gases not trapped by the molecular sieve were expected to be present in the carrier gas.

2:2 Apparatus and procedure.

2:2:1 Pulse-flow microreactor.

2:2:1:1 General description.

The apparatus consisted essentially of a microreactor situated in the carrier gas line of a gas chromatograph. Reactants were introduced into the gas stream by means of a gas sample valve situated upstream in relation to the microreactor. After reaction, the products were carried to the chromatograph for analysis. A diagram of the system is depicted in Figure 2:2 while the apparatus is shown in Figure 2:3.

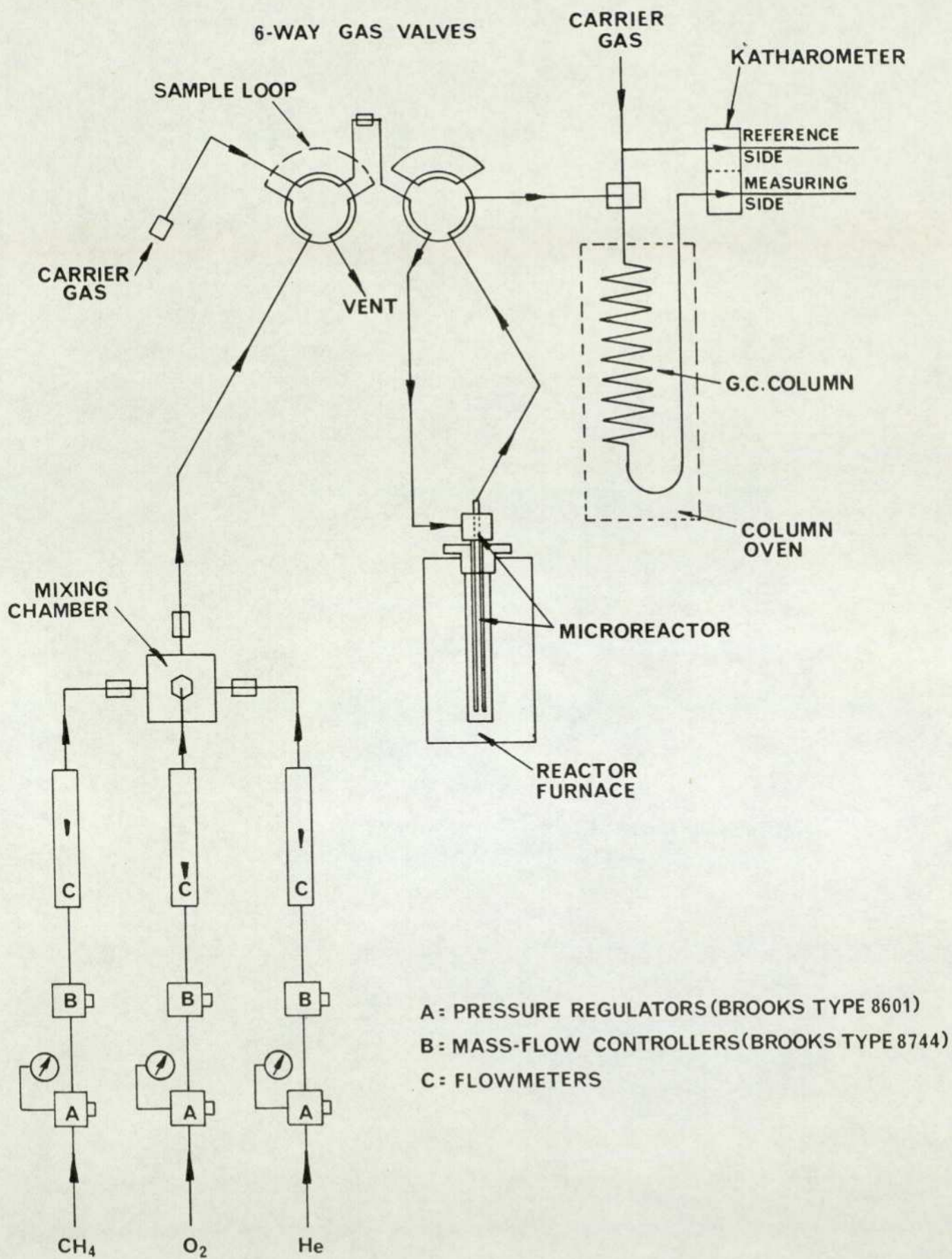


FIG. 2.2 PULSED FLOW MICROREACTOR SYSTEM

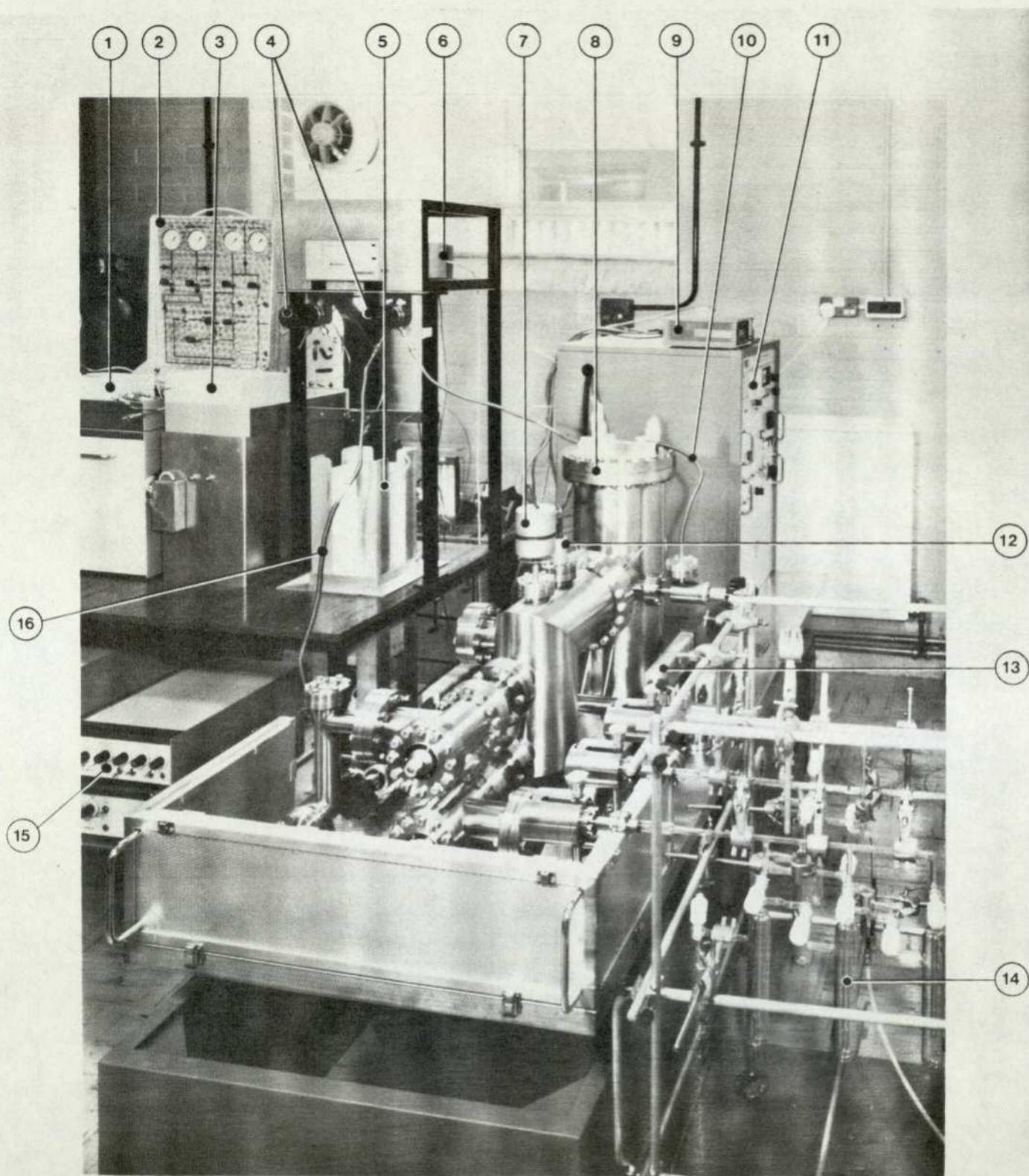


FIGURE 2.3. ULTRA-HIGH VACUUM STATIC GAS-HANDLING APPARATUS.

KEY TO FIGURE 2:3.

1. Katharometer detector.
2. Carrier gas control unit.
3. Flame ionization detector.
4. Six-way gas sample valve.
5. Microreactor furnace.
6. Temperature controller for furnace.
7. Baratron pressure gauge ($0-10^3$ Torr).
8. Liquid nitrogen cooled trap above diffusion pump.
9. Baratron head and display unit.
10. Sample line evacuation section.
11. Control unit for pumping system.
12. Ionization gauge ($10^{-3} - 10^{-10}$ Torr).
13. Bake-out heater.
14. Gas handling and purification lines.
15. Gas chromatograph control units.
16. Sample line to reactor.

Reactants were initially generated using a flow system with gases supplied from cylinders and controlled by pressure regulators (Brooks type 8601) and mass flow controllers (Brooks type 8744). These gases were mixed at ambient pressure in a stainless steel mixing chamber (volume = 500 cm³) from which the sample loop was supplied (Figure 2:2). The disadvantages of this system were the difficulty of adding low concentrations of poisons to the gas mixture, the difficulty of purifying the reactants and the problem of measuring low flow rates with associated long mixing times. Consequently, an ultra-high vacuum static gas handling apparatus was constructed by Vacuum Generators Limited for generation of precisely monitored gas mixtures free from contaminants.

A diagram of the vacuum apparatus is shown in Figure 2:4. The glass traps used to store and purify reactants are shown in Figure 2:5. Gases from cylinders were passed into these traps, condensed and distilled from trap to trap using liquid nitrogen baths. Flow between traps was controlled by greaseless PTFE stopcocks (Youngs Limited, London). Glass to metal seals joined these traps to all metal leak valves which admitted the reactants to the stainless steel main chamber. All joints were sealed with copper gaskets to avoid the use of greases and pumping was provided by an oil diffusion pump (Edwards EO4) backed by a rotary pump (Edwards ED200). Use of 'Santovac 5' oil (a polyphenylether supplied by the Monsanto Company) and a baffled, 5 litre capacity, liquid nitrogen trap for

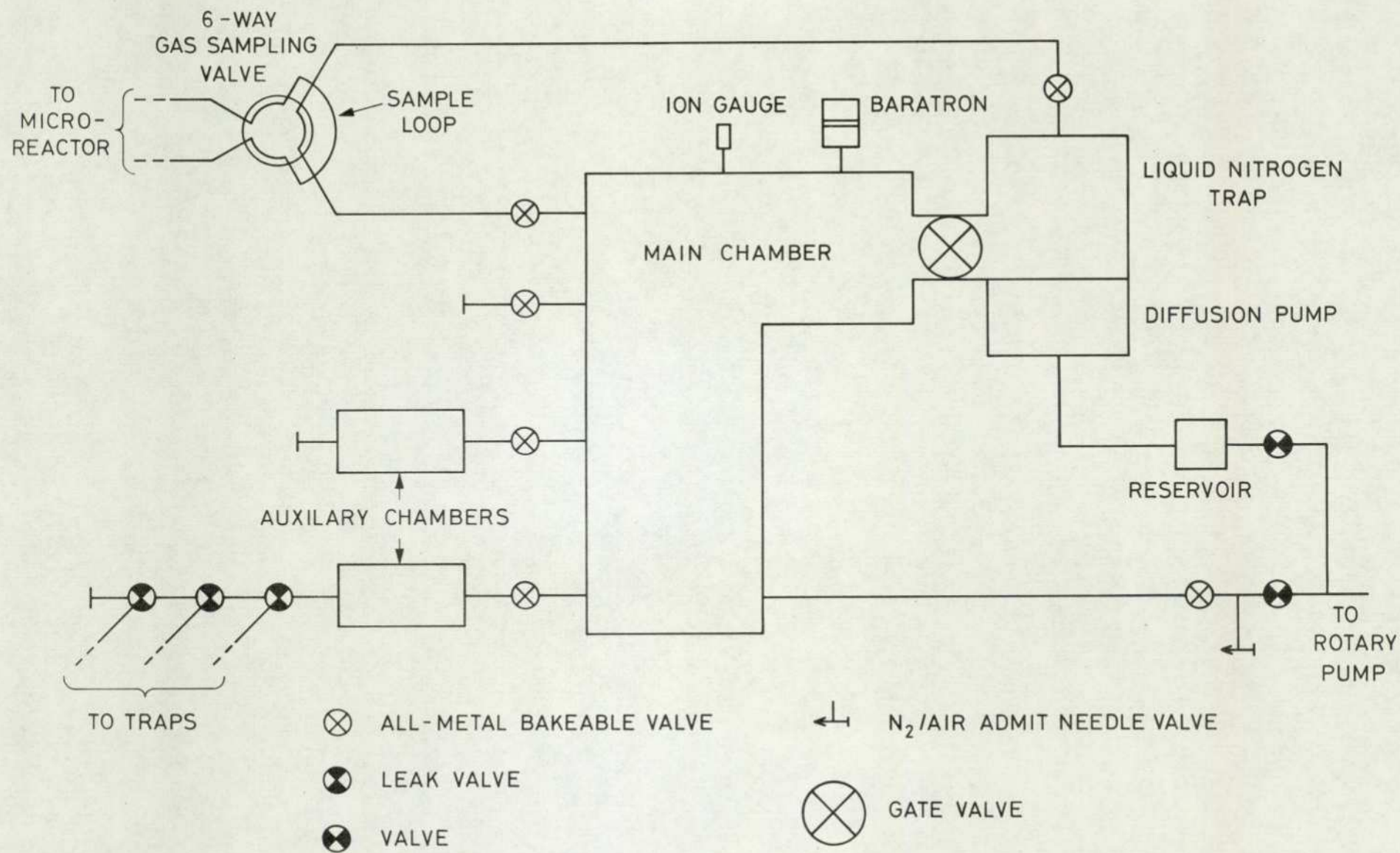


FIG. 2.4 ULTRA HIGH VACUUM STATIC GAS-HANDLING APPARATUS

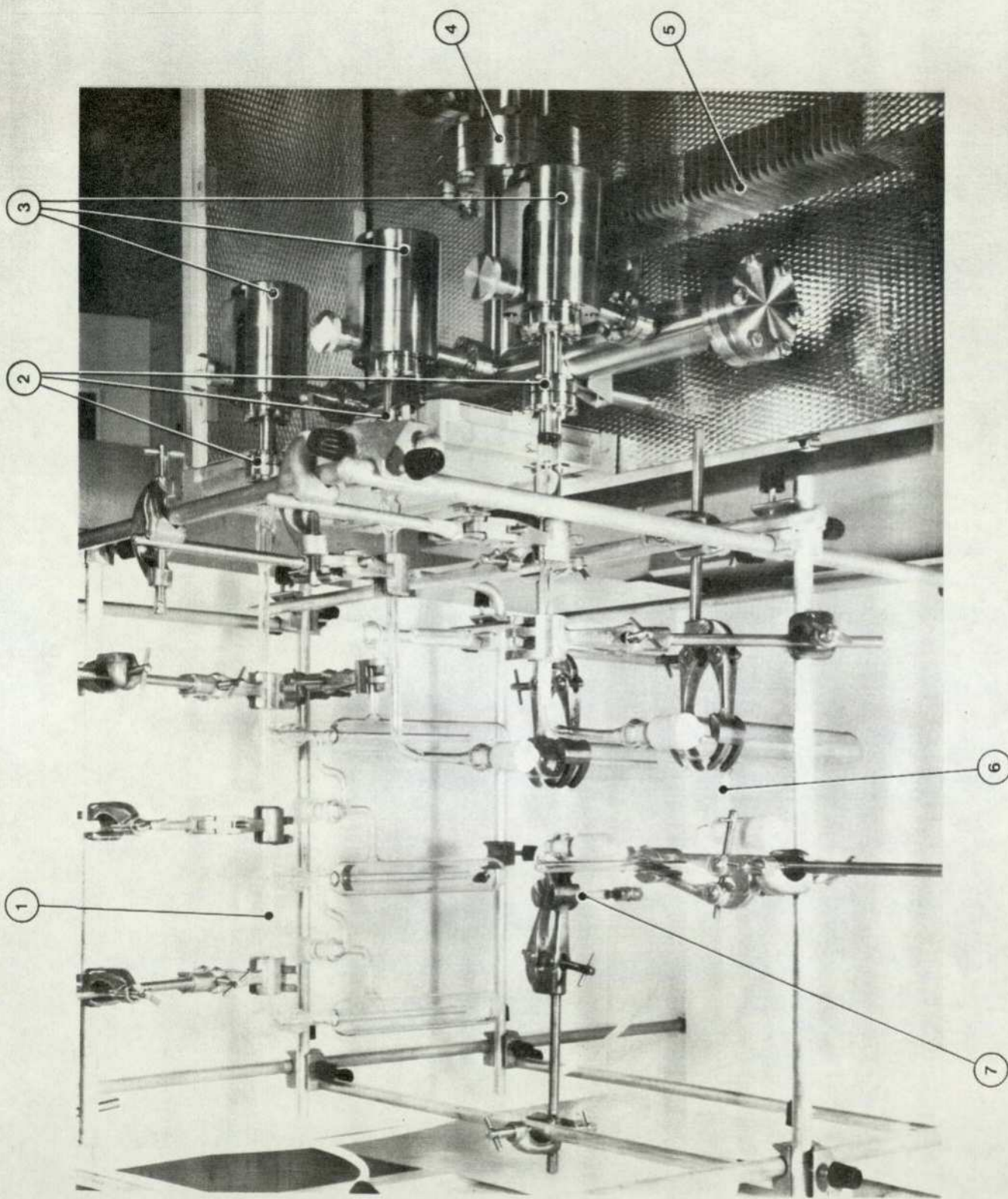


FIGURE 2.5. GLASS TRAP SYSTEM FOR STORAGE AND PURIFICATION OF GASES.

KEY TO FIGURE 2:5.

1. Hydrocarbon and inhibitor handling and purification section.
2. Glass to metal seals.
3. Bakeable all metal leak valves.
4. Line to U.H.V. apparatus.
5. Bake-out heater.
6. Oxygen handling and purification line.
7. Helium or nitrogen handling line.

the diffusion pump meant that an ultimate vacuum of less than 5×10^{-10} Torr in the main chamber was achieved. Contamination of the storage chambers was avoided by a bake-out facility enabling the stainless steel section to be heated to 525K for several hours while pumping was continued.

The pressure in the main chamber was monitored by an ionisation gauge (Vacuum Generators Model TCS9; 1×10^{-10} Torr) or a choice of two calibrated capacitance manometers (MKS Instruments Baratron model 221A, 0-1000 Torr and model 220B, 0-10 Torr). Mercury manometers were avoided to prevent contamination of the reactants by mercury, a possible catalyst poison. Flexible stainless steel tubing connected the main chamber to the sample loop (Figure 2:6).

Generation of the reactant mixtures (normally methane, oxygen and diluent with, or without inhibitor) involved purification of the gases followed by mixing at the required partial pressures in the main working chamber. The gases, obtained from cylinders, were passed through traps cooled in liquid nitrogen. Gases such as methane, a solid at these temperatures, were distilled at least twice, the middle fraction being collected each time. Alternatively, for gases obtained at high purity, such as oxygen, about a third of the liquefied volume was pumped away after degassing, and the rest was retained for use. Each reactant was in turn allowed to warm up and admitted to the main chamber via the leak valve at a pre-determined partial pressure measured on the Baratron manometer (these pre-calibrated instruments gave an absolute measurement of pressure).

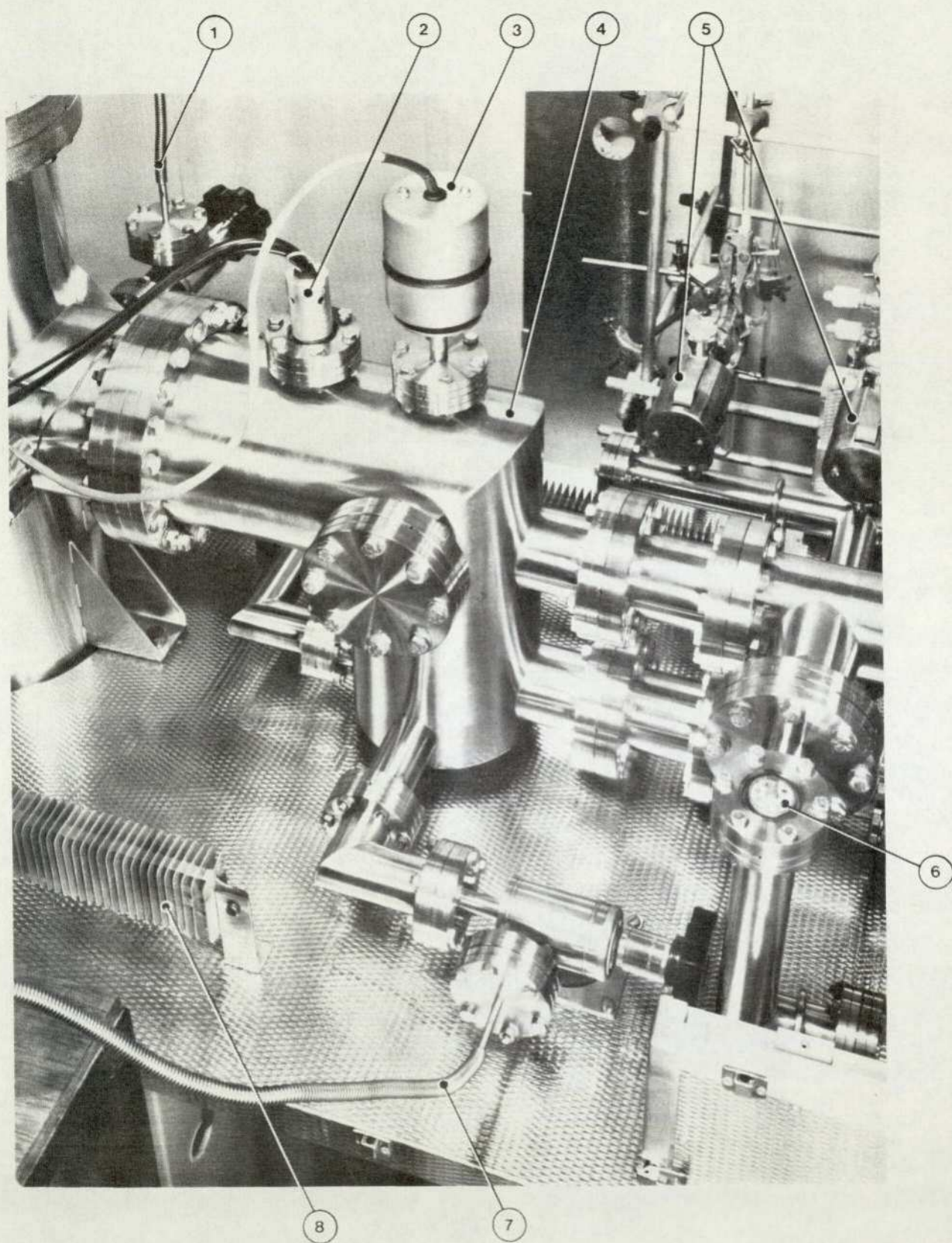


FIGURE 2.6. MAIN STORAGE CHAMBER FOR GASES AND VAPOURS.

KEY TO FIGURE 2:6.

1. Flexible sample line.
2. Ionization gauge head.
3. Baratron head (0 - 10^3 Torr).
4. Bakeable U.H.V. gas mixing chamber.
5. Leak valve to gas purification lines.
6. Ionization gauge connector.
7. Flexible sample line.
8. Bake-out heater.

The leak valve was closed, the liquid nitrogen bath was raised and the process was repeated using the next component, care being taken to ensure that the pressure of the gas to be admitted was greater than that in the main chamber before the leak valve was opened. At least 20 minutes were allowed for the mixture to equilibrate. In addition to the use of pressure measurements, the composition of the reactant mixtures was measured by gas chromatography.

Expansion of the gas mixture into the evacuated sample loop was achieved by opening the interconnecting valve between the flexible coupling and the main chamber. After sample injection, this valve was closed and the contents of the sample loop and flexible coupling were pumped away for re-filling.

2:2:1:3 Sample injection.

Injection of the reactant gases into the carrier gas stream was achieved by using a six-way valve (Perkin Elmer Model F17) with an associated sample loop. A second six-way valve, connected to the outlet from the first, either diverted the flow through the catalyst or by-passed the microreactor straight to the gas chromatograph for analysis.

The sample loop was chosen with the requirement that a rectangular pulse of reactant gas reached the catalyst with minimum mixing with the carrier gas. A loop of volume 5 cm^3 (at N.T.P.) was used, made of stainless steel, length ca. 30 cm, overall diameter 6 mm. This size was chosen

for the following reasons:

- (1) The smaller surface area obtained with a larger diameter sample loop reduced adsorption of the poisons on the walls.
- (2) Shorter equilibration times were obtained using a short loop thus reducing leakage. Although the loop could be evacuated so that 5×10^{-8} Torr was obtained in the main chamber, there was a measurable leak rate because the six-way valve was not constructed to operate under high vacuum.
- (3) The volume of the loop was large enough to minimise the effects of reactants mixing with the carrier gas. Smaller diameter tubing with the same volume reduced the mixing of carrier gas and reactants still further but consideration of factors (1) and (2) resulted in the choice of 6 mm overall diameter.

Measurement of the sample pulse shape was achieved by attaching a microkatharometer (Taylor-Servomex Mk 158, the response time of which was 3×10^{-3} seconds) to the outlet of the six-way valve. By varying the sample loop diameter and volume, the peak shape was recorded on a chart recorder and the degree of mixing could be found from the concentration profile of the pulse.

2:2:1:4 The microreactor.

The microreactor was designed with the requirement that a small catalyst bed evenly heated throughout its length be exposed to a rectangular pulse of gas whose composition was changed only by the catalyst itself.

The construction of the microreactor is shown in Figure 2:7 and is similar to that used by Keene (1969). The inner (2 mm i.d.) and outer (5 mm i.d.) tubes of the reactor were made from silica and held in place by a stainless steel head with viton rubber O-ring seals. The annular gap between these tubes was minimised, less than 1 mm separating their walls. Silica wool plugs (ca. 2.0 mm long) were used to keep the catalyst bed (ca. 15 mm long, 2 mm diam.) in place. The carrier gas flow (carrier gas pressure = 40 psig) after passage through the catalyst bed was carefully measured to detect any restriction to flow caused by a tightly packed bed.

The furnace was constructed with three separate windings and operated using a Eurotherm type 070 temperature controller with a Ni-Cr/Ni-Al thermocouple. A similar thermocouple, connected to a Comark model 1601 electronic thermometer, monitored the bed temperature. Temperature profiles along the reactor tube are shown in Figure 2:8. A longitudinal variation of $\pm 2\text{K}$ over 5 cm was observed while over the length occupied by the catalyst bed, the temperature varied by only 1K. To ensure that hot spots were not created by catalytic reactions, a thermocouple was inserted into the bed while typical reaction mixtures were passed through the catalyst. The only examples of severe temperature fluctuations along the catalyst bed were observed when an unsupported palladium catalyst was exposed to highly oxidising or reducing conditions (see section 3:2).

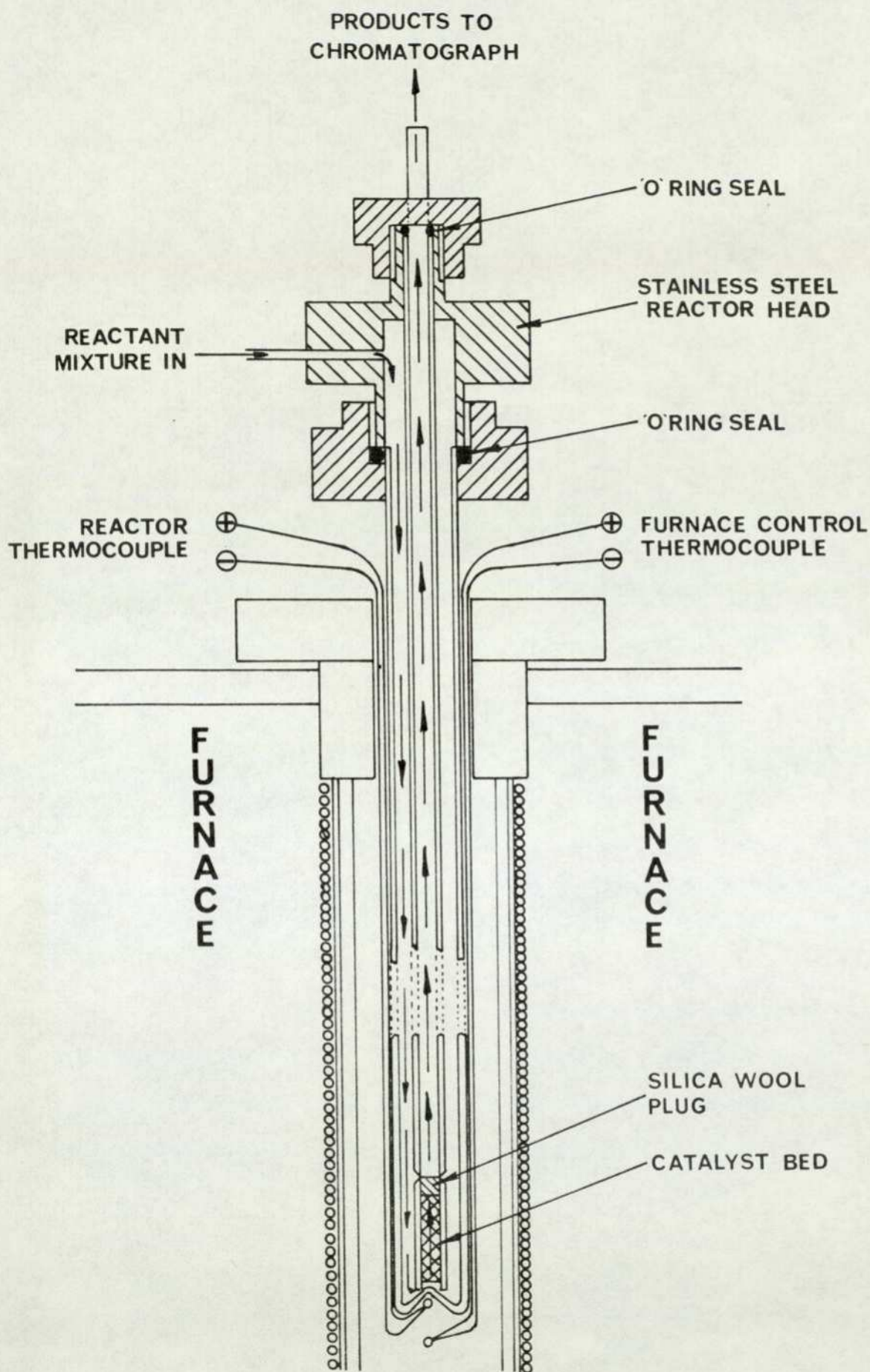


FIG. 2.7 THE MICROREACTOR

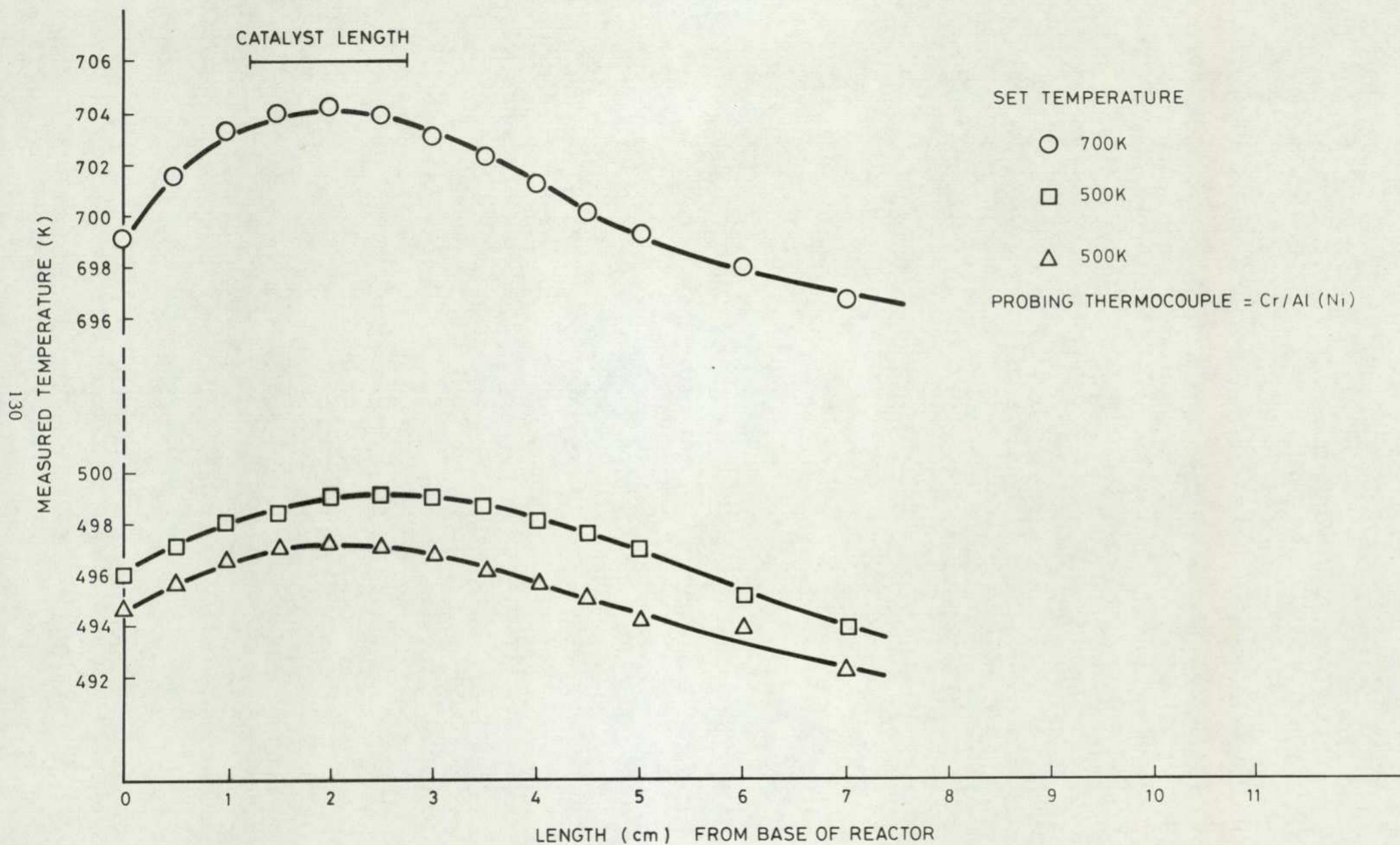


FIG.2.8 TEMPERATURE PROFILE ACROSS FURNACE

2:2:1:5 Analysis of reactants and products by gas chromatography.

2:2:1:5:1 The gas chromatograph.

The identification and quantification of the reactants and products was achieved using a gas chromatograph (Pye Unicam model 104). This was connected to the microreactor via 3.2 mm diam. stainless steel tubing which could be heated, using heating tape, to ca. 400K to prevent adsorption of products or inhibitors on the walls. The need to analyse compounds with widely different boiling points such as hydrogen and water made it necessary to choose more than one column packing. Furthermore, the flame ionisation detector generated no signal when water, carbon dioxide or carbon monoxide were present and a katharometer detector was used for these compounds.

2:2:1:5:2 Separation of components.

A complete analysis of the reactants and products was achieved using the following columns:

- (i) Silica gel (80 - 100 mesh; 1.83m x 6.35 mm) in stainless steel tubing maintained at 323K.
- (ii) Carbosieve B (60 - 80 mesh; 1.25m x 3.2 mm) in stainless steel tubing maintained at 323K.
- (iii) Poropak Q (956x; 2.2m x 6.35 mm) in glass tubing maintained at 373K.

Silica gel and Carbosieve B were suited to the separation of low boiling gases such as hydrogen, oxygen, carbon monoxide and methane. In addition, Carbosieve B was suitable for the separation of water, formaldehyde and methanol when

heated to ca. 400K. Poropak Q, a porous styrene polymer, was used to separate higher boiling components such as water and ethylene (Table 2:1).

The column temperature was thermostatically controlled to $\pm 1.5\text{K}$ with the possibility of temperature programming if required. In addition, as the separation of components depends on the flow rate and the pressure as well as the temperature, the flow was maintained constant at $25\text{ cm}^3\text{ min}^{-1}$ (N.T.P.) and checked every day. The columns were reconditioned when necessary (about once every three months for the silica gel column) using the conditions specified by the manufacturers for each column.

2:2:1:5:3 Detectors.

The katharometer detector (Pye Unicam model 44) was connected to the column outlet preceding a dual heated flame ionisation detector (FID - Pye Unicam model 64) linked by 3.2 mm o.d. stainless steel tubing. The choice of two detectors meant that carbon monoxide, oxygen, carbon dioxide and water could be analysed using the katharometer while hydrocarbons could be analysed using the FID, the sensitivity of which was greater than that of the katharometer. Helium was used as a carrier gas to improve the sensitivity of the katharometer to all components with the exception of hydrogen. The temperature of the katharometer was controlled to $\pm 0.05\text{K}$ while the flows through the reference and measuring cells were balanced to $25 \pm 0.5\text{ cm}^3\text{ min}^{-1}$ using a bubble flow meter. The temperature of the FID was maintained at $373 \pm 0.05\text{K}$.

Component	Retention time.		
	Silica gel ⁺	Carbosieve B [†]	Poropak Q [*]
H ₂	1 min. 6 sec.		
O ₂	1 min. 50 sec.	22 sec.	1 min. 21 sec.
N ₂	1 min. 52 sec.		
CO	2 min. 18 sec.	1 min. 33 sec.	1 min. 16 sec.
CH ₄	3 min. 4 sec.	47 sec.	1 min. 31 sec.
C ₂ H ₆	15 min. 6 sec.		
CO ₂	25 min. 53 sec.	2 min. 30 sec.	1 min. 59 sec.
C ₂ H ₄	32 min. 24 sec.		
C ₃ H ₈	68 min. 30 sec.		7 min. 40 sec.
H ₂ O		2 min. 10 sec.	4 min. 21 sec.
neo-C ₅ H ₁₂			36 min.
CH ₂ Cl ₂			11 min. 5 sec.
CH ₃ OH			3 min. 48 sec.
C ₂ H ₅ OH			6 min. 12 sec.
CH ₃ COOH			13 min. 10 sec.

+ 1.83 m x 6.35 mm; 80-100 mesh; temperature = 323K.

† 1.25 m x 3.2 mm; 60-80 mesh; temperature = 323K.

* 2.2 m x 6.35 mm; 956x; temperature = 373K.

Table 2:1 Retention times of various components on three chromatographic columns.

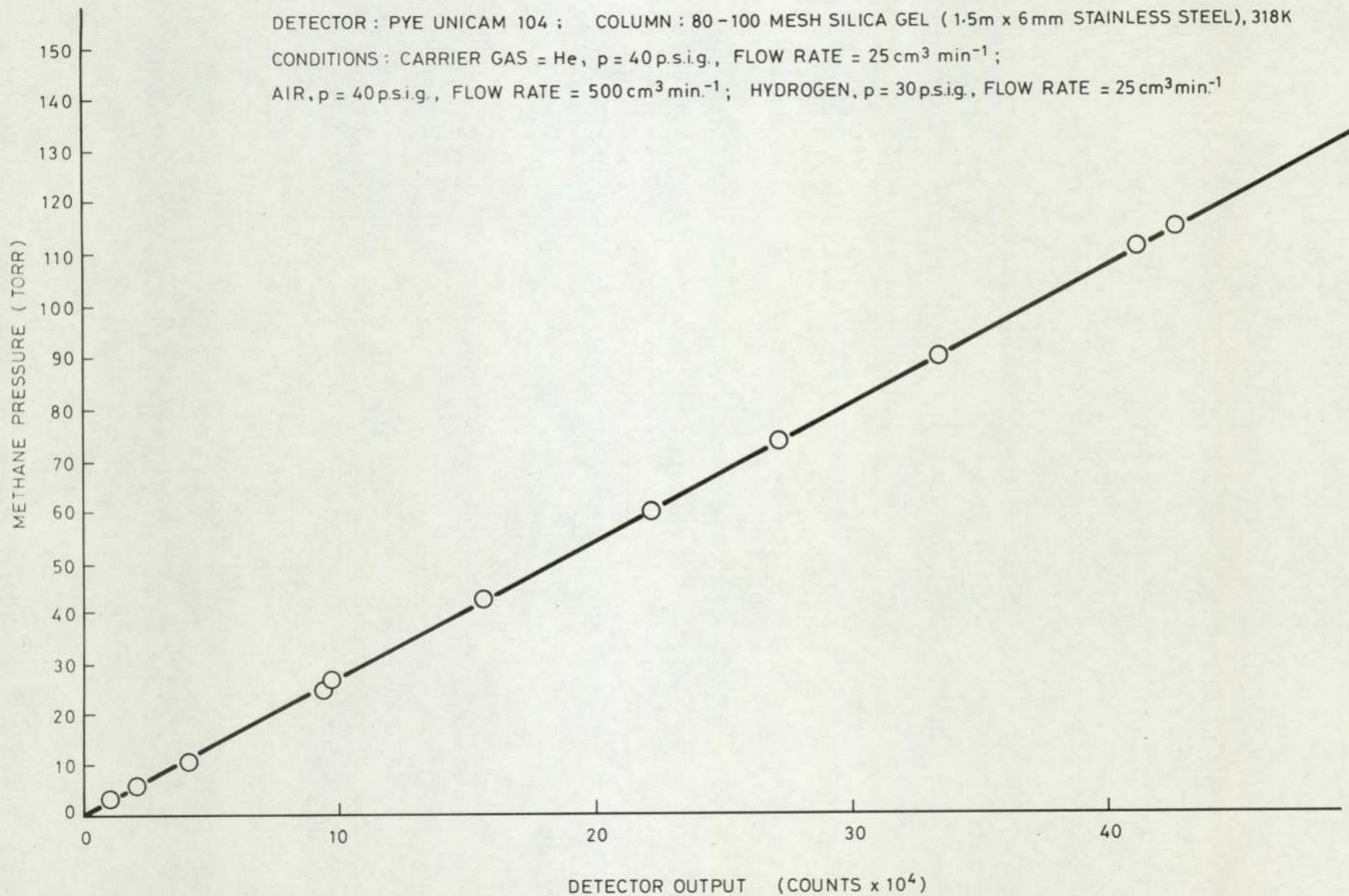
The detector outputs were monitored with an integrator (Laboratory Data Control model 308) and chart recorders. Calibration of the gas used in rate determinations (usually methane or carbon dioxide) was carried out every day. A calibration curve for methane is shown in Figure 2:9 from which it can be seen that the detector (FID) response is linear to methane over these concentrations. The hydrogen and air supply for the detector flame was regulated using pressure controllers (Brooks type 8601) and mass flow controllers (Brooks type 8744) to give a flow rate of $500 \text{ cm}^3 \text{ min}^{-1}$ of air at 40 psig and $25 \text{ cm}^3 \text{ min}^{-1}$ of hydrogen at 30 psig. This gave a steady flame, the output from which was not appreciably altered by small changes in the air or hydrogen flow rates.

2:2:1:6 Catalyst conditioning.

Supported catalysts were conditioned by heating to 775K in a flow of helium (ca. $25 \text{ cm}^3 \text{ min}^{-1}$) for at least 15 hours. During conditioning, the microreactor was disconnected from the chromatograph to prevent corrosion and deterioration of the column by acid gases evolved during decomposition of the precious metal salts. Hydrogen was sometimes used instead of helium for conditioning and was obtained by connecting a hydrogen cylinder to the sample valve via a two-stage regulator. The purpose of the conditioning was to decompose the precious metal salts to the precious metal or its oxide. Conditioning at temperatures of less than 775K produced a catalyst whose performance was unstable on exposure to methane/oxygen mixtures. At temperatures above 775K, severe agglomeration of palladium was

FIG.2.9 TYPICAL CALIBRATION CURVE FOR METHANE OBTAINED BY FLAME IONISATION DETECTOR

DETECTOR : PYE UNICAM 104 ; COLUMN : 80-100 MESH SILICA GEL (1.5m x 6mm STAINLESS STEEL), 318K

CONDITIONS : CARRIER GAS = He, $p = 40$ p.s.i.g., FLOW RATE = $25 \text{ cm}^3 \text{ min}^{-1}$;AIR, $p = 40$ p.s.i.g., FLOW RATE = $500 \text{ cm}^3 \text{ min}^{-1}$; HYDROGEN, $p = 30$ p.s.i.g., FLOW RATE = $25 \text{ cm}^3 \text{ min}^{-1}$ 

expected to occur, especially in hydrogen atmospheres.

2:2:1:7 Operation of microreactor.

Following conditioning, the catalyst was exposed to pulses of reactants supplied by the sample loop and carried through the catalyst by helium.

The contact time was varied by alteration of the following parameters:

- a) Carrier gas flow.
- b) Catalyst bed length.
- c) Pulse volume.

Variation in the temperature of the catalyst bed altered the rate of the reaction. Typical measurements of the activation energy for methane oxidation by a particular catalyst were made by passing methane/oxygen mixtures of the same composition through the catalyst over a range of temperatures. Reaction orders with respect to a particular component of the gas sample were measured by varying the partial pressure of that component in the gas mixture while the partial pressures of other active components were kept constant.

A study of methane oxidation by reduced or oxidised palladium catalysts required that the catalyst was exposed to pulses of oxygen or hydrogen followed by methane or methane/oxygen mixtures. In order to oxidise or reduce the catalyst, an injection port was fitted between the sample loop and the microreactor by means of which oxygen or hydrogen could be injected into the gas stream using a

syringe. Alternatively, the sample loop and gas handling apparatus were used or a cylinder of the required gas was connected directly to the sample valve via a two-stage regulator using the same method as that adopted for conditioning the catalyst.

The effect of poisons on the catalyst was studied by passing methane/oxygen mixtures containing small amounts of poisons through the catalyst and measuring the effect of the poison on the reaction rate. The possibility of adsorption of poisons on the walls of the sample loop and on the side of the flexible tubing from the loop to the microreactor was prevented by heating these lines to ca. 400K using heating tape.

2:2:2 Catalytic beads.

The catalytic beads were exposed to gas in a stainless steel reactor (volume = 10 litres). This was connected via an all-metal valve to the ultra-high vacuum gas handling apparatus described in section 2:1:2 and could be evacuated to a pressure of 2×10^{-8} Torr with heating at 525K to remove contaminants. Gas samples for analysis were withdrawn from the reactor by means of flexible stainless steel tubing and injected into the carrier gas stream of a gas chromatograph via a six-way valve.

A static gas reactor was chosen rather than a flow system as it was easier to purify and generate very low concentrations of inhibitors and poisons using a static system. The large volume of the reactor (10 litres) was chosen to

provide an adequate operating time for the catalytic beads without seriously depleting the hydrocarbons present (methane consumption by the catalytic bead was ca. $1.0 \mu\text{l sec}^{-1}$). Furthermore, at least six beads could be tested at the same time reducing any inconsistencies observed when only single beads were operated.

The catalytic bead, with a 10Ω resistance in series, formed one arm of a Wheatstone bridge. The other arm consisted of a 100Ω resistance in series with a variable resistor. The circuit diagram is given in Figure 2:10. The coil was heated using a power supply which maintained the bead at constant resistance and hence constant temperature and the out-of-balance voltages across the bridge were measured using a digital voltmeter (Fluke model 8050A).

On exposure to combustible gas mixtures, heat is generated at the catalyst surface. Operation at constant resistance means that the heat generated by the catalytic process is compensated by a reduction in the electrical power input to the bead. Since the power generated = $(\text{current})^2 \times \text{resistance}$, the current through the bead is reduced and the voltage across the bead (the parameter normally measured) is also reduced. This is effectively a Wheatstone bridge in that at balance, the current across the bead and the 10Ω resistor is the same and the current across the variable resistor and the 100Ω resistor is also the same.

The bead was maintained at the desired temperature, which was determined by the voltage across, and the current in, the

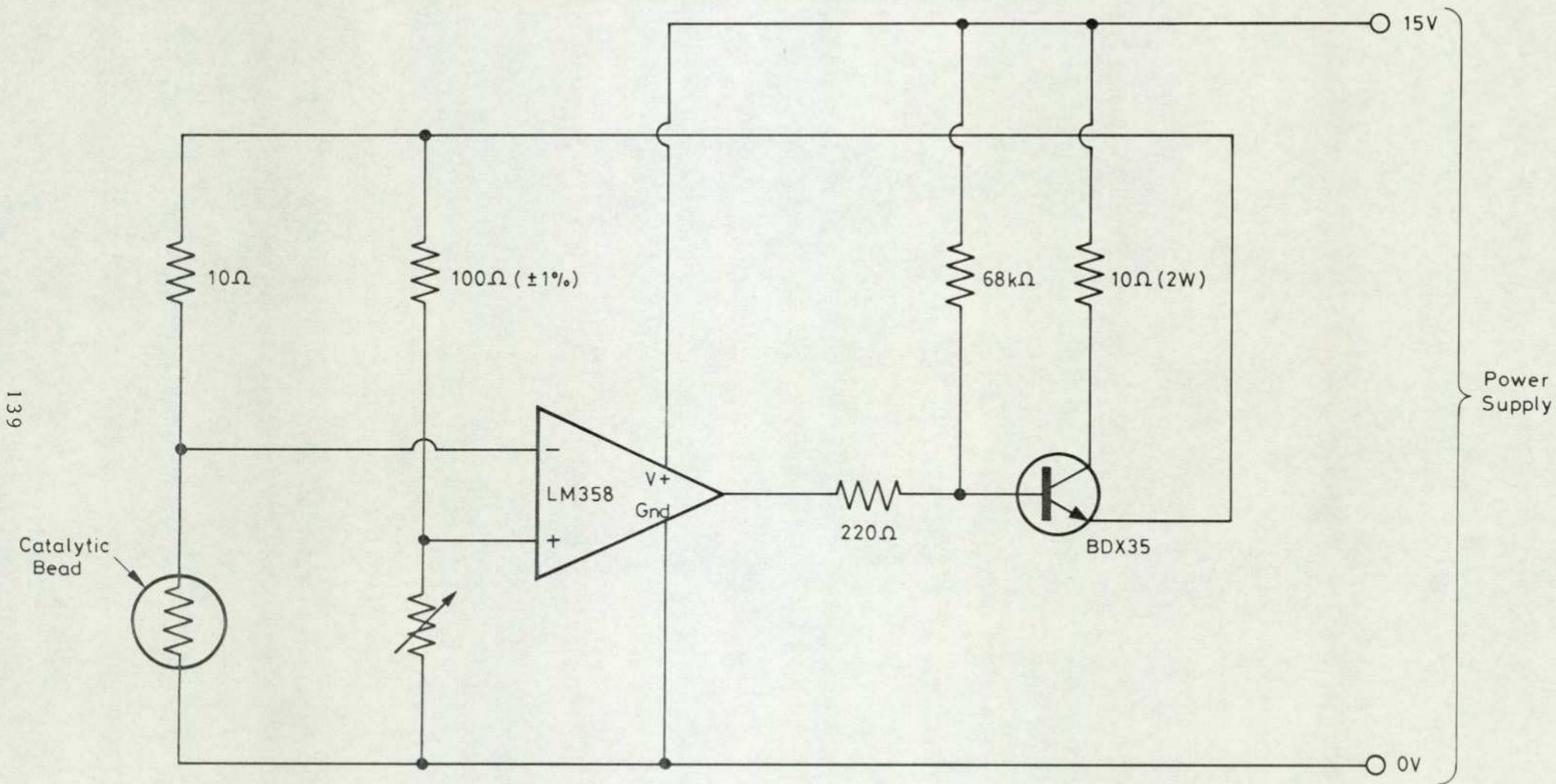


FIG. 2-10 CONSTANT RESISTANCE CIRCUIT USED TO POWER CATALYTIC BEADS

bridge in an atmosphere of oxygen and nitrogen at 760 Torr. The reactor was evacuated and the appropriate gas mixture, containing a large excess of oxygen, was introduced. Nitrogen was used as a diluent to bring the pressure up to 760 Torr. The balance in the bridge and hence the temperature of the calorimeter were maintained by decreasing the electrical power to the bridge. This reduction in the power required to maintain the bead at constant temperature was calculated from voltage measurements across the bead using a digital voltmeter. The rate of hydrocarbon oxidation was obtained from the difference in electrical power consumption of the bead, ΔP , viz.

$$\frac{dn}{dt} = \frac{\Delta P}{\alpha \Delta H}$$

Atmospheres containing methane and an inhibitor were prepared by filling a side arm of the gas-handling apparatus with the required pressure of inhibitor (measured using the 1×10^{-3} to 1 Torr Baratron capacitance manometer); this was then expanded into a pre-diluted mixture of hydrocarbon and oxygen in nitrogen in the main chamber. Sufficient time for mixing (at least five minutes) was allowed before final expansion into the reactor vessel. The concentration of inhibitor in which the beads were operating was calculated from the expansion factors. By this means concentrations as low as 5 mg m^{-3} of polyorganosiloxanes could be generated.

The catalytic beads were activated by heating in a gas mixture containing 7% v/v methane in air at atmospheric pressure for five minutes. This caused the bead to glow red and produced a catalyst whose activity, in the absence of poisons, remained reasonably stable over the period required

for its use. In addition, the beads were powered at constant resistance in an atmosphere containing oxygen (ca. 100 Torr) and then in a vacuum for five minutes before each test so that the surface was substantially similar each time. Checks on the activity and reproducibility of bead operation were carried out using a 2.5% v/v methane-in-air mixture.

2:2:3 Measurement of surface area of support.

2:2:3:1 Introduction.

Dynamic surface area measurements involving nitrogen adsorption at temperatures close to the boiling point of nitrogen were carried out using a flow system introduced by Nelsen and Eggertsen (1958) and developed by Farey and Tucker (1971). This technique differs from static methods involving pressure-volume measurements, in that the amount of adsorbed gas is determined by concentration measurements in a continuous-flow system. The method has the advantage that measurements are rapid and it is applicable over a wide range of surface areas, even as low as $0.1 \text{ m}^2 \text{ g}^{-1}$. Unlike the static B.E.T. methods, however, only the adsorption process can be studied; hence pore-size distributions cannot be determined.

In a continuous-flow method, a stream of helium containing known partial pressures of nitrogen is passed over the sample. After the sample has been cooled in liquid nitrogen, the amount of nitrogen adsorbed is determined using a previously calibrated microkatharometer detector. The

amount of nitrogen desorbed is similarly measured. In effect, this method is a modified type of gas chromatography in which the column material is the sample itself and the mobile gas phase is a known mixture containing a suitable adsorbate (N_2) and an inert gas (He). From the adsorption isotherm, the surface area may be determined using the method of Brunauer, Emmett and Teller (1938).

2:2:3:2 The apparatus and its operation.

2:2:3:2:1 Flow apparatus.

A diagram of the apparatus is shown in Figure 2:11 and the different pressures in the lines are indicated while a photograph of the apparatus is given in Figure 2:12.

The sample to be measured was placed in a silica glass reactor tube that allowed passage of gas down the outer tube, through the sample and up the inner tube. This is identical to the sample tube used in the microreactor, thus enabling transfer of samples from one apparatus to the other with the minimum of disturbance and exposure to the atmosphere. The sample was degassed by heating it in a movable furnace.

In order that the thermal histories of the reference and sample lines should be identical there was a loop in the reference arm which could be cooled in a liquid nitrogen bath. In practice, however, this proved unnecessary and caused instability in the base-line measurements. It was found essential to provide a coiled copper tube (0.32 cm

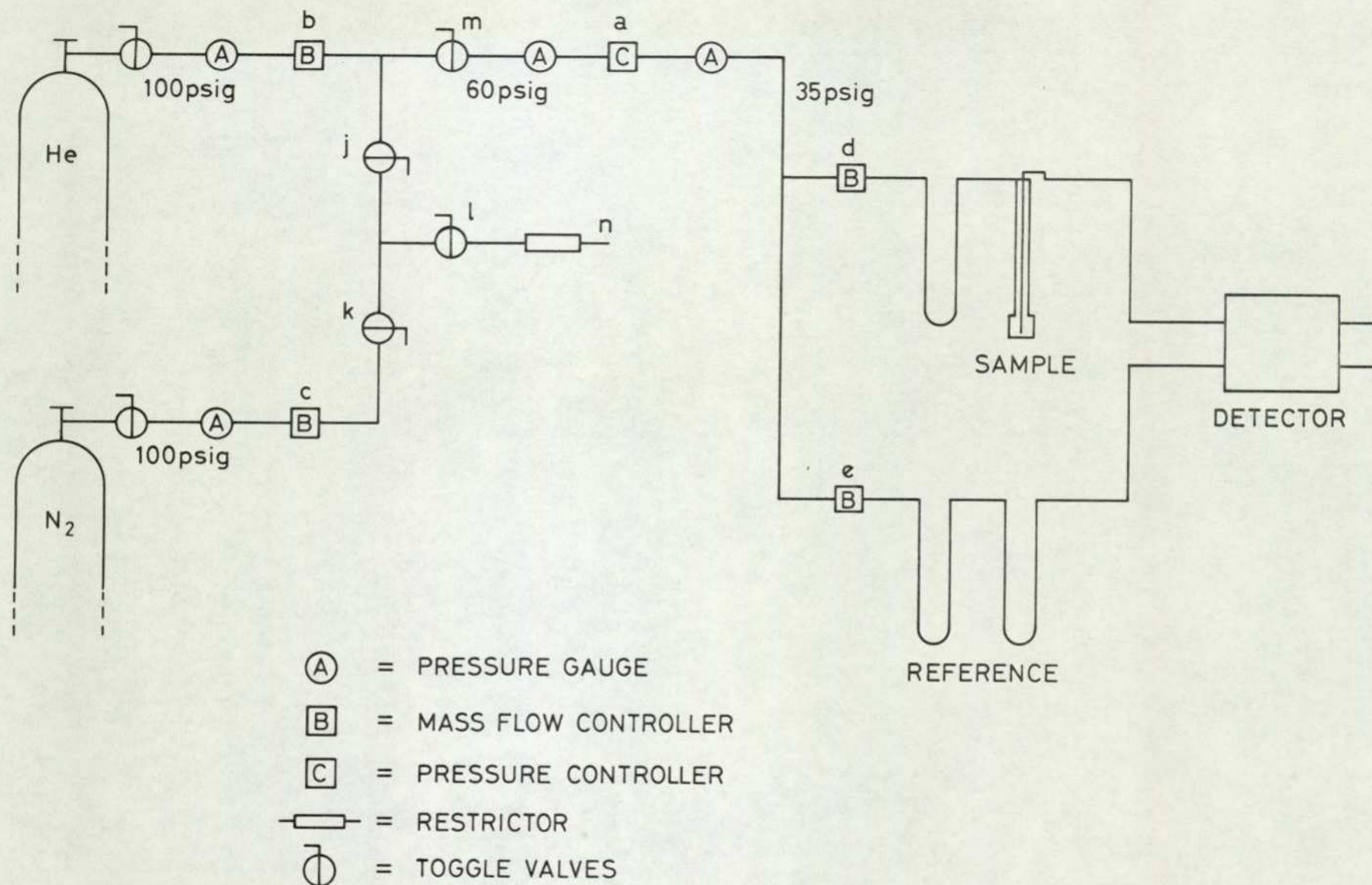


FIG. 2-11 CONTINUOUS FLOW SURFACE AREA MEASUREMENT APPARATUS

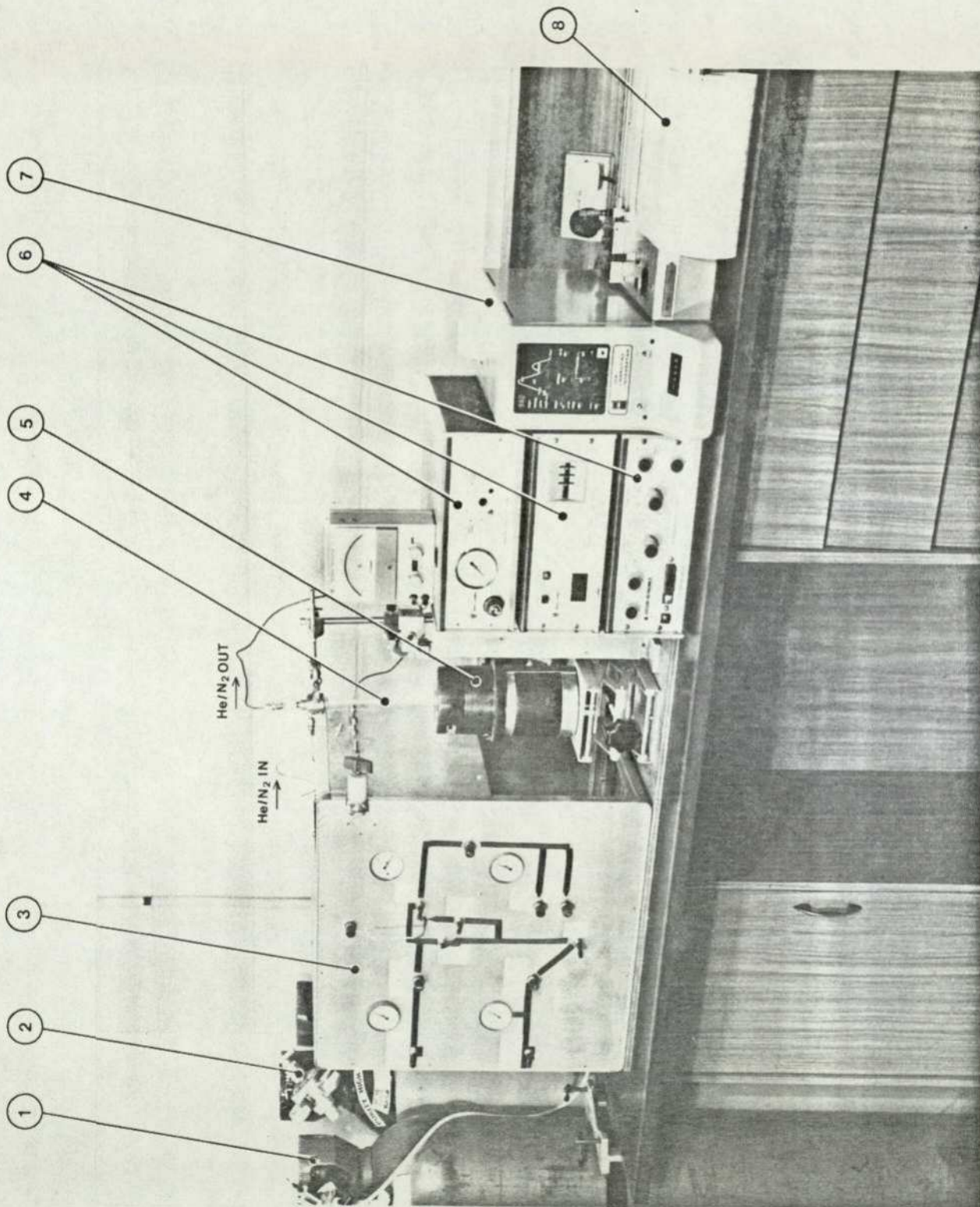


FIGURE 2.12. CONTINUOUS FLOW APPARATUS FOR SURFACE AREA MEASUREMENT.

KEY TO FIGURE 2:12.

1. Helium cylinder.
2. Nitrogen cylinder.
3. Gas control and mixing point.
4. Sample tube.
5. Dewar vessel containing liquid nitrogen.
6. Katharometer and controls.
7. Computing integrator.
8. Chart recorder.

in diameter and 100 cm long) in the measuring line directly after the sample. This enabled the adsorbed gas to warm up to room temperature before it reached the katharometer, which was heated to 323K.

2:2:3:2:2 Measurement of liquid nitrogen temperature.

Since it was essential to know the saturation vapour pressure of nitrogen under the conditions where the surface area was determined, the temperature of the liquid nitrogen used to cool the sample was measured using a platinum resistance thermometer. The thermometer (Cryogenic Calibrations Limited, model E109 - 25.5, resistance $R_0 = 25.4850\Omega$) was operated at a fixed current (2.0 mA) and the voltage output from the thermometer was found when it was immersed in liquid nitrogen contained in a Dewar flask (9 cm diameter, 18 cm depth). By applying Ohm's law,

$$V = IR$$

where V = voltage

I = current

R = resistance,

the resistance of the thermometer at the temperature of liquid nitrogen, R_t , can be found. Using the Callendar equation:

$$R_t = R(1 + \alpha T)$$

where α = first order temperature coefficient of resistivity for platinum,

T = temperature of liquid nitrogen,

a value of T was obtained. This was found to be 77.6K for "fresh" liquid nitrogen supplied by Liquidaire Limited.

From standard tables (British Standard, 1969) the saturation

vapour pressure of nitrogen at that temperature was shown to be 778 Torr.

2:2:3:2:3 Calibration of detector.

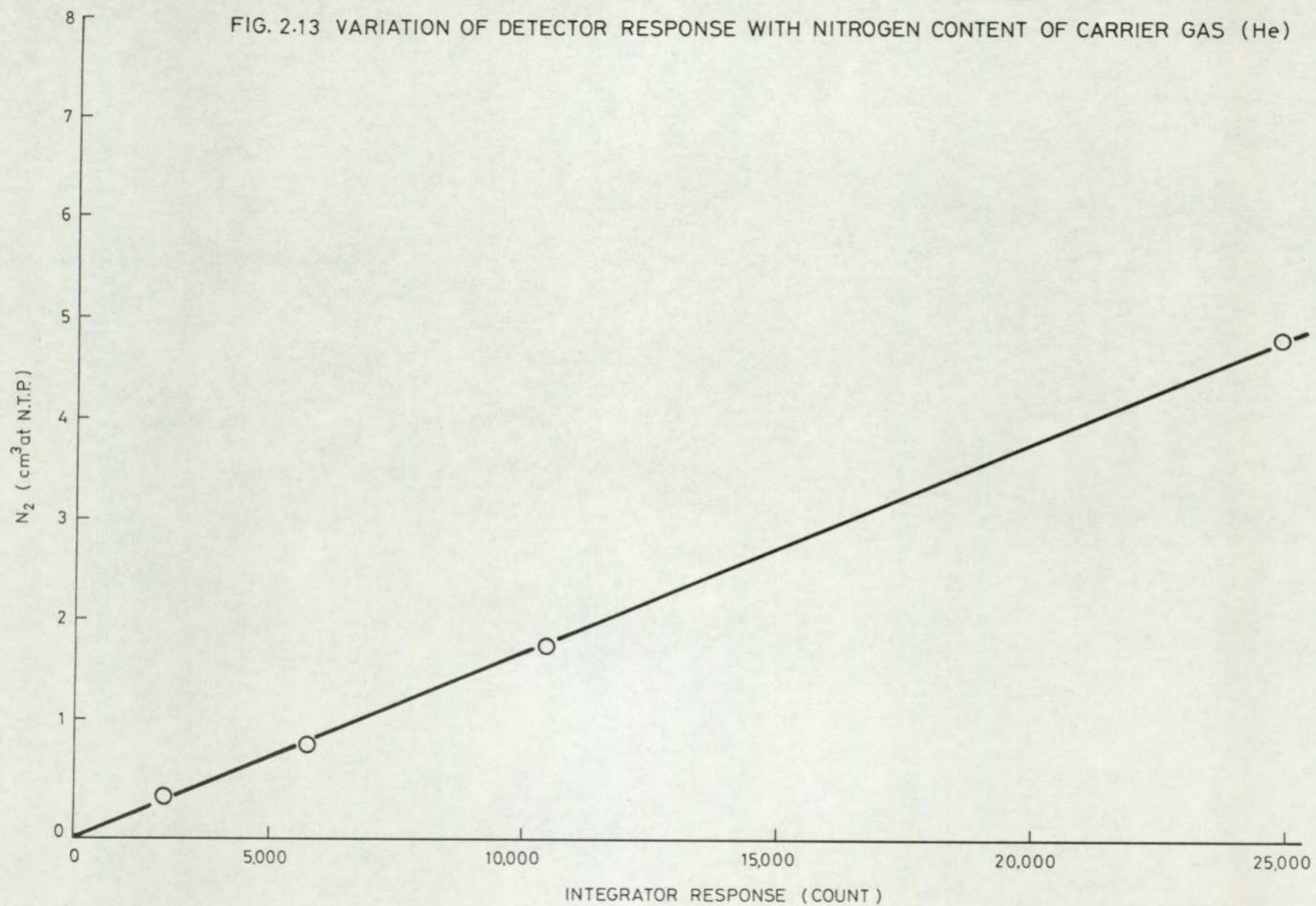
The microkatharometer was calibrated for nitrogen by injection of pulses of known volume of this gas via a gas sample valve through the sample at room temperature and measurement of the detector output by means of an integrator. Over the range 0 to 5 cm³(N.T.P.) of nitrogen, the detector response was linear (Figure 2:13).

2:2:3:2:4 Nitrogen adsorption measurements.

The continuous flow apparatus was operated according to the method of Farey and Tucker (1971). Valve j was closed and the nitrogen flow was set at the fixed flow resistance n at a value within the range 2 to 40 cm³min⁻¹. Valve m was closed, valve j was opened and the combined nitrogen and helium flow was measured at n. The flow controller, b, was adjusted to give a helium flow between 50 and 70 cm³min⁻¹. Valve l was then closed, valve m was opened and the pressure was set at 35 psig by pressure controller, a. The flow from the detector was then set at 25 cm³min⁻¹ by flow controllers, d and e.

To ensure equilibration of the gas mixture, at least fifteen minutes were allowed before nitrogen adsorption was measured. This was especially important at low partial pressures of nitrogen. Inadequate mixing was indicated by a broadening of the adsorption peak. Nitrogen flow rates of less than 2 cm³min⁻¹ were avoided as inconveniently

FIG. 2.13 VARIATION OF DETECTOR RESPONSE WITH NITROGEN CONTENT OF CARRIER GAS (He)



long equilibration times (>1.5 h) were required.

A range of sample sizes (0.1 - 0.5 g) was investigated; the lower the surface area, the greater was the amount of sample required. Each sample was degassed at 500K in flowing helium for 1 hour. Urwin (1969) has shown that, for titanium (IV) oxide, temperatures between 425 and 525K are required to achieve optimum results. Gammage, Fuller and Holmes (1969) found that 473K was the minimum outgassing temperature for porous thorium (IV) oxide required to remove water from the micropores.

As in previous work, (Nelsen and Eggertsen, 1958) the desorption peak was used for quantitative measurements (Figure 2:14).

2:2:3:2:5 Calculation of results.

Measurements were carried out on samples of γ -aluminium (III) oxide, thorium (IV) oxide and titanium (IV) oxide, both before and after heat treatment, using the B.E.T. method.

The B.E.T. equation was applied, viz:

$$\frac{P}{(P_o - P)V_a} = \frac{1}{V_m c} - \frac{P}{P_o} \cdot \frac{(c - 1)}{V_m c}$$

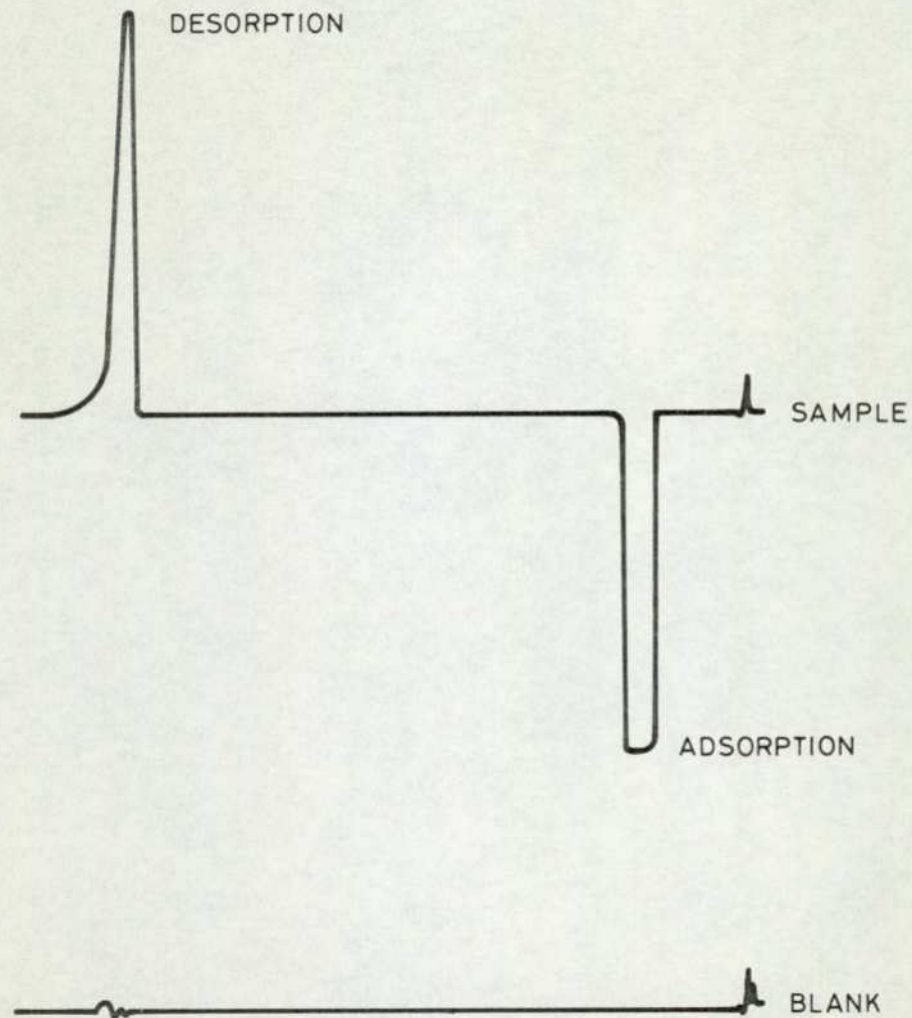
where P = equilibrium pressure

P_o = saturation vapour pressure of nitrogen at
the temperature of adsorption

c = constant

V_a = volume of nitrogen adsorbed

FIG.2.14 TYPICAL NITROGEN ADSORPTION AND DESORPTION CURVES FOR AN EMPTY SAMPLE TUBE (BLANK) AND A TUBE CONTAINING SAMPLE.



V_m = volume of nitrogen required to form a monolayer.

A plot of $\frac{P}{(P_o - P)V_a}$ against P/P_o gives a straight line of slope $\frac{c - 1}{V_m c}$ and intercept $1/V_m c$, from which V_m can be calculated. The range of linearity over which the slope can be measured is usually restricted to values of P/P_o from 0.05 to 0.30.

The specific surface area of the powder, S , was then determined from:

$$S = \frac{V_m \sigma N}{V_o w}$$

where N = Avagadro's constant

V_o = ideal molar gas volume ($22,410 \text{ cm}^3$)

w = weight of sample (g)

σ = average area occupied by each nitrogen molecule (0.162 nm^2)

A minimum of three points was taken for each B.E.T. plot and the surface area was calculated using a linear fit programme in the Data General Nova 2 computer.

In order that a comparison could be made between the conventional static methods of measuring surface area and the continuous flow method, two samples were selected whose surface areas had been measured using static methods. Their surface areas were then re-measured in the continuous flow apparatus. The results agree within the limits imposed by use of the different techniques (Table 2:2).

Sample	Surface area ($\text{m}^2 \text{g}^{-1}$)	
	Continuous flow method	Static method
TiO ₂	10.7	12.1*
Sample B	74	86.**

* Supplied by Tioxide International; area measured using a Strohlein Area Meter.

** Supplied by Portsmouth Polytechnic; area measured using a conventional static apparatus.

Table 2:2 Comparison of surface areas measured in static and flow systems.

2:2:4 Characterisation of catalysts.

2:2:4:1 Scanning electron microscopy.

In the scanning electron microscope, a finely focussed electron beam impinges on the specimen surface. The energy of the electron beam may be varied (typically from 1-50 keV) and the secondary electrons emitted from the specimen are detected using a scintillator photomultiplier. Alternatively, back-scattered electrons or emitted X-rays may be detected. Secondary electrons come from within about the first 10 nm of the specimen, whereas back-scattered electrons, due to their greater energy, may diffuse from within about the first 100 nm of the sample when high voltages are applied. The surface topography may be studied because the yield of secondary electrons depends on the angle of incidence of the electron beam. Another advantage is the large depth of field obtainable with this technique.

Scanning electron micrographs were obtained using a JEOL JSM 35 instrument. To prevent charging of the sample, the surface was sputter-coated with ca. 50 nm of gold before examination.

Identification of the elements present in the samples undergoing microscopic examination was achieved using an energy dispersive X-ray analyser (Philips Limited). During bombardment of the sample by the electron beam, vacancies are created by loss of electrons from the inner shells (K-shells) of the atoms present in the sample. These "excited" atoms may revert to the ground state by movement of an L-shell electron into the K-shell. The energy loss necessary for this

transition is emitted as electromagnetic radiation in an X-ray quantum characteristic of the atom from which it was generated. These X-rays are collected in an X-ray analyser and spectral lines are displayed on a cathode ray tube. The technique is limited to elements of atomic number greater than 11.

2:2:4:2 Transmission electron microscopy.

The particle size distribution of precious metals was examined using a JEOL JEM 100C transmission electron microscope. This technique requires that a beam of electrons passes through the sample for analysis. Hence, thin specimens are required and two methods were utilised for their preparation.

Initially, powder samples were lightly crushed and ultrasonically dispersed in 2-methylpropan-2-ol (which readily wets the oxide support), transferred to a microscope slide and dried. A carbon film (ca. 50 nm thick) was then evaporated over the sample. The carbon-catalyst film was floated off in distilled water and placed on a copper grid 3 mm in diameter. Later samples were obtained by mixing the powder catalyst with Spurr low-viscosity resin and, after curing, sectioning the product in an ultramicrotome (Reiker OM3), using a diamond knife; the resulting sections were mounted on a carbon-coated copper grid. The latter technique had the advantage that thin sections were obtained without possible damage to the sample caused by grinding.

The bombardment of atoms by electrons or X-rays produces vacancies in inner electron shells with subsequent excitation of the atoms (Figure 2:15). The kinetic energy of the ejected electron, E_{kin} , causing the vacancy may be related to the energy required to bind it to the atom by the relationship,

$$E_{kin} = h\nu - (E_f - E_i) = h\nu - E_b$$

where $h\nu$ = energy of exciting beam, and

E_i , E_f and E_b = energy of initial, final and binding states respectively.

Variation of the photon energies, (He^I 212eV, He^{II} 40.8eV, $Al\ k_\alpha$ 1486eV, $Mg\ k_\alpha$ 1254.6eV) supplies information on both inner-core levels and valence levels. Core level spectroscopy is referred to as X-ray photoelectron spectroscopy (XPS), while ultra violet photoelectron spectroscopy (UPS) provides information on valence levels using He^I and He^{II} radiation only.

The excited atom with an electron vacancy in its inner level (K-shell) may revert to the ground state losing energy by emitting a second electron (Auger electron) and/or by emitting X-rays (X-ray fluorescence). The former event occurs by filling of the inner (K-shell) vacancy by an outer (L-shell) electron with the energy released by this transition being transferred to another L-shell electron, which is ejected with an energy characteristic of the atom. This process is called a $KL_I L_{III}$ transition.

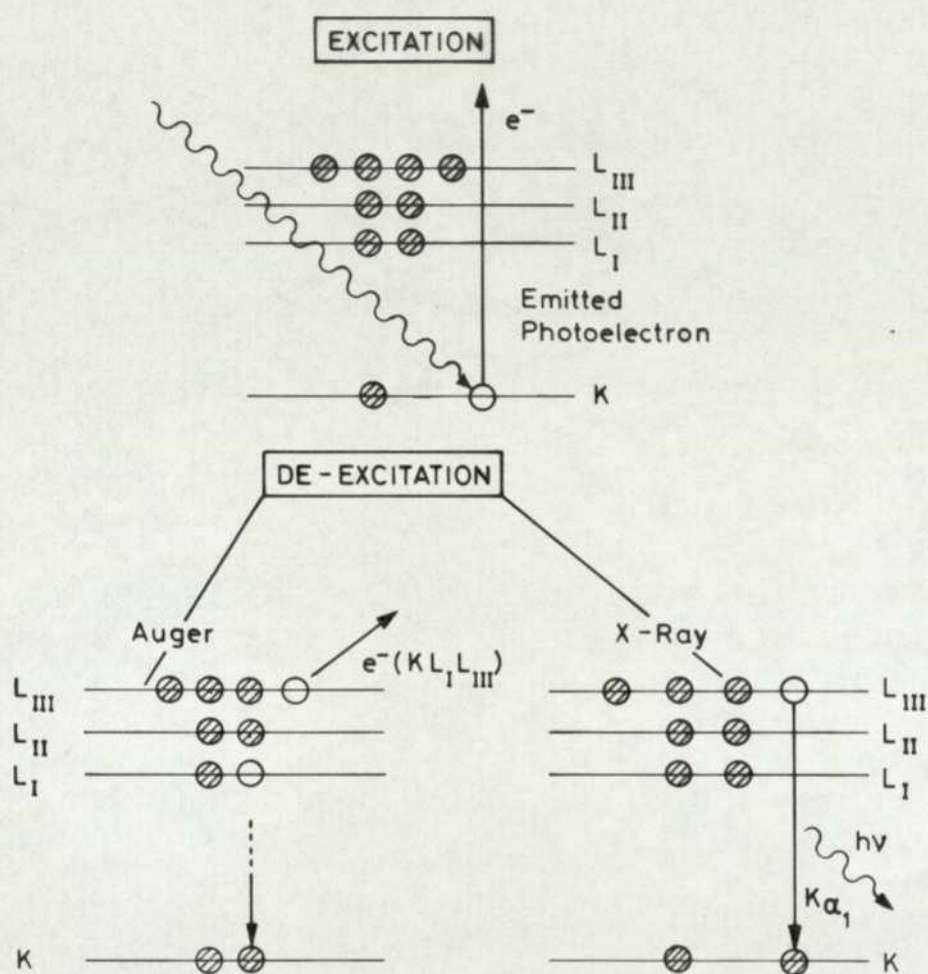


FIG. 2.15 THE PRODUCTION OF AUGER ELECTRONS OR X-RAY FLUORESCENCE FOLLOWING THE CREATION OF AN ATOMIC INNER SHELL VACANCY.

2:2:4:3:1 X-ray photoelectron spectroscopy.

X-ray photoelectron spectra were obtained using a V.G. scientific ESCA Mark 11 spectrometer. The X-ray source was provided using aluminium K_{α} radiation of 1486.6eV, while the powdered catalysts were pressed into indium foil for mounting in the instrument. Etching of the catalyst surface by bombardment with argon ions was possible using this instrument.

2:2:4:3:2 Auger electron spectroscopy.

Auger electron spectra were obtained using a JEOL JAMP 10 scanning Auger microprobe. This type of instrument has been described in the literature (le Gressus, Massignon and Sopizet, 1977) and has been modified so that electron beam intensities of less than 10^{-10} Amps can be used routinely to reduce electron beam damage to the surface of the sample. The powder catalysts were either ultrasonically dispersed in propanone before being transferred to the sample block of the instrument or pressed into indium metal which was attached to the sample block by means of copper clips.

Section 3. RESULTS.

- 3:1 Homogeneous oxidation of methane.
- 3:2 Adsorption of oxygen by precious metal catalysts.
- 3:3 Heterogeneous oxidation of methane.
 - 3:3:1 Tests for the presence of intraparticle diffusion.
 - 3:3:2 Activity of various precious metal/ support combinations towards methane oxidation.
 - 3:3:3 Orders of reaction with respect to methane and oxygen.
 - 3:3:4 Variation of the rate of methane oxidation with temperature.
 - 3:3:5 Effect of oxygen adsorption on the rate of reaction.
 - 3:3:6 Influence of methods of catalyst preparation on catalytic activity.
 - 3:3:7 Formation of partial oxidation products.
- 3:4 Pyrolysis of methane on supported palladium and platinum catalysts.
- 3:5 Oxidation of methane in the absence of gaseous oxygen by palladium (II) and platinum (IV) oxides.
- 3:6 Precious metal particle size distributions for various supported catalysts.
- 3:7 Contribution of catalyst supports towards methane oxidation.
 - 3:7:1 Reactions of methane on catalyst supports.

- 3:7:2 Effect of heating on catalyst supports.
- 3:8 Inhibition of methane oxidation over supported catalysts.
 - 3:8:1 Effect of the products of reaction on heterogeneous methane oxidation.
 - 3:8:2 Inhibition of methane oxidation by chlorinated hydrocarbons.
 - 3:8:3 Inhibition of methane oxidation by brominated hydrocarbons.
 - 3:8:4 Inhibition of methane oxidation over powdered catalysts by hexamethyldisiloxane.
 - 3:8:5 Inhibition and poisoning of hydrocarbon oxidation over catalytic beads by hexamethyldisiloxane.
- 3:9 Physicochemical studies of poisoned catalysts.
 - 3:9:1 Transmission electron microscopy.
 - 3:9:2 X-ray photoelectron spectroscopy.
 - 3:9:3 Auger electron spectroscopy.

3:1 Homogeneous oxidation of methane.

Tests for the occurrence of homogeneous oxidation of methane in the heated section of the microreactor were undertaken using an empty silica reactor tube. Under the conditions where much of the work on the heterogeneous oxidation of methane was carried out (temperature = 573 - 723K, $[\text{CH}_4]_0^* = 4.2 \times 10^{-5}$ mol, $[\text{O}_2]_0^* = 1.8 \times 10^{-5}$ mol, pulse volume = 5 cm³), less than 1% methane was consumed. Above 723K, small amounts of carbon dioxide were formed but even at 873K, only 3.2% of the methane reacted.

The method used to clean the silica reactor tube seemed to have some effect on the extent of methane conversion. Washing the tube with fuming nitric acid (specific gravity = 1.50) rather than detergent/water/methanol reduced the methane consumption. Furthermore, over the temperature range 800 - 900K, the methane conversion (3% at 873K) did not increase with temperature. This indicates that methane oxidation on the walls of the reactor tube may well be contributing to the overall reaction and some "sooting" of the reactive silica sites may occur under these conditions.

3:2 Adsorption of oxygen by precious metal catalysts.

Palladium differs from other precious metals in forming an oxide which is stable at temperatures between 523K and 1173K (see Section 1:7:1). It is between these temperatures that the heterogeneous oxidation of methane is normally studied and the possible significance of oxide formation on

* $[\text{CH}_4]_0$ and $[\text{O}_2]_0$ are initial concentrations expressed as mol per 5 cm³ reactant pulse; they are expressed for simplicity, simply as the number of mol in this volume.

the behaviour of palladium during methane oxidation requires investigation. Accordingly, the adsorption of oxygen by supported palladium catalysts was studied over a range of temperatures. In addition, a platinum catalyst was investigated for comparison purposes and the interaction of oxygen with the catalyst support was studied for a sample of γ -aluminium (III) oxide. The results are given in Table 3:1 and Figures 3:1, 3:2, 3:3 and 3:4.

From these, the following observations were made:

- (i) At 823K, palladium supported on γ -aluminium (III) oxide adsorbed nearly one hundred times more oxygen than was adsorbed by platinum. This is not unexpected since platinum metal forms only a thin surface oxide layer at this temperature, whereas oxygen can migrate into the bulk of the palladium as well as forming a surface oxide.
- (ii) γ -aluminium (III) oxide did not take up appreciable amounts of oxygen at temperatures as high as 923K. After the support had been conditioned in flowing helium at 773K for 3 hours, however, it adsorbed about ten times more oxygen than it did before. Thus, passage of helium through the catalyst at high temperatures reversibly removed oxygen from the support.
- (iii) The amount of oxygen adsorbed per gram of supported palladium varied considerably depending both on the support and the loading on that support. Over the temperature range 600-823K, the oxygen uptake per gram of supported palladium was greater on 2.7% Pd on TiO_2 than on 8.7% Pd on TiO_2 (Figure 3:2). These results are supported by studies

Catalyst/support	Uptake of oxygen (mol per gram precious metal)	
	623K	683K
1% Pd on $\gamma\text{-Al}_2\text{O}_3$	4.95×10^{-3}	9.01×10^{-3}
10.78% Pd on $\gamma\text{-Al}_2\text{O}_3$	1.45×10^{-3}	2.65×10^{-3}
25% Pd on $\gamma\text{-Al}_2\text{O}_3$	1.27×10^{-3}	2.50×10^{-3}
5% Pd on ThO_2	0.15×10^{-3}	0.20×10^{-3}
2.7% Pd on TiO_2	0.86×10^{-3}	-
8.7% Pd on TiO_2	0.20×10^{-3}	0.25×10^{-3}
5% Pt on $\gamma\text{-Al}_2\text{O}_3$	0.02×10^{-3}	0.02×10^{-3}
$\gamma\text{-Al}_2\text{O}_3$	0.05×10^{-4}	$0.05 \times 10^{-4*}$

* Oxygen uptake per gram of support.

Oxygen pulse volume = $0.1 - 0.5 \text{ cm}^3$ (N.T.P.)

Catalyst bed length = 1.5 cm.

Helium flow rate = $25 \text{ cm}^3 \text{ min}^{-1}$.

Table 3:1 The uptake of oxygen by supported precious metal catalysts.

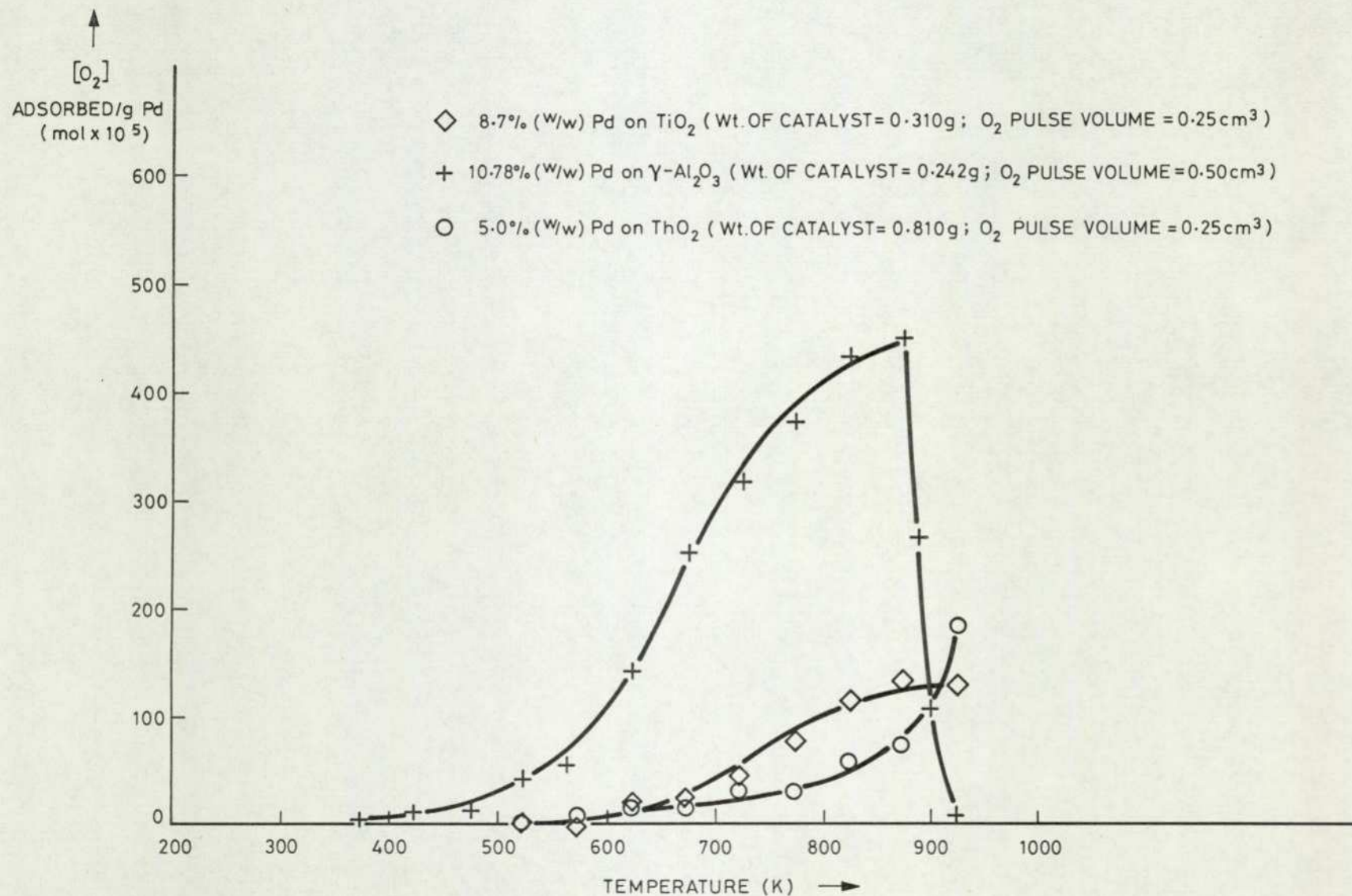


FIG. 3.1 VARIATION WITH TEMPERATURE OF THE ADSORPTION OF OXYGEN FOR SUPPORTED PALLADIUM CATALYSTS

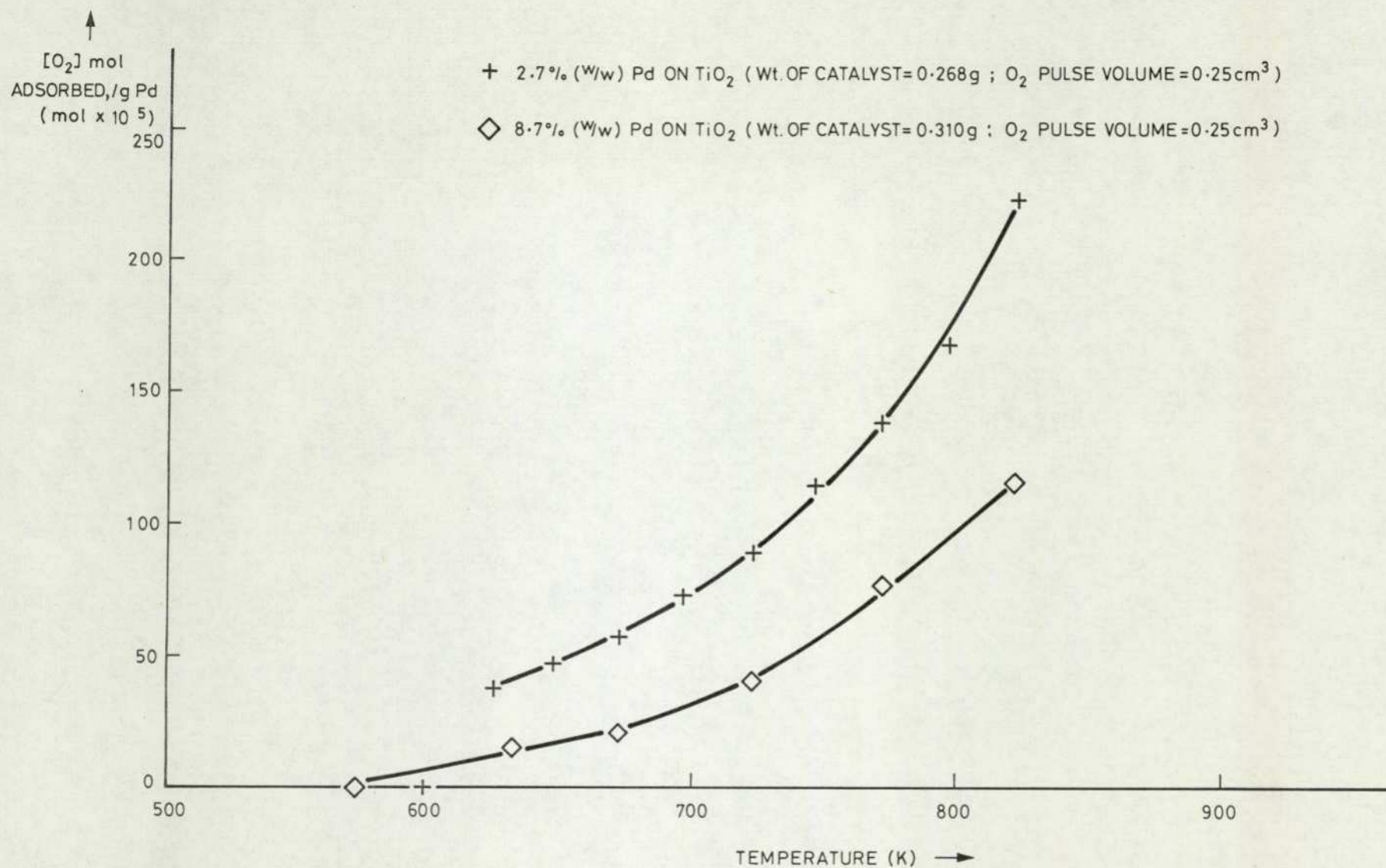


FIG.3.2 VARIATION WITH TEMPERATURE OF THE ADSORPTION OF OXYGEN FOR Pd/ TiO_2 CATALYSTS

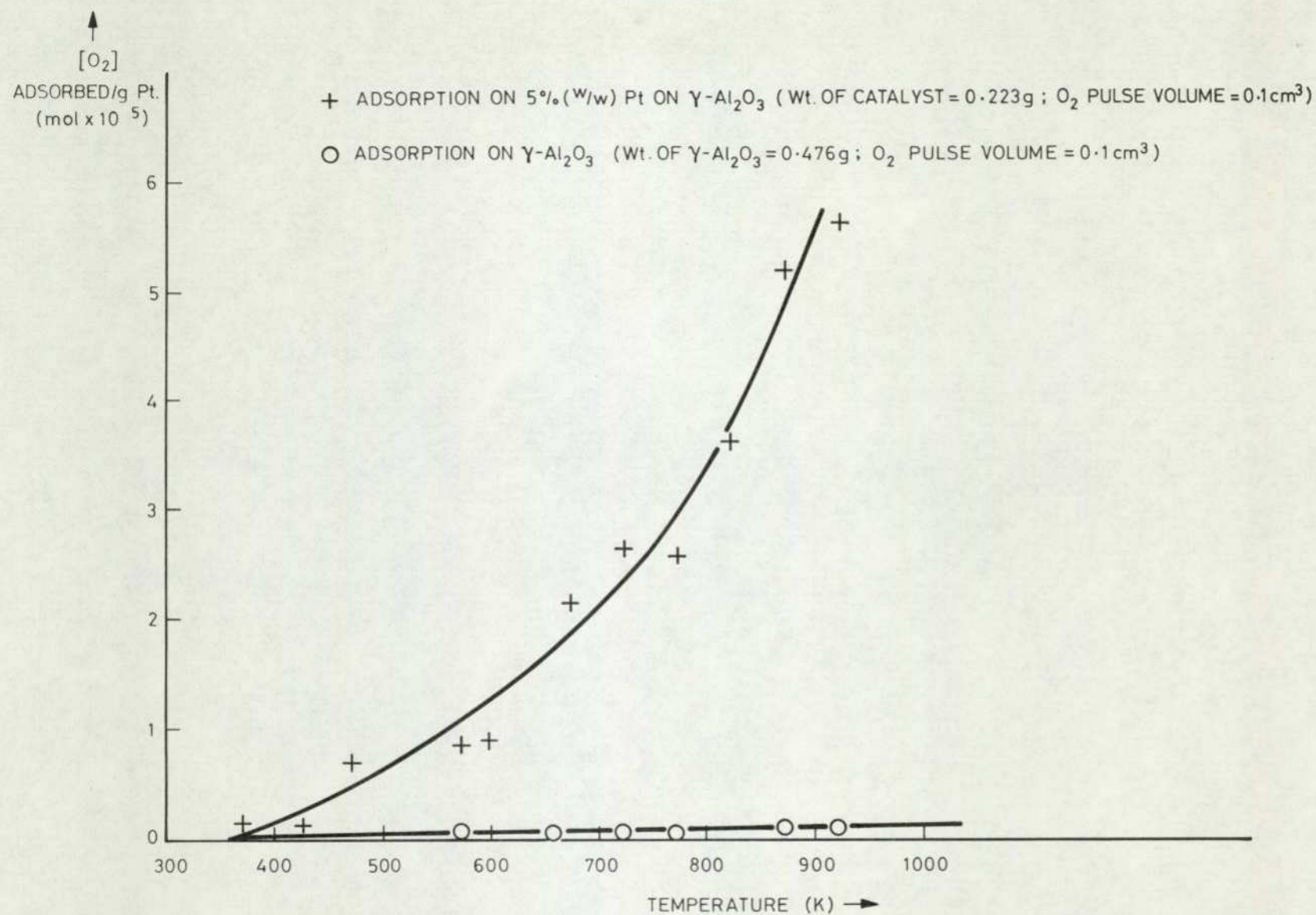


FIG. 3.3 VARIATION WITH TEMPERATURE OF THE UPTAKE OF O_2 ON A 5% (w/w) Pt. ON $\gamma\text{-Al}_2\text{O}_3$ CATALYST.

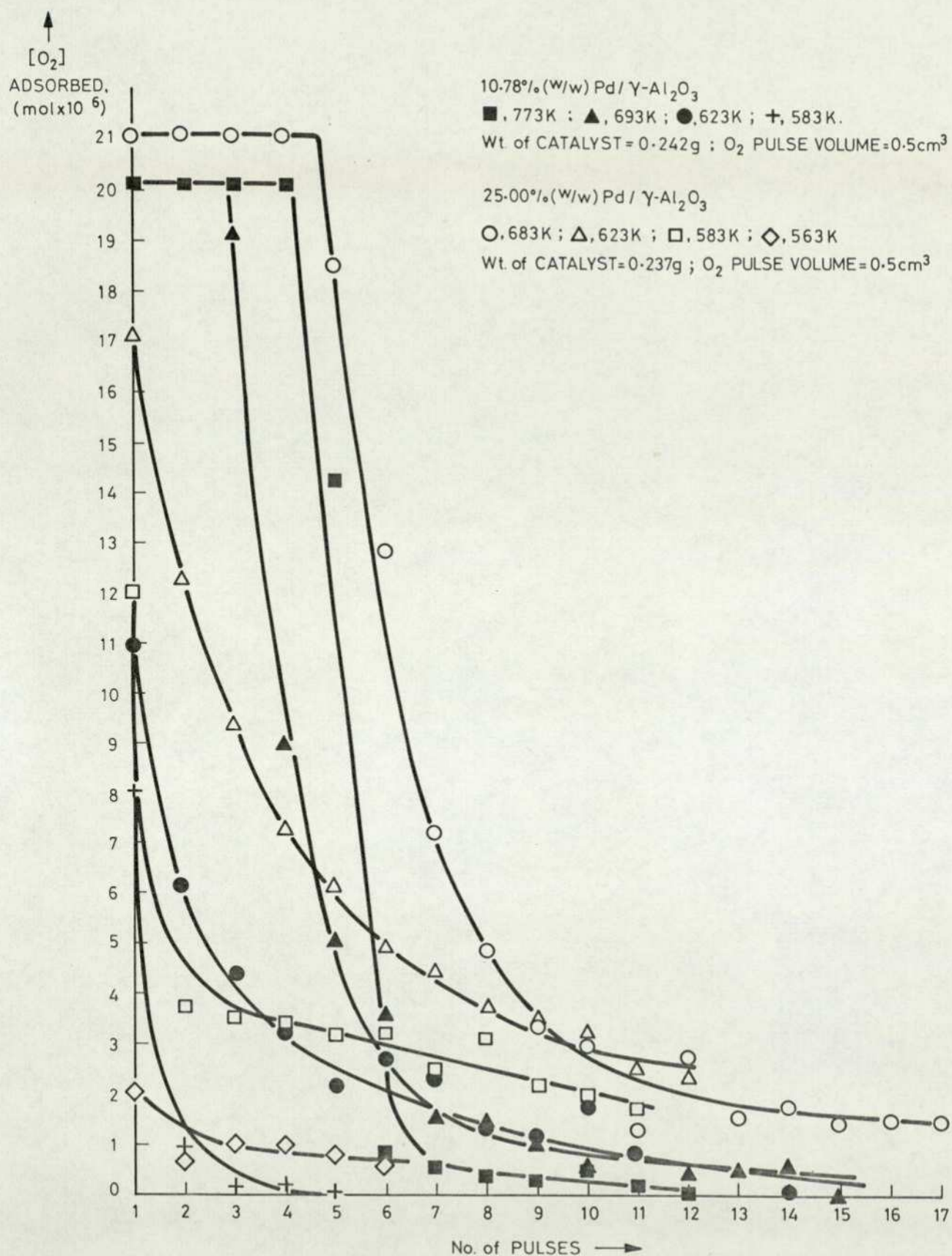


FIG. 3.4 VARIATION WITH PULSE NUMBER OF THE ADSORPTION OF OXYGEN FOR Pd / γ-Al₂O₃ CATALYSTS AT VARIOUS TEMPERATURES.

using transmission electron microscopy in which it was found that when catalysts containing high loadings of palladium were examined, poor dispersion of palladium was observed with a resultant shift in the particle size distribution (see section 3:6). A correlation was obtained between the amount of oxygen adsorbed at these temperatures and the particle size distribution of the palladium.

The oxygen uptake per gram of supported palladium at 873K was four times greater on 10.78% Pd on $\gamma\text{-Al}_2\text{O}_3$ than on 8.7% Pd on TiO_2 and over six times greater than on 5% Pd on ThO_2 .

(iv) The optimum temperature for the adsorption of oxygen on a palladium on γ -aluminium (III) oxide catalyst was 873K. At higher temperatures, the ability to take up oxygen declined markedly so that, at 923K, adsorption was negligible. In the case of palladium supported on both thorium (IV) oxide and titanium (IV) oxide, oxygen adsorption maxima were observed at 923K and 873K respectively. With increasing temperature, however, an equilibrium was set up. The oxide gradually decomposes with time but the rapid decomposition observed for palladium on γ -aluminium (III) oxide is not found.

(v) The rate of oxygen uptake depended both on the temperature and on the metal loading on the support. Thus, with a 10.78% Pd on $\gamma\text{-Al}_2\text{O}_3$ catalyst, adsorption at 773K was more rapid than with 25% Pd on $\gamma\text{-Al}_2\text{O}_3$. It can be seen from Figure 3:4 that the oxygen adsorption curves at fixed temperatures are flatter for the catalyst with a high palladium

loading. Compared with the formation of the surface oxide, oxygen diffusion into the bulk is slow.

(vi) Once supported palladium (II) oxide was formed at 773K, it was stable at that temperature and no loss of oxygen was observed even after 30 minutes in flowing helium. For the period over which the oxygen adsorption was measured at 773K, no decomposition to gas-phase oxygen and palladium metal occurred. At higher temperatures, however, there may be some loss of oxygen into the gas flow although no broadening of the oxygen adsorption peaks was observed below temperatures of 923K in the case of palladium on thorium (IV) oxide and of 887K in the case of palladium on titanium (IV) oxide. Furthermore, it was observed (section 3:2:(ii)) that, after 3 hours at this temperature, the support ($\gamma\text{-Al}_2\text{O}_3$) lost a significant amount of oxygen and when the catalyst/support was left overnight at 773K in flowing helium, further oxygen loss occurred.

Measurement of the uptake of oxygen by supported palladium over a range of temperatures revealed that the adsorption of oxygen obeyed the Arrhenius equation:

$$k_{\text{ads.}} = A \exp\left(-\frac{E_{\text{ads.}}}{RT}\right)$$

where $k_{\text{ads.}}$ is the rate of oxygen adsorption, $E_{\text{ads.}}$ is the energy of activation for adsorption and A, R and T have their usual meanings. From the variation of the rate constant for oxygen adsorption with temperature, activation energies for this process were calculated for a number of catalysts (Table 3:2 and Figures 3:5 and 3:6). These activation energies can be compared with the values of

Catalyst/support.	Activation energy (kJ mol ⁻¹)	
	673-873K	473-673K
8.7% Pd on TiO ₂	61.0	-
2.7% Pd on TiO ₂	43.0	-
5% Pd on ThO ₂	46.6	-
10.78% Pd on γ-Al ₂ O ₃	22.8	45.2
25% Pd on γ-Al ₂ O ₃	53.0	-

Oxygen pulse volume = 0.5 cm³ (N.T.P.).

Catalyst length = 1.5 cm.

Helium flow rate = 25 cm³ min⁻¹.

Table 3:2. Energies of activation observed for the
adsorption of oxygen on supported palladium
catalysts.

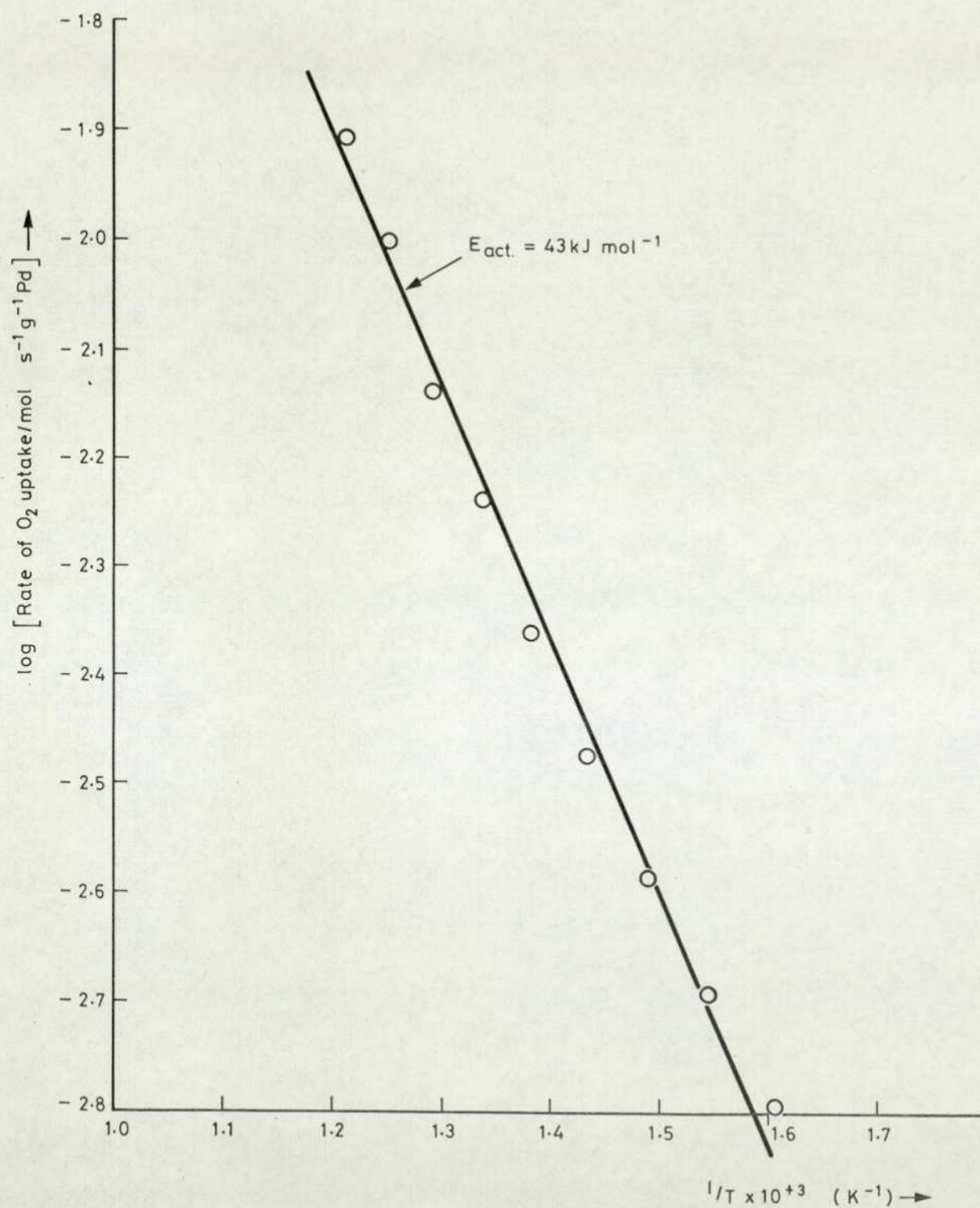


FIG. 3.5 VARIATION OF THE RATE OF OXYGEN UPTAKE WITH RECIPROCAL TEMPERATURE FOR A 2.7% Pd (W/W) ON TiO_2 CATALYST.
(PULSE VOL = 0.5 cm^3 ; $[\text{O}_2]_0 = 10.31 \times 10^{-6} \text{ mol}$; Wt OF CATALYST = 0.268 g)

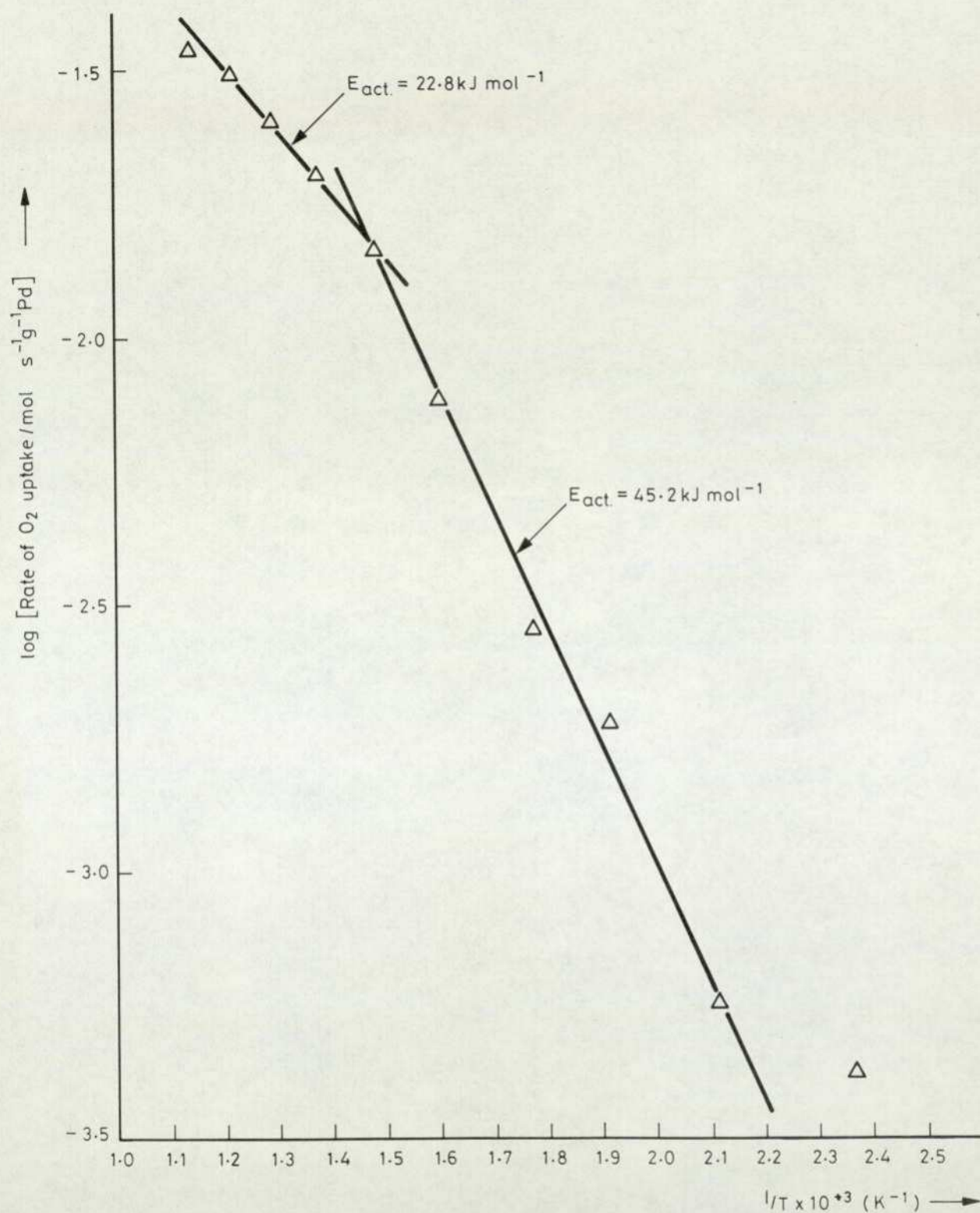


FIG. 3.6 VARIATION OF THE RATE OF OXYGEN UPTAKE WITH RECIPROCAL TEMPERATURE FOR A 10.78% (W/W) Pd ON γ -Al₂O₃
(PULSE VOL = 0.5 cm³; [O₂]₀ / PULSE = 10.31 × 10⁻⁶ mol; Wt of CATALYST = 0.242 g)

84 kJ mol^{-1} (Ertl and Koch, 1972) and 71.4 kJ mol^{-1} (Campbell, Foyt and White, 1977) obtained for the oxidation of bulk palladium metal. This suggests that, the better the distribution of palladium over the support and the smaller the palladium particle size, the lower is the activation energy for the oxidation of that palladium.

The temperature range over which the activation energies were calculated was 673 - 873K. Below 673K, a break in the line occurred for palladium on γ -aluminium (III) oxide and an activation energy of 45.2 kJ mol^{-1} was obtained over the temperature interval 473 - 673K (Figure 3:6).

3:3 Heterogeneous oxidation of methane.

3:3:1 Tests for the presence of intraparticle diffusion.

Intraparticle diffusion may have a significant effect on the catalytic oxidation of methane over a porous catalyst (Thomas and Nobe, 1968). The effects of pore diffusion should, however, diminish with a decrease in particle size. In other words, if pore diffusion effects are significant, decreasing the pellet size should increase the activity per unit mass of catalyst.

The proof that pore diffusion plays no part in methane oxidation over titanium (IV) oxide-supported palladium catalysts was demonstrated for two 2.7% Pd on TiO_2 catalysts of different particle sizes. One contained particles of diameter 150-251 μm , while the other contained particles of diameter 75-150 μm .

The results in Table 3:3 show that the rate constant for methane oxidation was the same over both catalysts. Particle size effects were insignificant. This was true both for oxygen-rich and for methane-rich reactant mixtures over equilibrium catalysts at 683K.

3:3:2 Activity of various precious metal/support combinations towards methane oxidation.

The activity of a number of supported precious metal catalysts has been assessed in terms of the conversion of methane per pulse, expressed as follows:

$$\text{Conversion} = \frac{\text{number of mol of methane converted}}{\text{total number of mol of methane in pulse}} \times 100\%$$

The results are given in Table 3:4 and refer to catalysts operating under equilibrium conditions. Pulses of methane, oxygen and helium ($[\text{CH}_4] : [\text{O}_2] = 2:1$ or $1:2$) with volume 5 cm^3 were passed through the catalyst bed until equilibrium was achieved. The methane conversion was then measured.

The support appears to play a significant role in the activity of the precious metal towards methane oxidation. The order of activity of supported palladium catalysts was found to be:



Increasing the loading of palladium on the support raised the methane conversion for both oxygen-rich and methane-rich reactant mixtures. However, the activity per unit mass of palladium decreased with increased loading.

Catalyst/support.	Particle size. (μm)	Temperature. (K)	Reaction rate for methane oxidation (mol sec^{-1}).
2.7% Pd on TiO_2	251-150	683	1.3×10^{-4} *
2.7% Pd on TiO_2	150-75	683	1.4×10^{-4} *
2.7% Pd on TiO_2	251-150	683	3.1×10^{-4} +
2.7% Pd on TiO_2	150-75	683	3.0×10^{-4} +

* $[\text{CH}_4]_0 = 4.3 \times 10^{-5} \text{ mol}$, $[\text{O}_2]_0 = 1.7 \times 10^{-5} \text{ mol}$.

+ $[\text{CH}_4]_0 = 1.8 \times 10^{-5} \text{ mol}$, $[\text{O}_2]_0 = 4.3 \times 10^{-5} \text{ mol}$.

Catalyst weight = 0.04g.

Catalyst bed length = 1.5 cm.

Pulse volume = 5 cm^3 .

Table 3:3 The effect of particle size on the catalytic activity for methane oxidation over 2.7% Pd on TiO_2 .

Catalyst/support	Methane conversion (%)			
	Methane:oxygen ratio = 2:1 ^(a)		Methane:oxygen ratio = 1:2 ^(b)	
	623K	683K	623K	683K
2.7% Pd on TiO ₂	10	22	14	35
20% Pd on TiO ₂	22	30	57	100
40% Pd on TiO ₂	32	-	68	100
2.7% Pd on γ -Al ₂ O ₃	21	33	34	55
10.8% Pd on γ -Al ₂ O ₃	-	40 [*]	41	85
3% Pd on ThO ₂	13	29	-	-
2.7% Pd on α -Al ₂ O ₃	9	12	-	-
2.7% Pt on TiO ₂	5	18	-	-
2.7% Pt on γ -Al ₂ O ₃	17	28	-	-
10% Pt on γ -Al ₂ O ₃	31	45 [*]	-	-
3% Pt on ThO ₂	8	25	-	-

* all O₂ consumed.

(a) $[\text{CH}_4]_0 = 4.2 \pm 3 \times 10^{-5}$ mol, $[\text{O}_2]_0 = 1.9 \pm 2 \times 10^{-5}$ mol.

(b) $[\text{CH}_4]_0 = 1.8 \pm 2 \times 10^{-5}$ mol, $[\text{O}_2]_0 = 3.6 \pm 2 \times 10^{-6}$ mol.

Pulse volume = 5 cm³.

Catalyst bed length = 1.5 cm.

Table 3:4 The effect of the support and the precious metal loading on methane conversion by some supported catalysts.

When supported on $\gamma\text{-Al}_2\text{O}_3$, platinum catalysts exhibited similar high activity to palladium and methane conversion again increased with metal loading. Slightly higher methane conversions were obtained over supported palladium catalysts when compared with supported platinum catalysts at the same temperatures and precious metal loadings.

3:3:3 Orders of reaction with respect to methane and oxygen.

Studies of the effects of varying the partial pressures of methane and oxygen yielded the respective orders of reaction. In the case of palladium on titanium (IV) oxide catalysts, the reaction order was zero in oxygen and first order in methane at low temperatures and conversions (Tables 3:5 and 3:6). This suggests that the catalyst surface is saturated with adsorbed oxygen and the rate-determining step involves either the adsorption or the activation of methane. At high temperatures and high loadings, titanium (IV) oxide-supported palladium catalysts gave a positive order with respect to oxygen (0.2 to 0.4).

Palladium supported on γ -aluminium (III) oxide and on thorium (IV) oxide gave an order of reaction with respect to oxygen which was close to zero. The order with respect to methane was 0.6 ± 0.1 and 1.0 ± 0.1 for palladium on γ -aluminium (III) oxide and on thorium (IV) oxide respectively. The reaction orders for a platinum catalyst (2.7% Pt on TiO_2) resembled those of the palladium catalyst: i.e. zero order with respect to oxygen and 0.8 ± 0.1 with respect to methane.

Catalyst/support	Temperature (K)	$[O_2] : [CH_4]$	Methane converted (%)	Order w.r.t. oxygen
2.7% Pd on TiO_2^*	583	2:1-10:1	20	0 ± 0.1
2.7% Pd on TiO_2^*	623	2:1-10:1	50	0 ± 0.1
2.7% Pd on TiO_2^+	683	2:1-4:1	12	0 ± 0.1
2.7% Pd on TiO_2^+	773	2:1-4:1	56	0 ± 0.1
2.7% Pd on $\gamma-Al_2O_3^+$	598			0.2 ± 0.1
2.7% Pd on $\gamma-Al_2O_3^+$	640	1:2-8:1	15	0.1 ± 0.1
10.8% Pd on $\gamma-Al_2O_3^+$	623	2:1-5:1	25	0.1 ± 0.1
13.1% Pd on $\gamma-Al_2O_3^+$	683	1:4-6:1	50	0.2 ± 0.1
25% Pd on $\gamma-Al_2O_3^+$	623	2:1-8:1	20	0.1 ± 0.1
3% Pd on ThO_2	623	1:5-6:1	10	0.2 ± 0.1
2.7% Pt on TiO_2^+	585	1:1-5:1	10	0 ± 0.1
8.5% Pd on TiO_2^+	723	1:5-2:1	50-90	0.4 ± 0.1
40% Pd on TiO_2^*	623	2:1-4:1	60-80	0.2 ± 0.1
40% Pt on TiO_2^+	660	2:1-8:1	15	0 ± 0.1

Catalyst length = 1.5 cm.

* Catalyst weight = 0.33 g.

+ Catalyst weight = 0.04 g.

Pulse volume = 5 cm^3 .

Catalyst bed length = 1.5 cm.

Table 3:5 The orders of reaction with respect to oxygen for methane oxidation over some supported palladium and platinum catalysts.

Catalyst/support.	Temperature (K)	$[O_2]:[CH_4]$	Methane converted (%)	Order w.r.t. methane
2.7% Pd on TiO_2	710	2:1-8:1	10-30	1.1 ± 0.1
2.7% Pd on TiO_2	773	3:1-4:1	40-80	1.0 ± 0.1
2.7% Pd on $\gamma-Al_2O_3$	635	2:1-12:1	10-20	$0.6^*, 0.6^+ \pm 0.1$
2.7% Pd on ThO_2	623	1:5-6:1	10-20	1.0 ± 0.1
2.7% Pt on TiO_2	585	1:1-5:1	10	$0.8^*, 0.9^+ \pm 0.1$

* Order calculated on the amount of carbon dioxide produced.

+ Order calculated on the amount of methane consumed.

Catalyst bed length = 1.5 cm.

Pulse volume = 5 cm^3 .

Table 3:6 The orders of reaction with respect to methane for methane oxidation over some supported palladium and platinum catalysts.

Determination of the order of reaction with respect to methane by measurement of the carbon dioxide produced obviously provided information only on methane oxidation. Calculations involving the amount of methane consumed included methane loss by pyrolysis. The orders calculated in terms of methane consumption for 2.7% Pt on TiO_2 and 2.7% Pd on $\gamma\text{-Al}_2\text{O}_3$ catalysts did not vary significantly from the orders calculated from the amount of carbon dioxide produced.

A constant pulse size for each methane/oxygen mixture was achieved by variation of the amount of helium in the sample. The results used for measurement of the orders of reaction were those obtained over a catalyst in equilibrium with the reactant mixture. To achieve equilibrium, successive pulses of the reactant mixture were passed over the catalyst until a constant conversion level was obtained.

3:3:4 Variation of the rate of methane oxidation with temperature.

The activation energies for methane oxidation were determined over a number of supported precious metal catalysts. Measurements were made for catalysts operating under equilibrium conditions using the same reactant concentration over the temperatures concerned. The production of oxides of carbon (both carbon dioxide and carbon monoxide were produced at high temperatures, especially over platinum and rhodium catalysts) was taken as a measure of the reaction rate. A correction for the variation in contact time with temperature was applied using the formula:

$$\text{Contact time, } t_c = \frac{\text{catalyst volume}}{\text{carrier gas flow rate}} \times \frac{T}{T_o}$$

where T = catalyst temperature (K)

T_o = ambient temperature (K)

Some first-order Arrhenius plots are shown in Figures 3:7 and 3:8, while values of the activation energies are given in Table 3:7. These plots show a linear relationship between $\log$ (reaction rate) and reciprocal temperature. There is, however, a discontinuity which appears at higher temperatures in many of the plots. The temperature at which this behaviour occurs depends on the catalyst, the support and the composition of the reactant gas mixture.

Platinum catalysts, and to a lesser extent rhodium catalysts, underwent a sudden rise in activity at this transition point. For a 3% Pt on ThO_2 catalyst methane conversion doubled between furnace temperatures of 644 and 645K, all oxygen being consumed at the higher temperature. The methane conversion increased by a factor of eight between 610 and 633K during methane oxidation over 2.7% Pt on $\gamma\text{-Al}_2\text{O}_3$. Carbon monoxide appeared as a reaction product above 623K while the quantity of carbon dioxide produced increased only by 10% at temperatures as high as 773K.

Palladium catalysts underwent a more gradual transition. All the oxygen in the reactant mixture was consumed at temperatures well below those at the break in the Arrhenius plot. Carbon dioxide production increased with temperature up to, and above, the transition point and carbon monoxide began to appear as a reaction product at the transition point.

Catalyst/support	$[O_2] : [CH_4]$	Activation energy		Transition temperature (K)
		A (kJ mol ⁻¹)	B (kJ mol ⁻¹)	
2.7% Pd on TiO ₂	1:2.5	83±5	35±5	720
2.7% Pd on γ-Al ₂ O ₃	1:1.5	84±5	23, 24±5	680
2.7% Pd on γ-Al ₂ O ₃	1:2.5	89±5	45±5	717
2.7% Pd on SiO ₂ / Al ₂ O ₃	1:2.5	92±5	45±5	683
2.7% Pd on ThO ₂	1:2.5	85±5	34±5	654
2.7% Pt on TiO ₂	1:2.5	116±5	19±5	610
2.7% Pt on γ-Al ₂ O ₃	1:2.5	114±5	24±5	630
3.1% Pt on ThO ₂	1:2.5	108±5	22±5	644
2.7% Rh on TiO ₂	1:2.5	94±5	25±5	723
1% Rh on γ-Al ₂ O ₃	1:2	100±5	27±5	721
2.7% Pt-Rh(95-5) on TiO ₂	1:2.5	124±5	25±5	685
2.7% Pt-Rh(93-7) on γ-Al ₂ O ₃	1:2.5	82±5	27±5	721
2.7% Pd on ThO ₂	2:1	95±5	24±5	707
10.8% Pd on γ-Al ₂ O ₃	2:1	84±5	-	-
20% Pd on SnO ₂	2:1	75±5	-	-

$[CH_4]_o = 4.2 \pm 0.4 \times 10^{-6}$ mol, $[O_2]_o = 1.9 \pm 0.2 \times 10^{-6}$ mol.

$[CH_4]_o = 1.8 \pm 0.1 \times 10^{-6}$ mol, $[O_2]_o = 3.6 \pm 0.1 \times 10^{-6}$ mol.

Catalyst length = 1.5 cm. Pulse volume = 5 cm³.

Table 3:7 Activation energies for the oxidation of methane over various supported catalysts.

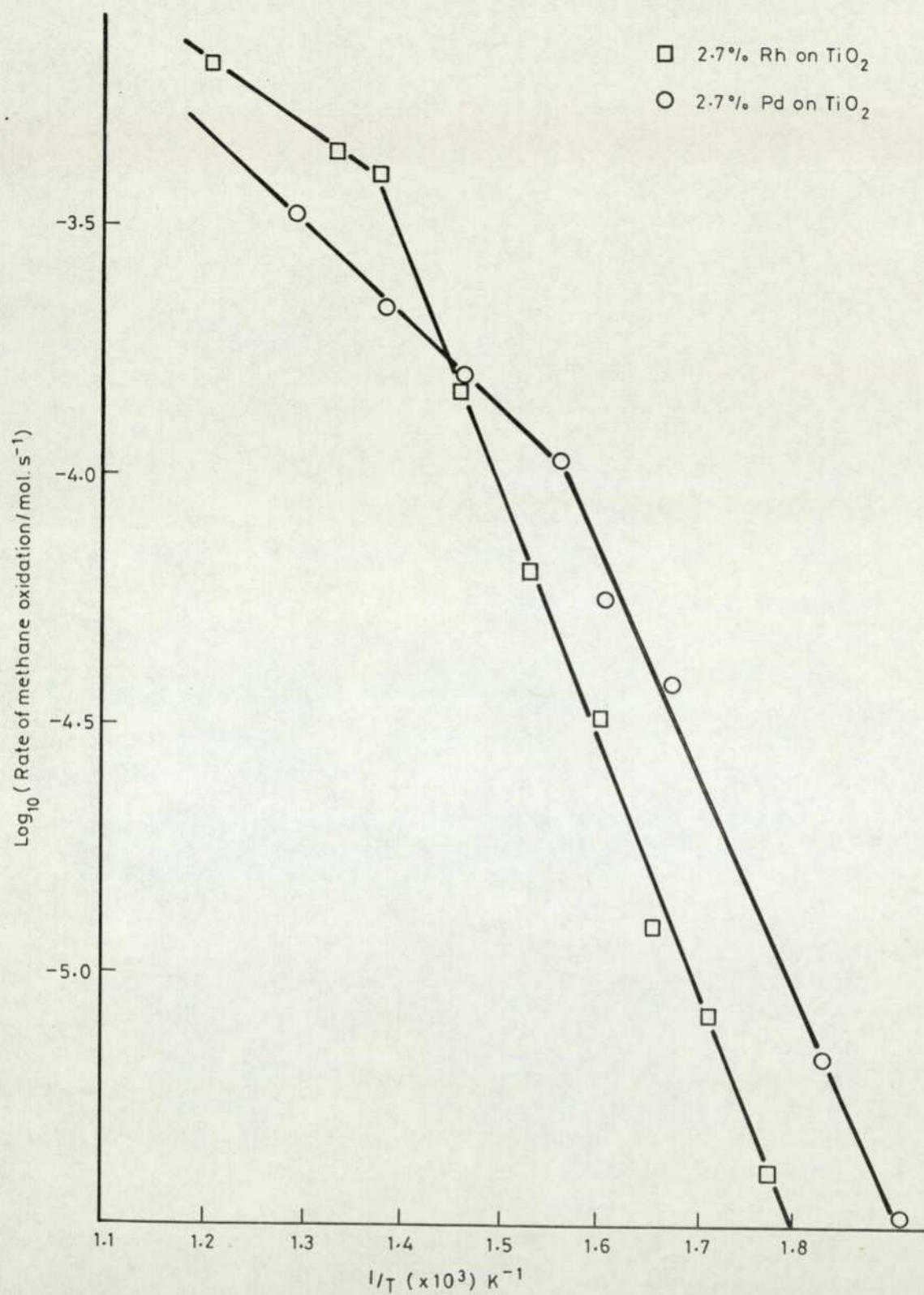


FIG. 3.7 ARRHENIUS PLOTS FOR THE OXIDATION OF METHANE OVER TITANIUM(IV) OXIDE - SUPPORTED CATALYSTS.

$[\text{CH}_4]_0 = 4.2 \times 10^{-5} \text{ mol}$, $[\text{O}_2]_0 = 1.9 \times 10^{-5} \text{ mol}$, Pulse volume = 5 cm^3

Catalyst length = 1.5 cm

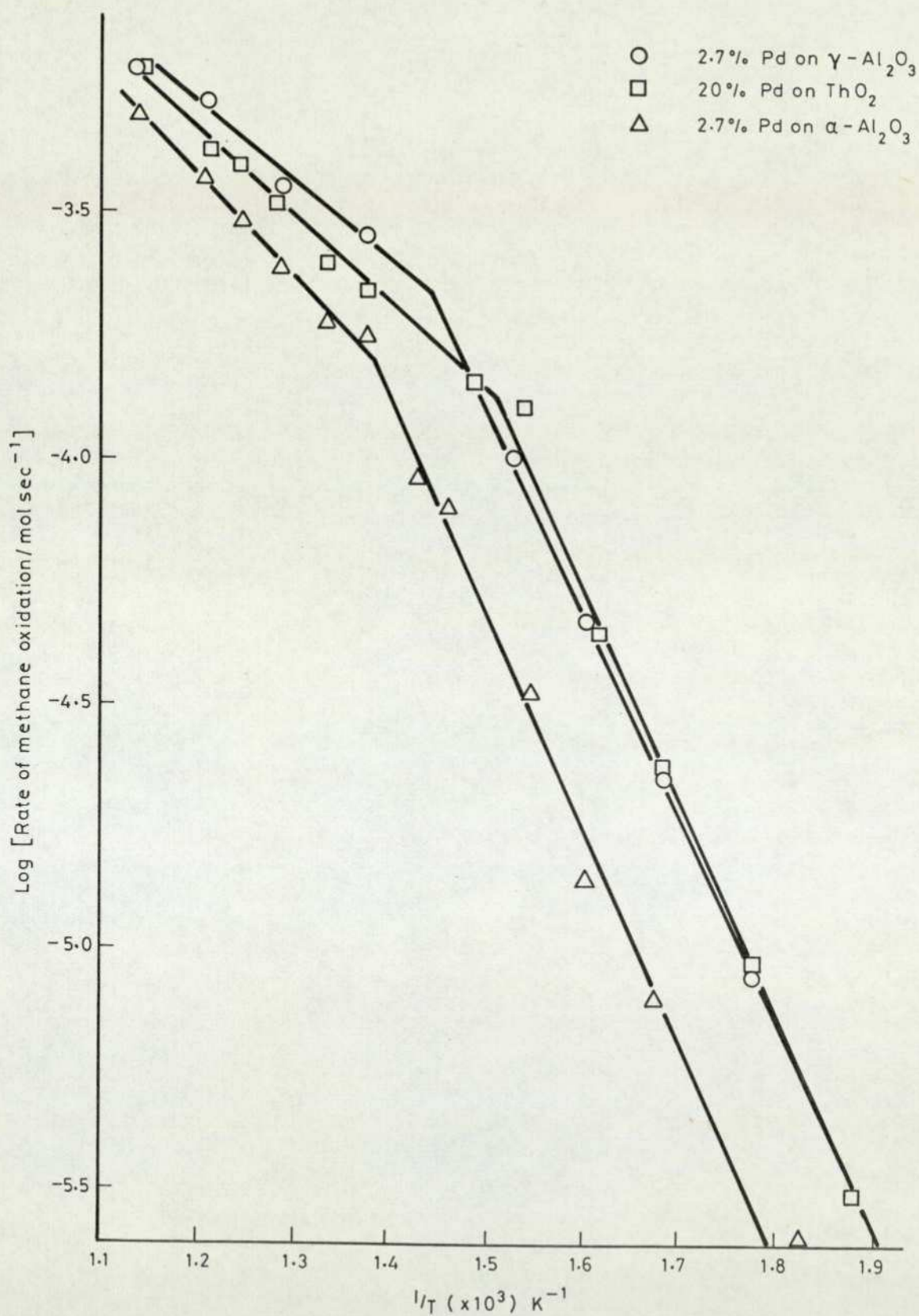


FIG. 3.8 ARRHENIUS PLOTS FOR THE OXIDATION OF METHANE OVER SOME SUPPORTED CATALYSTS

$[\text{CH}_4]_0 = 4.2 \times 10^{-5} \text{ mol.}$, $[\text{O}_2]_0 = 1.9 \times 10^{-5} \text{ mol.}$, Pulse volume = 5 cm^3

Catalyst bed length = 1.5 cm

The sharp transition with the rapid rise in methane conversion observed for platinum catalysts did not occur with supported palladium catalysts.

Values of the activation energies for methane oxidation over a number of supported catalysts are shown in Table 3:7. The activation energies obtained for platinum catalysts ($108-116 \text{ kJ mol}^{-1}$) were higher than those found for palladium catalysts ($75-95 \text{ kJ mol}^{-1}$). After the transition point the opposite was observed, with platinum catalysts tending towards low activation energies for methane oxidation ($19-24 \text{ kJ mol}^{-1}$). Rhodium catalysts were intermediate between those based on platinum and palladium with activation energies of $94-100 \text{ kJ mol}^{-1}$ before, and $25-27 \text{ kJ mol}^{-1}$ after, the transition point. The results for palladium are in excellent agreement with activation energies obtained by Anderson, Stein, Feenan and Hofer (1961) ($E_A = 88-92 \text{ kJ mol}^{-1}$ for Pd on $\gamma\text{-Al}_2\text{O}_3$), and Cullis, Keene and Trimm (1971) ($E_A = 80-90 \text{ kJ mol}^{-1}$ for palladium sponge).

Increasing the loading of a palladium on γ -aluminium (III) oxide catalyst from 2.7% (w/w) Pd to 10.8% (w/w) Pd had little effect on the activation energy. Changing the methane: oxygen ratio from 1:2 to 2:1 for a 2.7% Pd on ThO_2 catalyst raised the transition point temperature but the activation energy before the transition point remained substantially the same.

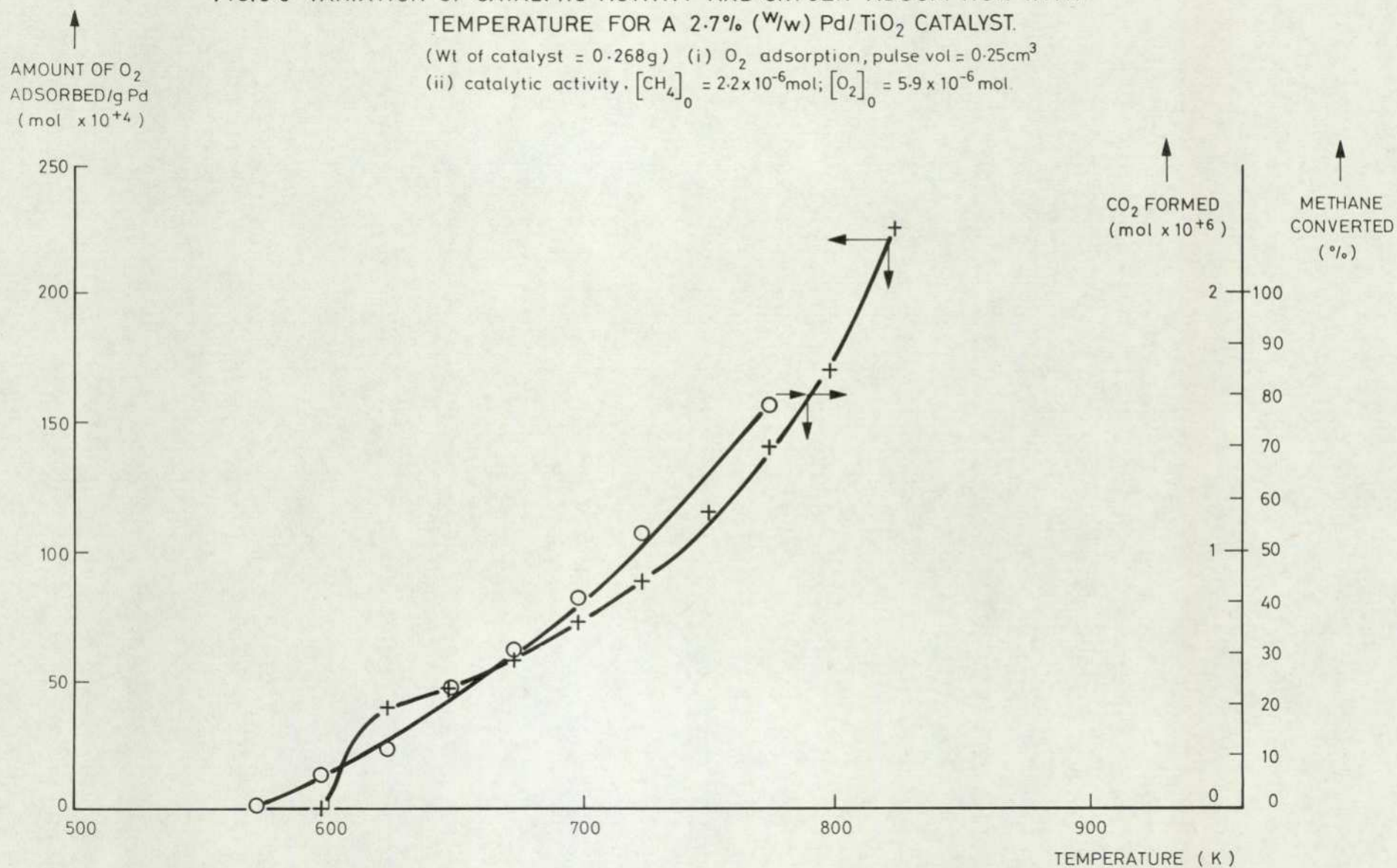
3:3:5 Effect of oxygen adsorption on the rate of reaction.

In order to determine whether or not the ability to adsorb oxygen was related to the catalytic activity of the precious metal, the variation of the oxygen uptake with temperature was compared with the extent of methane oxidation over the same temperature range. The amount of carbon dioxide produced was taken as a measure of the catalytic activity. The ability of the supported palladium catalyst to adsorb oxygen closely reflected the ability of that catalyst to oxidise methane (Figure 3:9). Very little methane conversion occurred at temperatures at which palladium (II) oxide was expected to be present in small quantities but increased with oxygen adsorption.

The importance of adsorbed oxygen on the reaction was also confirmed by a study of methane oxidation using catalysts that had been pre-reduced at 550K with pulses of hydrogen (volume = 1 cm^3) before exposure to methane/oxygen reactant mixtures at temperatures increasing from 573K by steps of 20K. Two catalysts were examined (5% Pd on ThO_2 and 2.7% Pd on TiO_2); both of these showed a low activity with the initial reactant pulse, when compared with subsequent pulses, until a certain temperature was reached (648K in the case of the TiO_2 -supported catalyst and 633K for Pd on ThO_2). Above these temperatures, identical activity was observed for all pulses. Below this temperature, the first reactant pulse was not in equilibrium with the surface during methane oxidation. Presumably there is competition for oxygen between palladium to form the oxide and methane

FIG.3.9 VARIATION OF CATALYTIC ACTIVITY AND OXYGEN ADSORPTION WITH TEMPERATURE FOR A 2.7% (W/W) Pd/TiO₂ CATALYST.

(Wt of catalyst = 0.268g) (i) O₂ adsorption, pulse vol = 0.25cm³
(ii) catalytic activity, [CH₄]₀ = 2.2 × 10⁻⁶mol; [O₂]₀ = 5.9 × 10⁻⁶mol.



to undergo oxidation. Raising the temperature favours palladium oxidation at the expense of methane oxidation.

Pre-oxidation of the catalyst before exposure to pulses of methane and oxygen had little effect on methane conversion for all pulses at temperatures between 650 and 700K. From 725-775K the first reactant pulse through the catalyst gave a lower methane conversion than subsequent pulses. Thus, an oxygen-rich surface at these temperatures inhibited methane oxidation for the first pulse. Equilibrium was achieved only on passage of the second pulse through the catalyst.

3:3:6 Influence of methods of catalyst preparation on catalytic activity.

The effects of catalyst pre-treatment and the nature of the metal precursor on the heterogeneous oxidation of methane have been investigated for a number of supported palladium catalysts. The use of palladium (II) nitrate rather than palladium (II) chloride as the precious metal salt from which the catalyst was prepared had little influence on the subsequent activity. Such behaviour was not observed, however, for catalysts prepared from palladium (II) oxide. Mechanical mixing of the titanium (IV) oxide support with palladium (II) oxide produced a catalyst whose activity for methane oxidation was significantly lower than that of catalysts which were obtained by the thermal decomposition of palladium (II) chloride or palladium (II) nitrate dispersed on the same support.

The effect of catalyst pre-treatment on catalytic

activity is shown in Figure 3:10. A series of 2.7% Pd on $\gamma\text{-Al}_2\text{O}_3$ catalysts was pre-treated in a range of atmospheres (helium, oxygen or hydrogen + helium) at 673K. Exposure to pulses of methane/oxygen ($[\text{CH}_4]_0 = 4.5 \times 10^{-5}$ mol, $[\text{O}_2]_0 = 1.8 \times 10^{-5}$ mol) at 683K showed that equilibration of the catalyst had not occurred completely at 673K. Subsequent exposure to pulses of methane and oxygen was necessary to activate the catalyst fully. In the case of the 2.7% Pd on $\gamma\text{-Al}_2\text{O}_3$ catalyst pre-treated in oxygen, the low activity was maintained despite efforts to improve the activity using pulses of methane and oxygen at 683K.

3:3:7 Formation of partial oxidation products.

Carbon dioxide and water were the only reaction products observed in appreciable quantities during the heterogeneous oxidation of methane over palladium catalysts at temperatures below 650K. The chromotropic acid test indicated that formaldehyde was present only in very small quantities. After exposure to the products of reaction, a chromotropic acid/sulphuric acid mixture gave a very faint pink colour on warming to 335K for 15 minutes. Other partial oxidation products, such as methanol, were not detected using chromatographic analysis.

Carbon monoxide was rarely found during methane oxidation at temperatures below 650K but its production depended on the methane:oxygen ratio of the reactant mixture. Methane-rich mixtures produced carbon monoxide at temperatures which were low when compared with those needed for oxygen-rich mixtures. For example, over a 3% Pd on ThO_2 catalyst, carbon

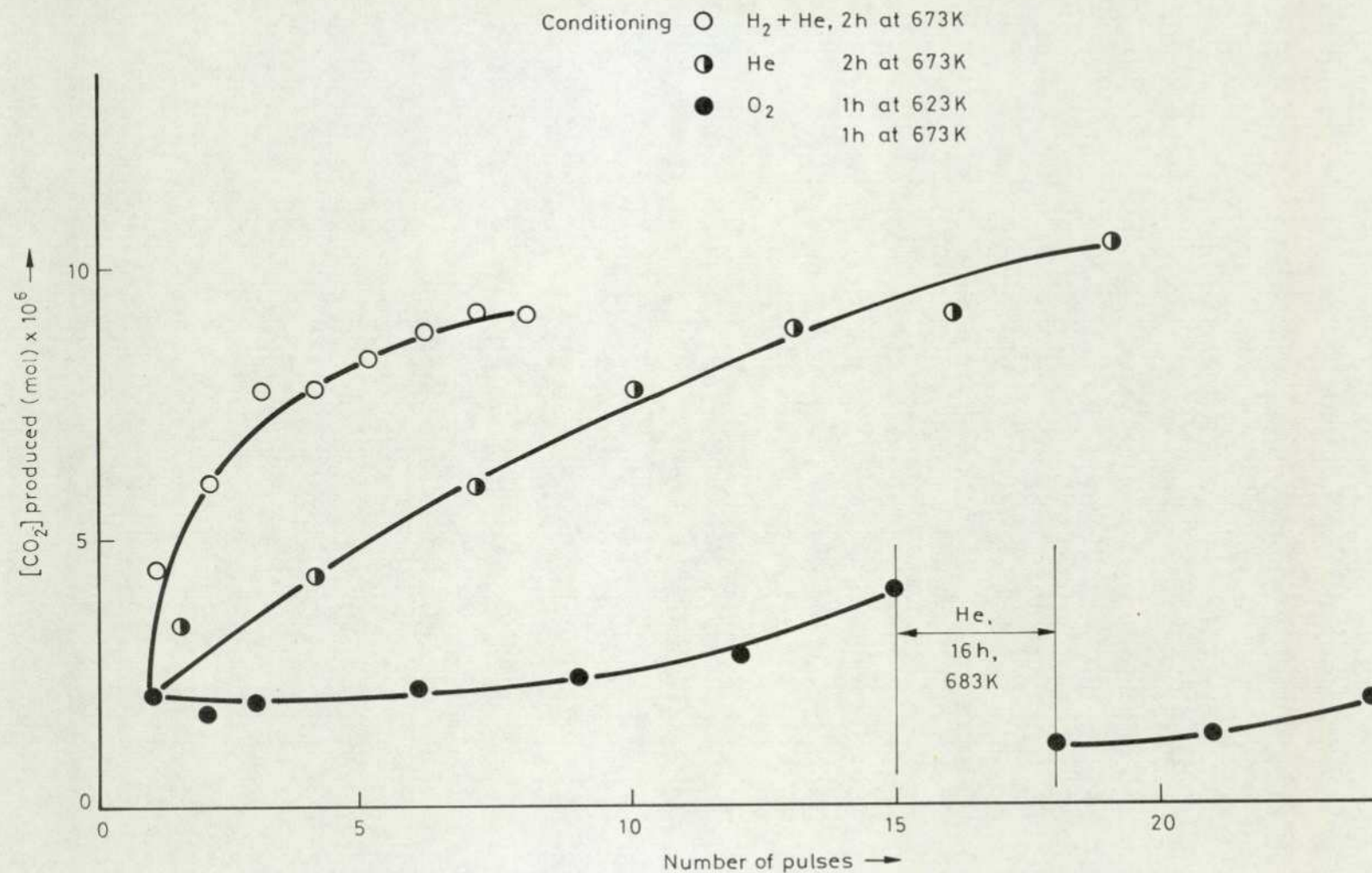


FIG. 3.10 EFFECT OF CATALYST PRE-TREATMENT ON THE PRODUCTION OF CARBON DIOXIDE AT 683K DURING METHANE OXIDATION OVER 2.7% Pd γ - Al_2O_3

$[\text{CH}_4]_0 = 4.2 \times 10^{-5} \text{ mol.}$, $[\text{O}_2]_0 = 1.9 \times 10^{-5} \text{ mol.}$, Pulse volume = 5 cm^3 , Catalyst weight = 0.04g

monoxide (0.9×10^{-6} mol) was produced at 683K only on consumption of at least 95% of the oxygen in the reactant mixture ($[\text{CH}_4]_0 = 4.2 \times 10^{-5}$ mol, $[\text{O}_2]_0 = 1.9 \times 10^{-5}$ mol) (Table 3:8). Similar results were obtained for 3% Pt on ThO_2 .

The pyrolysis of methane on palladium and platinum catalysts yielded both hydrogen and ethane as well as carbonaceous deposits on the catalyst surface (see section 3:4). The use of helium as a carrier gas prevented quantitative analysis of the low concentrations of hydrogen formed due to the similarity in thermal conductivity of hydrogen and helium and the subsequent low sensitivity of the katharometer detector to hydrogen.

Some indication that carbon was deposited even in the presence of oxygen was obtained from the carbon balances measured before and after reaction. For a 2.7% Pd on TiO_2 catalyst, the amount of methane consumed lay within $\pm 6\%$ of the oxides of carbon formed when the methane:oxygen ratio of the reactant mixture was less than 0.5. Above this ratio (i.e. methane:oxygen ratio > 0.5) the quantity of methane consumed far exceeded that of oxides of carbon produced.

Attempts to balance the oxygen consumed with the production of carbon dioxide and water were complicated by concurrent oxidation of the palladium. A reservoir of oxygen in the form of palladium (II) oxide compensated for the lack of oxygen in the reactant mixture under methane-rich conditions. The opposite is true with oxygen-rich mixtures

(a) 3% Pd on ThO₂

$[O_2]_o$ (mol x 10 ⁵)	$[CH_4]_o$ (mol x 10 ⁵)	Temperature (K)	[CO] produced (mol x 10 ⁶)
1.9	4.2	773	7
1.9	4.2	683	0.9
1.9	4.2	623	0
5.5	6.6	773	5.6
5.4	4.2	773	3.8
5.4	2.9	773	1.1
5.4	2.2	773	0
5.4	1.2	773	0

(b) 3% Pt on ThO₂

1.7	4.1	773	4.6
1.7	4.1	683	0.4
1.7	4.1	623	0
9.9	4.1	773	0

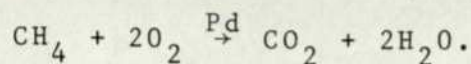
Catalyst weight = 0.20 g.

Pulse volume = 5 cm³.

Catalyst bed length = 1.5 cm.

Table 3:8 The effect of the methane:oxygen ratio on carbon monoxide production over supported palladium and platinum catalysts.

where oxygen oxidises the palladium as well as the methane. Only at the stoichiometric point (methane:oxygen ratio = 0.5) does the oxygen loss balance the oxides of carbon produced and the methane loss according to the equation:



3:4 Pyrolysis of methane on supported palladium and platinum catalysts.

The interaction of methane with supported palladium was investigated over the temperature range in which the catalytic oxidation of methane is normally studied. This reaction is of particular interest as deposition of carbon may occur with subsequent loss of catalytic activity (Cullis, Keene and Trimm, 1971). This is an important consideration when methane-rich mixtures are used.

Some difficulty was experienced in obtaining a clean catalyst which was free from oxygen. In order to prepare a clean metallic surface, the catalyst was first exposed to oxygen at 723K and then reduced at this temperature by exposure to ten pulses of hydrogen (20 cm^3). Finally, helium ($25 \text{ cm}^3 \text{ min}^{-1}$) was passed through the catalyst at 723K for 15 min to remove any hydrogen trapped in the palladium. No evidence of the formation of oxides of carbon was observed when methane was passed over the catalyst at high temperatures. This indicated the effectiveness of the cleaning process. Surface cleaning was then repeated before methane pyrolysis was investigated.

The breakdown of methane on a clean 5% Pd on ThO₂ catalyst occurred at temperatures above 540K (Figures 3:11 and 3:12). At 873K almost 50% of the methane introduced was pyrolysed on the catalyst surface. Hydrogen was detected at temperatures as low as 600K. It must be pointed out, however, that at temperatures typical of those at which methane oxidation was studied (<730K), only 5% or less of the methane underwent conversion.

Two methods were utilized for the recovery of the carbonaceous residue left by the pyrolysed methane. Either oxygen was passed over the catalyst at 723K and the carbon dioxide produced was measured by gas chromatography, or hydrogen was passed over the catalyst at 723K and the methane produced was measured. The former method had two disadvantages. Firstly, some of the oxygen that was passed through the catalyst to oxidise the methane concurrently oxidised the palladium; thus no check on the oxygen consumed in oxidising the carbonaceous residue could be made. Secondly, when using oxygen, the amount of carbon dioxide recovered was not as great on a molar basis as the amount of methane recovered by hydrogen treatment. Thus, hydrogen pulses (1.0 cm³) were passed through the catalyst at 723K until no more methane was formed. Passage of oxygen through the catalyst after hydrogen produced no carbon dioxide; all accessible carbon had evidently already been removed.

The amount of carbon present on the catalyst was estimated by determining the amount of methane formed after

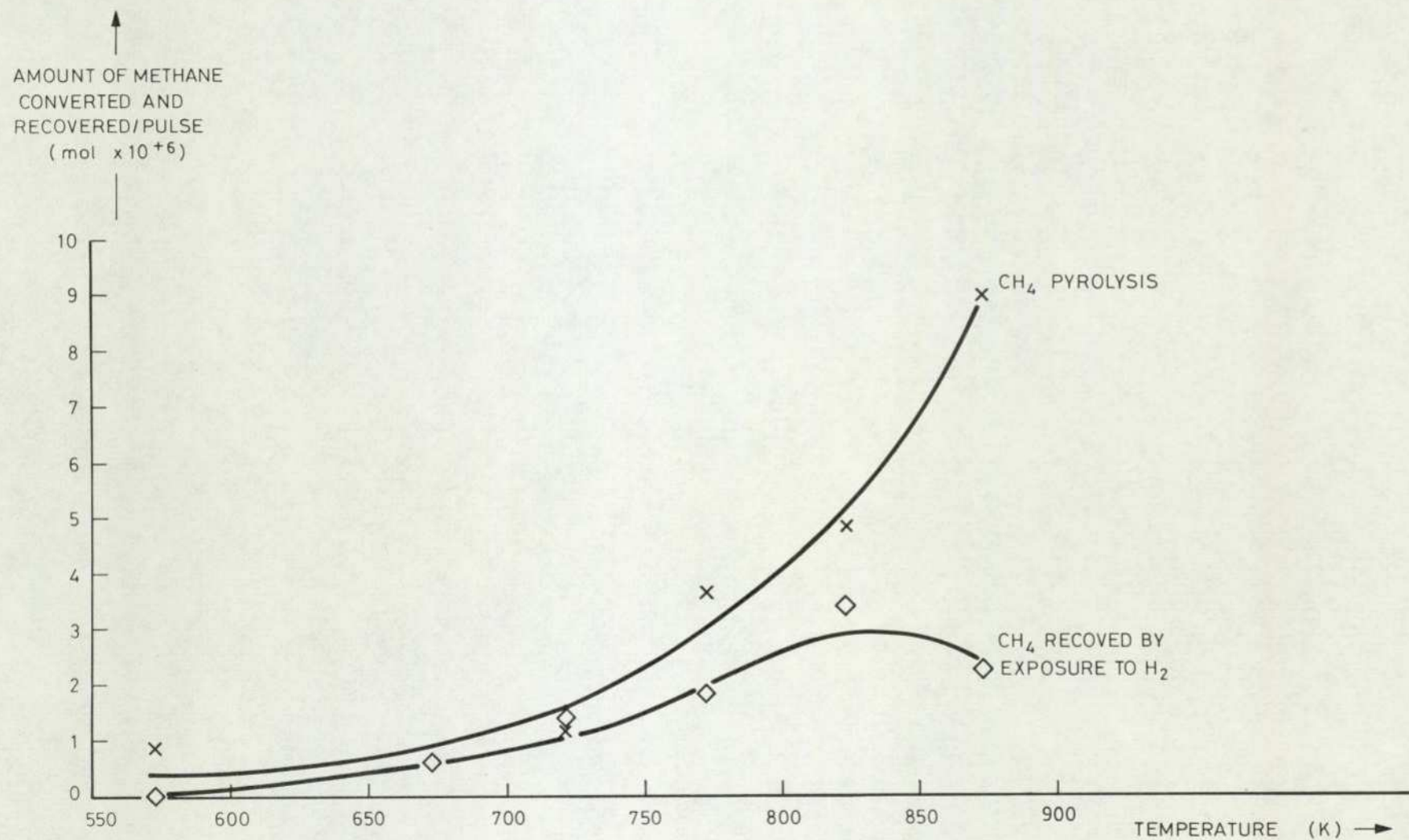


FIG. 3.11 METHANE PYROLYSIS AND RECOVERY ON 5% (w/w) Pd / ThO₂, VARIATION WITH TEMPERATURE
(Wt OF CATALYST = 0.810 g ; CH₄ PULSE VOL = 0.5 cm³ ; H₂ PULSE VOL = 1 cm³)

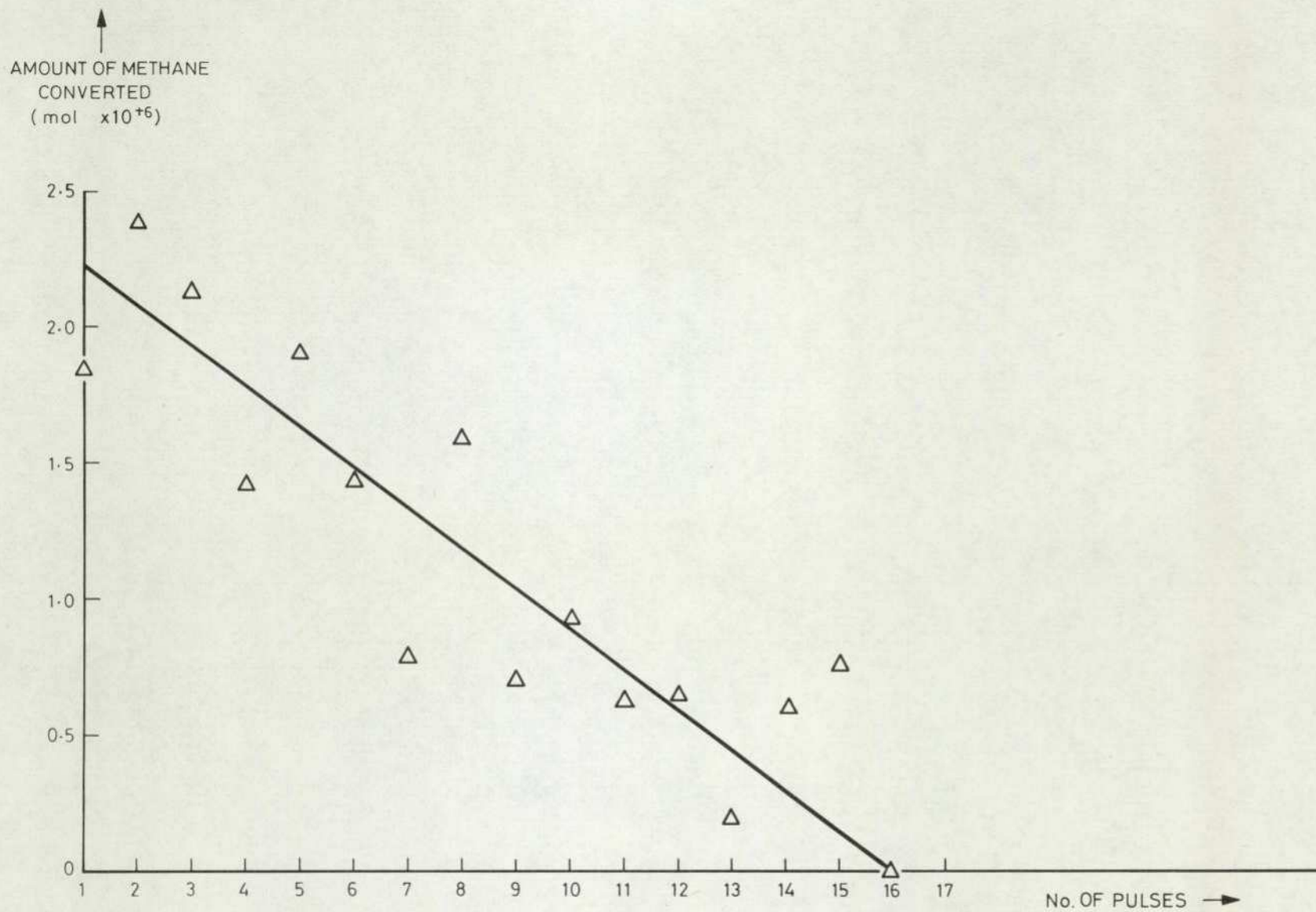
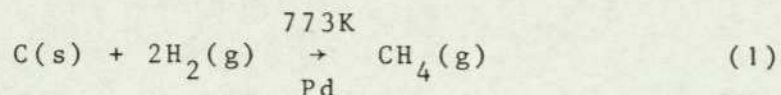


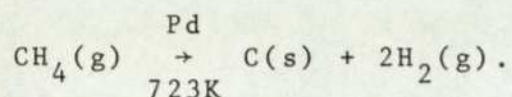
FIG. 3.12 METHANE PYROLYSIS ON 5% (W/W) Pd ON ThO₂ VARIATION OF AMOUNT OF METHANE CONVERTED WITH NUMBER OF REACTANT PULSES.
(Wt OF CATALYST = 0.810g; PULSE VOL = 0.5cm³)

exposure to hydrogen, assuming the following relationship:



Carbonaceous products formed after hydrocarbon pyrolysis in the presence of platinum group metals often contain hydrogen (Paal, Fryer and Thomson, 1973).

Equation (1) was assumed to be obeyed, however, since the amount of hydrogen produced during pyrolysis experiments was almost twice the methane lost corresponding to the equation:



It would appear, therefore, that the pyrolysis of methane over palladium catalysts produced almost exclusively elemental carbon. Recovery of this carbon by reduction with hydrogen and measurement of the methane evolved showed that only about half of this carbon was recoverable as methane. Thus, a coating of carbon was built up under reducing conditions.

A supported platinum catalyst (2.7% Pt on TiO_2) produced ethane as well as hydrogen at temperatures of 557-943K in the presence of methane (Figure 3:13). A peak in ethane formation occurred at 735K giving a yield at this temperature of only 0.002%. The methane was pyrolysed more rapidly over the supported platinum catalyst than over the titanium (IV) oxide itself, (see section 3:7:1). Only 0.5% conversion of a 0.5 cm^3 ($2.4 \times 10^{-5} \text{ mol}$) pulse of methane took place at 730K over the 2.7% Pt on TiO_2 catalyst. Some carbonisation

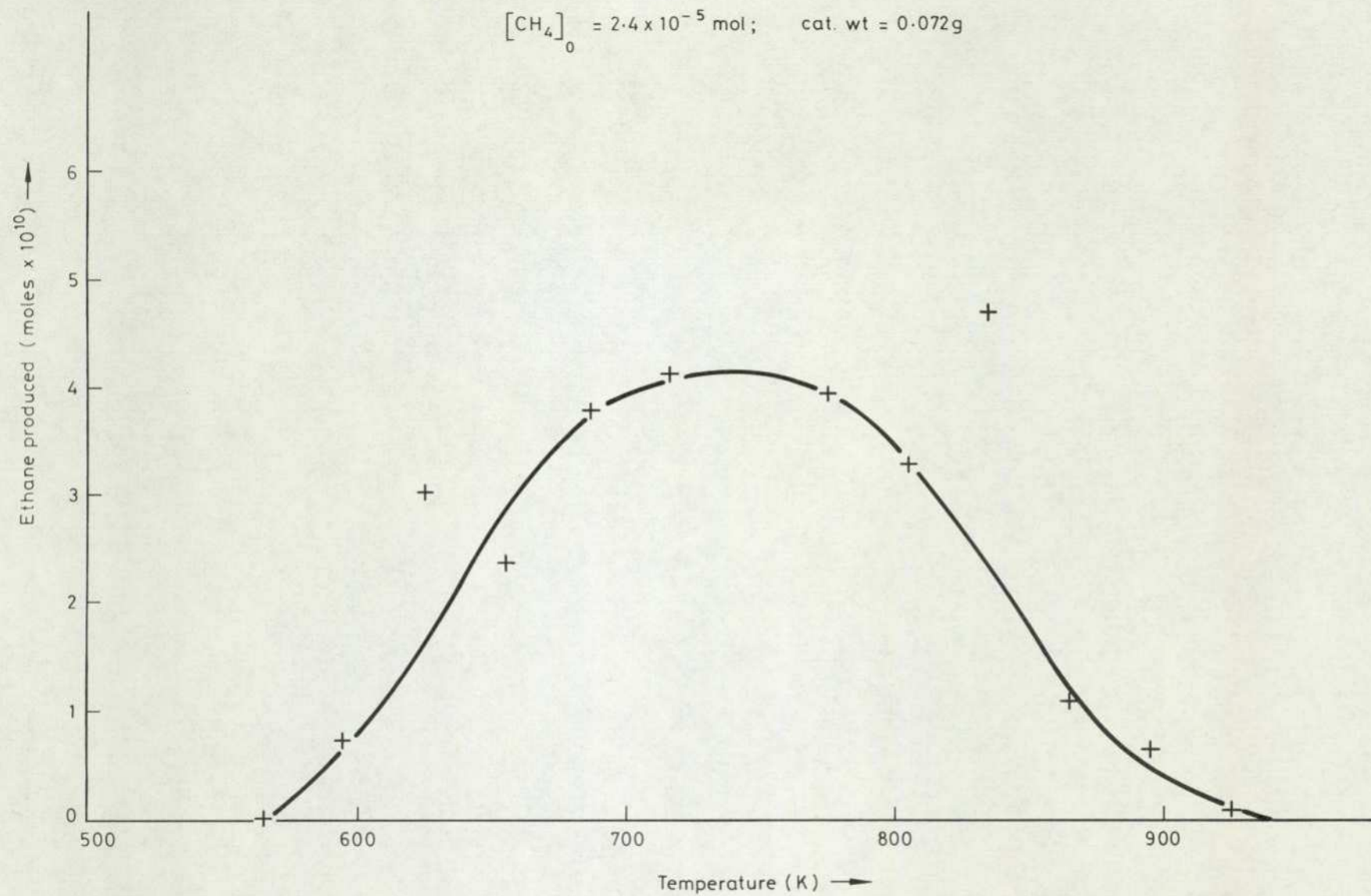


FIG. 3.13 PRODUCTION OF ETHANE FROM PYROLYSIS OF METHANE OVER 2.7% Pt/TiO₂

occurred on the catalyst surface and part of this carbon was recoverable as methane by injection of pulses of hydrogen through the catalyst.

3:5 Oxidation of methane in the absence of gaseous oxygen by palladium (II) and platinum (IV) oxides.

The oxidation of methane in the absence of gaseous oxygen was investigated over platinum (IV) and palladium (II) oxides, both supported and unsupported. The catalysts were oxidised by passage of 8 pulses of oxygen (volume = 0.5 cm^3) through the catalysts at predetermined temperatures (625-775K). More drastic treatment such as flowing oxygen through the catalyst bed at high temperatures, caused irreversible loss of catalytic activity, the effects of which are discussed later. After oxidation, a pulse of methane ($[\text{CH}_4]_0 = 1.04 \times 10^{-6} \text{ mol}$) was passed over the precious metal oxide and the carbon dioxide produced was measured. This was repeated over a range of temperatures using a fully oxidised catalyst.

It was found that platinum (IV) oxide was a more active catalyst for methane oxidation than palladium (II) oxide, requiring lower temperatures (Figures 3:14 and 3:15). Carbon monoxide, too, was produced at lower temperatures on the 2.7% PtO_2 on ThO_2 catalyst than on the 2.7% PdO on ThO_2 catalyst. Unexpectedly, oxygen was detected after passage of methane over the platinum catalyst due, presumably, to its desorption during adsorption of methane.

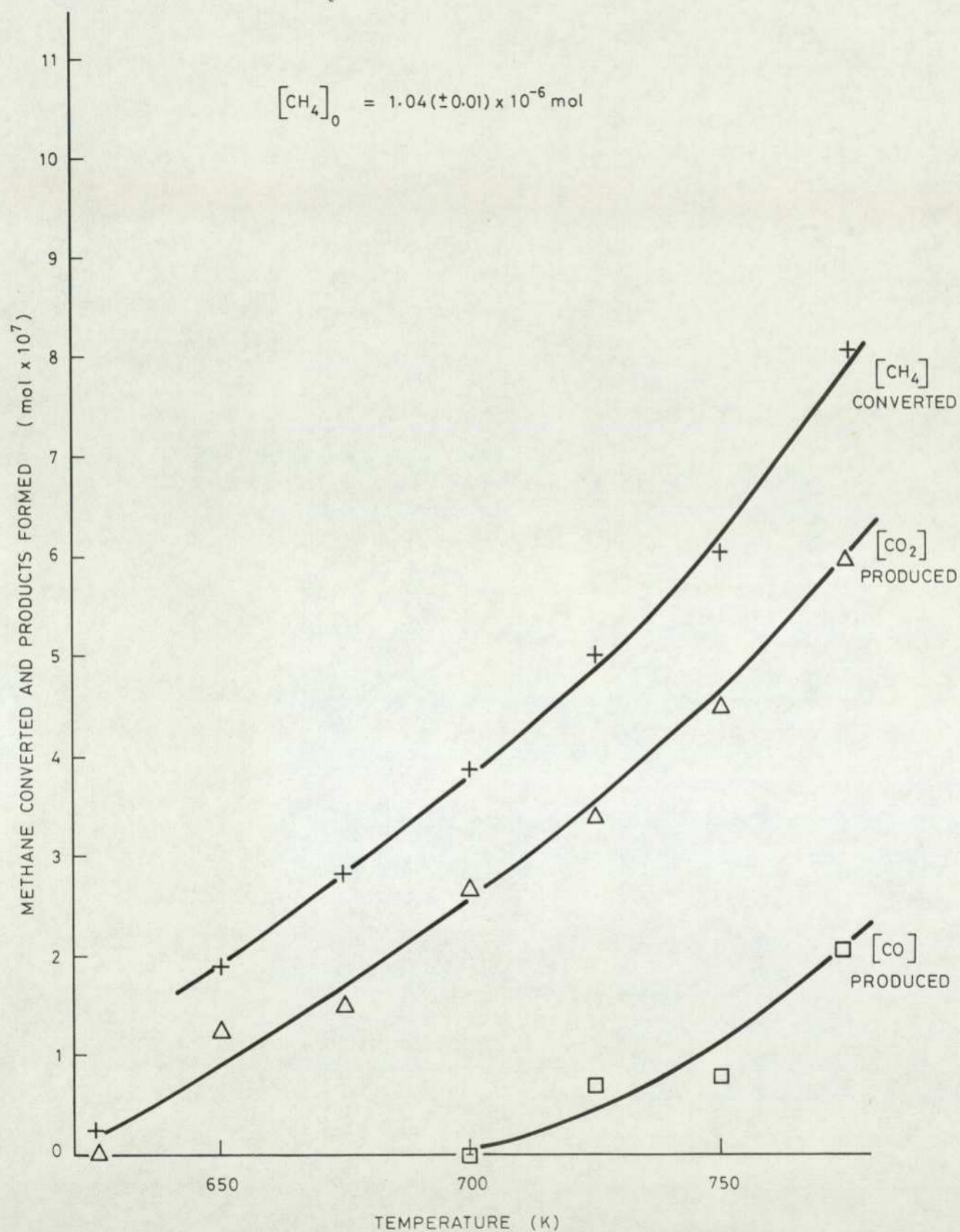


FIG.3.14 METHANE OXIDATION OVER OXIDISED 2.7% Pd/ThO₂

Oxidised by passing $8\text{cm}^3\text{min}^{-1}\text{O}_2$, 15 min. at 625K

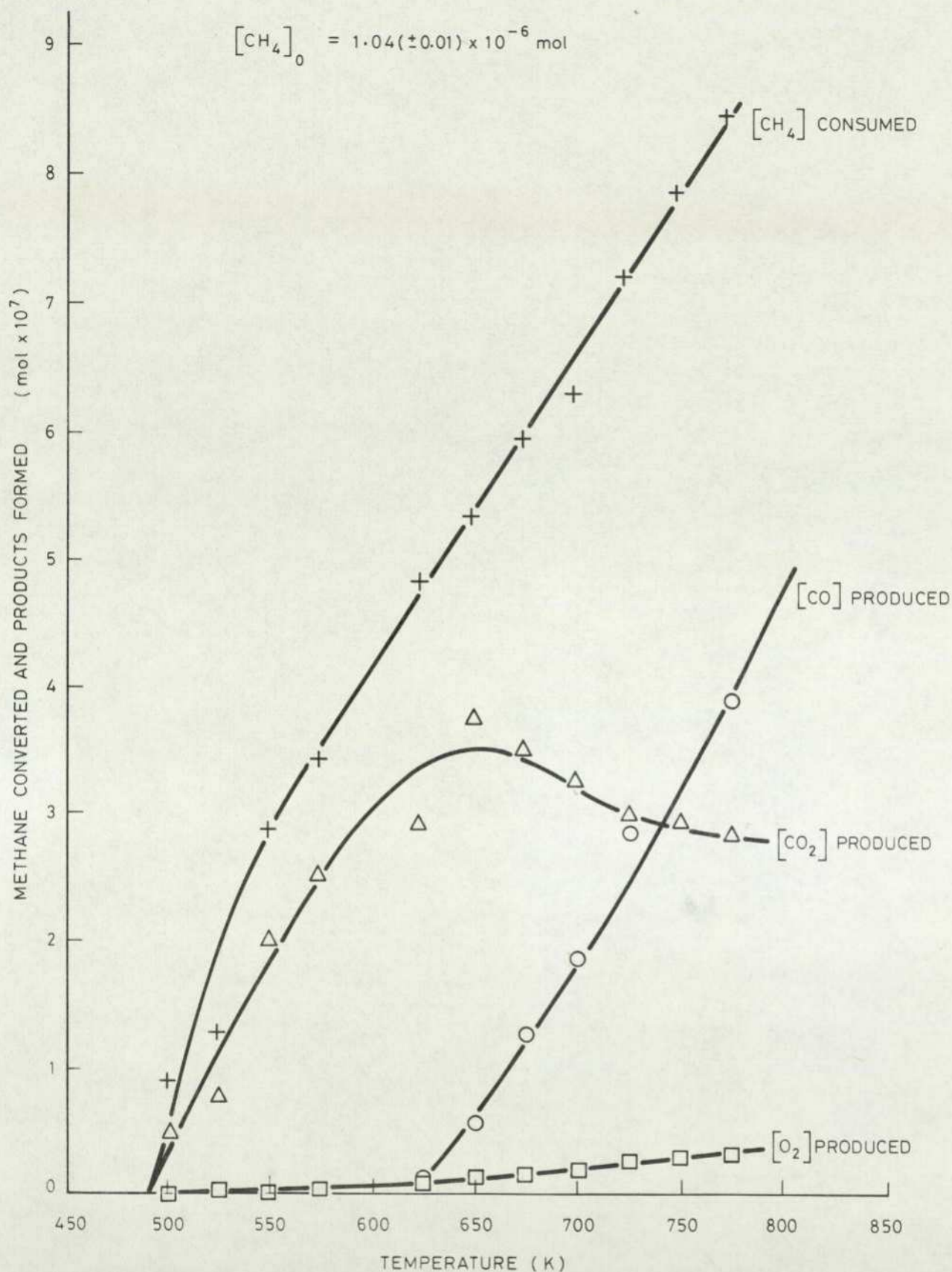


FIG.3.15 METHANE OXIDATION OVER OXIDISED 2.7% Pt/ThO₂
Oxidised by passing 9cm³ min.⁻¹ O₂, 20 min. at 625K

The dependence of the rate of reaction on methane concentration was determined, for both platinum (IV) and palladium (II) oxides by measuring the methane consumption (which takes place as a result of both pyrolysis and oxidation) over a range of conversion levels from 10% to 30%. The results are given in Figures 3:16 and 3:17 and indicate orders with respect to methane of 0.5 ± 0.1 and 0.7 ± 0.1 for palladium (II) oxide and platinum (IV) oxide respectively. Calculation of the order with respect to methane from the amount of carbon dioxide produced gave a value of 0.6 ± 0.1 for palladium (II) oxide and 0.8 ± 0.1 for platinum (IV) oxide. The concurrent pyrolysis of methane evidently had little effect on the order of reaction for methane oxidation.

Measurements were made of the variation in the rate of methane oxidation with temperature for both supported and unsupported catalysts. The linear plots of log (reaction rate) against reciprocal temperature yielded activation energies (Table 3:9).

The amount of oxygen adsorbed by the catalyst was at least twice the amount of the methane in the reactant pulse, ensuring that there was ample oxygen to oxidise all the methane present to carbon dioxide and water. The amount of carbon dioxide produced by the oxidation of methane was the same, on a molar basis, as the amount of oxygen which had to be passed through the catalyst to re-oxidise the precious metal. The balance between carbon dioxide produced and methane consumed indicated, however, that not all the methane consumed was totally oxidised. The presence of

Catalyst	Activation energy (kJ mol ⁻¹)	Temperature range (K)
PdO*	48	500-600
PtO	55	500-600
2.7% Pd on ThO ₂ ⁺	39	625-750
2.7% Pd on ThO ₂ **	51	640-755
2.7% Pt on ThO ₂ ⁺⁺	23	550-773

* Oxidised at 675K.

** Oxidised at 775K.

+ Oxidised at 625K.

++ Oxidised at 625K.

$[\text{CH}_4]_0 = 2.2 \times 10^{-5} \text{ mol.}$

Pulse volume = 5 cm³.

Table 3:9 Observed activation energies for the oxidation of methane over palladium (II) and platinum (IV) oxides.

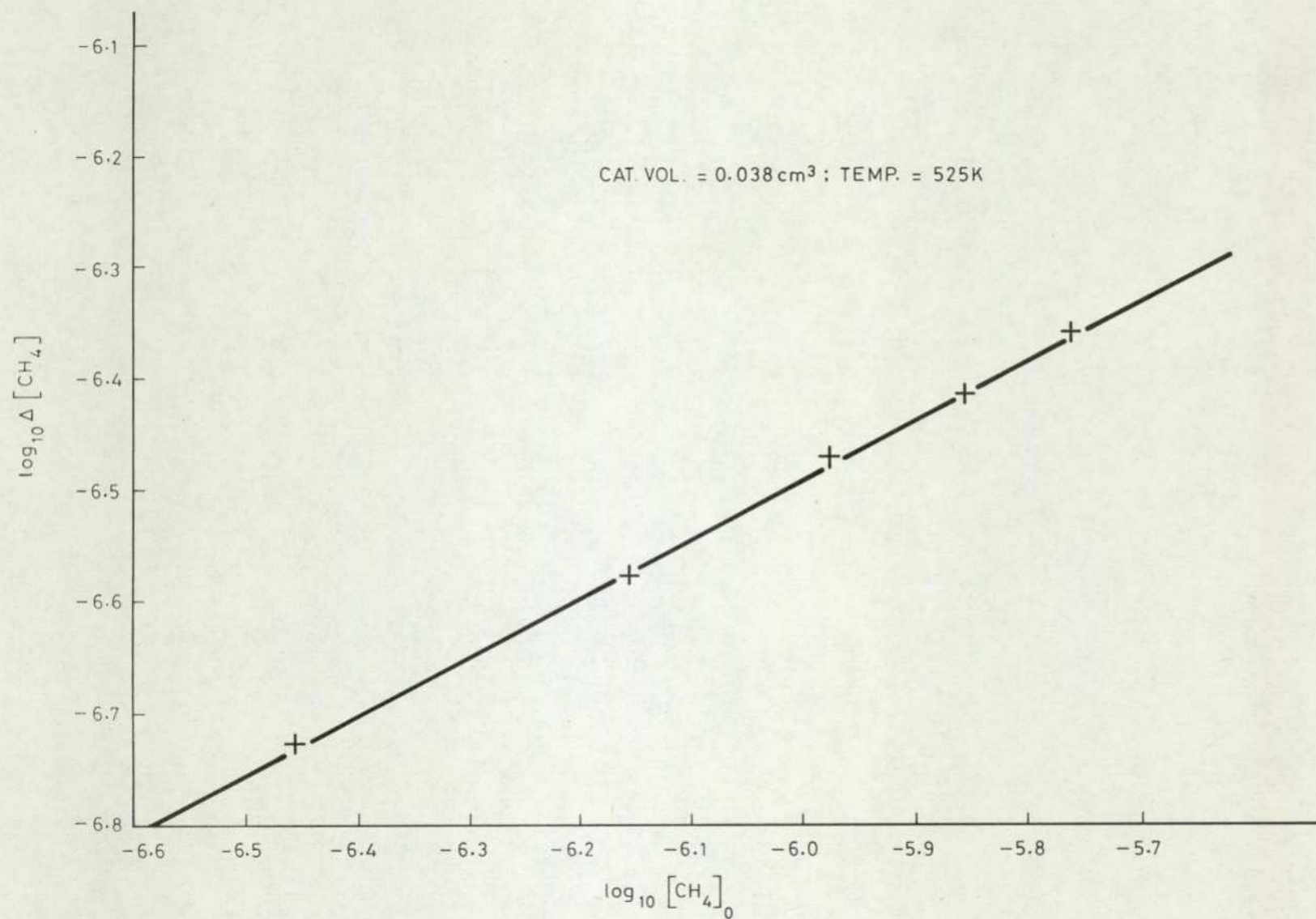


FIG 3.16 VARIATION (WITH INITIAL METHANE CONCENTRATION) OF METHANE CONSUMPTION
IN THE PRESENCE OF PALLADIUM (II) OXIDE

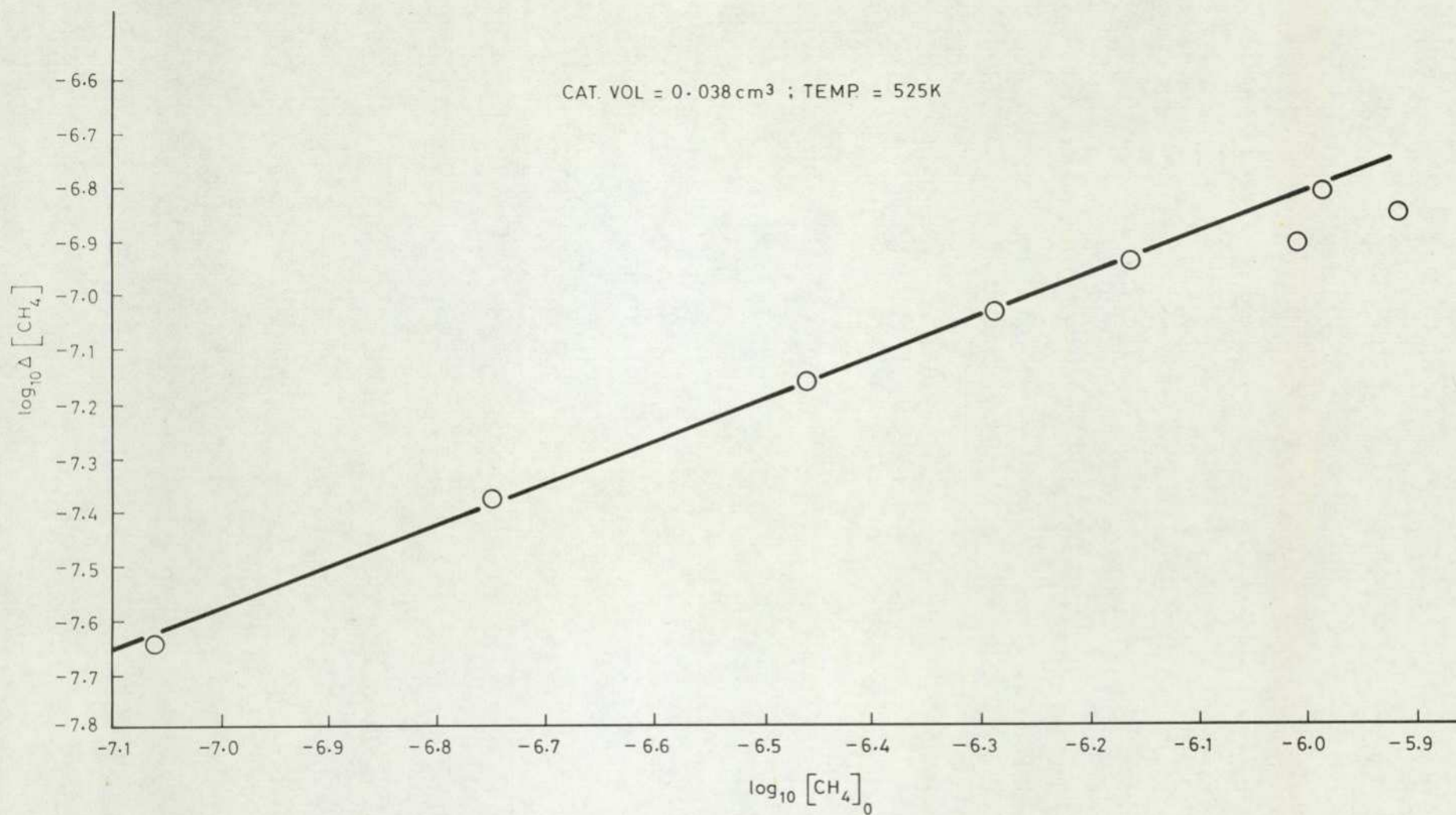


FIG.3.17 VARIATION (WITH INITIAL METHANE CONCENTRATION) OF METHANE CONSUMPTION
IN THE PRESENCE OF PLATINUM (IV) OXIDE

formaldehyde was not observed using the chromotropic acid test. Methane was pyrolysed to carbon that was not recoverable.

Significant differences in the catalytic activity of the palladium (II) oxide were observed depending on the technique used to re-oxidise the catalyst. Prolonged oxidation (oxygen flowing through the catalyst for 20 min. at 775K or 625K; flow rate = $9 \text{ cm}^3 \text{ min}^{-1}$) caused a loss of catalytic activity which was irreversible. Attempts to recover activity by reduction with hydrogen followed by re-oxidation were unsuccessful. However, oxidation under milder conditions (pulses of 0.1 cm^3 of oxygen through the catalyst at 625K) caused no loss in subsequent activity.

Examination, by scanning electron microscopy, of a sample of palladium (II) oxide, the catalytic activity of which had deteriorated on exposure to oxygen at 775K, revealed that considerable morphological changes had occurred when compared with a sample of "fresh" palladium (II) oxide. A "fresh" sample (Plate 3:A,x200) consisted of particles ca. $250 \text{ }\mu\text{m}$ in diameter which at higher magnification (Plate 3:B,x20,000) showed a flat surface with a certain amount of debris. In contrast, exposure of palladium (II) oxide to oxygen at 775K caused the particles to agglomerate and form loosely bound clumps ca. 2 mm in diameter. Flaking of the surface material occurred (Plate 3:C,x200) and at higher magnification (Plate 3:D,x20,000) instead of the flat surface observed for the "fresh" oxide, particles of palladium (II) oxide were found of size 0.1 to $0.5 \text{ }\mu\text{m}$. These drastic

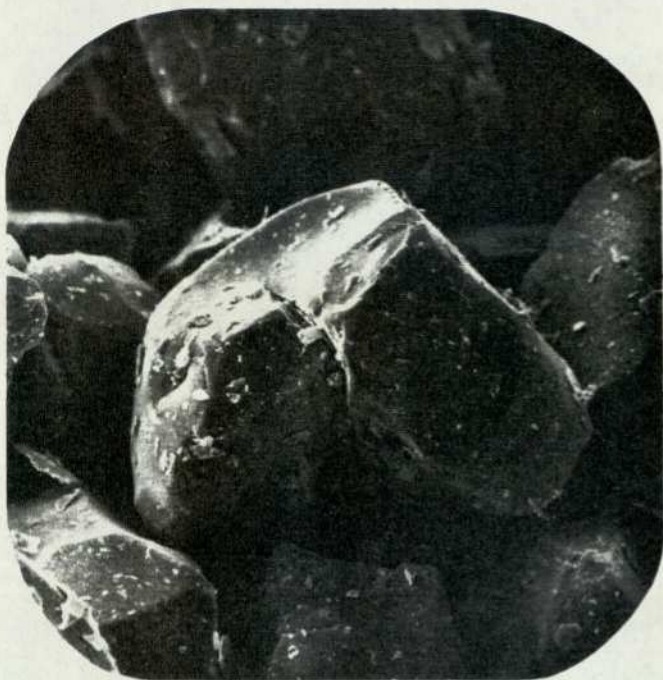


Plate 3:A.

Palladium (II) oxide.

x200.

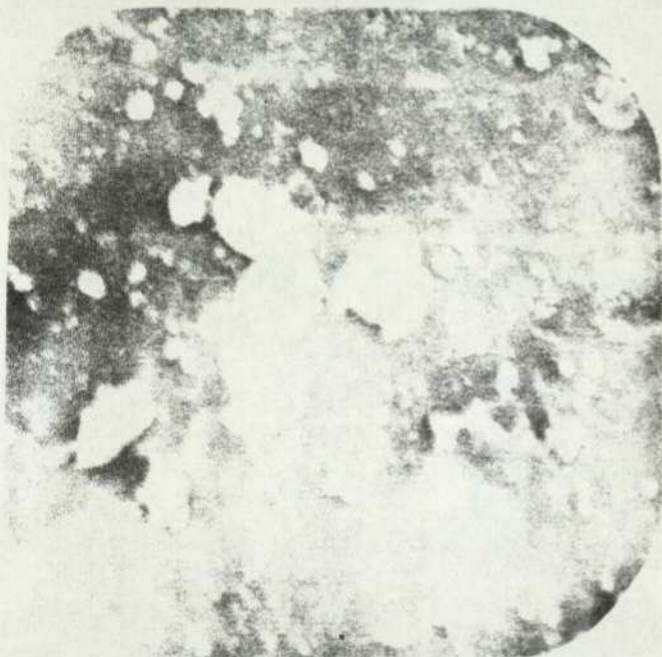


Plate3:B.

Palladium (II) oxide.

x20,000.

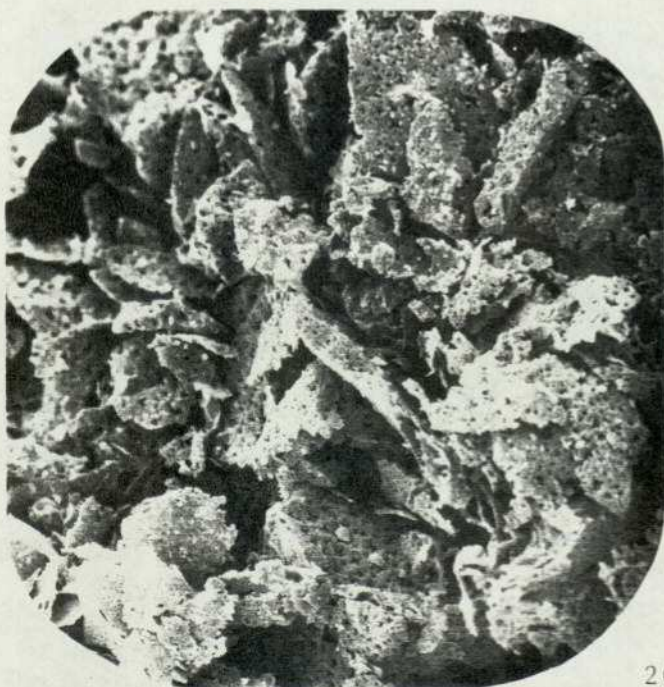


Plate 3:C.

Palladium (II) oxide

exposed to oxygen at

775K.

x200.

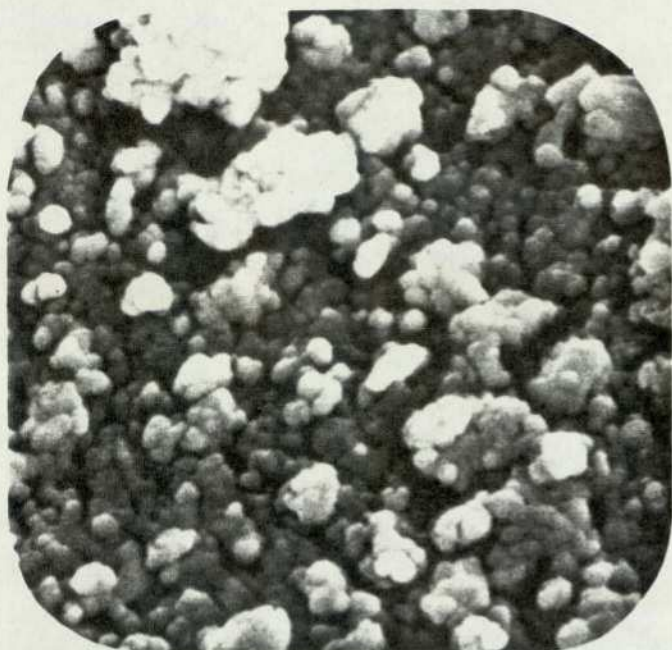


Plate 3:D.

Palladium (II) oxide
exposed to oxygen at
775K.

x20,000.

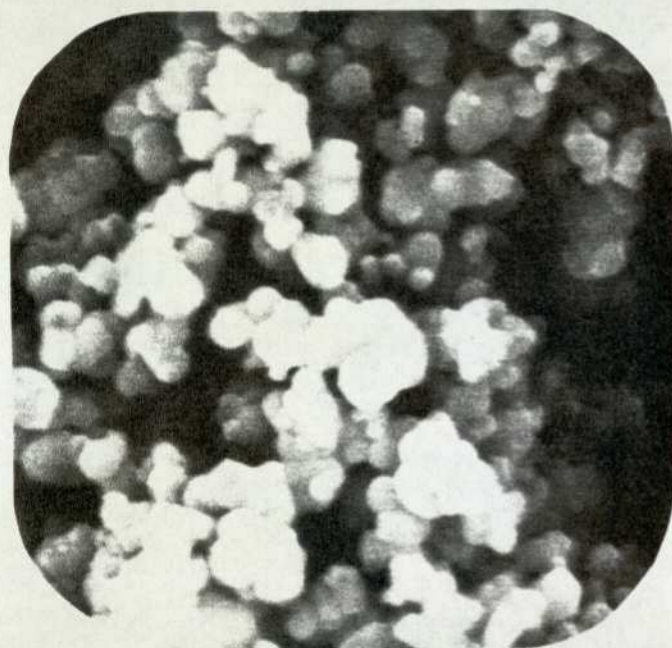


Plate 3:E.

Platinum (IV) oxide.

x20,000.

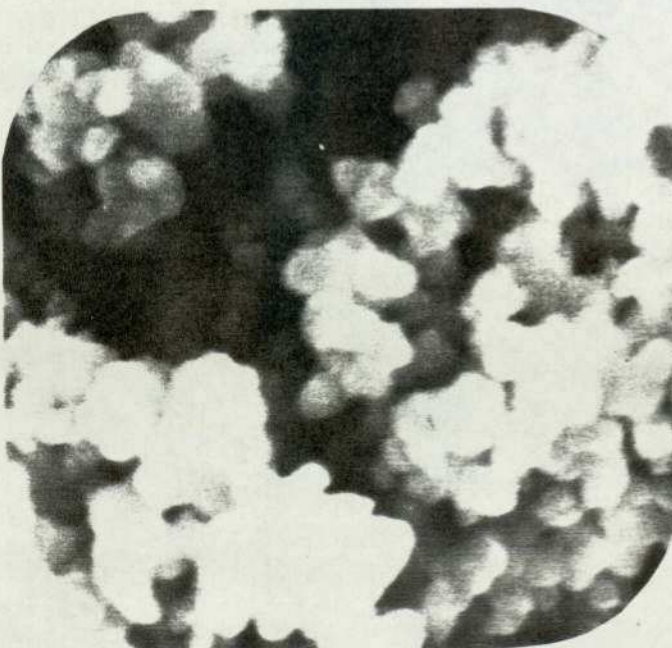


Plate 3:F.

Platinum (IV) oxide
exposed to oxygen at
775K.

x20,000.

changes presumably caused the irreversible loss of catalytic activity.

Unlike palladium (II) oxide, platinum (IV) oxide when exposed to flowing oxygen (at 773K for 20 min) suffered no deterioration in either morphology (Plates 3:E, 3:F) or catalytic activity. It was noticed, however, that a platinum mirror formed on the walls of the reactor tube, indicating the greater volatility of the platinum as opposed to the palladium oxides. This occurred for both supported and unsupported catalysts and may well impose a limit on the useful lifetime of platinum catalysts under these conditions.

The massive sintering that occurred when palladium (II) oxide was heated in oxygen led to an investigation into the temperature profiles across the catalyst bed on exposure to oxidising and reducing atmospheres. Beds of 2.7% Pd on $\gamma\text{-Al}_2\text{O}_3$ as well as platinum (IV) oxide and palladium (II) oxide themselves were subjected to successive oxidation-reduction cycles at 620K and transient temperature rises were measured using a probing thermocouple. Temperature profiles are shown in Figures 3:18, 3:19 and 3:20 and the following conclusions can be drawn:

- a) The reaction of hydrogen with the precious metal oxides was the most exothermic reaction, although that with carbon monoxide was only a little less so. Methane and methane/oxygen mixtures caused much less exothermic behaviour.
- b) The highest temperature rises were observed over palladium (II) oxide. Non-isothermal behaviour was very much reduced in the presence of γ -aluminium (III) oxide, while platinum

Temperature measuring probe : Cr/Al thermocouple (Ni)
 Catalyst bed length = 18mm : Temperature = 620K

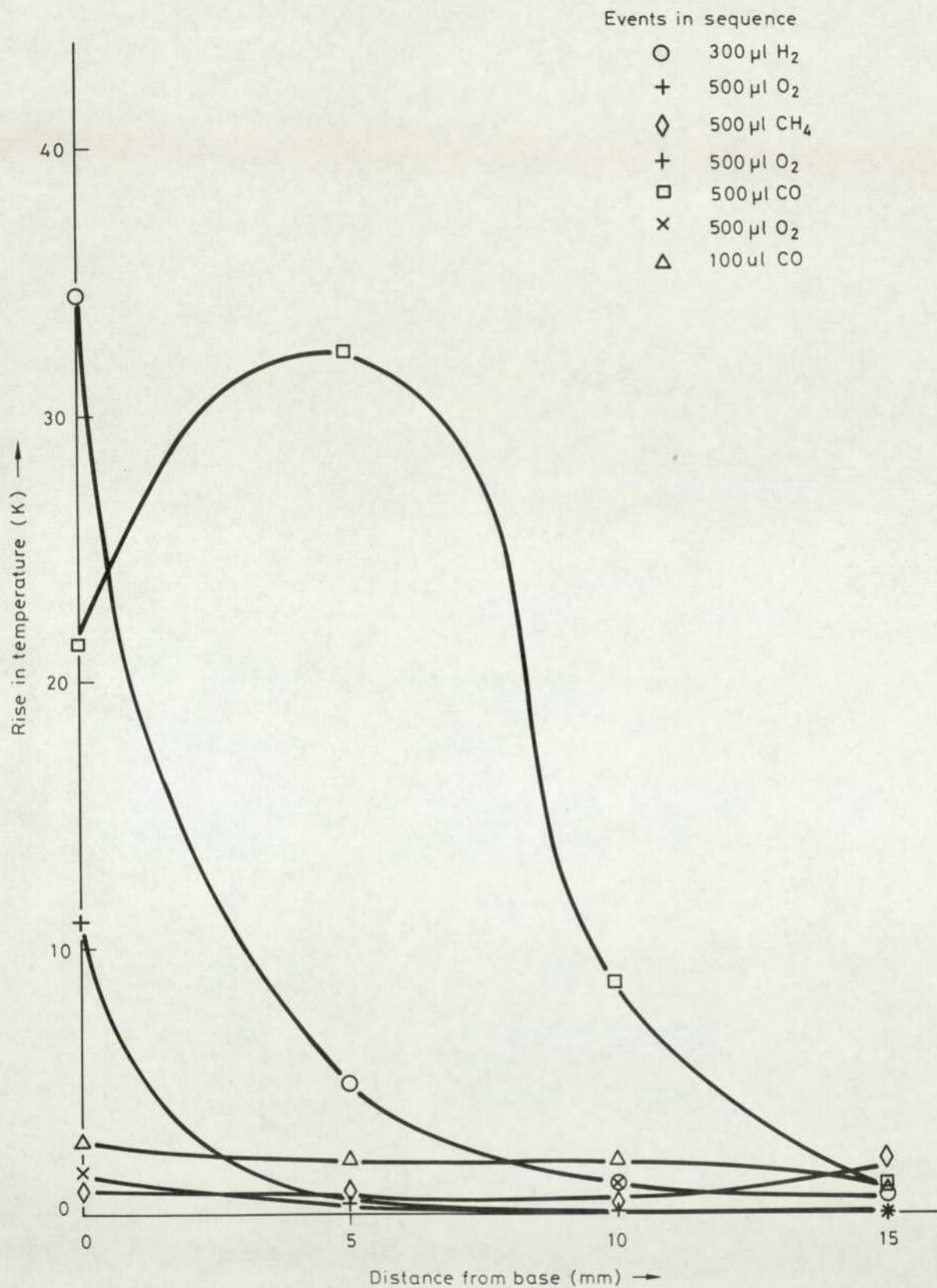


FIG.3.18 TEMPERATURE PROFILE ACROSS PALLADIUM (II) OXIDE BED DURING OXIDATION/ REDUCTION

Catalyst Bed Length = 18 mm

Temperature measuring probe : Cr/Al thermocouple (Ni)

Temperature = 620K

Events in sequence

1. × 300 μ l H_2
2. ○ 500 μ l O_2
3. △ 500 μ l CH_4
4. ◇ 100 μ l O_2
5. □ 100 μ l H_2
6. ○ 500 μ l O_2
7. + 100 μ l CH_4

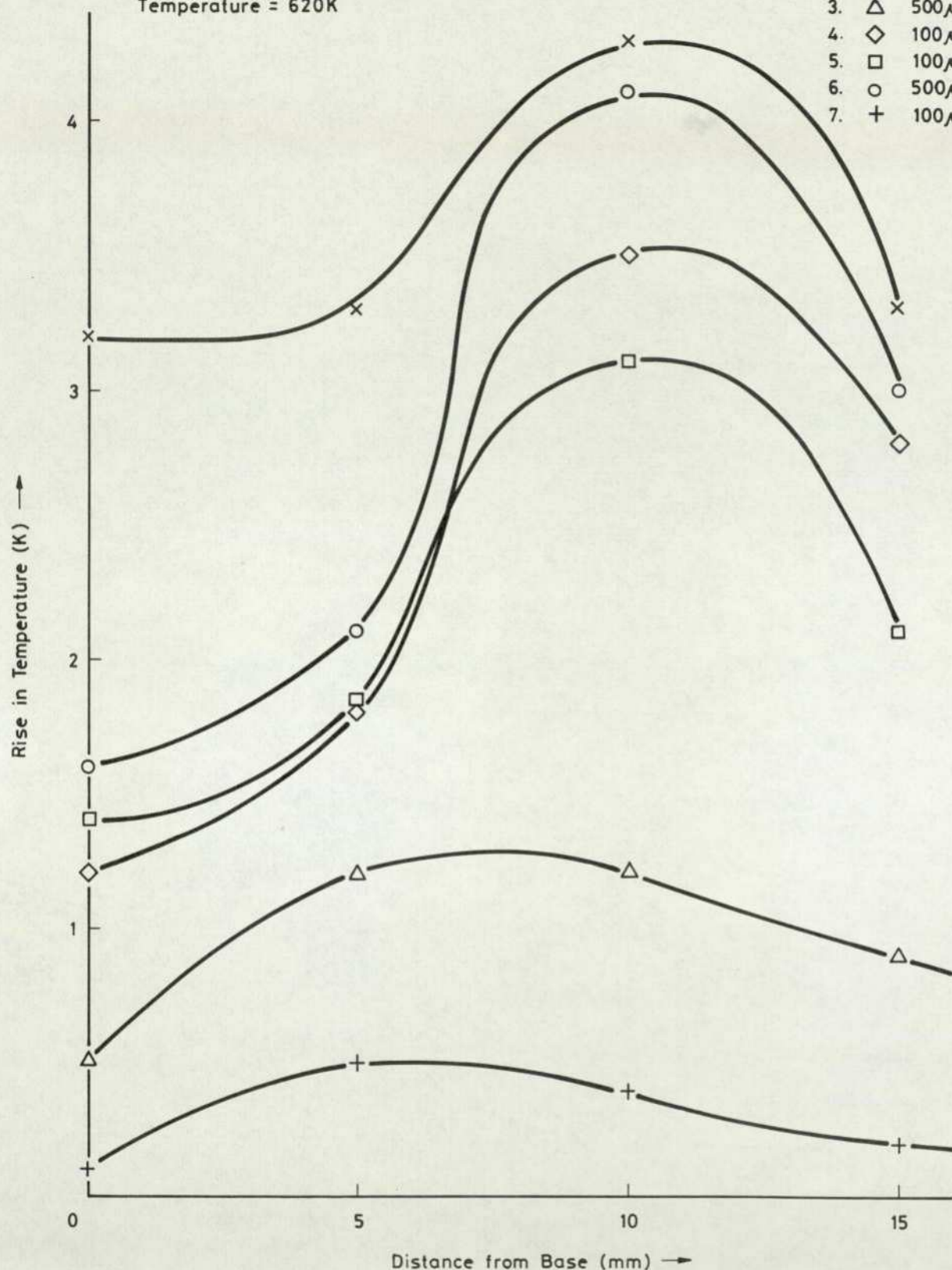


FIG.3.19 TEMPERATURE PROFILE ACROSS PLATINUM (IV) OXIDE BED DURING OXIDATION/REDUCTION

Catalyst Bed Length = 18 mm

Temperature measuring probe = Cr/Al thermocouple (Ni)

Temperature = 620K

Events in sequence

1. ○ 300 μ l H_2
2. + 500 μ l O_2
3. □ 500 μ l CH_4
4. + 500 μ l O_2
5. ◆ 500 μ l CO
6. x 300 μ l O_2
7. △ 100 μ l H_2
8. ◇ 200 μ l O_2 + 200 μ l CH_4

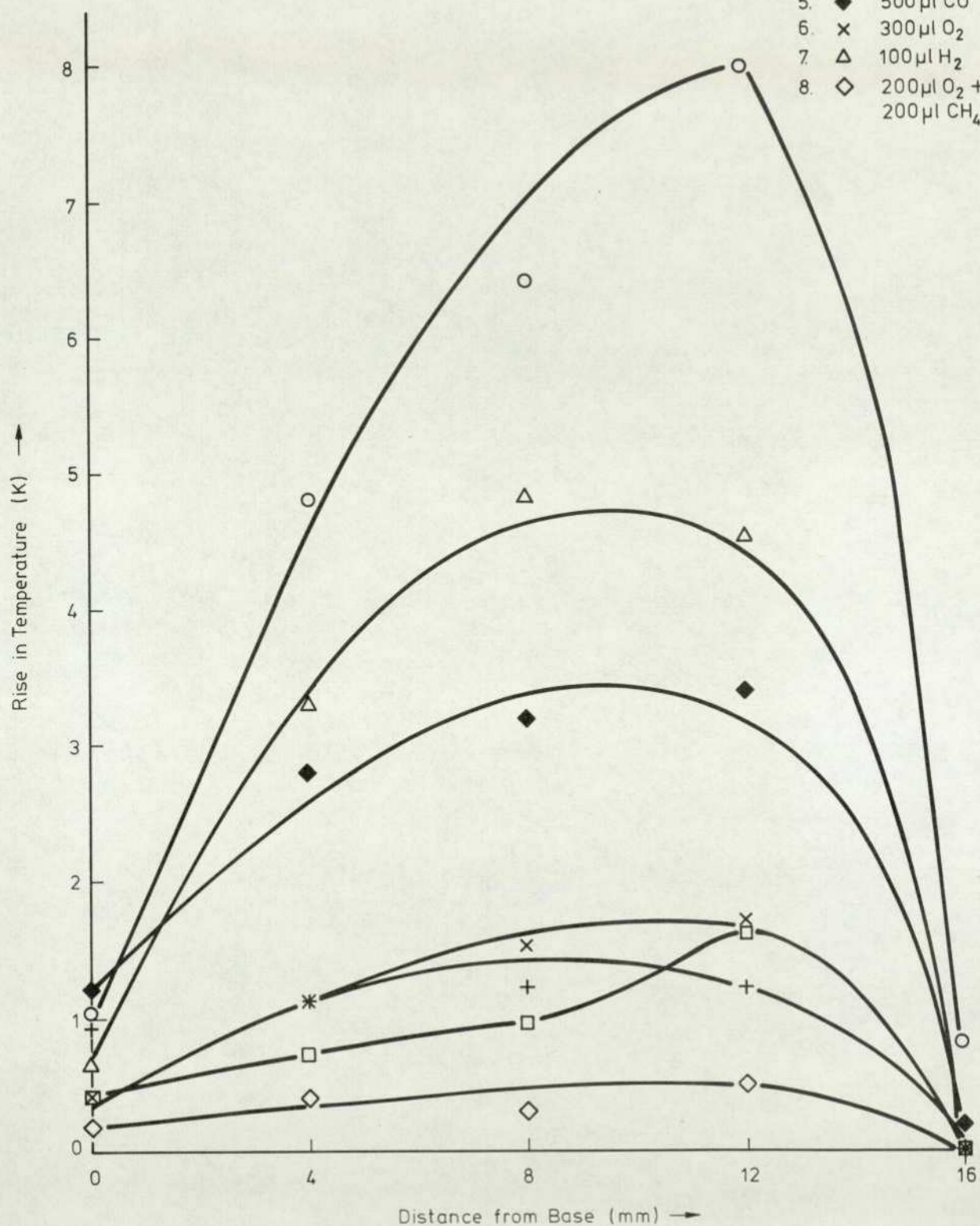


FIG.3.20 TEMPERATURE PROFILE ACROSS 2.7% Pd (w/w) ON γ - Al_2O_3 BED DURING OXIDATION/REDUCTION

(IV) oxide showed only a moderate rise in temperature.

c) Over palladium (II) oxide, the temperature increase was greatest at the inlet point. For platinum (IV) oxide and 2.7% PdO on $\gamma\text{-Al}_2\text{O}_3$, the heat distribution was more even over the whole catalyst bed, the highest temperatures being recorded just beyond the middle of the bed.

d) Under typical experimental conditions, the oxidation of methane over the supported palladium (II) oxide catalyst took place almost isothermally ($\pm 0.3\text{K}$ over the whole bed). Care had to be taken, however, when hydrogen or carbon monoxide were passed over a previously oxidised catalyst, especially palladium (II) oxide.

3:6 Precious metal particle size distributions for various supported catalysts.

A number of catalysts were examined using transmission electron microscopy and the average particle size of the precious metal was determined. The results shown in Table 3:10 were obtained by measuring the diameters of precious metal particles obtained from micrographs at magnifications of $\times 50,000$ to $\times 300,000$. The precious metal particles were identified as black spots on the lighter background of the support. Use of scanning-transmission electron microscopy with EDAX revealed that these dark spots consist of high levels of palladium when compared with the lighter areas which were identified as the support.

The measurement of the particle sizes of palladium and platinum on thorium (IV) oxide and palladium on tin (IV) oxide was not possible because the precious metal was

Catalyst/support	Mean precious metal particle diameter (nm)	Maximum temperature to which catalyst was exposed (K)	Range of precious metal particle diameters (nm)
2.7% Pd on TiO_2^+	11	773	2-32
8.5% Pd on TiO_2^+	13	773	2-26
8.7% Pd on TiO_2^*	10	773	2-26
2.7% Pd/Pt(3/1) on TiO_2	4	773	<1-20
2.7% Pt on TiO_2	2.4	773	<1-14
2.7% Pd on $\gamma\text{-Al}_2\text{O}_3$	13	773	2-32
10.8% Pd on $\gamma\text{-Al}_2\text{O}_3$	26	923	<1-70
25% Pd on $\gamma\text{-Al}_2\text{O}_3$	26	773	5-70
2.7% Pt on $\gamma\text{-Al}_2\text{O}_3$	2.8	773	<1-9

+ prepared from palladium (II) oxide.

* prepared from palladium (II) chloride.

Conditions:-

Accelerating voltage = 100 kV.

Magnification = x50,000 to x300,000.

All catalysts above were conditioned in flowing helium ($25 \text{ cm}^3 \text{ min}^{-1}$) at 773K for 16h before being exposed to methane/oxygen pulses at 773K. Further heating to 923K was applied to 10.8% Pd on $\gamma\text{-Al}_2\text{O}_3$ in the presence of oxygen.

Table 3:10 Precious metal particle size distributions for various supported catalysts.

indistinguishable from the support. The electron beam hardly penetrated thorium (IV) oxide, thus masking the palladium and platinum. For tin (IV) oxide and titanium (IV) oxide, the inability to distinguish the precious metal from the support may be due to either the small size of the palladium particles present or the lack of contrast between the support and the precious metal, which may be accentuated by strong metal-support interactions (tin (IV) oxide). Bond, Fuller and Molloy (1977) were also unable to find palladium particles on tin (IV) oxide and postulated that the particle diameter was so small as to be beyond the resolution of the instrument. In the present case this seems unlikely as the average particle size of a catalyst containing a high loading of palladium (e.g. 20% Pd on SnO_2) would be expected to lie well within the resolution of the microscope used for these studies (1 nm). This suggests that palladium is present but is indistinguishable both in contrast and in particle size from the smaller tin (IV) oxide particles (see Plate 3:G). As with titanium (IV) oxide, platinum may be observed on the tin (IV) oxide surface as it has a higher atomic number making it more opaque to the electron beam.

Catalysts with high precious metal loadings show a tendency towards large metal particle sizes. Low concentrations of precious metals provide smaller particle sizes. Hence increased loading does not necessarily lead to increased dispersion but to agglomeration of particles (Table 3:10). Histograms of two palladium on γ -aluminium (III) oxide catalysts shown in Figure 3:21 demonstrate the tendency towards large particle diameters for high loadings.

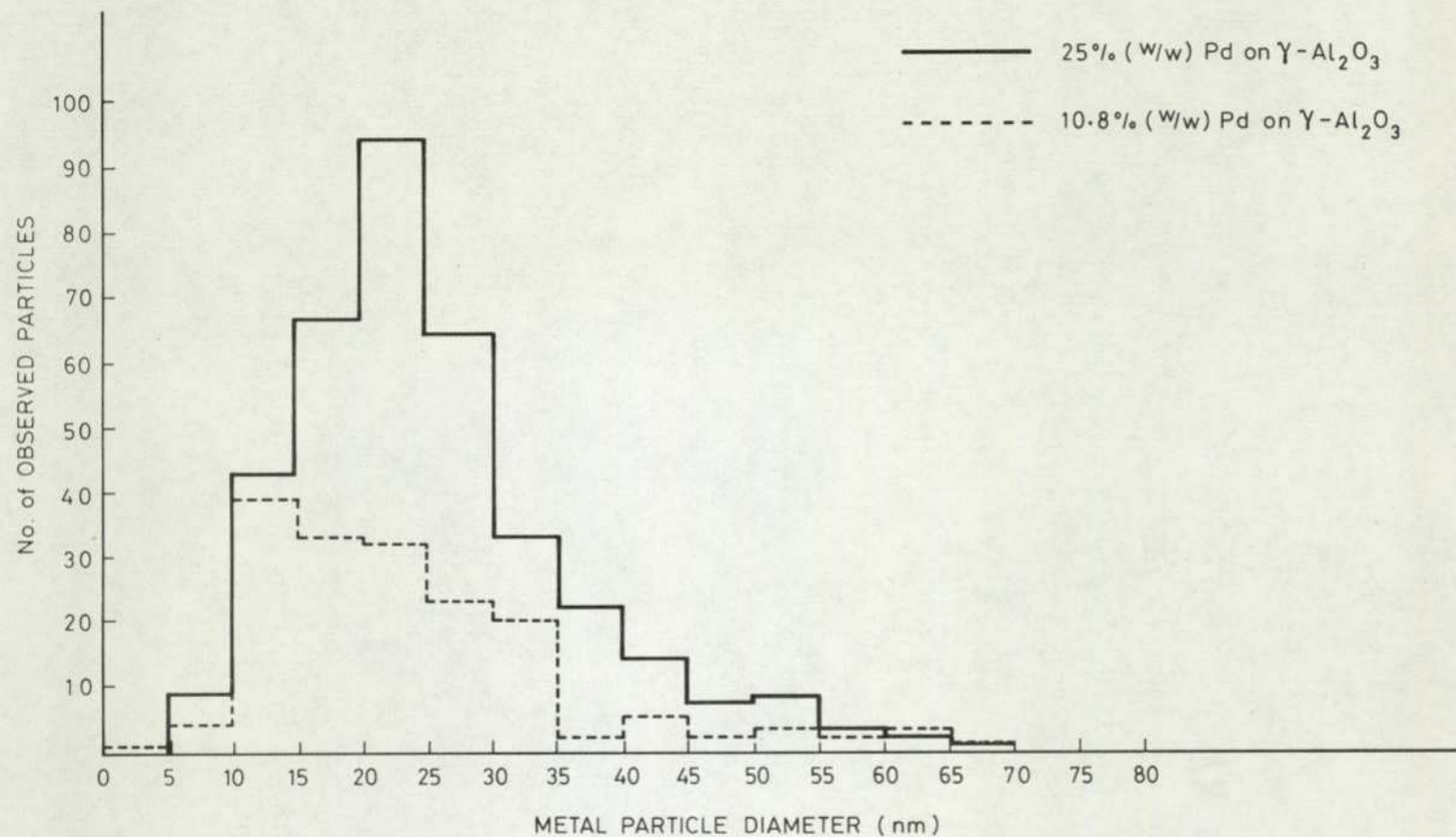


FIG. 3.21 AVERAGE PALLADIUM PARTICLE DIAMETER DISTRIBUTION FOR 25% Pd/ γ - Al_2O_3 AND 10.8% Pd/ γ - Al_2O_3

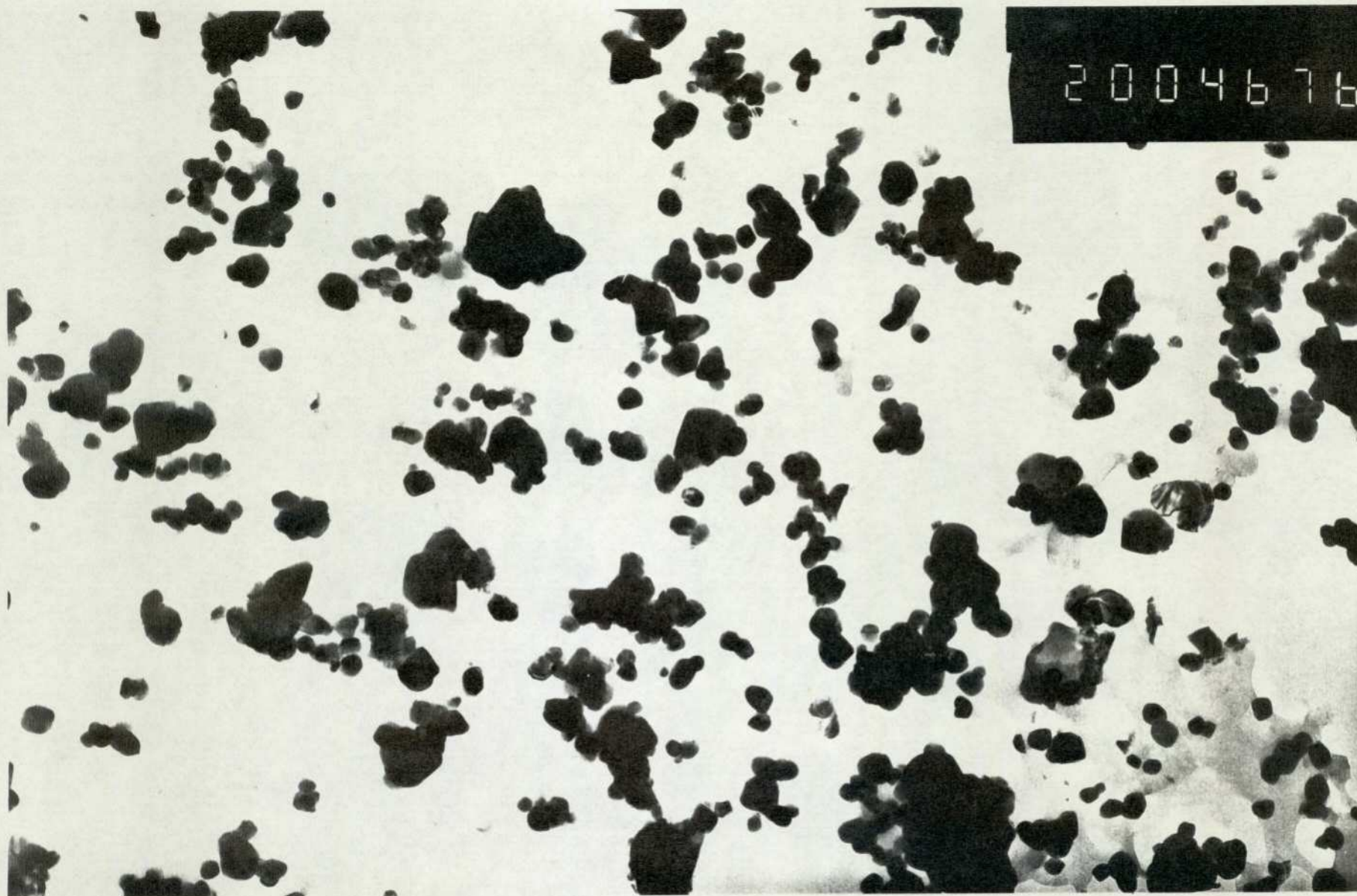


Plate 3:G.

20% Pd on SnO_2 .

x60,000.

Both catalysts had been exposed to oxygen at high temperatures (923K for 10.8% Pd on $\gamma\text{-Al}_2\text{O}_3$ and 775K for 25% Pd on $\gamma\text{-Al}_2\text{O}_3$) and despite the higher temperatures to which it was exposed, the 10.8% Pd catalyst retained the same average particle size as the 25% Pd catalyst.

The effect of prolonged heating on the palladium particle size of a 2.7% Pd on $\gamma\text{-Al}_2\text{O}_3$ catalyst is shown in Figure 3:22. This catalyst was heated for 40 days in flowing air (21% oxygen in nitrogen, flow rate = $25\text{ cm}^3\text{ min}^{-1}$) at temperatures of 723K to 1023K and the catalytic activity towards methane oxidation was measured periodically. In addition, the palladium particle size distribution was measured both before and after heat treatment at 823K. While the catalytic activity towards methane oxidation is almost unaffected by heating, the particle size increases greatly. Gas testing was carried out using a 5 cm^3 methane/oxygen pulse ($[\text{CH}_4]_0 = 3.61 \times 10^{-5}\text{ mol}$, $[\text{O}_2]_0 = 1.91 \times 10^{-5}\text{ mol}$) at 683K and 773K. The production of carbon dioxide was taken as a measure of catalytic activity.

Heating a 2.7% Pd/Pt (Pd:Pt = 1:1 by weight) on a TiO_2 catalyst at 1023K for 35 days caused the formation of a Pd-Pt alloy. This was revealed using X-ray diffraction, the line spacings being intermediate between those of palladium and platinum and thus indicating the presence of a single alloy phase. The line breadth suggested that the primary crystallite diameter of the Pd-Pt alloy was between 100 and 150 nm. Under the transmission electron microscope, discrete metal particles were not observed. Some "blistering"

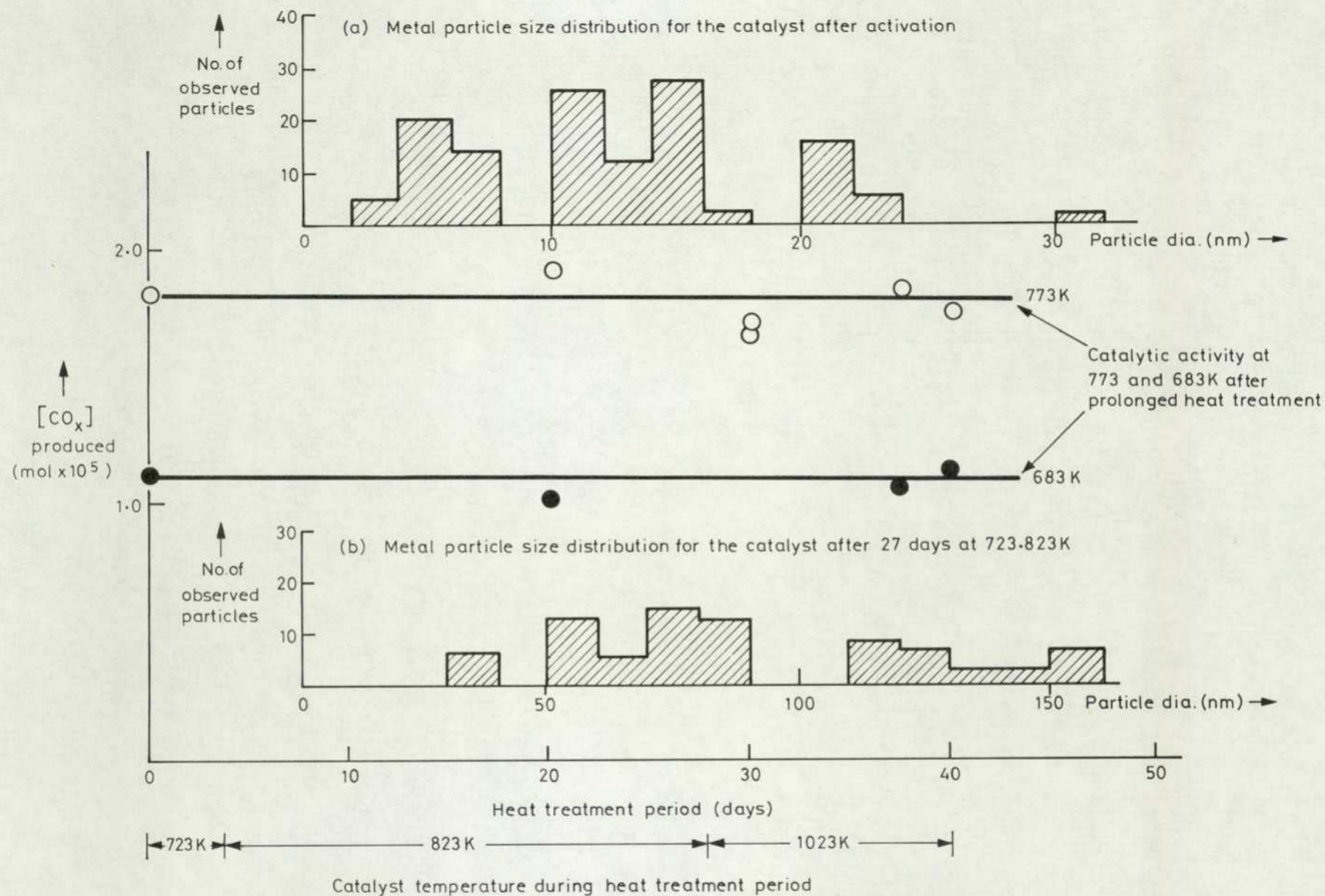


FIG.3.22 EFFECT OF PROLONGED HEATING IN AIR ON THE ACTIVITY AND METAL PARTICLE SIZE DISTRIBUTION OF A 2.7% Pd ON γ -Al₂O₃ CATALYST

of the surface occurred (Plate 3:H) and examination under polarised light suggested that the catalyst contained a ternary Pd-Pt-Ti alloy.

3:7 Contribution of catalyst supports towards methane oxidation.

3:3:1 Reactions of methane on catalyst supports.

The contribution of the support itself towards the heterogeneous oxidation of methane by supported precious metal catalysts may be significant in the overall reaction. As well as support-precious metal interactions, the support may itself be active in methane oxidation. Accordingly, a number of catalyst supports, thorium (IV) oxide, γ -aluminium (III) oxide, silicon (IV) oxide, titanium (IV) oxide, (89% anatase - 11% rutile and pure rutile) and tin (IV) oxide were exposed to methane, both in the presence and in the absence of gaseous oxygen at 873K. Silicon (IV) oxide, in the form of silica gel, was included as it was thought that the presence of Lewis acid sites usually found on silica would promote the reaction. The results in the absence of oxygen are given in Figure 3:23 and Table 3:11.

High temperatures are required before methane will react with almost all the supports in the absence of gaseous oxygen, tin (IV) oxide being the only exception. Anatase, which would be expected to be less stable than rutile, produced carbon monoxide at temperatures above 825K, a phenomenon not observed with the other supports. The formation of carbon monoxide can probably be ascribed to the participation of

Support	Methane conversion (% at 873K)	
	(1) In the absence of gaseous O_2^* .	(2) In the presence of gaseous O_2^+ .
ThO_2	0.8	7.1
$\gamma-Al_2O_3$	1.1	2.3
TiO_2 (89% anatase - 11% rutile)	1.6	8.6
TiO_2 (rutile)	1.5	-
SiO_2	1.8	-
Silica reactor tube.	-	3.2
SnO_2	25	100

* $[CH_4]_0 = 2.8 \times 10^{-7}$ mol.

+ $[CH_4]_0 = 4.1 \times 10^{-5}$ mol, $[O_2]_0 = 1.9 \times 10^{-5}$ mol.

Catalyst bed length = 1.5 cm.

Table 3:11 The activities of oxide supports towards
pyrolysis and oxidation of methane.

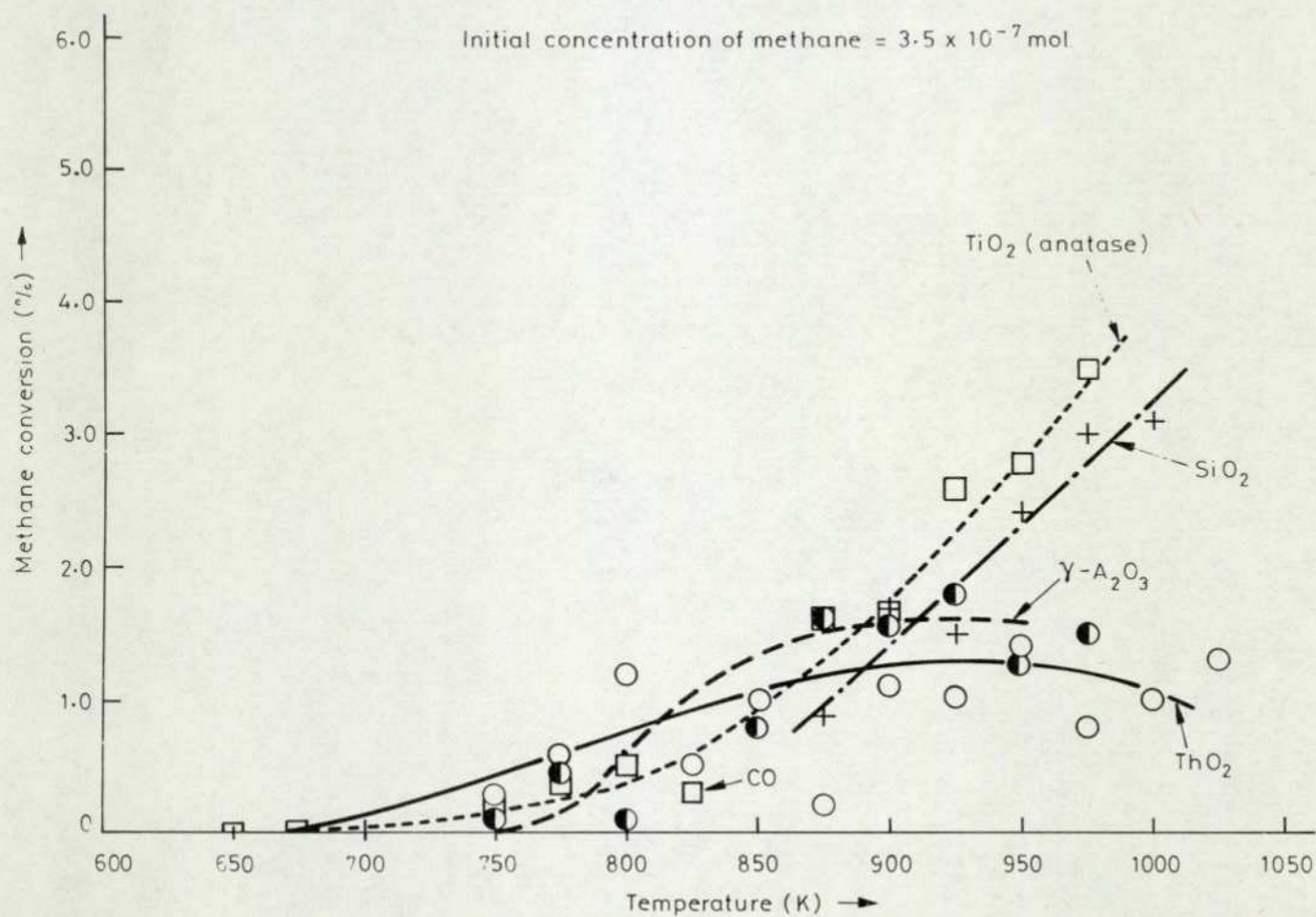


FIG. 3.23 VARIATION WITH TEMPERATURE OF THE ACTIVITY OF SOME CATALYST SUPPORTS TOWARDS THE CONVERSION OF METHANE



Plate 3:H. 2.7% Pd/Pt on TiO calcined at 1023K for
35 days in flowing air. x200,000.

lattice oxygen from titanium (IV) oxide. Pyrolysis of methane on rutile produced no carbon monoxide but a small section of the catalyst bed turned grey due, possibly, to loss of oxygen and formation of lower oxides of titanium (titanium (II) oxide is black) or to carbon deposition.

In the presence of oxygen, some methane oxidation occurred. Once again, tin (IV) oxide was exceptionally active, converting significant amounts of methane to carbon dioxide and water at temperatures as low as 650K. As temperatures of 873K are higher than those normally used for a study of catalytic oxidation of methane over supported precious metals, the contribution to the overall reaction of the support alone would be expected to be small in almost all cases. Tin (IV) oxide may, however, play a significant role in methane oxidation.

3:7:2 Effect of heating on catalyst supports.

Prolonged heat treatment at temperatures of up to 1273K for several days was applied to γ -aluminium (III) oxide, titanium (IV) oxide and thorium (IV) oxide. Samples of each oxide were heated in a furnace in still air and a small quantity was submitted for examination by electron microscopy and for surface area determination. The results are given in Tables 3:12 and 3:13.

Both γ -aluminium (III) oxide supplied by B.D.H. which was used as a support for the aluminium (III) oxide-supported catalysts and that prepared by calcination of aluminium (III) nitrate nonahydrate, showed that on continued

Sample	Heat treatment temperature (K)	Time (h)	Surface area ($\text{m}^2 \text{g}^{-1}$)
1*	-	-	45±3
1	-	-	43±3
1	600	8	53±4
1	600	24	60±4
1	600	48	53±4
1	600	88	56±4
1	600	104	57±4
1	800	16	67±4
1	800	32	71±5
1	800	56	61±4
1	800	115	53±4
1	800	183	54±4
1	1273	9	20±1
1	1273	178	6.8±0.8
1	1273	323	10.6±0.8
11+	600	12	66±5
11	1000	120	61±4
11	1100	28	67±5
11	1100	124	73±5
11	1100	196	54±4
11	1100	360	43±3
11	1273	0.5	59±4
11	1273	3	23±1
11	1273	323	4.8±0.5

* Sample 1 Al_2O_3 (B.D.H.) + Sample 11 Al_2O_3 (prepared by thermal decomposition of $\text{Al}_2(\text{NO}_3)_6 \cdot 9\text{H}_2\text{O}$).

Table 3:12 Effect of heat treatment on the surface area of some aluminium (III) oxides.

Sample	Heat treatment temperature (K)	Time (h)	Surface area ($\text{m}^2 \text{g}^{-1}$)
III	-	-	10.7 ± 1.0
IV	-	-	6.8 ± 0.8
IV	900	24	5.8 ± 0.5
IV	1100	118	5.8 ± 0.5
IV	1273	9	2.9 ± 0.2
IV	1273	81	2.5 ± 0.2
IV	1273	178	1.7 ± 0.2
IV	1273	323	1.6 ± 0.2
V	1273	6	0.04 ± 0.01
VI	-	-	2.5 ± 0.2

Sample III TiO_2 (rutile).

Sample IV starting material TiO_2 (Hopkin and Williams; 89% anatase + 11% rutile).

Sample V ThO_2 (calcined 1273K).

Sample VI ThO_2 (Hopkin and Williams).

Table 3:13 Effect of heat treatment on the surface area of titanium (IV) oxide and thorium (IV) oxide.

heat treatment, the surface area first increased to a maximum and then decreased again (Figure 3:24). The higher the temperature, the higher the maximum and the sharper the fall-off. Furthermore, at 1100K, the surface area continued to decrease with time without levelling off. At 1273K no maximum was observed and the surface area decreased to a constant, low value.

Initial heating of γ -aluminium (III) oxide at 873K caused the growth of spherical particles (diameter 50-250 nm) on the surface (Plate 3:I). These may be associated with the loss of water from the alumina (γ -aluminium (III) oxide supplied by B.D.H. contained 3% added water) and could contribute to the increase in surface area. Raising the temperature initiated further alteration to the aluminium (III) oxide surface with the appearance of cracks which probably resulted from enlargement of the micropores. The surface area was considerably decreased at 1273K and evidence of sintering can be seen (Plate 3:J). The spherical particles formed on the surface at 600K were still present at higher temperatures.

The melting point of aluminium (III) oxide is 2319K, the Huttig temperature (that at which surface molecules become mobile) is ca. 773K and the Tamman temperature (that at which bulk molecules become mobile) is ca. 1160K. Hence surface changes may be expected above 773K and bulk changes above 1160K, accompanied by loss of water and by phase transformations. The probable transformations brought about by heating γ -aluminium (III) oxide have been identified by

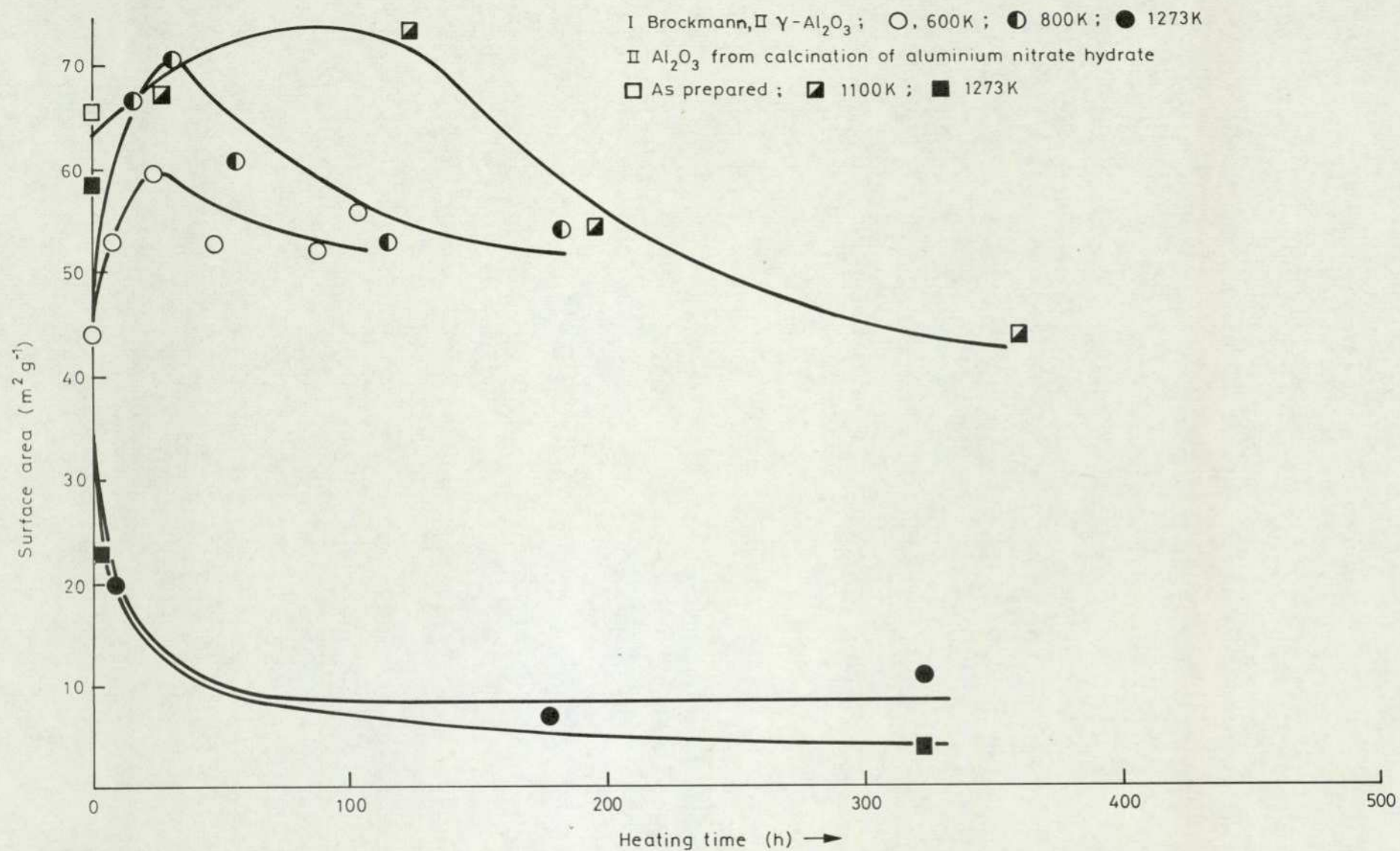


FIG. 3.24 EFFECT OF HEAT TREATMENT ON THE SURFACE AREA OF ALUMINA

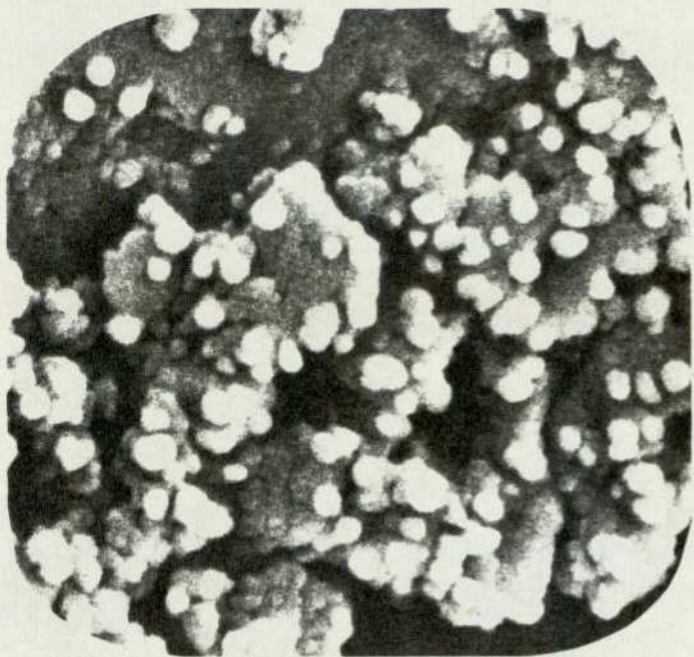


Plate 3:I.

Aluminium (III) oxide
(BDH) calcined at 873K
for 12h.
x40,000.

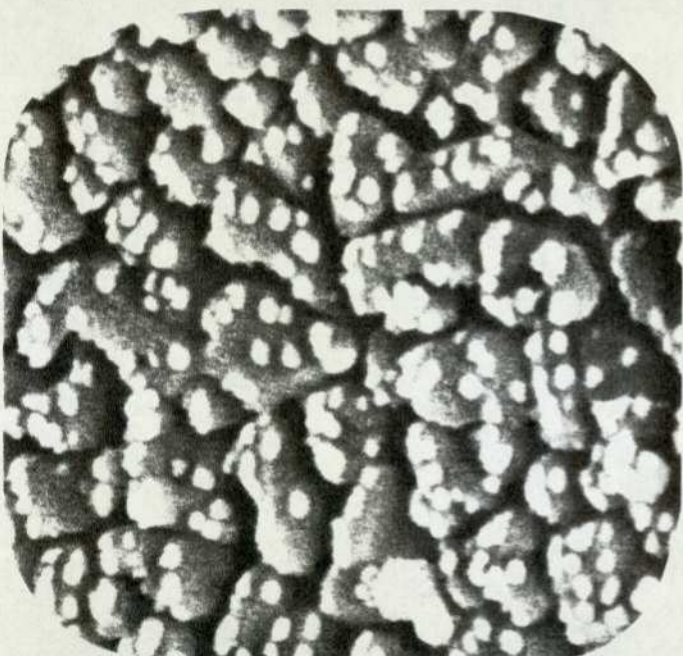


Plate 3:J.

Aluminium (III) oxide
(BDH) calcined at 1273K
for 323h.
x40,000.

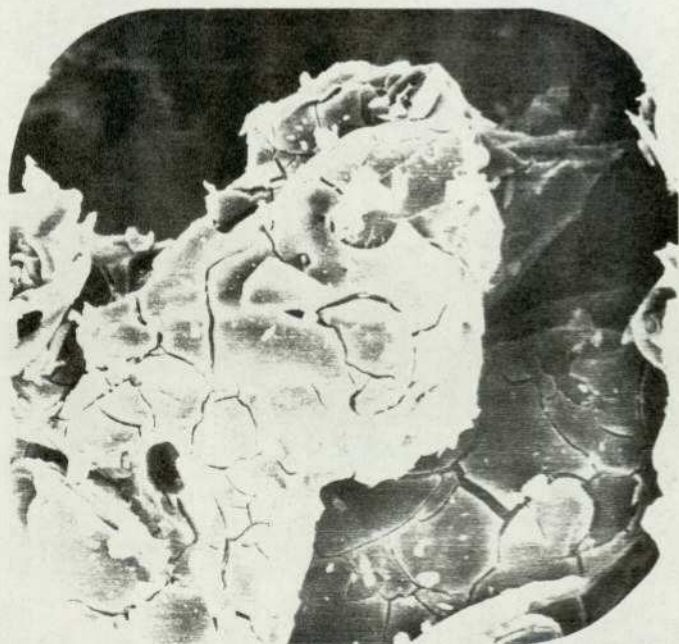
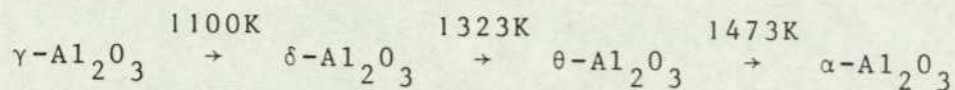


Plate 3:K.

Aluminium (III) oxide
(from $\text{Al}_2(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$)
calcined at 773K for 72h.
and 873K for 24h.
x240.

Gauguin, Graulier and Papee (1975):



(the temperatures are only approximate).

Prolonged heating (105h at 1273K) of γ -aluminium (III) oxide caused the formation of α -aluminium (III) oxide, although κ -, θ -, and γ -aluminium (III) oxide were still present. δ -Aluminium (III) oxide is formed without a basic change in structure and consequently without alteration of mechanical properties. On the other hand, alumina, with which a θ -phase is formed around 1073K, loses its mechanical strength; subsequently, loss of surface area may be expected to occur.

The behaviour of γ -aluminium (III) oxide formed from the nitrate and of that supplied by B.D.H. was similar. Electron microscopy (Plates 3:K and 3:L) revealed that the former had an irregular surface with "blow holes" formed by escaping gas during thermal decomposition. These were absent on the Brockmann grade II γ -aluminium (III) oxide. Despite the differences in macrostructure, the surface areas of the two samples were almost the same indicating similar microporous structures. Loss in porosity caused by heating the sample at 1273K for 333h is shown in Plate 3:M.

An S-shaped adsorption isotherm was obtained for titanium (IV) oxide (Hopkin and Williams) unlike the smooth curve found for γ -aluminium (III) oxide (Figure 3:25). The surface area ($6.4 \text{ m}^2 \text{ g}^{-1}$) is also much lower than for

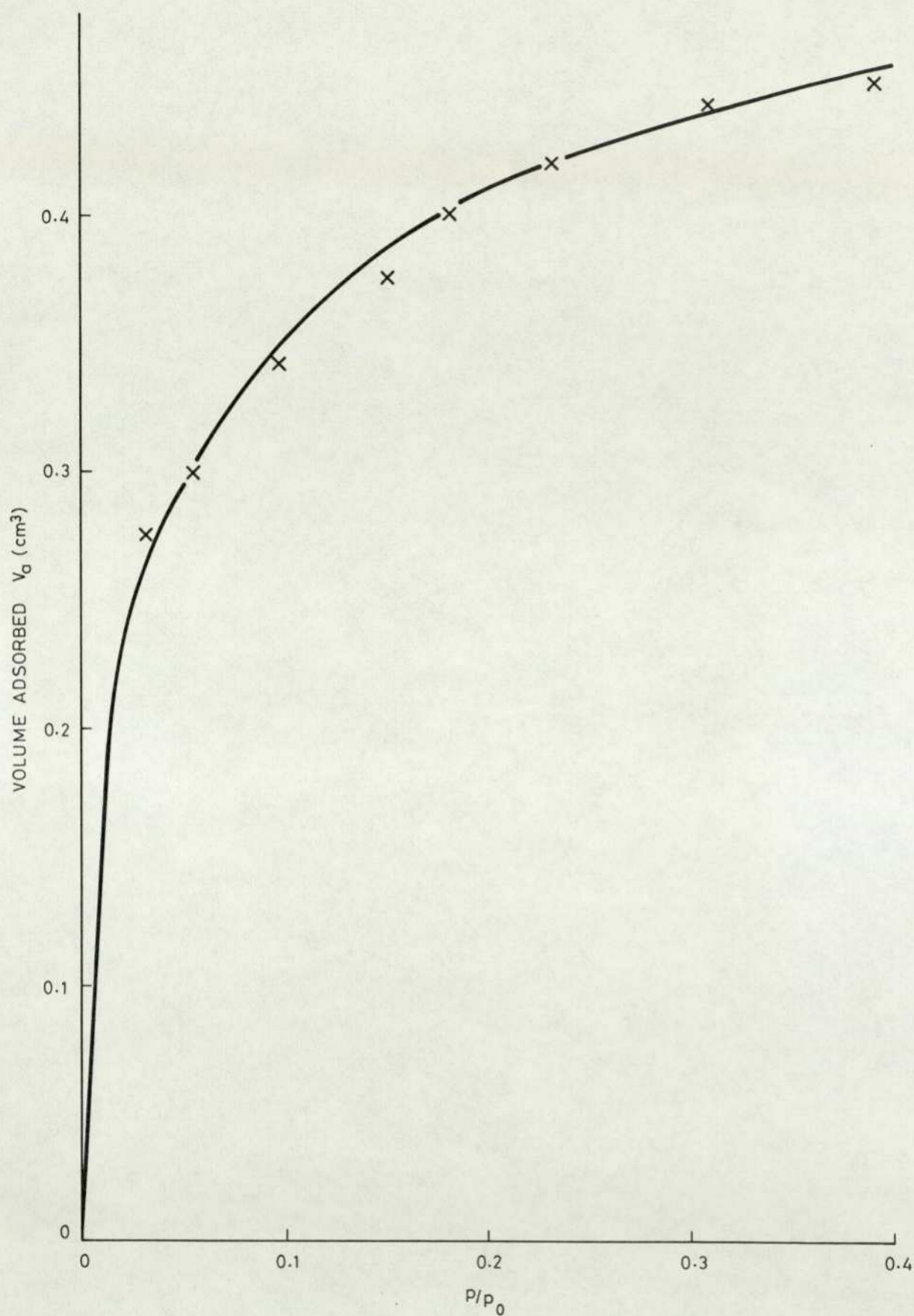


FIG. 3.25 ADSORPTION ISOTHERM FOR NITROGEN ON $\gamma\text{-Al}_2\text{O}_3$

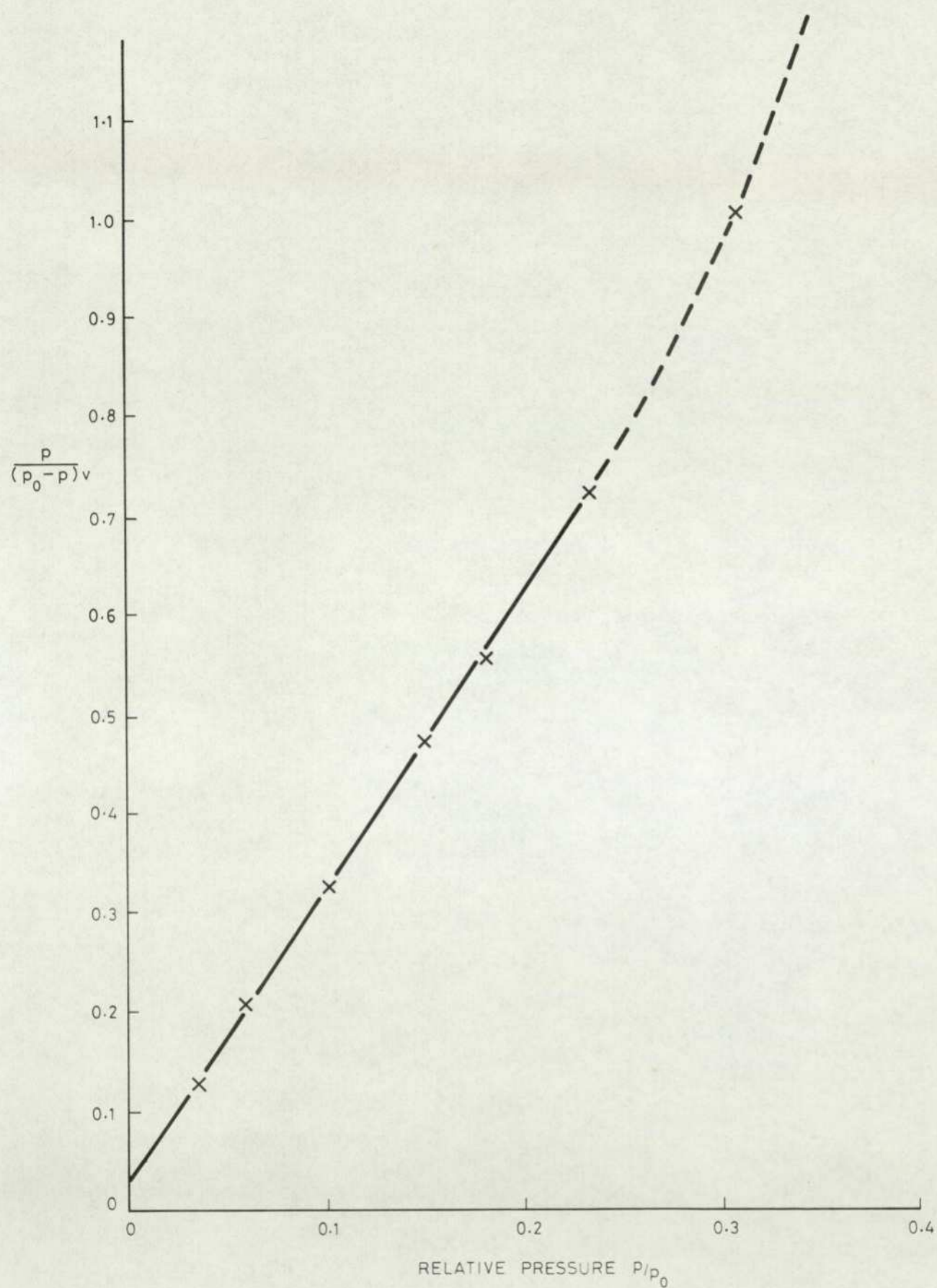


FIG. 3-26 B.E.T. PLOT CORRESPONDING TO ADSORPTION ISOTHERM IN FIG. 3-25

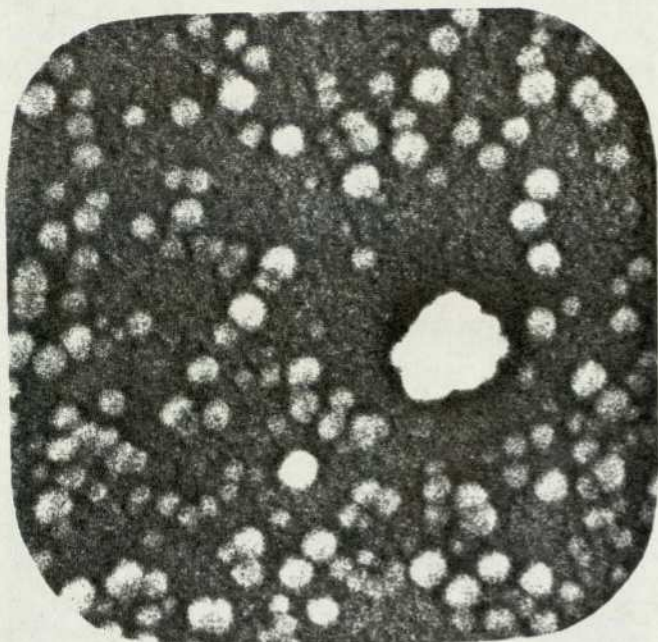


Plate 3:L.

Aluminium (III) oxide
 (from $\text{Al}_2(\text{NO}_3)_6 \cdot 9\text{H}_2\text{O}$)
 calcined at 773K for 72h.
 and 873K for 24h.
 x40,000.

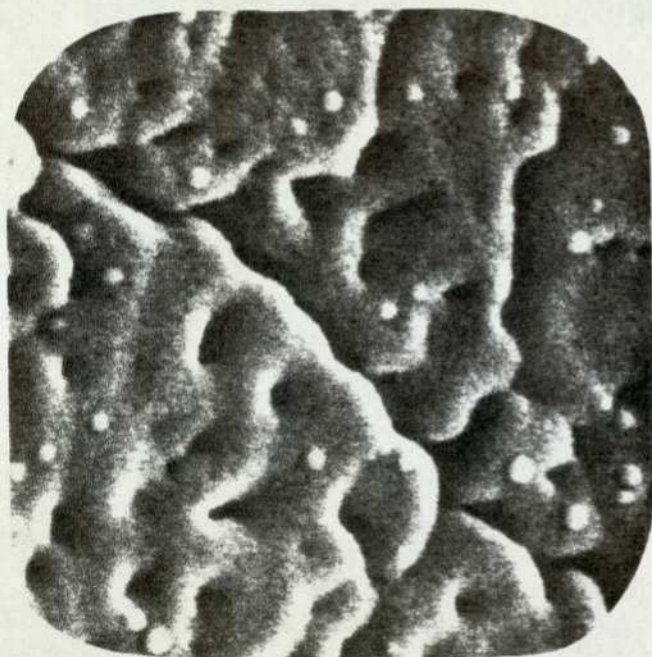


Plate 3:M.

Aluminium (III) oxide
 (from $\text{Al}_2(\text{NO}_3)_6 \cdot 9\text{H}_2\text{O}$)
 calcined at 1273K for
 323h.
 x40,000.

γ -aluminium (III) oxide. Heat treatment at 900K and 1100K caused a small decrease in the surface area, whereas at 1273K, the surface area declined sharply, reaching a plateau at around $2\text{m}^2\text{g}^{-1}$ after 5h of heating (Figure 3:27).

Electron microscopy revealed no microporous structure for the titanium (IV) oxide which may account for its low surface area compared with that of γ -aluminium (III) oxide. When TiO_2 was heated at the lower temperatures, the characteristic rounded particles, ca. 25 nm in diameter were unchanged as shown in Plate 3:N. Prolonged heating at 1273K, however, caused sintering and agglomeration of the crystallites with a subsequent reduction in the surface area (Plates 3:O,P).

The surface area of thorium (IV) oxide ($2.5\text{m}^2\text{g}^{-1}$) was lower than that of both titanium (IV) oxide and aluminium (III) oxide, although all three supports underwent a reduction in surface area on being heated above 1273K. Scanning electron microscopy revealed that thorium (IV) oxide, supplied by Hopkin and Williams Limited, had a flat featureless surface (Plate 3:Q), whilst that obtained from the decomposition of thorium (IV) nitrate contained massive fissures (Plate 3:R). These may have been formed as a result of disintegration of the microporous structure but their contribution to the surface area was small. No microporous structure was observed for either sample of thorium (IV) oxide at magnifications up to x40,000.

Finally, several hundred gas detectors in the form of microcalorimetric beads, prepared by coating a platinum coil

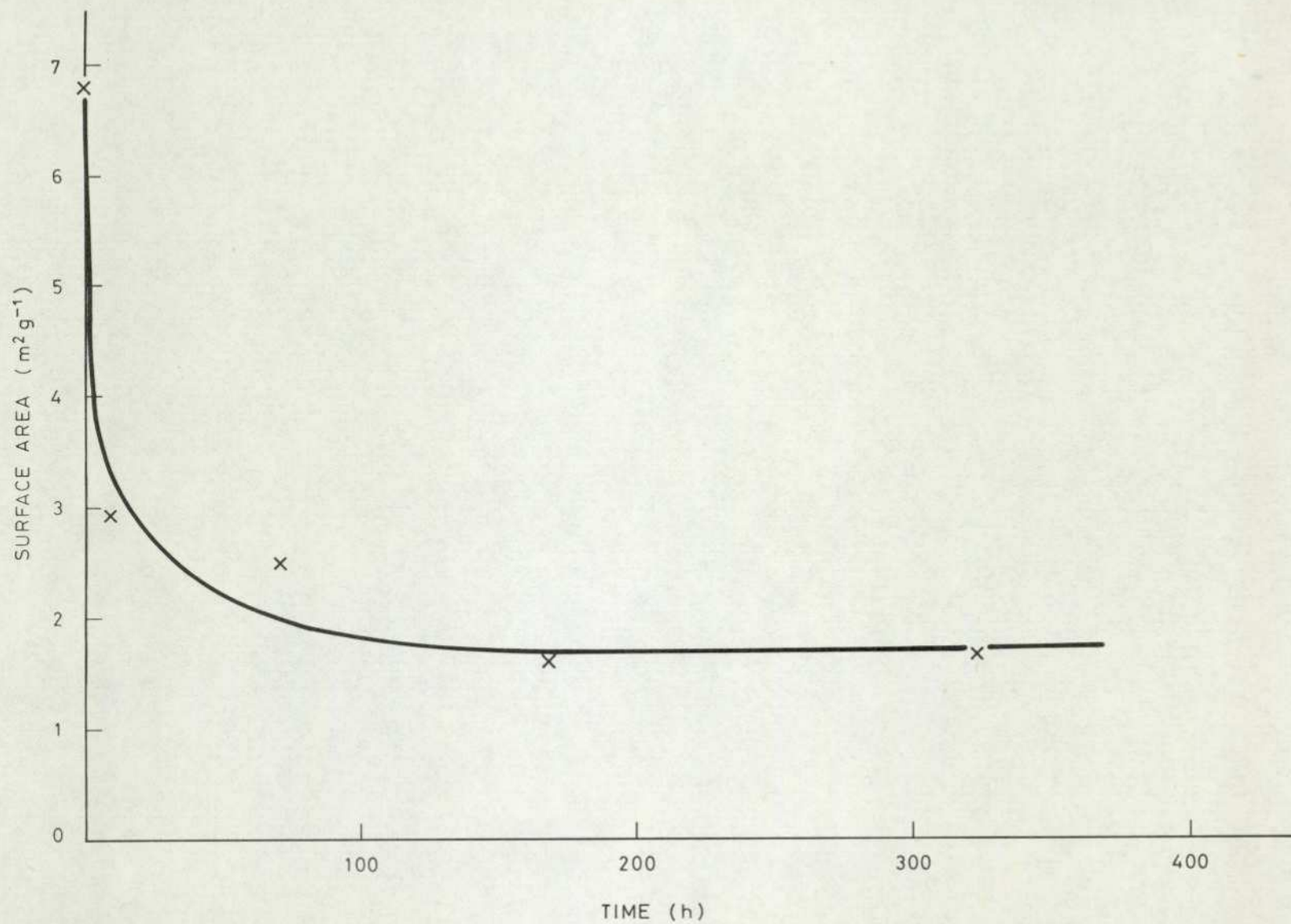


FIG.3.27 EFFECT OF HEAT TREATMENT ON THE SURFACE AREA OF TiO_2 (1273K)

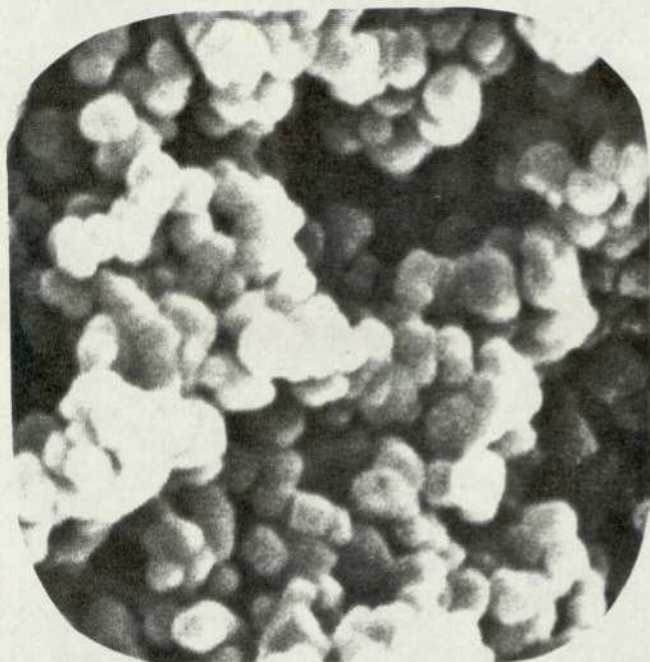


Plate 3:N.

Titanium (IV) oxide.

x40,000.

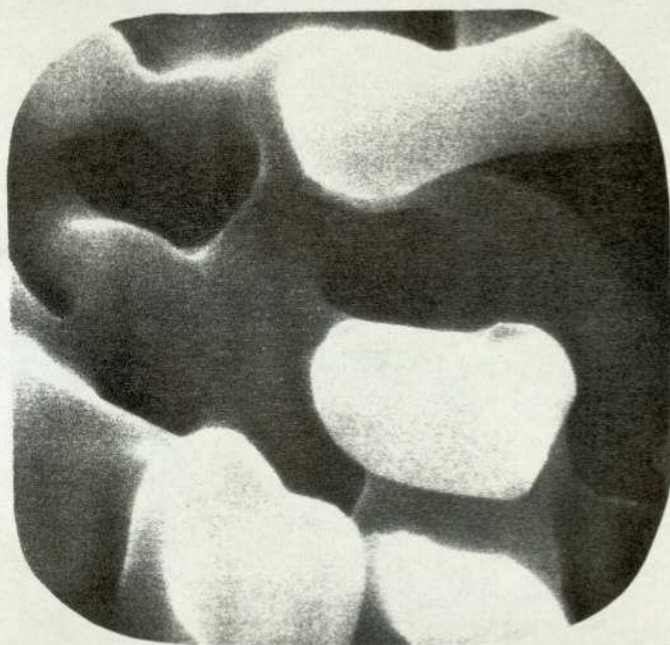


Plate 3:O.

Titanium (IV) oxide
calcined at 1273K for
178h.

x40,000.

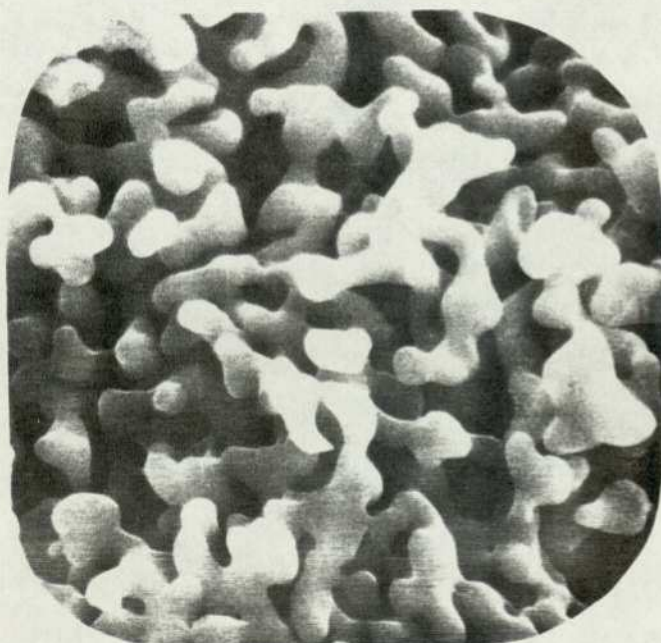


Plate 3:P.

Titanium (IV) oxide
calcined at 1273K for
178h.

x10,000.

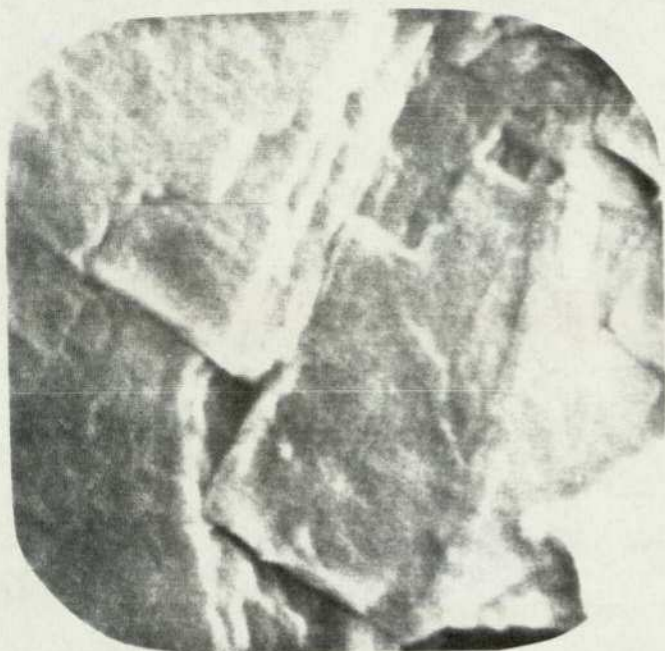


Plate 3:Q.

Thorium (IV) oxide.

x40,000.

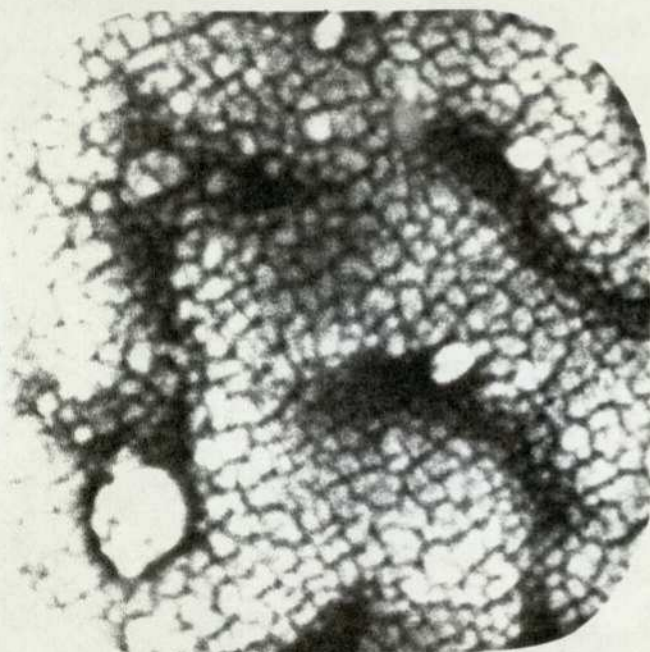


Plate 3:R.

Thorium (IV) oxide

(from $\text{Th}(\text{NO}_3)_4 \cdot 6\text{H}_2\text{O}$)

calcined at 1373K for

1h.

x40,000.

with aluminium (III) oxide, then thorium (IV) oxide and finally palladium, were examined in the continuous flow apparatus. The adsorption isotherm was similar to that obtained for γ -aluminium (III) oxide (B.D.H.). The specific surface area ($5.8 \text{ m}^2 \text{ g}^{-1}$) was considerably higher than that of thorium (IV) oxide calcined at 1373K for 1h, and it is probable that there is some contribution from the γ -aluminium (III) oxide which is incompletely covered by the thorium (IV) oxide.

3:8 Inhibition of methane oxidation over supported catalysts.

3:8:1 Effect of the products of reaction on heterogeneous methane oxidation.

At low temperatures, carbon dioxide and water were the major products of reaction. The effect of these compounds on methane oxidation was studied using a 2.7% Pd on $\gamma\text{-Al}_2\text{O}_3$ catalyst. Carbon dioxide ($0\text{--}4.0 \times 10^{-5} \text{ mol}$) was found to have little effect on the oxidation reaction; its ability to inhibit methane oxidation was no greater than that of an inert gas (Figure 3:28).

Water, on the other hand, had a temporary inhibiting effect on the catalyst (Figure 3:29). The degree of inhibition depended both on the amount of water passed through the catalyst and the length of time for which the catalyst was allowed to stand in flowing helium after exposure to the water vapour. To demonstrate the importance of the latter factor, a 2.7% Pd on $\gamma\text{-Al}_2\text{O}_3$ catalyst was exposed to a known amount of water ($2.8 \times 10^{-5} \text{ mol}$) at 625K

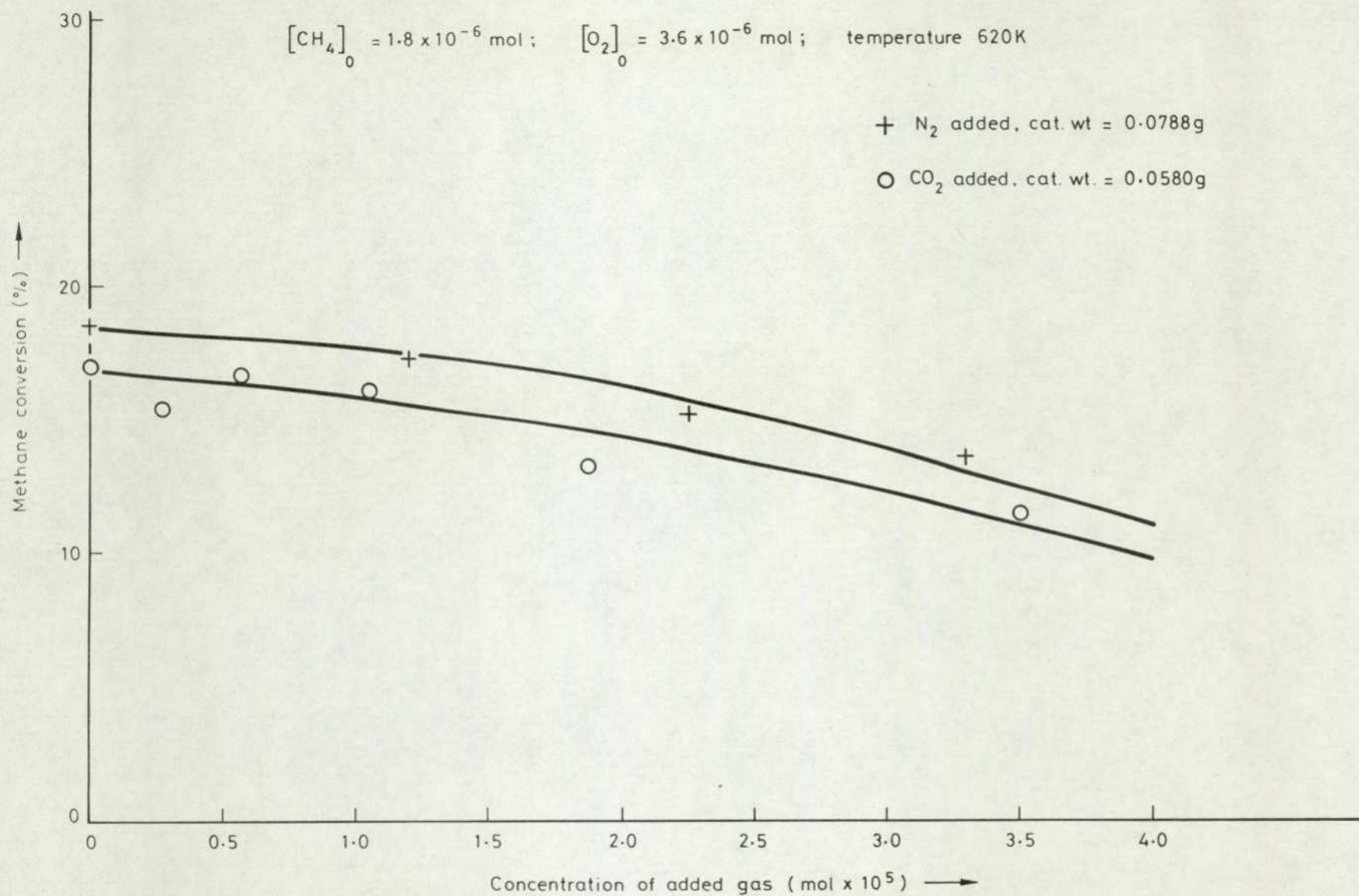


FIG.3.28 EFFECT OF A DILUENT GAS (N_2) AND CARBON DIOXIDE ON METHANE OXIDATION OVER 2.7% Pd ON $\gamma\text{-Al}_2\text{O}_3$

$[\text{CH}_4]_0 = 1.8 \times 10^{-6} \text{ mol}$; $[\text{O}_2]_0 = 3.6 \times 10^{-6} \text{ mol}$; Temperature = 625 K ; catalyst weight = 0.0735g ,

During recovery run, (+) catalyst exposed to successive aliquots of $2.78 \times 10^{-5} \text{ mol H}_2\text{O}$

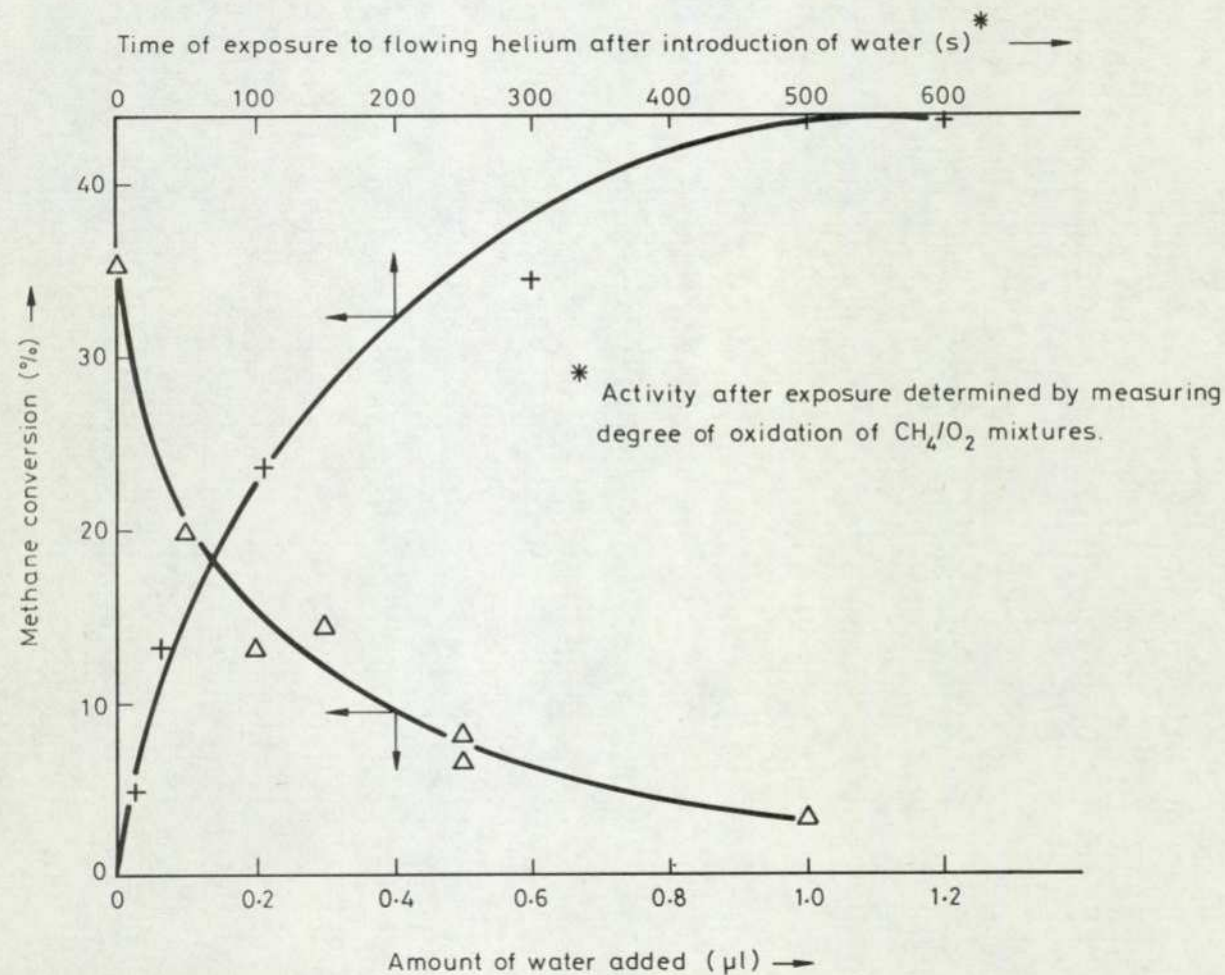


FIG.3.29 EFFECT OF WATER VAPOUR AND RECOVERY TIME ON METHANE OXIDATION OVER 2.7% Pd ON $\gamma\text{-Al}_2\text{O}_3$

and left in flowing helium at that temperature for a measured period of time. A pulse of methane/oxygen ($[\text{CH}_4]_0 = 1.8 \times 10^{-6}$ mol, $[\text{O}_2]_0 = 3.6 \times 10^{-6}$ mol) was then passed over the catalyst and the methane conversion was measured. The variation in methane conversion with the time during which the catalyst remained in flowing helium is also shown in Figure 3:29. When the catalyst was exposed to a smaller quantity of water typical of that present during methane oxidation (1.4×10^{-6} mol), inhibition at 625K was negligible. Introduction of four times that amount of water (5.6×10^{-6} mol), however, halved the catalytic activity and thirty times the amount (4.2×10^{-5} mol) almost totally inhibited oxidation.

3:8:2 Inhibition of methane oxidation by chlorinated hydrocarbons.

Results were obtained of the influence of some chlorinated hydrocarbons (dichloromethane, trichloromethane and 1,2-dichloroethane) on the oxidation of methane over supported palladium and platinum catalysts. Small amounts of inhibitor (1.63 – 13.6×10^{-8} mol) were mixed with the methane/oxygen mixtures ($[\text{CH}_4]_0 = 1.8 \times 10^{-6}$ mol; $[\text{O}_2]_0 = 3.6 \times 10^{-6}$ mol) and passed over an equilibrium catalyst, the uninhibited activity of which had already been determined. Recovery was attempted by removal of the inhibitor from the reactant mixture followed by successive pulses of the reactants through the catalyst at the same temperature as that used for the inhibition reaction. Lengthy periods during which the catalyst remained in flowing helium without exposure to reactants were used in case this treatment was responsible for

some recovery. In addition to the nature of the inhibitor, the extents of inhibition and of subsequent recovery depended on the temperature, the support, the concentration of the inhibitor and the nature of the precious metal used (Table 3:14).

The effect of temperature on the inhibition is shown in Figure 3:30. High temperatures enhanced the activity of the catalyst but inhibition occurred more rapidly than at lower temperatures. Recovery, too, was more rapid at high temperatures. At 650K, a 2.7% Pd on $\gamma\text{-Al}_2\text{O}_3$ catalyst underwent no recovery, while at 730K the initial activity was almost re-established after the catalyst had been exposed to pulses of methane and oxygen at that temperature.

The nature of the support had a significant effect on the degree of deactivation of the precious metal (Figures 3:31, 3:32). For palladium catalysts both the rate of inhibition and the rate of recovery were affected by the support. 20% Pd on tin (IV) oxide showed high activity in the absence of inhibitors, but a rapid decrease in methane conversion was observed on exposure to chloroform, followed by a rapid recovery, even at 650K, when the chloroform was removed from the gas stream. Palladium on thorium (IV) oxide and on γ -aluminium (III) oxide underwent lower rates of deactivation with no recovery when the chloroform was removed. 2.7% Pd on titanium (IV) oxide was rapidly deactivated but showed some recovery at 650K.

The loading of the precious metal had little effect either

Catalyst/support	Inhibitor	Degree of inhibition $\frac{A_o - A_i}{A_o} \times 100\%$	Degree of recovery* $\frac{A_r - A_i}{A_o} \times 100\%$
2.7% Pd on $\gamma\text{-Al}_2\text{O}_3$	CHCl_3	90%	0%
2.7% Pd on $\gamma\text{-Al}_2\text{O}_3$	CH_2Cl_2	70%	15%
2.7% Pd on $\gamma\text{-Al}_2\text{O}_3$	$\text{CH}_2\text{ClCH}_2\text{Cl}$	60%	25%
2.7% Pd on $\gamma\text{-Al}_2\text{O}_3$	CH_2Br_2	70%	0%
2.7% Pt on $\gamma\text{-Al}_2\text{O}_3$	CHCl_3	50%	100%
2.7% Pt on $\gamma\text{-Al}_2\text{O}_3$	CH_2Br_2	30%	0%
2.7% Pd on TiO_2	CHCl_3	95%	25%
2.7% Pd on ThO_2	CHCl_3	100%	5%
2.7% Rh on TiO_2	CHCl_3	86%	15%
20% Pd on SnO_2	CHCl_3	95%	80%
20.6% Pd on $\text{SnO}_2\text{-Al}_2\text{O}_3$	CHCl_3	70%	0%
25% Pd on $\gamma\text{-Al}_2\text{O}_3$	CHCl_3	75%	0%
25% Pd on $\gamma\text{-Al}_2\text{O}_3$	CH_2Br_2	90%	0%

A_o = Initial activity. A_i = Inhibited activity.

A_r = Recovered activity.

* Recovery was attempted by passage of CH_4/O_2 pulses through the catalyst at 650K in flowing helium.

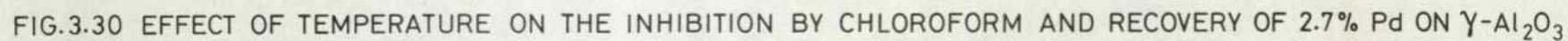
Catalyst weight = 0.05-0.08g.

$[\text{CH}_4]_o = 1.8 \times 10^{-6}$ mol.

$[\text{O}_2]_o = 3.6 \times 10^{-6}$ mol.

$[\text{Inhibitor}] = 1.36 \times 10^{-7}$ mol.

Table 3:14 The effect of inhibitors on methane oxidation over supported precious metal catalysts at 650K.



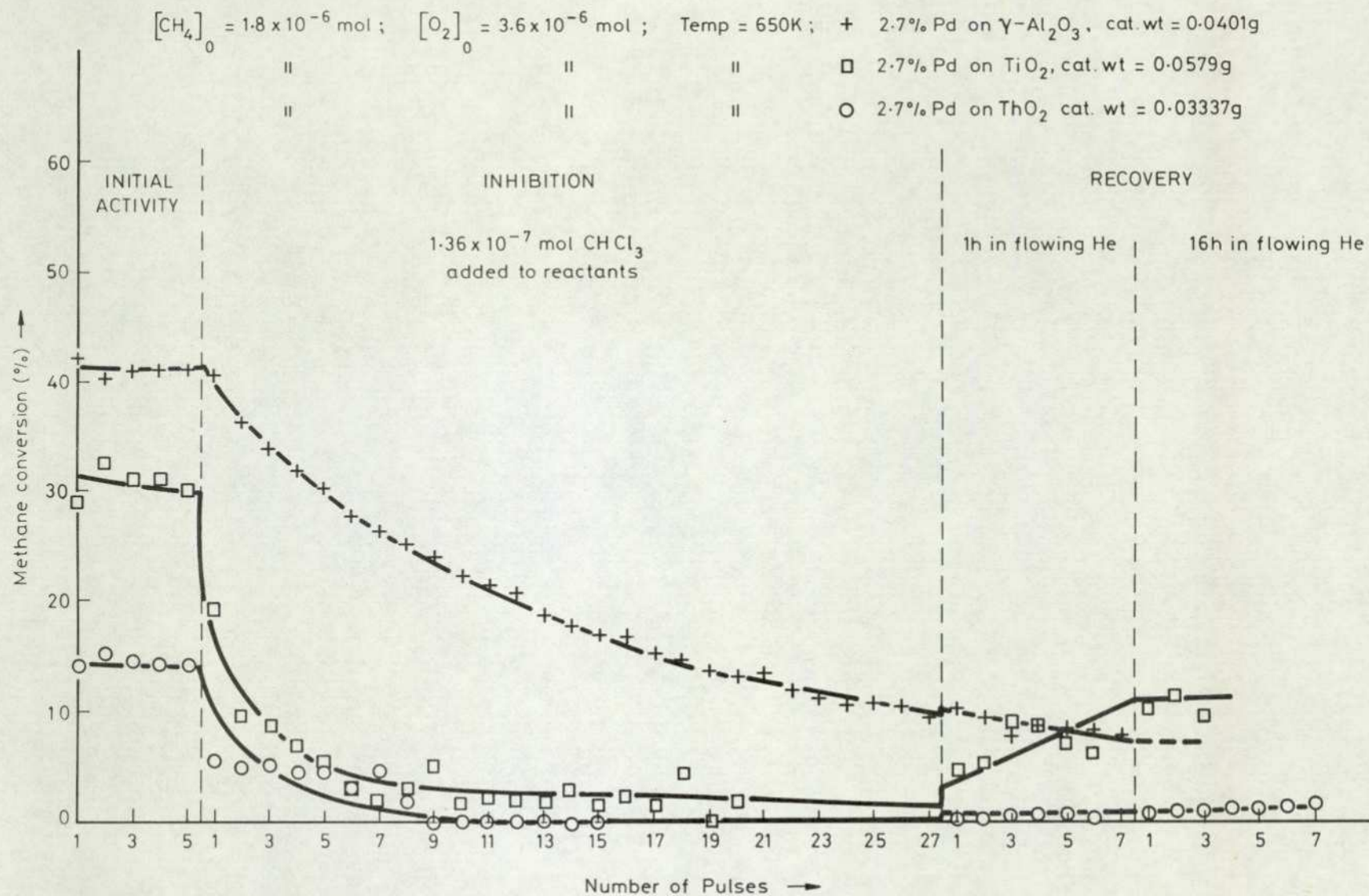
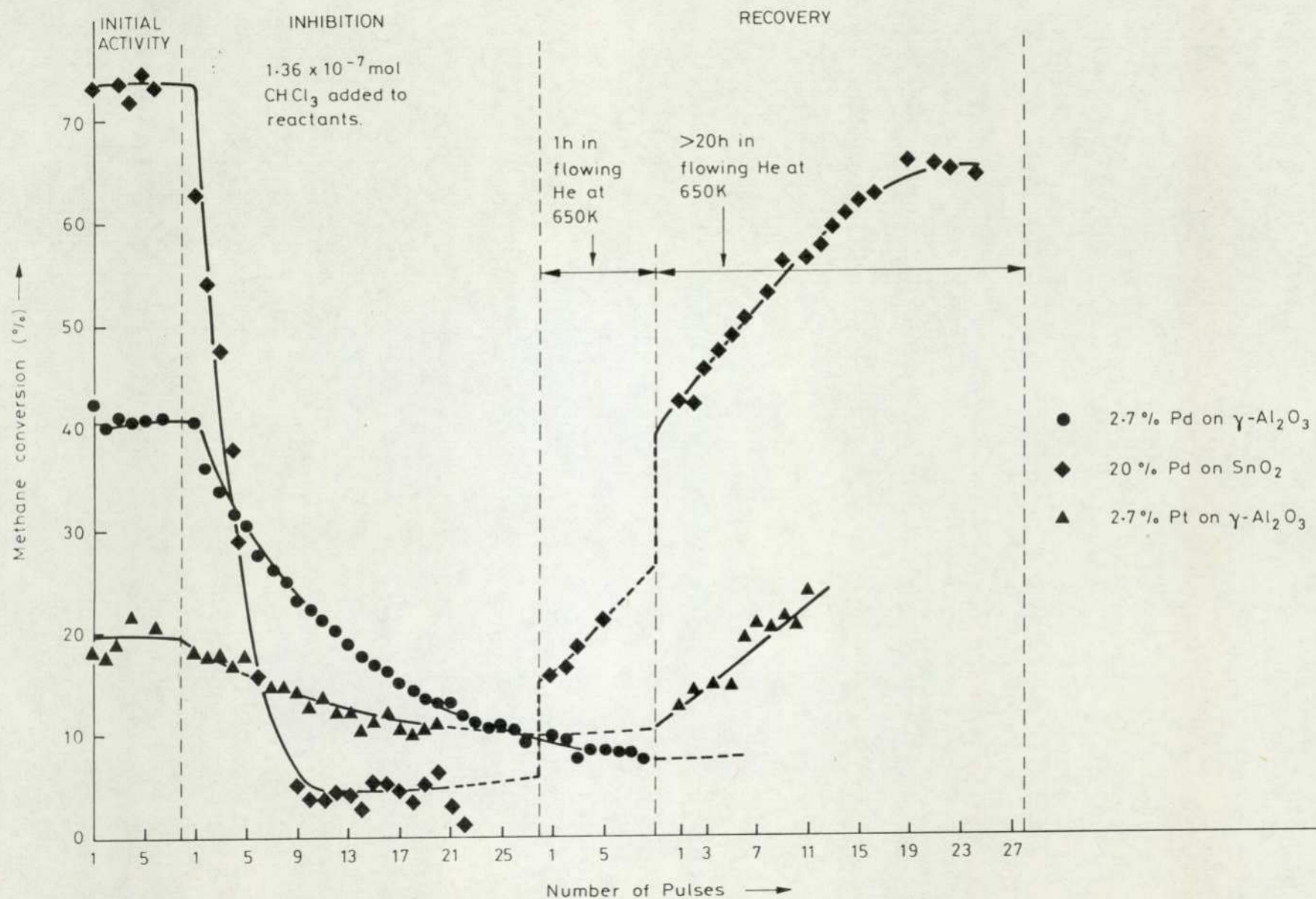


FIG.3.31 INHIBITION OF METHANE OXIDATION BY CHLOROFORM AND RECOVERY OF PALLADIUM CATALYSTS ON DIFFERENT SUPPORTS

FIG.3.32 THE INHIBITION BY CHLOROFORM AND RECOVERY OF SOME PALLADIUM CATALYSTS AT 650K

$$[\text{CH}_4]_0 = 1.8 \times 10^{-6} \text{ mol}; \quad [\text{O}_2]_0 = 3.6 \times 10^{-6} \text{ mol}; \quad \text{cat. volume} = 0.051 \text{ cm}^3$$

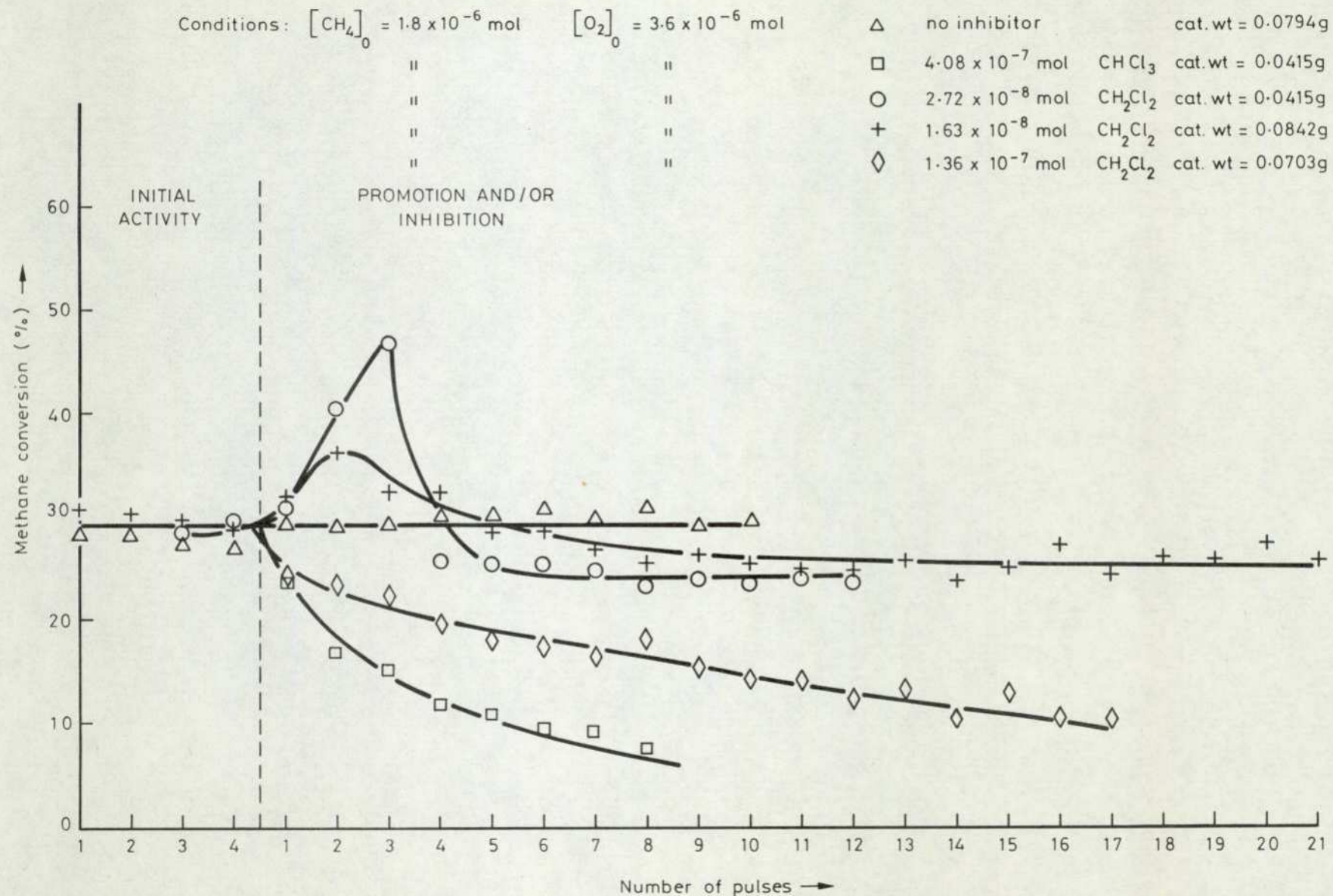


on the degree of inhibition or on the extent of recovery of the catalyst. From Table 3:14, however, it appears that trichloromethane caused a greater reduction in activity for 2.7% Pd on $\gamma\text{-Al}_2\text{O}_3$ catalysts than did dichloromethane and 1,2-dichloroethane. Furthermore, no recovery was observed for catalysts poisoned with trichloromethane, whereas some recovery occurred when the other chlorocarbons were used. Recovery was effected by allowing the catalyst to stand in flowing helium at 650K for several hours or by pulsing methane/oxygen mixtures ($[\text{CH}_4]_0 = 1.8 \times 10^{-6}$ mol; $[\text{O}_2]_0 = 3.6 \times 10^{-6}$ mol) through the catalyst. Recovery was more rapid when methane/oxygen mixtures were passed through the catalyst rather than helium alone.

Platinum catalysts were more resistant than palladium catalysts to inhibition by chlorinated hydrocarbons. From Figure 3:32 it can be seen that for supported platinum catalysts, slow inhibition was followed by rapid recovery, whereas for γ -aluminium (III) oxide-supported palladium, rapid deactivation occurred with little or no recovery.

Exposure of a 2.7% Pd on $\gamma\text{-Al}_2\text{O}_3$ catalyst to dichloromethane at low concentrations at first increased the activity for methane oxidation (Figure 3:33). This occurred for the first few pulses only, inhibition then replacing this initial rise in activity. This promotion was not found at high inhibitor concentrations where the activity declined rapidly and continuously. The higher the concentration of inhibitor, the more rapid the decline in activity. A low concentration of dichloromethane (1.63×10^{-8} mol) caused a loss in activity of only 5%.

FIG.3.33 EFFECT OF CONCENTRATION OF INHIBITOR ON METHANE OVER 2.7% Pd (W/W) ON γ - Al_2O_3 AT 650K



Oxidation of dichloromethane (2×10^{-5} mol) was carried out at 675K over a 2.7% Pd on $\gamma\text{-Al}_2\text{O}_3$ catalyst that had been previously exposed to oxygen at high temperatures. Water, carbon monoxide and carbon dioxide were the only products detected. Subsequent injection of oxygen through the catalyst at 675K produced carbon dioxide, indicating the presence of carbonaceous residues on the surface. Hence, of the total dichloromethane passed through the catalyst, 25% was converted to oxides of carbon, 25% was converted to recoverable carbonaceous residue and the remainder was adsorbed irreversibly on the catalyst surface. Measurements of the inhibition of methane oxidation by halocarbons were always based on methane consumption rather than carbon dioxide production because the carbon dioxide produced by halocarbon oxidation was indistinguishable from that produced by methane oxidation.

3:8:3 Inhibition of methane oxidation by brominated hydrocarbons.

The inhibition of methane oxidation over supported palladium catalysts by brominated hydrocarbons showed some similarities to that caused by chlorinated hydrocarbons. There were, however, some significant differences.

The results (Figures 3:34, 3:35 and 3:36) showed that inhibition by brominated hydrocarbons was irreversible, even exposure to temperatures as high as 730K not effecting recovery (whereas after inhibition by chlorinated hydrocarbons, exposure to methane/oxygen pulses at 730K brought about almost complete recovery (Section 3:8:2)). The loss in activity at

FIG.3.34 THE INHIBITION OF METHANE OXIDATION BY SOME HALOGENATED HYDROCARBONS AND THE RECOVERY OF
2.7% Pd ON γ - Al_2O_3

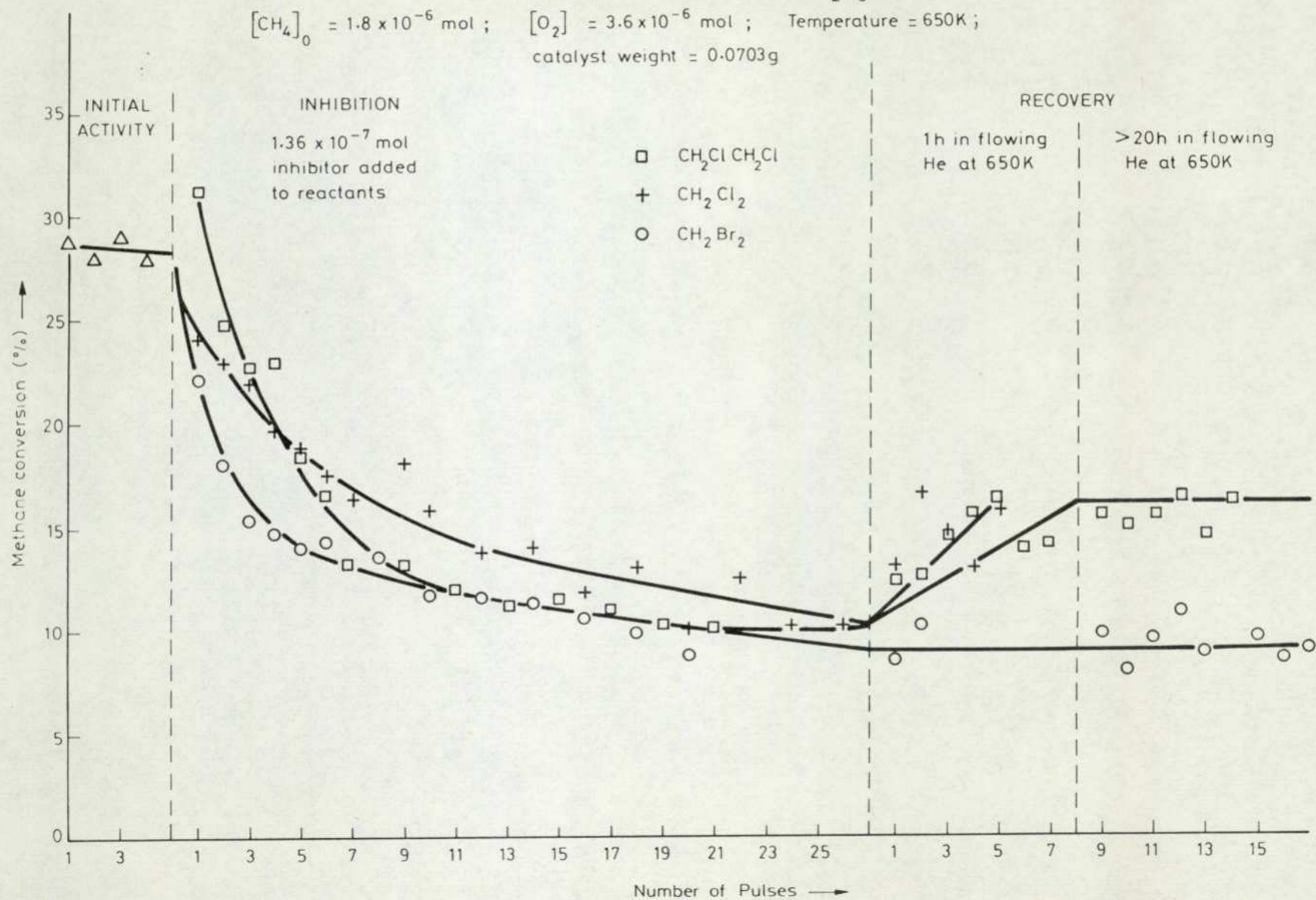
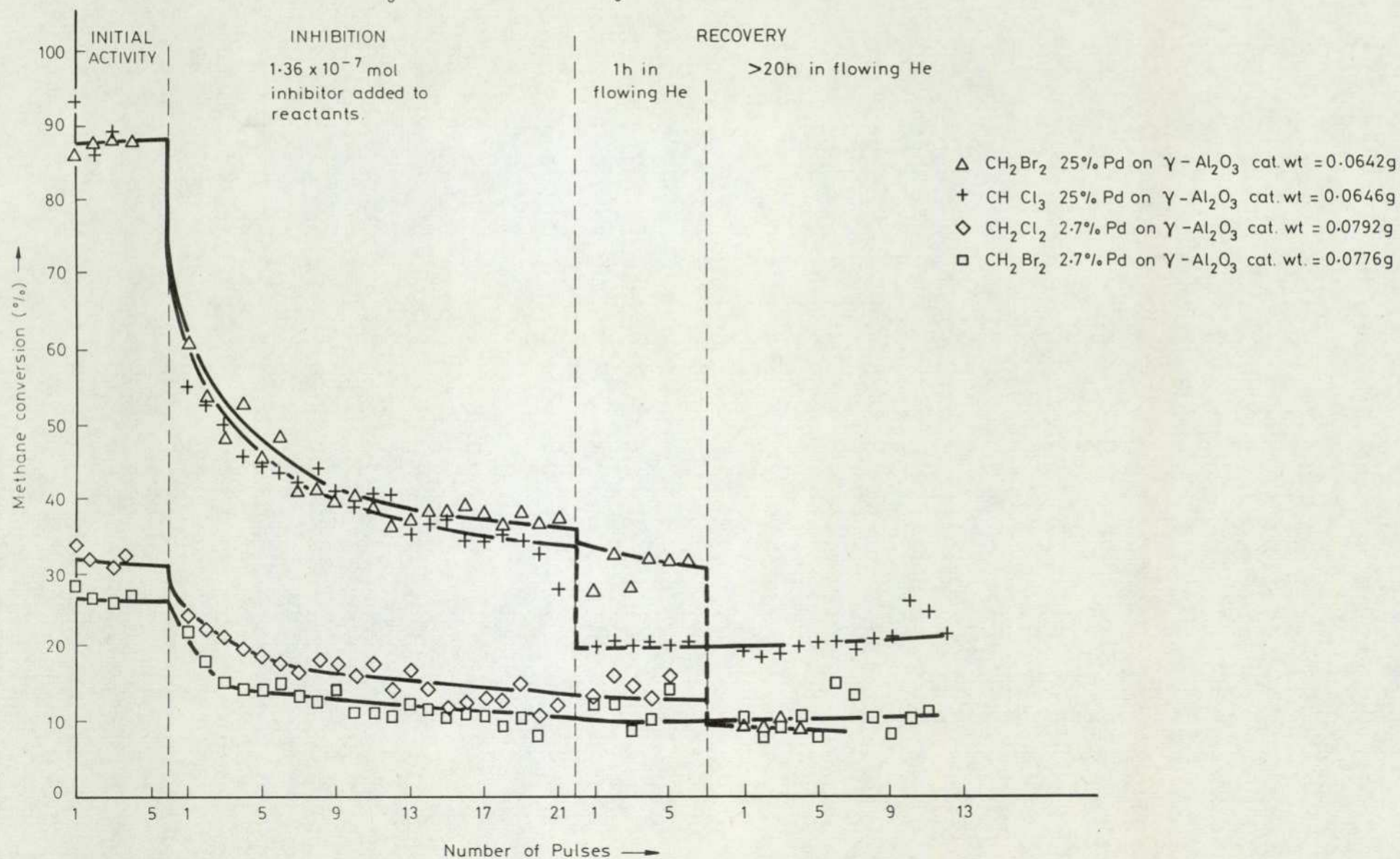


FIG.3.35 THE INHIBITION OF METHANE OXIDATION BY VARIOUS HALOGENATED HYDROCARBONS AND THE RECOVERY OF PALLADIUM ON ALUMINA CATALYSTS

$$[\text{CH}_4]_0 = 1.8 \times 10^{-6} \text{ mol}; \quad [\text{O}_2]_0 = 3.6 \times 10^{-6} \text{ mol}; \quad \text{Temperature} = 650 \text{ K}$$



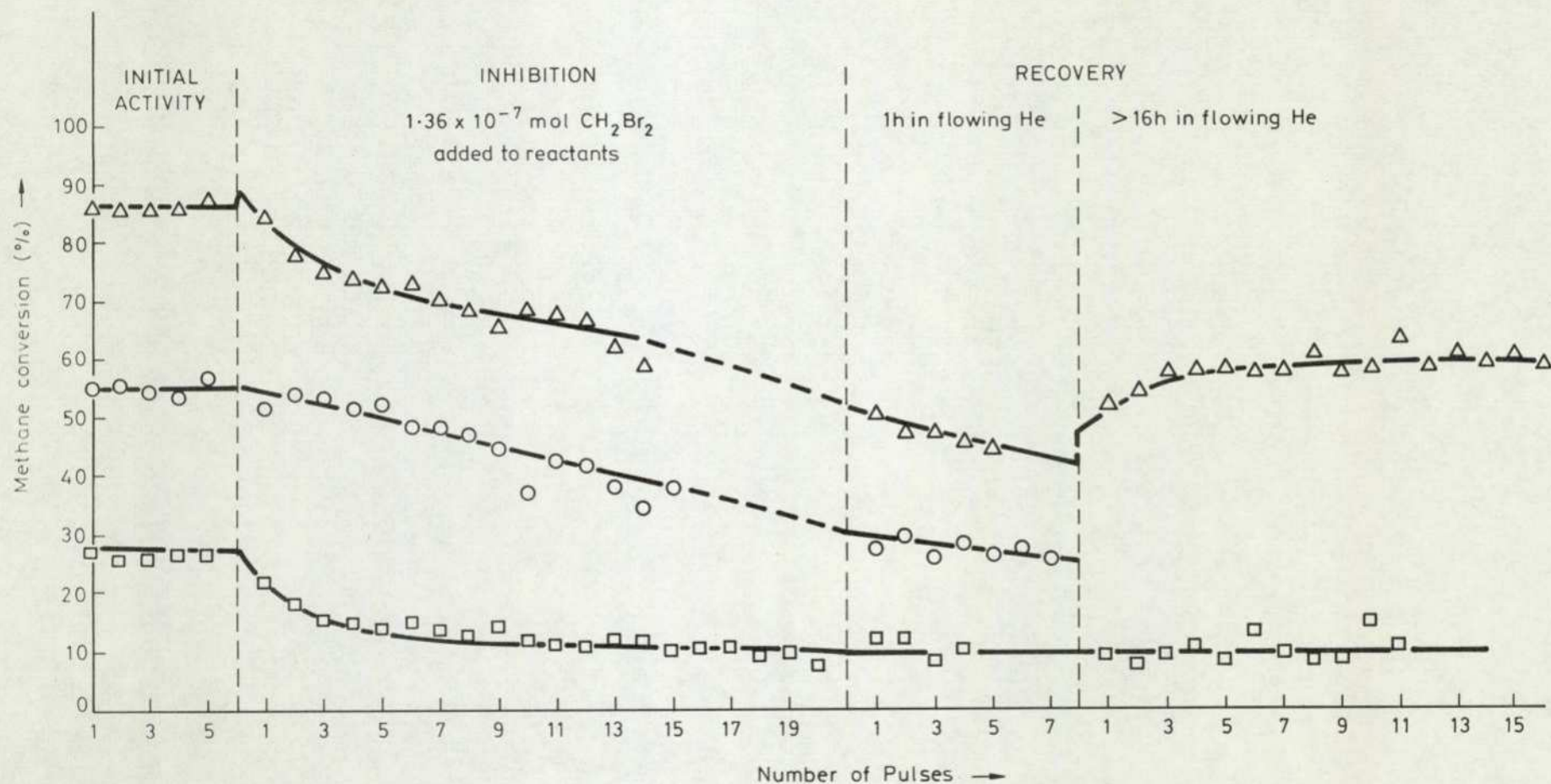


FIG.3.36 EFFECT OF TEMPERATURE ON THE INHIBITION BY DIBROMOMETHANE AND RECOVERY OF 2.7% Pd ON γ - Al_2O_3

low concentrations of dibromomethane was also more severe than for chloroform and dichloromethane (Figure 3:33).

3:8:4 Inhibition of methane oxidation over powdered catalysts by hexamethyldisiloxane.

A 2.7% Pd on $\gamma\text{-Al}_2\text{O}_3$ catalyst showed a rapid loss in activity when hexamethyldisiloxane (2.20×10^{-6} mol/pulse) was introduced into the methane/oxygen reactant mixture ($[\text{O}_2]_0 = 3.6 \times 10^{-6}$ mol, $[\text{CH}_4]_0 = 1.8 \times 10^{-6}$ mol). The results are given in Figure 3:37. The activity dropped to zero after nine pulses of inhibitor had been passed through the catalyst at 650K, over half the initial activity being lost in the first pulse. On removal of the inhibitor from the gas mixture, significant recovery of the activity for methane oxidation occurred which was accelerated by pulses of methane and oxygen through the catalyst. The shape of the deactivation and recovery curves are similar to those obtained for chlorinated hydrocarbons on supported palladium catalysts (Section 3:8:2).

A study of the thermal degradation of hexamethyldisiloxane was undertaken over a range of temperatures both in the absence and in the presence of a palladium catalyst. In both cases, methane was produced as a reaction product. In an empty silica reactor tube and in the absence of oxygen, methane was produced from the pyrolysis of hexamethyldisiloxane at temperatures above 900K and a white viscous liquid was deposited on the walls of the tube. This liquid probably consisted of polydimethylsiloxanes formed at these temperatures by polymerisation of hexamethyldisiloxane with accompanying

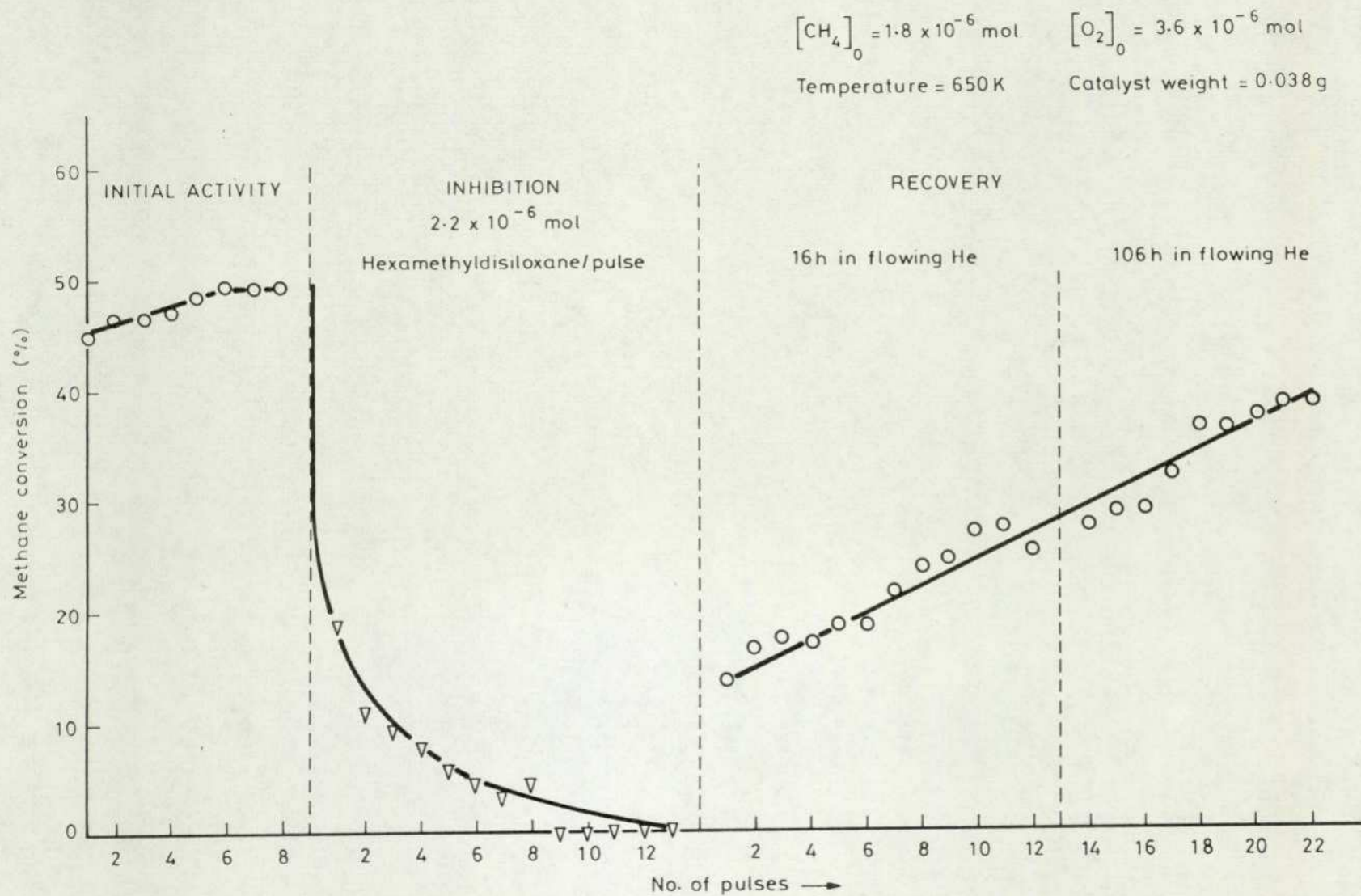


FIG. 3.37 INHIBITION OF METHANE OXIDATION OVER 2.7% Pd ON $\gamma\text{-Al}_2\text{O}_3$ BY HEXAMETHYLDISILOXANE

loss of methane (Kuz'minskii, Goldovskii, Dudenkova, Sunita and Orlov, 1965). With a 2.7% Pd on $\gamma\text{-Al}_2\text{O}_3$ catalyst and in the presence of oxygen, hexamethyldisiloxane decomposed to produce methane at temperatures above 500K, reaching a peak in production at 630K but falling to near zero at 725K. In addition, oxidation products such as carbon dioxide and carbon monoxide were observed. Carbon dioxide was produced at 625K, while carbon monoxide became the predominant product above 700K. The 2.7% Pd on $\gamma\text{-Al}_2\text{O}_3$ catalyst (weight 0.042g) was exposed to hexamethyldisiloxane (1.07×10^{-8} mol) in oxygen (3.23×10^{-6} mol).

3:8:5 Inhibition and poisoning of hydrocarbon oxidation over catalytic beads by hexamethyldisiloxane.

The effect of low concentrations of hexamethyldisiloxane on oxidation reactions was also studied using microcalorimetric beads. The beads (a minimum of four were used for each experiment) were first exposed to a butane/oxygen/nitrogen mixture for a period of time (usually ca. 1h) in a static reactor (volume = 10 l) and then exposed to a methane/oxygen/nitrogen mixture for a similar period. The initial activities for the oxidation of each gas mixture by the beads were measured as the difference in voltage output obtained across the beads (Table 3:15 and Figure 3:38). Exposure to hexamethyldisiloxane in methane/oxygen mixtures caused a drop in activity, the rate of which was dependent on the concentration of the inhibitor. Use of polydimethylsiloxane $((\text{CH}_3)_3\text{Si}[\text{O}-\text{Si}(\text{CH}_3)_2]_n-\text{O}-\text{Si}(\text{CH}_3)_3$ where $n = 2$ or 3) at the same concentration as hexamethyldisiloxane caused a similar loss in activity.

Catalyst poison	Concentration of poison (mg m ⁻³)	t ₅₀ (min)	t ₇₅ (min)	Recovery towards CH ₄ oxidn.	Recovery towards n-C ₄ H ₁₀ oxidn.
Hexamethyldi-siloxane	282	$\frac{1}{2}$	$\frac{1}{2}$	None	None
Hexamethyldi-siloxane	113	1	2	None	50%
Hexamethyldi-siloxane	23	5.3	14	None	100%
Polydimethyl-siloxane*	38	5	11	None	95%

* polydimethylsiloxane $(\text{CH}_3)_3\text{Si}-[\text{O}-\text{Si}(\text{CH}_3)_2]_n-\text{O}-\text{Si}(\text{CH}_3)_3$
where n = 2-3 (mainly 2).

t₅₀ = time taken for activity towards methane oxidation to drop by 50%.

t₇₅ = time taken for activity towards methane oxidation to drop by 75%.

Table 3:15 The effect of siloxanes on methane oxidation over catalytic beads.

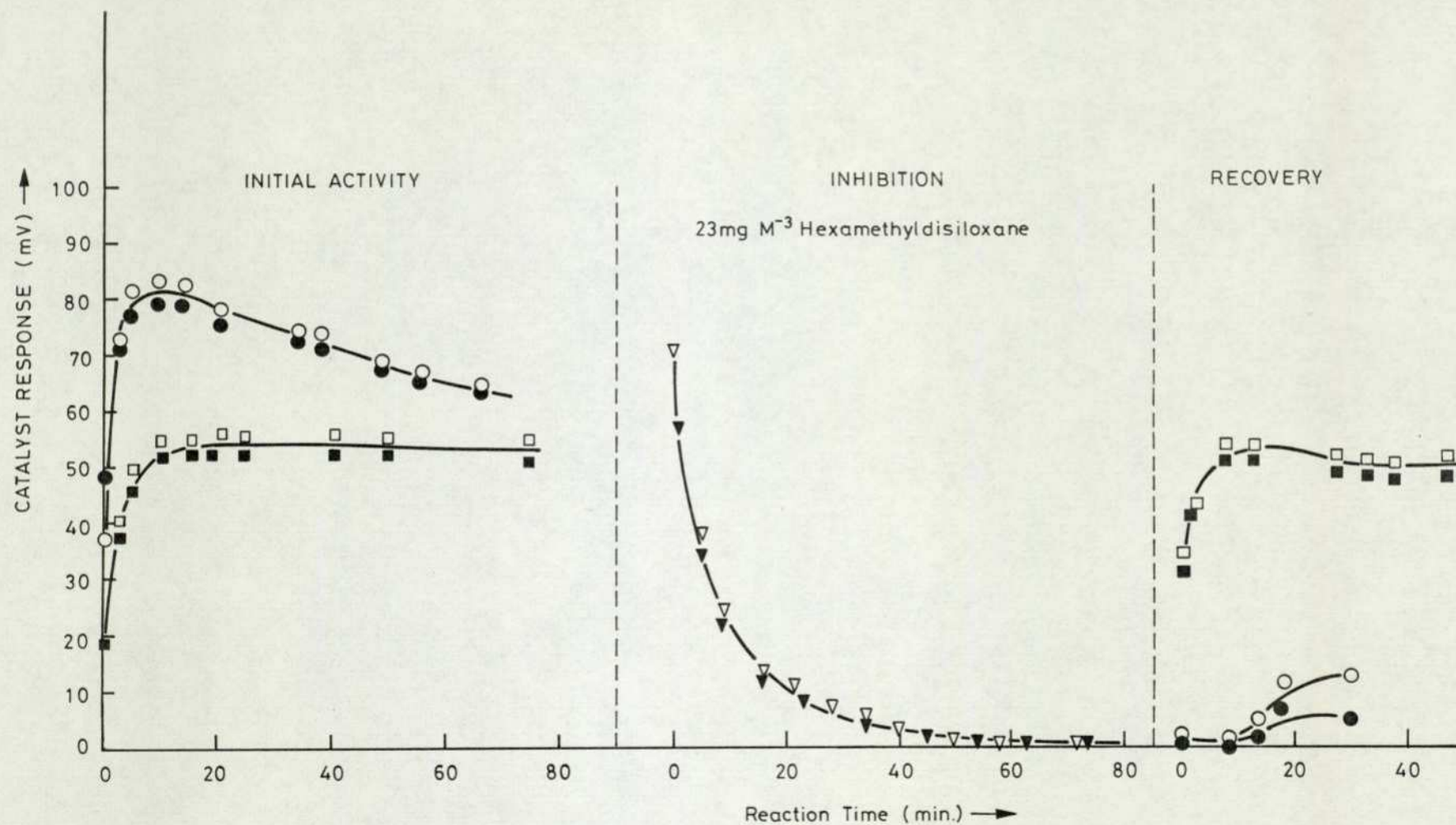


FIG. 3.38 INHIBITION OF HYDROCARBON OXIDATION BY HEXAMETHYLDISILOXANE OVER A CATALYTIC BEAD (Pd ON ThO₂/Al₂O₃)

Legend for Figure 3:38.

o, • PP_{O_2} = 156 Torr.

PP_{CH_4} = 19 Torr.

PP_{N_2} = 585 Torr.

∇, ▼ PP_{O_2} = 156 Torr.

PP_{CH_4} = 19 Torr.

PP_{N_2} = 585 Torr.

PP_{HMDS} = 0.0015 Torr.

□, ■ PP_{O_2} = 158 Torr.

$PP_{C_4H_{10}}$ = 5.7 Torr.

PP_{N_2} = 596 Torr.

Removal of the siloxane and introduction of methane-oxygen or butane-oxygen mixtures provided a measure of the ability of the catalyst to recover. Irreversible poisoning for methane oxidation was nearly always found, whereas in some cases there was total recovery with regard to butane oxidation.

3:9 Physicochemical studies of poisoned catalysts.

3:9:1 Transmission electron microscopy.

Particle size histograms were obtained from transmission electron micrographs for palladium and platinum on γ -aluminium (III) oxide and for rhodium on titanium (IV) oxide catalysts both before and after their exposure to inhibitors. The effect of trichloromethane on the palladium particle size can be seen in Figures 3:39 (a) and (b). Included in the diagram is a catalyst that had been conditioned in helium only. The palladium particle size increases after exposure to methane and oxygen at 750K (catalyst E0). This is to be expected, for oxygen at high temperatures has been found to cause an increase in palladium particle size (Section 3:6).

Exposure to trichloromethane (for catalysts EL, EP, EQ, EJ and EK) resulted in a shift in the palladium particle size. The number of particles with diameters of between 5 and 15 nm decreased, while there was a corresponding increase in the 25 to 35 nm range. The effect of the temperature at which the catalyst was exposed to trichloromethane vapour was negligible, and catalyst EK (730K)

FIG.3.39 (a) INFLUENCE OF EXPOSURE TO CHLOROFORM ON THE PARTICLE SIZE DISTRIBUTION OF 2.7%.(W/W) Pd ON γ -Al₂O₃ CATALYST

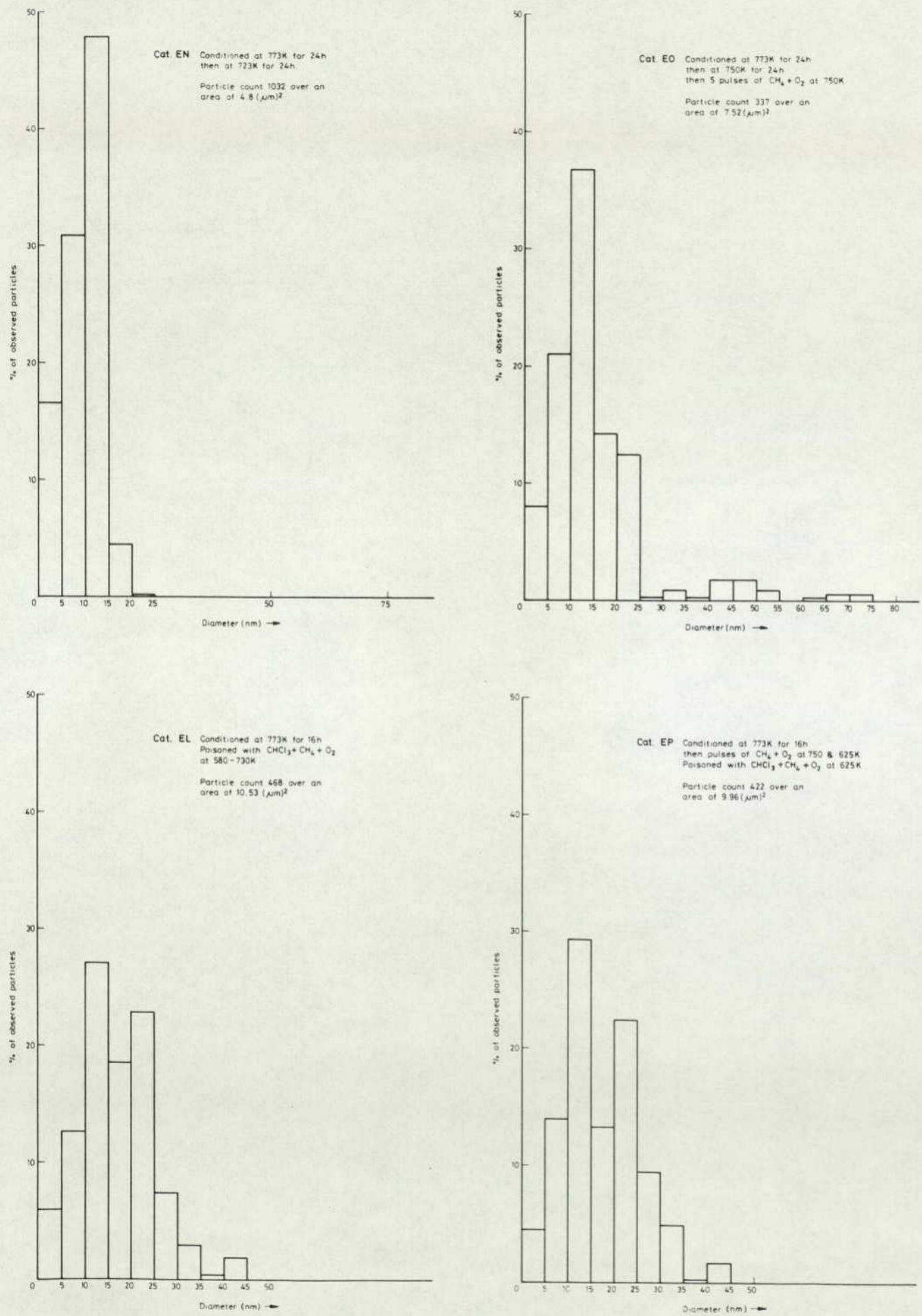
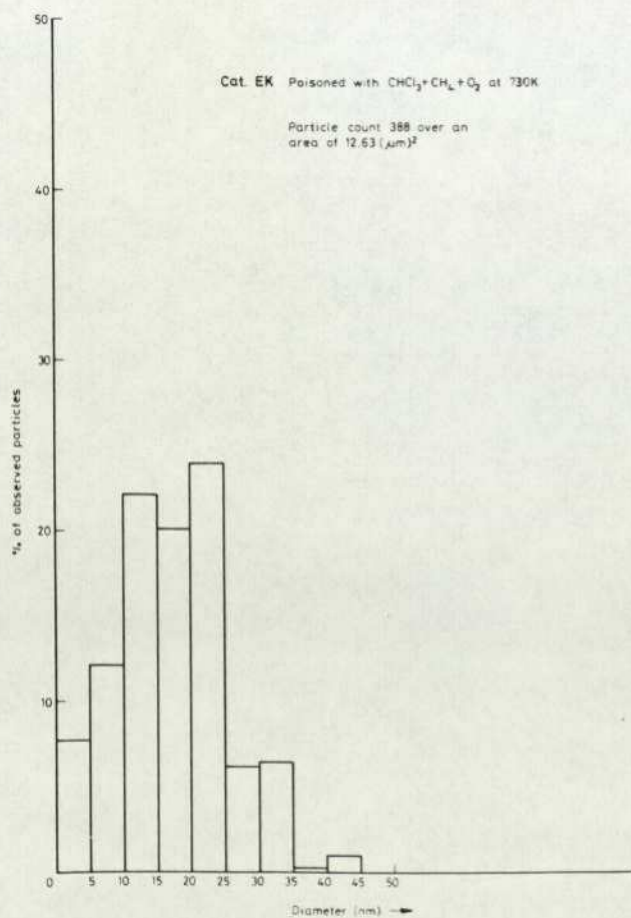
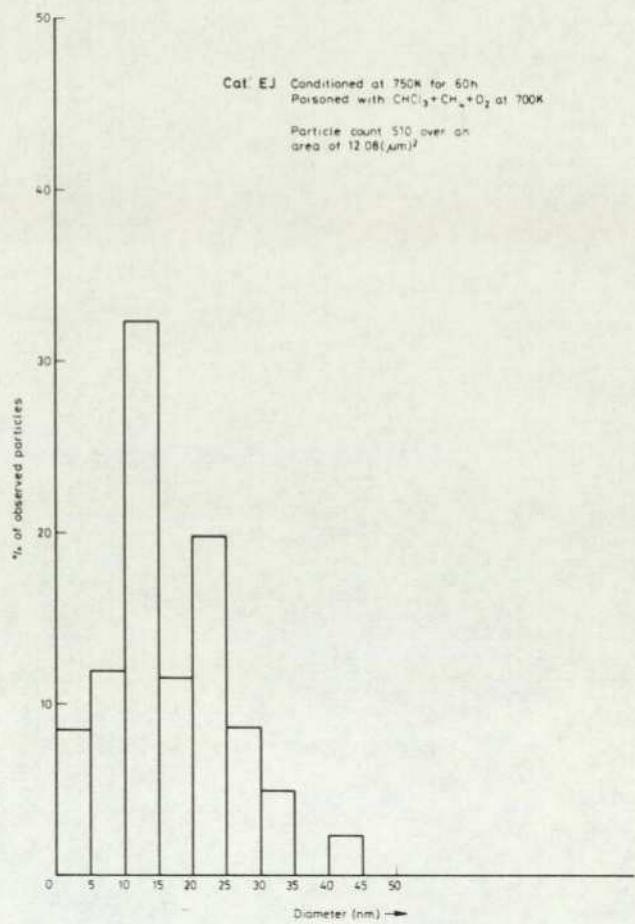
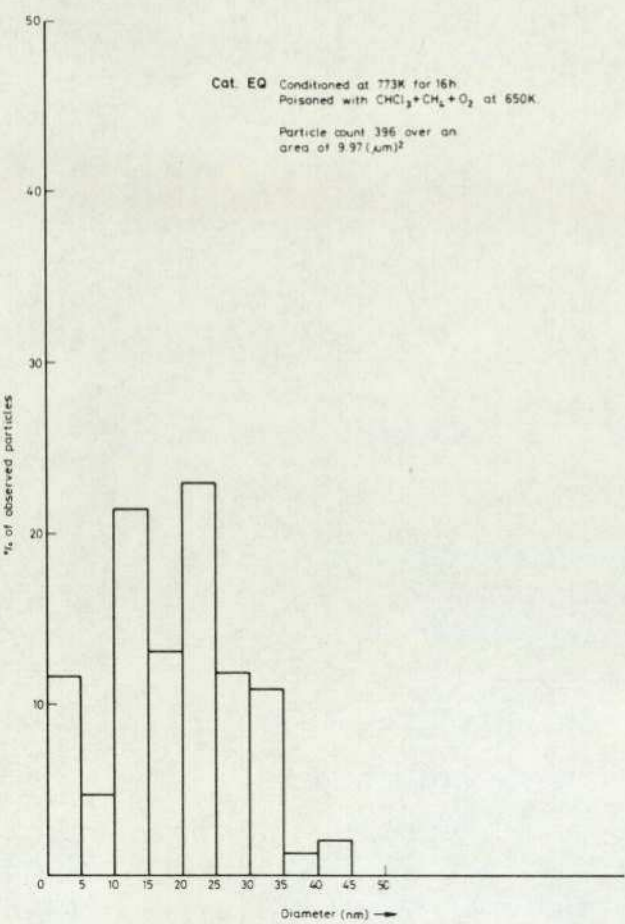


FIG. 3.39 (b)



contained particles of similar diameter to those of catalyst EP (625K).

The results obtained with a 2.7% Rh on TiO_2 catalyst are shown in Figure 3:40. Evidence for the growth of particles with diameters of 6 nm and above for the inhibited catalyst can be compared with the smaller diameters of the uncontaminated catalysts. This was not observed for the 2.7% Pt on $\gamma\text{-Al}_2\text{O}_3$ catalyst (Figure 3:41) where the halocarbon had an insignificant effect on particle size.

3:9:2 X-ray photoelectron spectroscopy.

Supported precious metal catalysts both exposed and unexposed to inhibitors, as well as the materials used for their preparation, were examined using X-ray photoelectron spectroscopy with aluminium K_α radiation as the X-ray source. Due to the insulating properties of the catalytic materials used, charging may occur on the sample surface causing shifts in the observed binding energies. To reduce errors in measurements due to charging, a reference line was used as an internal standard, from which other peaks were calculated. The reference line chosen was the $\text{O}_{1s_{1/2}}$ line at 532.0 eV. The $\text{C}_{1s_{1/2}}$ line was also present in all samples, even those not deliberately exposed to carbon-containing compounds, and may have represented atmospheric contamination. For that reason, it was considered unsuitable for use as a standard.

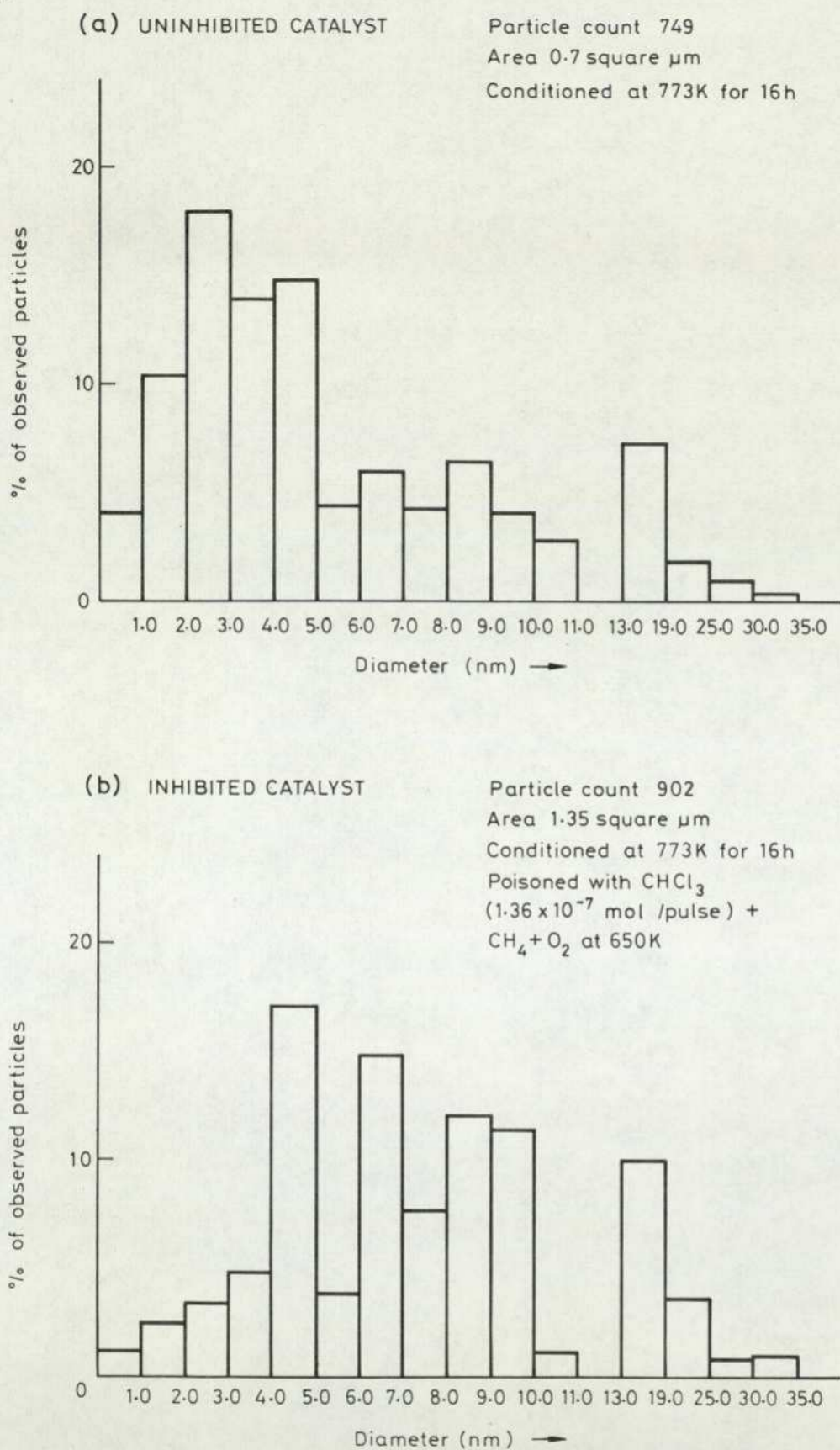


FIG.3.40 INFLUENCE OF EXPOSURE TO TRICHLOROMETHANE ON THE PARTICLE SIZE DISTRIBUTION OF 2.7% (w/w) Rh ON TiO_2 CATALYST

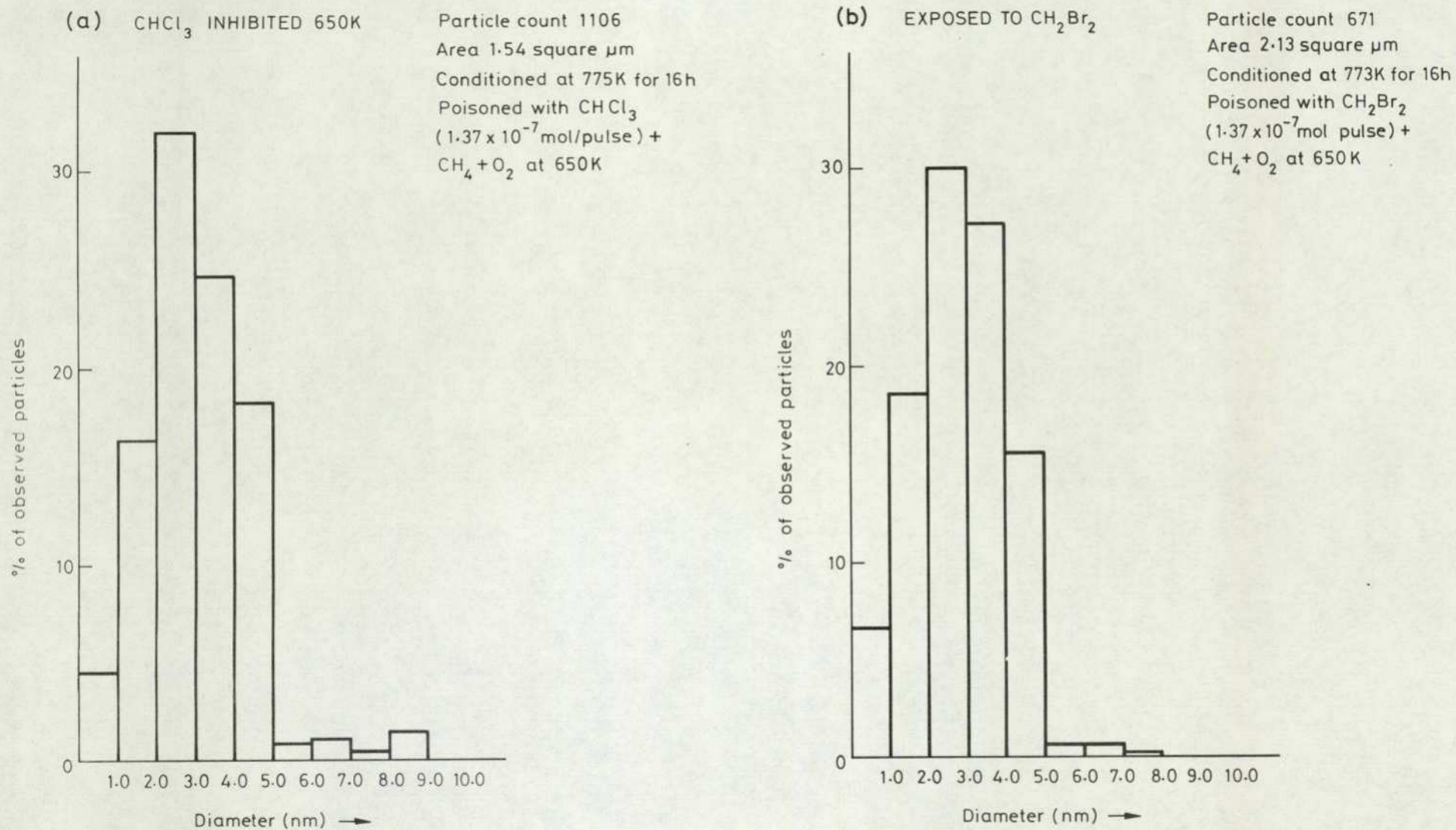


FIG.3.41 INFLUENCE OF EXPOSURE TO (a) TRICHLOROMETHANE AND (b) DIBROMOMETHANE ON THE PARTICLE SIZE DISTRIBUTION OF A 2.7% (W/W) Pt ON $\gamma\text{-Al}_2\text{O}_3$ CATALYST.

Peaks characteristic of the elements present on the surface of supported catalysts are shown in Table 3:16, together with those of standard samples. The palladium binding energies for both unsupported and supported palladium (II) oxide were ca. 3eV lower than those for pure palladium metal and hence information could be obtained concerning the oxidation state of the palladium. Examination of the $\text{Pd}_{3d_{3/2}}$ and $\text{Pd}_{3d_{5/2}}$ binding energies indicated that high loadings of palladium on titanium (IV) oxide (40% Pd on TiO_2) exhibited metallic character, while low loadings (2.7% Pd on TiO_2) contained palladium in the oxide form. This is to be expected for the larger palladium particles found at high loadings are more resistant to oxidation than are smaller, better dispersed particles at lower loadings. Exposure of a 2.7% Pd on $\gamma\text{-Al}_2\text{O}_3$ catalyst to methane-rich mixtures (reducing mixtures) shifted the palladium binding energies towards the values found for palladium metal.

Exposure of the catalysts to halocarbons caused some changes in the palladium and carbon binding energies on re-examination by XPS (Table 3:17). The $\text{C}_{1s_{1/2}}$ line had broadened and become a doublet. The carbon peak at the lower binding energy may be ascribed to carbon and carbon-halogen residues deposited on the catalyst during decomposition of the inhibitor. It was also found that samples of the catalysts deactivated by dichloromethane contained metallic palladium rather than the catalytically active palladium (II) oxide. This can be seen from the $\text{Pd}_{3d_{3/2}}$ and $\text{Pd}_{3d_{5/2}}$ electron binding energies which lie close to

Catalyst/compounds	Binding energies (eV)					
	$\text{Al}_{2p_{1/2,3/2}}$	$\text{Al}_{2s_{1/2}}$	$\text{C}_{1s_{1/2}}$	$\text{Pd}_{3d_{5/2}}$	$\text{Pd}_{3d_{3/2}}$	$\text{Cl}_{2p_{1/2,3/2}}$
Pd metal	-	-	284.5	335.1 ± 0.05	340.5 ± 0.05	-
Palladium (II) oxide	-	-	285.5	338.2 ± 0.05	343.6 ± 0.05	-
Palladium (II) chloride	-	-	284.3	337.3 ± 0.05	342.7 ± 0.05	199.5
$\text{Pd}(\text{NH}_3)_4\text{Cl}_2$	-	-	285.0	337.0 ± 0.1	343.3 ± 0.05	198.4
Al_2O_3	75.3	120.3	284.9	-	-	-
2.7% PdCl_2 on $\gamma\text{-Al}_2\text{O}_3$	-	-	284.9	337.3 ± 0.1	342.5 ± 0.1	199.3
2.7% Pd on $\gamma\text{-Al}_2\text{O}_3^*$	-	-	-	336.4	-	-
2.7% Pd on TiO_2	-	-	-	338.5 ± 0.1	343.9 ± 0.1	-
40% Pd on TiO_2	-	-	-	336.05 ± 0.05	341.05 ± 0.05	-
5.1% PdO on TiO_2	-	-	-	338.6	344.05	-
18.7% PdO on TiO_2	-	-	-	338.7	344.15	-

* Conditioned at 823K for 3h in flowing He then exposed to CH_4 -rich CH_4/O_2 pulses at 673K.

Table 3:16 Electron binding energies for a range of palladium catalysts, palladium compounds and catalyst supports.

Catalyst / compounds.	Binding energies (eV)					
	$\text{Al } 2p_{1/2,3/2}$	$\text{Al } 2s_{1/2}$	$\text{C } 1s_{1/2}$	$\text{Pd } 3d_{5/2}$	$\text{Pd } 3d_{3/2}$	$\text{Cl } 2p_{1/2,3/2}$
Palladium	-	-	284.5	335.1 ± 0.05	340.5 ± 0.05	-
Palladium (II) oxide	-	-	285.5	338.2 ± 0.05	343.6 ± 0.05	-
2.7% PdCl_2 on $\gamma\text{-Al}_2\text{O}_3$	-	-	284.9	337.3 ± 0.1	342.5 ± 0.1	199.3
2.7% Pd on $\gamma\text{-Al}_2\text{O}_3^1$	-	-	284.5	339.9 ± 0.1	342.0 ± 0.05	-
2.7% Pd on $\gamma\text{-Al}_2\text{O}_3^2$	-	-	283.8) 285.3)	335.5	340.7	199.6
2.7% Pd on $\gamma\text{-Al}_2\text{O}_3^3$	-	-	283.8(sh)	337.2	342.4	199.5) 197.1)
2.7% Pd on $\gamma\text{-Al}_2\text{O}_3^4$	-	-	283.8) 285.3)	337.2	342.5	197.8) 200.4)
2.7% Pd on $\gamma\text{-Al}_2\text{O}_3^5$	-	-	283.1) 286.0)	337.7	342.5	-
2.7% Pd on $\gamma\text{-Al}_2\text{O}_3^6$	75.3	-	284.6) 285.6)	337.4	342.8	-
2.7% Pd on $\gamma\text{-Al}_2\text{O}_3^7$	75.0	-	283.7) 285.2)	336.9	341.7	-

(sh) = shoulder.

1. Catalyst conditioned, exposed to CH_4/O_2 uninhibited.
2. Catalyst after deactivation with CH_2Cl_2 .
3. Catalyst after deactivation with CH_2Cl_2 and subsequent recovery.
4. Catalyst after deactivation with CCl_4 and subsequent recovery.
5. Catalyst after deactivation with CH_2Br_2 after 10% recovery.
6. 2.7% Pd on $\gamma\text{-Al}_2\text{O}_3^3$ after 3 months.
7. 2.7% Pd on $\gamma\text{-Al}_2\text{O}_3^3$ after 3 months - Ar^+ etched (7s.at 28 A); 1 nm surface removed.

Table 3:17 Effect of chlorinated hydrocarbons on binding energies for a 2.7% Pd on Al_2O_3 catalyst.

those obtained for palladium metal. Recovery of the palladium on γ -aluminium (III) oxide catalysts by exposure to methane/oxygen pulses ($[CH_4]_0 = 1.8 \times 10^{-6}$ mol; $[O_2]_0 = 3.6 \times 10^{-6}$ mol) with subsequent reactivation of the catalyst left the palladium in an oxidation state intermediate between that of the metal and the oxide. This was indicated by a shift in the position of the 3d binding energies from those obtained for Pd^0 to those found for Pd^{II} accompanied by simplification of the $C_{1s_{\frac{1}{2}}}$ signal. It appeared that the first step in recovery involved re-oxidation of the palladium followed by removal of the carbonaceous residue. This is shown for the 2.7% Pd on $\gamma-Al_2O_3$ catalyst (No. 5 in Table 3:17), for which a 10% recovery over the inhibited activity was obtained, which had Pd_{3d} binding energies typical of those for palladium (II) oxide but still retained a doublet for the $C_{1s_{\frac{1}{2}}}$ peaks. The 2.7% Pd on $\gamma-Al_2O_3$ catalyst, whose activity had almost recovered to a level similar to that obtained before inhibition, had a simple $C_{1s_{\frac{1}{2}}}$ peak at 283.8eV with only a shoulder at 286eV marking the presence of the other peak.

The electron binding energy levels of palladium dispersed on tin (IV) oxide were little different from those found for the catalyst and support separately (Table 3:18). This indicates that the interaction between palladium and tin (IV) oxide is of a physical nature only and no compounds of the type Pd-Sn-O are formed. After exposure to trichloromethane and without recovery in methane/oxygen, the 20% Pd on SnO_2/Al_2O_3 catalyst showed binding energies typical of those of palladium (II) oxide. This was not

Catalyst/support	Binding energy (eV)		
	C _{1s} _{1/2}	Pd _{3d} _{5/2}	Pd _{3d} _{3/2}
2.7% Pd on SnO ₂ ⁽¹⁾	286.3	337.3	342.6
20.0% Pd on SnO ₂ ⁽²⁾	286.4	337.9	342.9
20.0% Pd on SnO ₂ ⁽³⁾	286.4	338.2	343.4
20.6% Pd on SnO ₂ - Al ₂ O ₃ ⁽⁴⁾	284.8	338.0	342.7

- (1) No inhibitor, heated at 875K.
- (2) No inhibitor, heated to 720K.
- (3) Catalyst poisoned with pulses containing CHCl₃
(1.36 x 10⁻⁷ mol/pulse) at 650K; catalytic activity
recovered.
- (4) As (3) but catalytic activity not restored.

Table 3:18 Electron binding energies for some tin (IV)
oxide-supported palladium catalysts.

observed for the palladium on γ -aluminium (III) oxide catalyst, where palladium (II) oxide was formed only after recovery with methane/oxygen pulses; the inhibited catalyst contained palladium metal.

A number of platinum catalysts, both supported and unsupported, were also examined by XPS and the electron binding energies obtained from the spectra are shown in Table 3:19. A problem arose, however, due to overlap between the Pt_{4f} and the Al_{2p} lines. Only in the case of high loadings (10% Pt on $\gamma-Al_2O_3$) were the results conclusive. As with supported palladium, the active catalysts contained platinum whose binding energies resembled those of the oxide rather than the metal.

The stability of an inhibited catalyst surface was studied by storing a sample of 2.7% Pd on $\gamma-Al_2O_3$ that had partially recovered its activity after exposure to dichloromethane. It was re-examined by XPS after storage at room temperature for three months. There was little difference in the values of the electron binding energy levels of both the fresh and the stored catalysts. Argon ion etching by bombardment of the surface with Ar^+ ions removed atomic layers from the surface so that a depth profile of the elements of interest could be obtained. Carbon was still observed and the $C_{1s_{\frac{1}{2}}}$ peak had shifted slightly to lower binding energies as had the $Pd_{3d_{3/2}}$ and $Pd_{3d_{5/2}}$ lines. This indicates a return to more metallic character below the surface.

Catalyst/compound	Binding energy (eV)						
	Pt _{4f} _{7/2}	Pt _{4f} _{5/2}	Al _{2p} _{1/2,3/2}	C _{1s} _{1/2}	Al _{2s} _{1/2}	Pt _{4d} _{5/2}	Pt _{4d} _{3/2}
Platinum metal	71.3	74.9	-	284.9	-	-	-
Platinum oxide ⁽¹⁾	75.8	78.8	-	286.0	-	-	-
10% Pt on γ-Al ₂ O ₃	71.1	-	74.1	285.6	119.9	331.1	339.6
10% Pt on ThO ₂	74.1	76.5	-	283.2	-	-	-
2.7% Pt on γ-Al ₂ O ₃ ⁽²⁾	-	-	74.9	285.4	-	-	-
γ-Al ₂ O ₃	-	-	75.1	285.1	121.1	-	-
2.7% Pd on γ-Al ₂ O ₃ ⁽³⁾	-	-	75.1	-	-	-	-
PdCl ₂ on γ-Al ₂ O ₃ ⁽⁴⁾	-	-	74.8	-	-	-	-

(1) Adams catalyst.

(4) Pd catalyst poisoned with CCl₄.

(2) Poisoned with CH₂Br₂; inactive.

(5) Undecomposed.

Table 3:19 Electron binding energies in some platinum catalysts and compounds.

3:9:3 Auger electron spectroscopy.

Auger electron spectroscopic studies have shown some agreement with the results obtained using X-ray photoelectron spectroscopy. The Auger electron spectrum of a 25% Pd on $\gamma\text{-Al}_2\text{O}_3$ catalyst inhibited with CH_2Br_2 at 650K is shown in Figure 3:42. Results for catalysts contaminated by chlorinated hydrocarbons and for a 2.7% PdCl_2 on $\gamma\text{-Al}_2\text{O}_3$ sample can be seen in Figure 3:43. The peaks have been labelled with their corresponding elements according to standard tables (Palmborg, Riach, Weber and McDonald, 1972).

Both chlorine and bromine were found after exposure of the catalysts to the relevant inhibitors (CH_2Cl_2 and CH_2Br_2 respectively) but whereas bromine was found over most of the surface, chlorine was localised, being present only in certain areas. The relative intensity of the chlorine peak was much lower than that obtained for supported palladium (II) chloride. Carbon, too, was present on the catalyst surface although at 270eV it was difficult to separate from the Auger peak of palladium at 275-280eV. Its presence could be inferred only from a change in the expected height ratios of the three palladium peaks at ca. 240, 275 and 320eV. After injection of a high concentration ($1.5\text{ml} \equiv 2.3 \times 10^{-5} \text{ mol}$) of dichloromethane through a 2.7% Pd on $\gamma\text{-Al}_2\text{O}_3$ catalyst, carbon was relatively abundant on the surface.

The secondary electron and the adsorbed electron images

FIG. 3.42 AUGER ELECTRON SPECTRA FROM SURFACE OF SOME Pd/ γ - Al_2O_3 CATALYSTS EXPOSED TO CHLORINE COMPOUNDS

(a) 2.7% Pd Cl_2 on γ - Al_2O_3 ; (b) 25% Pd on γ - Al_2O_3 (FL) exposed to CHCl_3 (24 pulses containing 1.36×10^{-7} mol/pulse) at 650K;

(c) 2.7% Pd on γ - Al_2O_3 (GG) exposed to CH_2Cl_2 (1.5 μL) at 650K then H_2 (725K) and O_2 (675K)

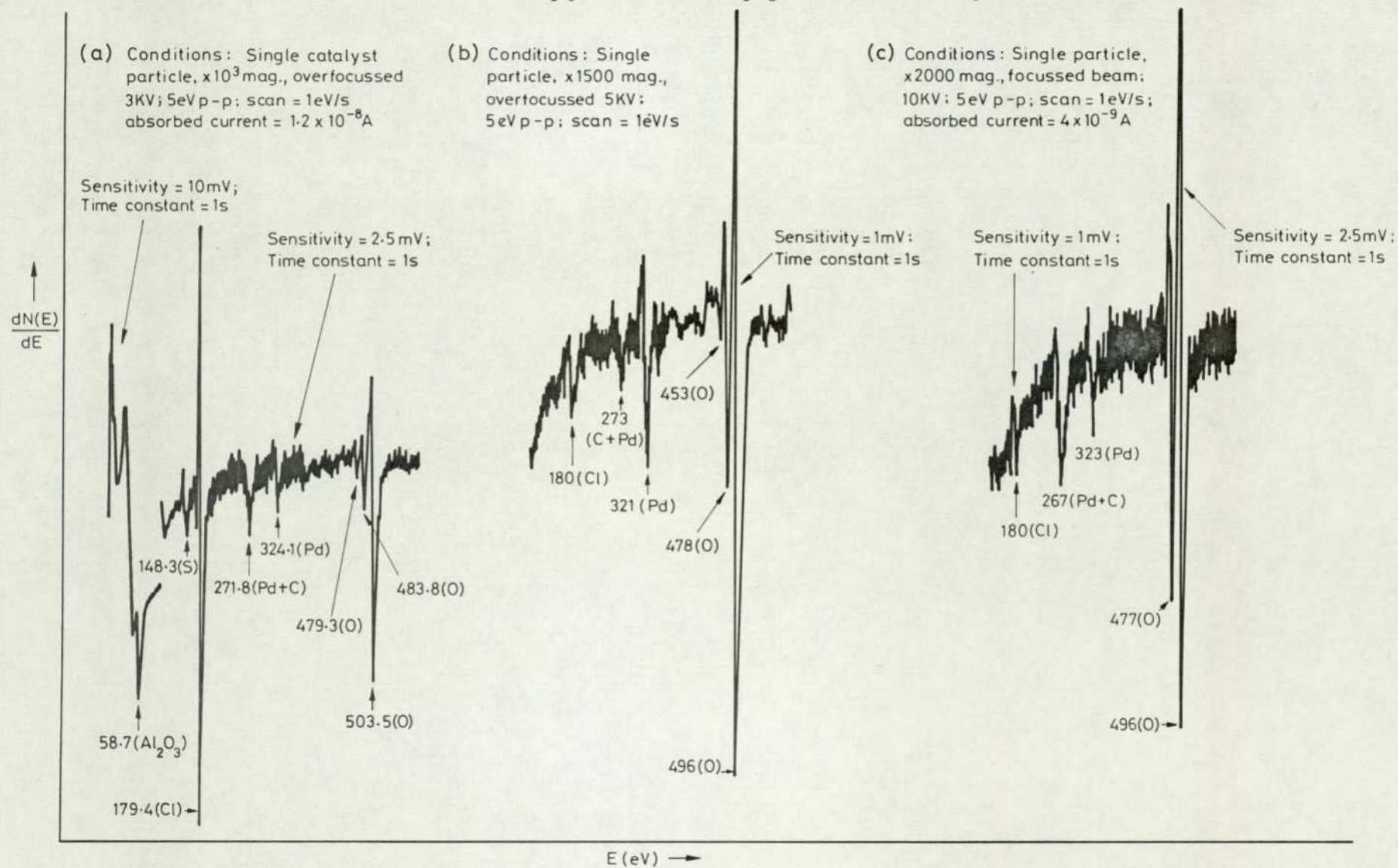
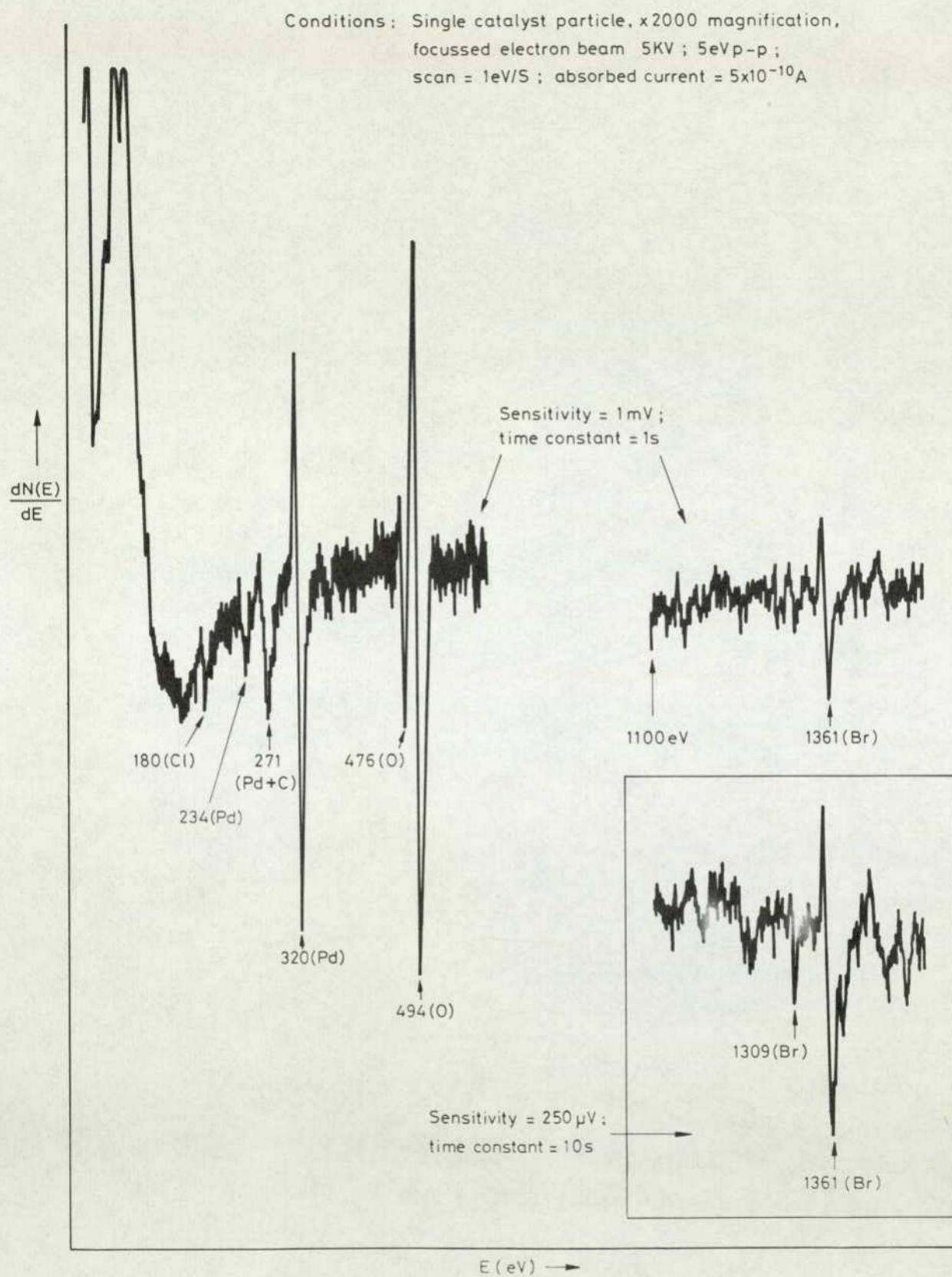


FIG.3.43 AUGER ELECTRON SPECTRUM FROM SURFACE OF A 25% (W/W)
Pd/ γ -Al₂O₃ (FP) CATALYST POISONED WITH CH₂Br₂ AT 650K



of the surface of a palladium on γ -aluminium (III) oxide catalyst which had been exposed to chloroform are shown in Plates 3S and 3T. Comparison of these micrographs with the palladium, chlorine and oxygen Auger images of the same area (Plates 3U, V and W) revealed that the palladium was concentrated in the upper right hand corner (the diffuse circular images are due to charging). Chlorine, too, could be found where palladium was present but oxygen was absent from this area. Hence, on chlorocarbon-contaminated catalysts, the palladium is not in the form of the oxide but is closely associated with chlorine.

The surface of a palladium on tin (IV) oxide catalyst exposed to hexamethyldisiloxane (20 pulses of 3×10^{-9} mol in a methane/oxygen mixture) whose activity had partially recovered at 650K was examined by Auger electron spectroscopy. The results of the analysis are shown in Table 3:20. Silicon and carbon were present on the immediate surface only, removal of only ca. 1.5 nm of the surface leaving little trace of these elements. Included in the table is a sample of silicon (IV) oxide for comparison purposes.

Catalytic beads which had been exposed to hexamethyldisiloxane were also examined by Auger electron spectroscopy. The results in Table 3:21 were obtained for beads operated for 1 hour in the presence of 2.55% v/v methane in nitrogen/oxygen at 760 Torr to which 0.0015 Torr hexamethyldisiloxane had been added. The activity of the beads towards methane oxidation was totally destroyed by this treatment, whereas the activity towards butane oxidation dropped by only 50%. The

Sample	Elements present ⁺				
	Sn	O	Pd	C	Si
20% Pd on SnO ₂ .					
As received	0.95	1	0.16	0.07	0.44
Ar ⁺ (10 secs)	1.03	1	0.21	-	0.05
Silicon (IV) oxide	-	1	-	-	0.14
Ar ⁺ (10 secs)	-	1	-	-	0.15

⁺ normalised to oxygen.

Auger electron generating conditions:- accelerating voltage = 5kV, vacuum = 5×10^{-10} Torr, absorbed current = 5×10^{-9} A, 5eV p-p, scan = 0.5 eV/s, fsd = 1mv, magnification = x4,500-7,500, defocussed beam.

Argon ion etching conditions:- accelerating voltage = 3kV, vacuum = 8×10^{-5} Torr, absorbed current = 20 mA, etch rate $\approx 10 \text{ nm min}^{-1}$.

Table 3:20 An Auger electron spectroscopic analysis of a 20% Pd on SnO₂ catalyst exposed to hexamethyl-disiloxane in the presence of methane/oxygen at 650K.

Bead type	Elements identified ⁺						
	Al	Si	S	C/Th*	Pd	Sn	O
Pd on ThO ₂ /Al ₂ O ₃							
as received	0.24	0.25	0.11	0.55	0.31	-	1.0
Ar ⁺ 15s.	0.22	0.22	0.12	0.49	0.57	-	1.0
Ar ⁺ 390s.	0.36	0.10	0.16	0.20	0.27	-	1.0
Pd on SnO ₂							
as received	-	0.15	-	0.60	1.25	0.46	1.0
Ar ⁺ 15s.	-	-	-	-	1.88	0.61	1.0
Ar ⁺ 390s.	-	-	-	-	1.23	0.43	1.0

⁺ normalised to oxygen.

* carbon and thoria peaks could not be identified separately.

Auger electron generating conditions:- accelerating voltage = 2kV; vacuum = 5×10^{-10} Torr; absorbed current = 2×10^{-9} A; 5eV p-p; scan = 1eV/s, 0-600eV scan; magnification = x700 (defocus).

Argon ion etch conditions:- accelerating voltage = 3kV; vacuum = 8×10^{-5} Torr; absorbed current = 20 mA; etch rate ≈ 10 nm min⁻¹.

Table 3:21 Auger analysis of the surface of catalytic beads exposed to hexamethyldisiloxane in the presence of methane/oxygen mixtures.



Plate 3:S.

Palladium on γ -aluminium
(III) oxide.

Secondary electron image.

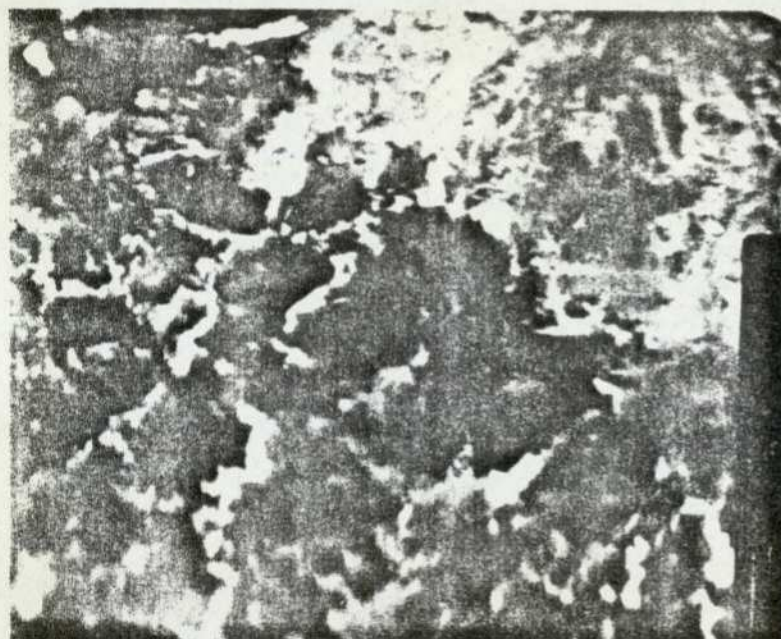


Plate 3:T.

Palladium on γ -aluminium
(III) oxide.

Adsorbed electron image.

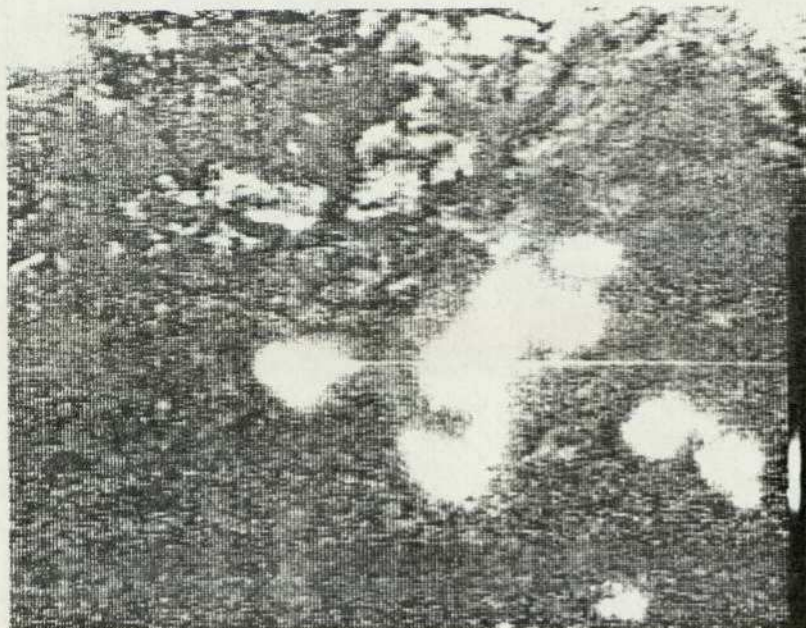


Plate 3:U.

Palladium on γ -aluminium
(III) oxide.

Palladium Auger image.

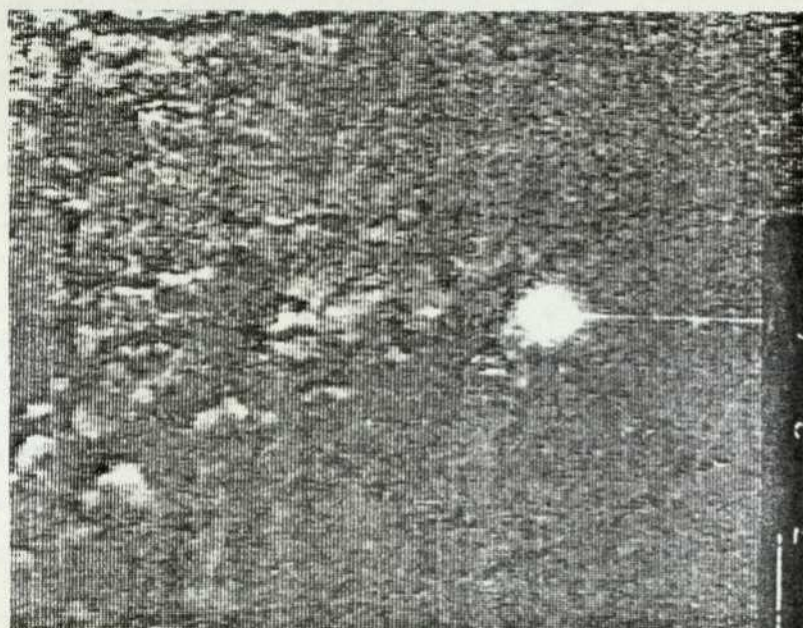


Plate 3:V.

Palladium on γ -aluminium
(III) oxide.

Oxygen Auger image.



Plate 3:W.

Palladium on γ -aluminium
(III) oxide.

Chlorine Auger image.

palladium on thorium (IV) oxide/aluminium (III) oxide bead contained sulphur on its surface as well as silicon. Sulphur is unlikely to be a contaminant from hexamethyldisiloxane and it may have been present before poisoning. Bombardment with argon ions reduced the silicon and palladium levels but the sulphur level increased slightly, indicating that it was probably associated with the support. The silicon too had penetrated deeply below the surface of the bead but its concentration decreased as succeeding atomic layers were removed.

The palladium on tin (IV) oxide beads which had been exposed to hexamethyldisiloxane showed differences in the Auger spectrum when compared with their palladium on thorium (IV) oxide/aluminium (III) oxide counterparts (Table 3:21). Although silicon was observed, it was only present in the first few atomic layers. Argon ion bombardment (3kV , 8×10^{-5} Torr, 20mA , $\approx 10 \text{ nm min}^{-1}$) for as little as 15 seconds was sufficient to remove the silicon. Carbon, too, was present only on the immediate surface.

Section 4. DISCUSSION.

- 4:1 Catalytic oxidation of methane.
 - 4:1:1 General considerations.
 - 4:1:2 Kinetics and mechanism.
 - 4:1:3 Partial oxidation products.
- 4:2 Thermal stability of catalysts and supports.
- 4:3 Carbon formation on precious metal catalysts.
- 4:4 Inhibition of methane oxidation by the products of reaction.
- 4:5 Inhibition of methane oxidation by halocarbons.
 - 4:5:1 Shape of poisoning curves.
 - 4:5:2 Inhibition.
 - 4:5:3 Recovery.
- 4:6 Inhibition and poisoning of hydrocarbon oxidation by organosiloxanes.
- 4:7 Conclusions.

4:1 Catalytic oxidation of methane.

4:1:1 General considerations.

The kinetics of methane oxidation over supported precious metal catalysts was studied in a region in which the rate of reaction was controlled only by the chemical processes at the catalyst surface. Homogeneous methane oxidation was insignificant over the temperature range in which the heterogeneous reaction was investigated. In addition, intraparticle diffusion was shown to be absent for a titanium (IV) oxide-supported palladium catalyst and chromatographic effects on the reactant pulse were avoided by the use of a sufficiently large pulse volume (5 cm^3).

The supports themselves, with the exception of tin (IV) oxide, did not oxidise or pyrolyse methane to any appreciable extent unless the temperature was raised to 723K or above. The effect of some supports on the behaviour of the precious metal was, however, significant. The activity and kinetics for methane oxidation, the degree of inhibition and recovery and the life expectancy of the catalyst were influenced by the support. In the case of tin (IV) oxide, the support itself oxidised methane appreciably even below 723K. A study of the behaviour of supported palladium catalysts must therefore include some attempt to understand the complex interactions that occur between the catalyst and its support.

4:1:2 Kinetics and mechanism.

The adsorption of oxygen on the catalyst surface is an essential step in the oxidation of methane over precious

metal catalysts. Optimum activity for methane oxidation was only achieved when sufficient oxygen was adsorbed from the methane/oxygen reactant mixture onto a previously reduced palladium surface. Examination by XPS of a supported palladium catalyst which had been exposed to pulses of methane/oxygen revealed that the palladium had similar binding energies to those obtained for palladium (II) oxide. The presence of palladium (II) oxide was observed even when the reactant mixture contained less than stoichiometric amounts of oxygen (i.e. was methane-rich). Thus not all the oxygen was consumed even under reducing conditions. A completely oxidised surface was, however, detrimental to methane oxidation, presumably because methane adsorption could then only occur on top of the strongly adsorbed oxide layer. Hence equilibrium was achieved only when the palladium surface was partially oxidised. This is in agreement with the results obtained by Cullis and Nevell (1976), who observed surface oxide formation prior to alkane (C_1 to C_4) oxidation for catalytic beads.

The zero order dependence of the reaction rate with respect to oxygen obtained for palladium and platinum catalysts suggests that oxygen is strongly bound to the surface. The formation of an oxide layer is accompanied at high temperatures by migration of oxygen into the bulk of the palladium (Campbell, Foyt and White, 1977). Activation energies obtained for oxygen adsorption on a number of supported palladium catalysts (42 to 61 kJ mol^{-1}) depended both on the support and on the loading of the precious metal and were lower than those obtained for oxygen migration into the bulk

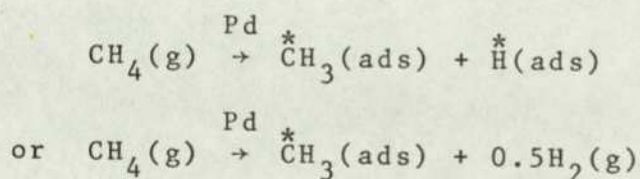
of the unsupported palladium (71.4 kJ mol^{-1} and 84 kJ mol^{-1} by Campbell, Foyt and White, 1977 and Ertl and Koch, 1972 respectively). At the temperatures at which these results were obtained (673-873K), it is the migration of oxygen into the bulk as well as surface oxidation that is being studied. The oxygen uptake depended both on the support and on the dispersion of the precious metal on it. As the loading of the precious metal increased, the oxygen uptake decreased due, presumably, to the inability of the larger palladium particles, obtained at poor palladium dispersions to adsorb sufficient oxygen. Indeed, XPS showed that there was more metallic character present in supported palladium at higher loadings than there was at lower loadings after exposure to identical methane/oxygen reactant mixtures at the same temperatures. This may be reflected in the positive orders with respect to oxygen obtained for methane oxidation over catalysts containing high loadings of palladium especially under methane-rich conditions.

The ability of the catalyst to adsorb oxygen was not dependent on particle size alone. There is some controversy as to the chemisorption stoichiometry of oxygen on precious metals especially on dispersed catalysts (Wilson and Hall, 1972; Sermon, 1972). A comparison between the particle sizes of palladium supported on titanium (IV) oxide and on aluminium (III) oxide measured by transmission electron microscopy revealed similar palladium dispersions over each support. It proved impossible to measure the palladium particle sizes of 2.7% Pd on TiO_2 prepared from palladium (II)

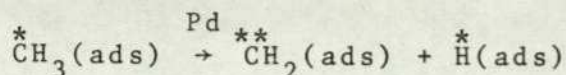
chloride but 8.7% Pd on TiO_2 had a smaller average palladium particle size than 2.7% Pd on $\gamma\text{-Al}_2\text{O}_3$. Oxygen adsorption was, however, significantly greater on 2.7% Pd on $\gamma\text{-Al}_2\text{O}_3$ than on 2.7% Pd on TiO_2 .

Strong metal-support interactions have been observed for precious metals supported on titanium (IV) oxide leading to a reduction in the hydrogen adsorbing capability of the precious metal (Horsley, 1979; Tauster and Fung, 1978). These interactions may be due either to metal-metal bonding between the noble metal and the titanium cations or, alternatively, to the formation of intermetallic compounds such as TiPd_3 formed under reducing conditions (Tauster, Fung and Garten, 1978).

Methane adsorption at temperatures similar to those required for its oxidation is probably dissociative. Hydrogen was formed during pyrolysis of methane over palladium catalysts at 600K and above, while ethane as well as hydrogen was produced over a platinum catalyst at 557K and above (Section 3:4). In addition, carbonaceous deposits were left on the catalyst surface, some of which were recoverable as methane by passage of hydrogen through the catalyst bed. Trapnell (1956) observed dissociative adsorption of methane on palladium:



The former process is thought to predominate. Further hydrogen abstraction from the adsorbed methyl group to form an adsorbed methylene group is quite possible at these temperatures,



If the palladium surface is covered with oxygen, it may be possible for methane to adsorb on a layer of oxygen. There is little information on hydrocarbon adsorption on palladium (II) oxide as oxidation of the hydrocarbon normally accompanies adsorption. Firth and Holland (1968) have postulated that methane and oxygen can both be adsorbed on a single palladium atom which is isolated from its neighbours on a zeolite support.

Oxidation of methane in the gas phase by adsorbed oxygen (an Eley-Rideal mechanism) has been proposed by some workers (Cullis and Nevell, 1976; Mezaki and Watson, 1966). This seems unlikely in the present study as methane oxidation was shown to be reduced at high oxygen coverages (Section 3:5). In addition, Cullis, Keene and Trimm (1971) observed inhibition of methane oxidation by small quantities of azomethane and methanol as did Firth (1966). A Langmuir-Hinshelwood mechanism thus seems more likely with both methane and oxygen adsorbed dissociatively on the palladium surface prior to reaction. Competition for adsorption sites appears to occur only at high coverage of oxygen. Brennan, Hayward and Trapnell (1960) observed that only 74% and 63% of the surfaces of palladium and platinum films respectively were covered with oxygen.

The activation energies for methane oxidation were, in most cases, obtained for methane-rich mixtures. A feature of the Arrhenius plots obtained for both palladium and platinum catalysts was the discontinuity in the straight line at higher temperatures. Activation energies for palladium catalysts below the transition point were in good agreement with published data (Section 3:3:4). Above this point almost total consumption of oxygen from reactant mixtures occurred and values of the activation energy were considerably reduced. The activation energies measured after the transition point thus correspond to the consumption of methane occurring by oxidation to both carbon monoxide and dioxide as well as pyrolysis on the catalyst surface. The values of the activation energy observed for this oxidation/pyrolysis process correspond to those obtained for methane oxidation on a previously oxidised palladium surface in the absence of gaseous oxygen, e.g. for palladium on thorium (IV) oxide, the activation energy for methane oxidation on a previously oxidised palladium surface was 39kJ mol^{-1} . The activation energy for oxidation of a 5% Pd on ThO_2 catalyst was 47kJ mol^{-1} . Addition of these two values gives 86kJ mol^{-1} which corresponds well with the activation energy for methane oxidation (85kJ mol^{-1}) obtained before the transition point. The activation energy at lower temperatures can thus be written as:

$$E_{A_{\text{total}}} = E_{A_{\text{Pd oxidn.}}} + E_{A_{\text{CH}_4 \text{ oxidn. on PdO.}}}$$

There is some agreement with the results for titanium (IV) oxide-supported palladium catalysts (Table 4:1) and the activation energy for methane oxidation over 2.7% PtO_2 on ThO_2 corresponds with that obtained after the transition point. This suggests that oxidation of the precious metal is no longer an important step in the reaction mechanism after the transition point. The adsorption and activation of methane is the activation energy-controlling step above the transition temperature.

It is possible that this change in the activation energy denotes a transfer from chemical control to diffusion control. It seems unlikely that this is pore diffusion as the more porous γ -aluminium (III) oxide-supported catalyst did not undergo this transition at lower temperatures than thorium (IV) oxide which was essentially non-porous. Furthermore, activation energies obtained after the transition point were considerably less than half those obtained before the transition point (for pore-diffusion the activation energy is reduced by one half). Measurements of the oxidation of methane were carried out at temperatures well below those at which bulk diffusion would be expected to occur and in the range in which diffusion was shown to be absent for 2.7% Pd on TiO_2 .

A rapid rise in activity occurred in the case of supported platinum at the transition point over a temperature range of less than 1K. Similar behaviour was observed by Schwartz, Holbrook and Wise (1971) during hydrocarbon oxidation over a platinum wire. This was believed to be due to

Catalyst/support	E_a (CH ₄ oxidation in the presence of gaseous O ₂)		E_a (CH ₄ oxidation in the absence of gaseous O ₂) (kJ mol ⁻¹)	E_a (precious metal oxidation) (kJ mol ⁻¹)
	Before transition (kJ mol ⁻¹)	After transition (kJ mol ⁻¹)		
2.7% Pd on ThO ₂	85±5	34±5	39±5	47±5
2.7% Pd on TiO ₂	83±5	35±5	23±5	43±5
2.7% Pd on γ-Al ₂ O ₃	89±5	45±5	-	45±5
3.1% Pt on ThO ₂	108±5	22±5	23±5	-

Table 4:1 Activation energies for methane oxidation with and without gaseous oxygen over supported precious metal catalysts and the activation energies for the oxidation of those catalysts.

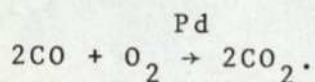
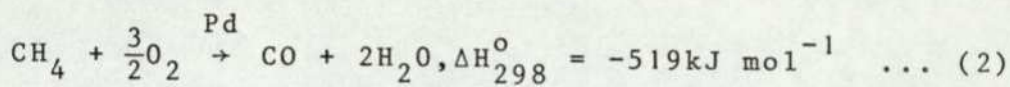
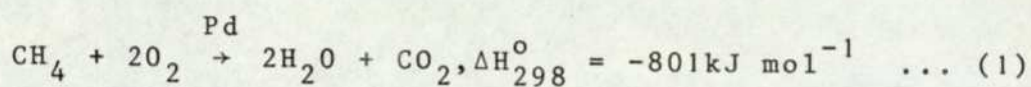
a transition from a region of kinetic to diffusion control. In these experiments the sudden rise in activity obtained for supported platinum catalysts increased in extent with the porosity of the support. That is, the rise in activity was more severe over platinum on γ -aluminium (III) oxide than over platinum on thorium (IV) oxide or titanium (IV) oxide. Trimm and Lam (1980) have observed a similar effect for platinum supported on porous aluminium (III) oxide under methane-rich conditions. The activity was ascribed to a rapid temperature increase produced by cracking of methane on the platinum, subsequent oxidation of the hydrogen produced by this cracking reaction causing a sudden rise in temperature and hence methane conversion. Certainly, hydrogen oxidation is highly exothermic but more so on palladium than on platinum as was observed over bulk catalysts using a thermocouple probe (Section 3:2). Increasing the amount of oxygen in the reactant mixture increased the temperature at which the exotherm occurred. For an oxygen-rich mixture, no exotherm was observed for platinum catalysts and the transition point increased for both palladium and platinum catalysts with increased pressure of oxygen in reactant mixtures with a constant partial pressure of methane. An explanation for the difference in catalytic activity of palladium and platinum may be found in their behaviour towards methane and oxygen. Palladium, unlike platinum, is able to adsorb oxygen into its bulk, thus providing a reservoir of oxygen which may prevent methane pyrolysis on its surface. In addition, methane was pyrolysed more rapidly over a platinum rather than a palladium catalyst. Cullis, Keene and Trimm (1971) observed that only 20% of

the active surface of a palladium catalyst was covered by carbon left by methane pyrolysis at 753K, while Trimm and Lam (1980) observed 50% coverage by carbon of a platinum on aluminium (III) oxide catalyst at 773K. No loss in activity for methane oxidation was observed on passage of successive methane-rich pulses (methane:oxygen ratio = 2:1) through a palladium catalyst. Passage of methane alone through the catalyst at similar temperatures, however, caused sooting of the catalyst surface with complete deactivation towards methane pyrolysis after 20 pulses.

The kinetics and mechanism of the oxidation of methane over catalytic beads have been extensively documented elsewhere (Section 1:6). A brief investigation was nevertheless undertaken to ensure that there was some agreement between the present results and those of other investigators. The beads were operated by heating to a temperature high enough to ensure that the rate of methane oxidation was independent of the catalyst temperature (ca. 800K). A logarithmic plot of the variation in methane consumption with methane concentration was linear and indicated a first order reaction. Pre-oxidation of the catalytic bead enhanced methane oxidation while pre-treatment in nitrogen reduced the activity when compared with pre-heating in air. The time to reach maximum activity was greatly reduced by this oxygen treatment. The initial activity of these beads was measured in both methane and n-butane before inhibition experiments were carried out.

4:1:3 Partial oxidation products.

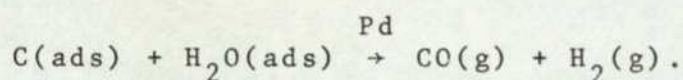
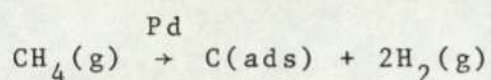
Carbon monoxide was produced over palladium and platinum catalysts only under methane-rich conditions after consumption of almost all the oxygen in the reactant mixture. Oxidation of carbon monoxide to carbon dioxide is a rapid reaction, occurring at temperatures much lower than those required for methane oxidation (Engel and Ertl, 1978). A reaction mechanism involving the total oxidation of methane via adsorbed intermediates may be postulated either involving direct oxidation of the hydrocarbon to carbon dioxide and water (scheme 1) or via a stepwise process involving carbon monoxide (scheme 2).



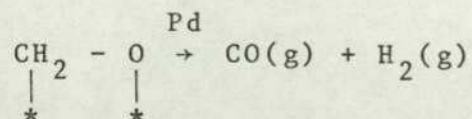
The reaction of carbon monoxide with palladium at temperatures above 475K involves a Rideal-Eley mechanism with reaction between chemisorbed oxygen and gaseous carbon monoxide (Close and White, 1975). The rate of oxidation decreased with temperature due to the short residence time of the carbon monoxide and the lack of chemisorbed oxygen at these temperatures. It is possible that carbon monoxide is produced during methane oxidation over palladium catalysts and that this is then desorbed and oxidised; but this seems unlikely as it would be expected that some carbon monoxide would have been observed in the reaction products at lower temperatures as was hydrogen. Carbon monoxide was not

observed even at temperatures as high as 723K when oxygen-rich mixtures were passed over the catalyst. The amount of carbon monoxide produced by the support would have been negligible as passage of methane-rich reactant mixtures over γ -aluminium (III) oxide, titanium (IV) oxide (79% anatase/11% rutile) or thorium (IV) oxide produced only carbon dioxide at temperatures up to 873K (Section 3:7:1).

Possible side reactions of the reactants and products may produce carbon monoxide e.g.

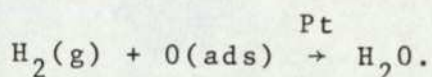


This reaction (the water-gas reaction) has been observed at temperatures as low as 850K over metal oxides such as NiO and CaO even for graphitic carbon (Berkmann, Morrell and Egloff, 1940). It seems most likely, however, that the carbon monoxide is formed at lower temperatures from the decomposition of a partially oxidised intermediate on the palladium surface when oxygen is lacking e.g.



Hydrogen was observed at temperatures as low as 650K when

methane-rich reactant mixtures were oxidised over a 2.7% Pt on $\gamma\text{-Al}_2\text{O}_3$ catalyst. It was also found over palladium catalysts but in both cases only in trace quantities. "Spillover" of hydrogen onto the catalyst support was not observed during pyrolysis of methane over palladium or platinum on titanium (IV) oxide. It may, however, have contributed towards the exothermic reaction that occurred when methane-rich mixtures reacted over 2.7% Pt on $\gamma\text{-Al}_2\text{O}_3$, as a spillover mechanism is known to take place from platinum on to aluminium (III) oxide (den Otter and Dautzenberg, 1978). Rapid oxidation of hydrogen to water would be expected in the presence of available oxygen over platinum at 330K and above (Gentry, Firth and Jones, 1974):



Neither carbon monoxide nor hydrogen were observed during methane oxidation over catalytic beads under the oxygen-rich conditions in which they were operated. Carbon dioxide and water were the only products identified.

4:2 Thermal stability of catalysts and supports.

Prolonged heating of supported precious metal catalysts led to a decrease in the dispersion of the precious metal. In addition, high temperatures caused structural and phase changes in the support with loss of surface area. Although minor changes in the surface area of the support occurred at low temperatures, massive agglomeration of the precious metal would be expected to result before the occurrence of any significant alteration in the structure of the supports used.

Increases in precious metal particle sizes are dependent on the temperature, the time at which the catalyst is held at that temperature and the metal concentration as well as the nature of the support and the atmosphere in contact with the catalyst during heating (Anderson, 1975). Platinum on γ -aluminium (III) oxide catalysts are normally more resistant to sintering in nitrogen or hydrogen atmospheres than are palladium on γ -aluminium (II) oxide catalysts, while the opposite is true in oxygen or in air (Swift, Lutinski and Tobin, 1966; Dodgson and Webster, 1976). Although the average diameter of the metal particles in a 2.7% Pd on γ -Al₂O₃ catalyst increased from 14 to 80 nm, there was little alteration in the catalytic activity towards methane oxidation. This means that the rate of methane oxidation is independent of particle size under the methane-rich conditions used for the experiment. Carballo and Wolf (1978) found that alteration in the average particle diameters of platinum supported on γ -aluminium (III) oxide had little effect on the rate of propylene oxidation.

The situation was more complicated in the case of 2.7% Pd/Pt (50-50) on TiO₂. In addition to the formation of a palladium-platinum alloy, the stability of which could well be affected by the production of palladium (II) oxide, strong metal-support interactions were observed. The presence of a Pd-Pt-Ti compound was indicated. Formation of a solid solution of platinum (IV) oxide in titanium (IV) oxide has been observed previously at temperatures of 1020-1470K by Hoekstra et al (1971), and this was not found for platinum on

γ -aluminium (III) oxide or on silicon (IV) oxide. Under reducing conditions, Tauster, Fung and Garten (1978) have shown that extensive compound formation occurs between precious metals and titanium (IV) oxide. Care should thus be taken in the use of supports which will interact strongly with the precious metals adsorbed on their surfaces, especially at high temperatures and under reducing conditions.

The massive sintering that occurred when unsupported palladium (II) oxide was exposed alternately to oxidising and reducing cycles was more severe than that obtained for supported palladium catalysts. This is hardly surprising, for adsorption of both hydrogen and oxygen into the bulk of the palladium is possible and the reaction of bulk as well as surface oxide produces significant temperature rises across the catalyst bed. The heat produced by supported palladium during exothermic reactions may be removed from the precious metal by heat transfer through the support to the reactor walls. Sintering was observed only after continuous passage of oxygen through unsupported palladium (II) oxide at 775K; exposure to transient pulses of oxygen or hydrogen caused less marked changes. The continuous passage of oxygen through 2.7% PdO on ThO₂ at 775K raised the activation energy for methane oxidation in the absence of gaseous oxygen when compared with that at 625K. This may, however, be due to an inhibition of methane oxidation over a catalyst which contains high levels of surface oxide, a situation which has also been observed by Schwartz, Holbrook and Wise (1971).

Platinum would be expected to have greater thermal stability in oxygen atmospheres than would palladium as it forms only a thin layer of surface oxide. The temperature rise along the platinum (IV) oxide bed during oxidation/reduction cycles was small. At high temperatures and in the presence of oxygen, however, platinum forms a gaseous oxide (Alcock and Hooper, 1960) and a platinum mirror was formed on the walls of the reactor tube when supported platinum catalysts were used for methane oxidation. This would seriously limit the operating life of a platinum catalyst used at high temperatures in oxidising conditions.

Particle growth on a catalyst support can occur by two distinct mechanisms, either by particle migration and coalescence or by transfer of metal atoms individually from one particle and their deposition on another either by diffusion across the surface or diffusion in the gas phase. Obviously, many factors control these processes but vapour phase diffusion may be more prevalent for platinum catalyst due to the volatility of the oxide. The cohesive energy of palladium is smaller than that of platinum which may encourage an agglomeration process rather than a vapour transport process.

Measurement of the surface area of three metal oxides used as catalyst supports (titanium (IV) oxide, γ -aluminium (III) oxide and thorium (IV) oxide) showed that high temperatures significantly altered their surface properties. At 1273K, rapid loss of surface area occurred for all three support materials. The major loss was observed within the

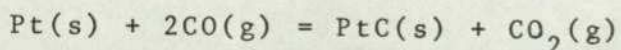
first few hours of heating and appeared to be due to sintering accompanied, in the case of γ -aluminium (III) oxide, by irreversible phase changes. Under these conditions, any microporous structure present grew to form a macroporous structure.

The requirements of the support material were that it should have a surface area as high as is necessary for good catalyst dispersion but should be stable at temperatures to which the support/catalyst is subjected. Changes in the support may cause changes in the catalyst distribution. Hence, the achievement of a high, but thermally unstable, surface area may not be desirable. The temperatures used for the heterogeneous oxidation of methane would not be expected to cause significant alterations to the surface areas of these supports. In practice, however, the support and the catalyst are present together and the precious metal may influence the stability of the support. The phase change from anatase to rutile occurring at temperatures of ca. 1273K, is accelerated by the addition of platinum group metals (Bystrov et al, 1973). In addition, formation of palladium-titanium complexes may be responsible for sintering of the support or oxygen may be removed from the support by the precious metal leaving lattice defects. Titanium (IV) oxide, especially anatase, turned yellow on being heated above 573K due to loss of oxygen. The presence of small amounts of chlorine on the surface of Pd on γ -Al₂O₃ catalysts formed by the decomposition of palladium (II) chloride (Bozon-Veraduz, Omar, Escard and Pontvianne, 1978) may also affect the properties of the support (Finch and Clark, 1970).

The resistance to thermal degradation of metal oxides which are used as catalyst supports may be increased by the addition of stabilizers. Metal oxides such as magnesium (II) oxide and cerium (IV) oxide will act as stabilizers for γ -aluminium (III) oxide (Gauguin et al, 1975). Diffusion of Al^{3+} cations away from the tetrahedral sites may be responsible for the metastability of the aluminium (III) oxide. The incorporation of magnesium into the tetrahedral position in the spinel cubic lattice may retard movement of Al^{3+} ions. The magnesium aluminate was found to be stable for 24 hours at 1273K with only a small loss of surface area.

4:3 Carbon formation on precious metal catalysts.

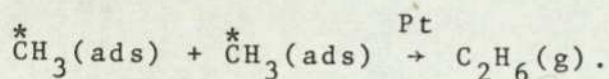
The deposition of a carbonaceous residue during pyrolysis or oxidation of methane over palladium or platinum catalysts was shown to occur at high temperatures under reducing conditions. This is not unusual for carbonaceous deposits are frequently observed on the surface of metallic catalysts during hydrocarbon reactions (Beeck, 1950a; Hattori and Burwell, 1978). The supports alone, with the exception of tin (IV) oxide, did not pyrolyse appreciable amounts of methane at temperatures of up to 873K. Carbon may also be produced by the breakdown of oxides of carbon on a reduced platinum surface. The reaction,



becomes thermodynamically feasible at temperatures above 700K. The rate of carbon monoxide formation was not decreased, however, by the formation of a carbon film on the

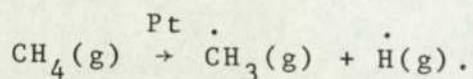
platinum surface (Hori and Schmidt, 1975).

The degree of pyrolysis of methane on precious metal catalysts increased with temperature producing hydrogen and, in some cases, ethane. The decomposition of a carbonaceous residue which was rich in carbon was presumably due to further hydrogen abstraction from adsorbed methylene groups. Ethane may have been produced over 2.7% Pt on TiO_2 by reaction between two adjacently adsorbed methyl groups,



The yield of ethane was low (0.002%). This may be due to a shortage of adjacent methyl groups, to strong adsorption of methyl groups or to further hydrogen abstraction from methyl groups.

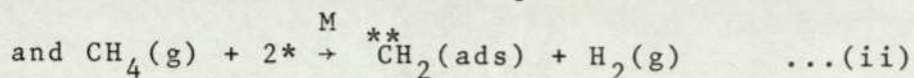
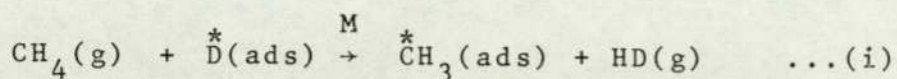
An alternative source of ethane may be combination of methyl radicals formed in the gas phase:



The short contact time (ca. 0.5s) and the low concentration of radicals produced would not be expected to favour high yields of ethane. Methyl radicals may be formed in the gas phase from ethane at temperatures of 773K and above (Tedder and Nechvatal, 1968), but platinum may well reduce this temperature considerably.

The difference in the ability of palladium and platinum to decompose methane cannot readily be explained in terms

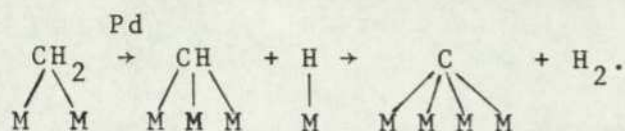
of the d-character of the precious metal or by geometric factors such as lattice spacings. Kemball (1953) observed that of the two reactions:



the former reaction occurred at an equal rate on both palladium and platinum films but the latter reaction was slower over palladium. Now palladium has more d-character (46%) than platinum (44%) and this would be expected to lower the heat of methane adsorption and hence raise the reaction rate (Trapnell, 1954), but this is not borne out by the above results. There is also a difference in the lattice spacings of palladium (0.137 nm interatomic distance) and platinum (0.138 nm interatomic distance), the smaller bond lengths usually being preferred for multiple bonding. This is not the case, however, reaction (ii) above being slower over palladium.

The ability to form both reversibly and irreversibly bound carbon indicated that the surface sites of these precious metals were non-uniform. Certainly, during pyrolysis of methane over palladium not all the surface carbon was recovered; hence the surface sites which were involved in residue formation were not involved in hydrogenation, a result confirmed by Anderson and Baker (1963). Carbon monoxide will bond in both a linear and a bridged form on the surface of palladium, the relative proportions of the two forms depending on particle size as well as being temperature- and pressure-dependent (Anderson, 1975).

Methane will itself form both linear- and bridge-bonded species (see above) and, as carbonaceous deposits were formed that mostly contained carbon alone, it would be expected that these would have been formed from multiply-bonded carbon atoms at the surface:



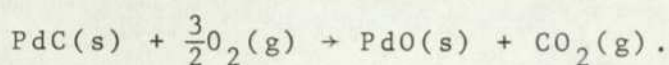
Keene (1969) observed that the (111) planes of palladium were responsible for bridge-bonding of methane. It was suggested that these bridge-bonded methylene radicals were responsible for irreversible carbon deposition, whereas methane which was bonded in linear form on the (100) planes was recoverable by hydrogenation. The (111) planes of platinum are more thermally stable than the (100) and (110) planes (Boudart, Aldag, Ptak and Benson, 1968) and hence may predominate at high temperatures causing a greater degree of irreversible poisoning.

The mechanism of carbon formation is uncertain but formation of C_4 and C_6 species have been observed during pyrolysis of ethylene over a platinum catalyst (Paal, Fryer and Thomson, 1973). Lobo and Trimm (1978) have found that the formation of carbon deposits on nickel from hydrocarbons at temperatures between 773 and 873K could be prevented if high partial pressures of hydrogen were present. Depending on the reaction conditions, several forms of carbon were observed by these workers. Filamentous and graphitic carbon were formed at high temperatures (700K in the case of nickel and as low as 623K for platinum (Paal, Fryer and

Thomson, 1973)). The amount of recoverable carbon on a 5% Pd on ThO₂ catalyst used for our experiments decreased with increasing temperature. This may be due to the formation of graphitic rather than amorphous carbon. High temperatures will encourage graphitisation but, although carbon may migrate into the bulk of the palladium, but not platinum, the precious metals do not form carbides. Carbonaceous deposits were partially recoverable by passage of hydrogen through the catalyst:



Oxygen was not as effective as hydrogen but an appreciable recovery as oxides of carbon was obtained,



When oxygen was passed over a catalyst which had previously been exposed to pure methane at 723K, oxidation of the residue formed by methane pyrolysis occurred at the same time as reoxidation of the palladium. More oxygen was taken up during the second rather than the first pulse. The residue formed from methane pyrolysis was probably blocking sites used either for the adsorption of oxygen and its incorporation into the bulk of the palladium or for the adsorption of oxygen and its reaction with the residue to form carbon dioxide. Pyrolysis of methane over a 5% Pd on ThO₂ catalyst was self-poisoning but there was no loss in activity when successive pulses of a methane-rich reactant mixture were oxidised over a palladium catalyst. In addition, a 2.7% Pd/Pt (50-50) on TiO₂ catalyst was exposed to a 1.4% v/v methane in air mixture at 683K for 21 days with no loss in catalytic activity. An adequate supply of

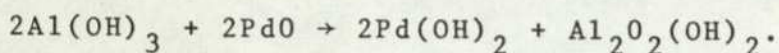
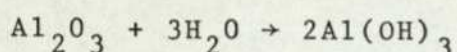
oxygen was thus necessary to prevent inhibition by carbon. Firth and Holland (1971) observed, however, that a 40% by volume of methane in air mixture caused maximum deposition of carbon on a palladium on aluminium (III) oxide catalytic bead. Loss in activity due to carbon deposition over a palladium catalyst was observed after operation in this methane concentration for only a few minutes (Baker and Firth, 1969).

The conditions in which methane oxidation over powder catalysts in a pulse flow microreactor was studied (temperature 580-723K; methane:oxygen ratio 2:1 $\rightarrow$ 1:10; contact time per pulse = ca. 0.5s) were unlikely to cause loss in activity due to carbon formation. Examination of palladium and platinum powder catalysts that had been exposed to methane-rich reactant mixtures by transmission electron microscopy revealed no evidence of carbon formation but catalysts exposed to methane in the absence of oxygen were not studied. A carbon line in the Auger spectrum other than that observed as a background for all catalysts was not identified. Raising the temperature may, however, enhance carbon deposition. Thus for catalytic beads operated for long periods in methane-rich conditions, as low a temperature as possible would be necessary to prevent deactivation by self-poisoning.

4:4 Inhibition of methane oxidation by the products of reaction.

A study of the inhibition of methane oxidation over

palladium catalysts has revealed that the products of reaction have little effect on the catalytic reaction. Water, when present in sufficient quantities, will, however, inhibit methane oxidation, the degree of inhibition increasing with increased water content of the reactant pulse. This is probably due to the strong affinity of the support for water; thus aluminium (III) oxide loses hydroxyl groups slowly at 570K and even after dehydration at 720-870K, surface hydroxyl groups are still present (Anderson, 1975). Addition of water will temporarily increase the number of hydroxyl groups on the surface which may be transferred to the palladium to form the hydroxide:



The inhibition of methane oxidation over 2.7% Pd on $\gamma\text{-Al}_2\text{O}_3$ by water vapour was reversible, recovery of the catalyst being rapid at the temperature of inhibition (625K). $\text{Pd}(\text{OH})_2$ (or $\text{PdO} \cdot \text{H}_2\text{O}$) loses water slowly on being heated and is not totally dehydrated at temperatures as high as 773K (Sidgwick, 1950). Confirmation that the support plays an active part in the inhibition of methane oxidation by water vapour was obtained from the fact that unsupported palladium catalysts are not deactivated by water vapour (Cullis, Nevell and Trimm, 1972).

The temporary inhibition by water indicates that the catalyst is temporarily unstable in the presence of water vapour. This effect would be expected to be chromatographic with the helium flow aiding the passage of water through the

catalyst bed. A highly porous, hydrophilic support would be expected to retain water more readily than a non-porous hydrophobic support. This may explain the difference in behaviour between catalytic beads studied in a static reactor and powder catalysts in a flow reactor. Catalytic beads undergo considerable deactivation by water vapour which is only partially reversed by heating in vacuo (Cullis, Nevell and Trimm, 1972). Furthermore, a build-up of water vapour may occur in a static reactor used for catalytic bead studies. Placing a bed of silica gel for drying the atmosphere in the reactor used for oxidation of methane over a catalytic bead, however, had no effect on the rate of deactivation. This indicates that deactivation was caused by water produced during the oxidation process rather than that adsorbed from the atmosphere.

A study of both the effect of temperature and the species formed by water adsorbed on the surface of the metal oxides used as supports may provide some insight into the degree of inhibition that may be expected. Thorium (IV) oxide requires temperatures as high as 1273K in vacuo before total dehydration of the surface occurs (Holmes, Fuller and Secoy, 1968) while hydroxyl groups are more readily removed from titanium (IV) oxide than from thorium (IV) oxide or aluminium (III) oxide. A fully hydrated titania surface has 11 OH groups per nm^2 with almost total dehydration at 640K (Munuera and Stone, 1971). Alumina has a surface hydroxyl concentration of ca. 8-12 OH groups per nm^2 at 770-870K (Anderson, 1975) and thoria has 7-8 OH groups per nm^2 at room temperature, while dehydration at 700K halves

this figure (Anderson, 1975). In addition to having a relatively large number of hydroxyl groups present on its surface, γ -aluminium (III) oxide would be expected to cause the most severe inhibition due to its porous nature and high surface area.

The ability of the support to transfer hydroxyl groups or water to the palladium surface must also play an important role in the degree of deactivation caused by water vapour. There is little information on this subject, although Cullis, Nevell and Trimm (1972) found that the order of deactivation was in broad agreement with the order of activity of a series of metal oxides for the dissociative adsorption of steam.

4:5 Inhibition of methane oxidation by halocarbons.

4:5:1 Shape of poisoning curves.

The shapes of the deactivation curves were generally similar to those found by Maxted (1951) and indicated that, in the absence of pore-mouth poisoning, the active sites were non-uniform with the most active of those sites being poisoned first. An increase in the concentration of halocarbon increased deactivation until a level was reached where no further loss in activity occurred. This would imply that some sites that are active for methane oxidation are resistant to inhibition by halocarbons. The absence of pore-mouth poisoning or blocking by these inhibitors was inferred from the absence of a porous structure for titanium (IV) oxide and thorium (IV) oxide. There was

little evidence from transmission electron micrographs that the palladium supported on the more porous γ -aluminium (III) oxide was deposited exclusively within the pores, yet the shape of the deactivation curve obtained for γ -aluminium (III) oxide-supported palladium did not differ greatly in form when compared with that of palladium supported on titanium (IV) oxide.

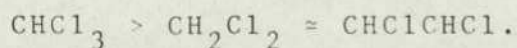
Further evidence for the absence of pore-mouth poisoning was obtained from measurement of the activation energy in the temperature region in which the inhibition was studied. This should be zero if the rate-controlling process is that of diffusion of reactants into the pores (Rajadhyaksha and Doraiswamy, 1976). In the case of 2.7% Pd on γ -Al₂O₃, the activation energy was ca. 56 kJ mol⁻¹ for methane oxidation at temperatures of 625-730K after inhibition with trichloromethane (10 pulses of 1.36×10^{-7} mol CHCl₃/pulse). Thus diffusion down the pores was not the poisoning process responsible for the shape of the poisoning curves.

4:5:2 Inhibition.

The initial promoting effect of small quantities (ca. 0.5 mol%) of di- and tri-chloromethane may be due to a change in the product spectrum. An increase in the selectivity towards partial oxidation products has been observed when chlorine-containing compounds are added to silver or palladium catalysts. The production of oxiran from the partial oxidation of ethylene over silver catalysts was

increased by the addition of 1,2-dichloroethane to the reactant mixture. Chlorine was adsorbed on the surface of silver and ethylene was desorbed. Oxygen uptake was reduced by the pre-adsorbed chlorine, only associative adsorption of the oxygen occurred and oxiran production was increased (Meisenheimer and Wilson, 1962). Rovida, Pratesi and Ferroni (1976) observed that the chlorine weakened the silver-oxygen bond, while oxygen had little effect on the adsorbed chlorine. The selectivity towards formaldehyde production observed by Cullis, Keene and Trimm (1970) during inhibition of methane oxidation by chlorocarbons over a palladium catalyst may also be explained by a shortage on the catalyst surface of dissociated oxygen which is necessary for total oxidation. Oxygen which is strongly adsorbed may not be as effective for methane oxidation as that less strongly adsorbed. A balance was thus obtained at low chlorocarbon concentrations where chlorine coverage was low enough to discourage strong oxygen adsorption but not high enough to inhibit weak adsorption.

It was found in this work that the presence of chlorocarbons in the reactant mixture caused a rapid loss in activity, the degree of which was dependent on the number of chlorine atoms in the molecule. Thus, the order of effectiveness of chlorocarbons for the inhibition of methane oxidation was found to be:



Temperature, too, played a significant role in the extent of both deactivation and recovery of chlorocarbon-inhibited

catalysts. At 625K, the activity of a 2.7% Pd on $\gamma\text{-Al}_2\text{O}_3$ catalyst, exposed to trichloromethane, dropped to 10% of its original value with no recovery, while at 730K it dropped to 40% but recovered to 80% of its initial value.

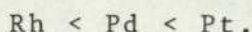
The interaction of halocarbons with precious metal surfaces thus produces a surface residue whose stability depends on the temperature and atmosphere. Chloromethanes decomposed on palladium and platinum films have been studied by Anderson and McConkey (1968). Adsorption was found to occur by an irreversible dissociative process, carbon-chlorine bonds breaking before carbon-hydrogen bonds. At 475-500K, the decomposition of methyl chloride gave hydrogen chloride and methane and left some carbonaceous residue on the catalyst surface. In the present work, the presence of a carbonaceous residue was confirmed. Bromine was found after exposure to dibromomethane whereas chlorine was localised and less readily observed. This result is not surprising as the carbon-halogen bond strengths are $\text{C-Cl} = 353 \text{ kJ mol}^{-1}$ and $\text{C-Br} = 294 \text{ kJ mol}^{-1}$. Thus bromine may dissociate on the surface away from the carbon residue, whereas chlorocarbon-inhibited catalysts retain the carbon fragment. In the presence of hydrogen, Anderson and McConkey (1968) observed the formation of higher hydrocarbons over palladium but not over platinum catalysts. This may reflect the difference in effectiveness of inhibition over these catalysts. Summers and Ausen (1978) observed that the Pt-Br bond was sufficiently

weak to permit rapid dissociation and subsequent reaction with surface sites of aluminium (III) oxide by hydrogen hexabromoplatinate (IV). By contrast, the Pt-Cl bond was stronger and underwent less dissociation and subsequent reaction with the aluminium (III) oxide sites occurred more slowly.

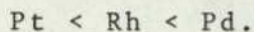
The effect of the deposition of carbon, as well as chlorine on the catalyst is difficult to assess. A shoulder on the carbon peak ($C_{1s\frac{1}{2}}$) observed on examining chlorocarbon-inhibited catalysts using XPS gradually disappeared as the catalytic activity recovered and was non-existent when steady-state activity was fully regained. This shoulder was not present when methane was pyrolysed on a reduced palladium surface and it may be ascribed to carbon that is still attached to halogen. The presence of carbon on the surface was confirmed by passage of oxygen through a catalyst which had been exposed to trichloromethane, when carbon dioxide was produced. Carbon itself was probably not wholly responsible for deactivation, as a supported palladium catalyst which had methane decomposed on its surface showed no loss in activity towards methane oxidation (Section 4:3). Hydrogen chloride and hydrogen bromide were found to be effective in inhibiting hydrocarbon oxidation over palladium catalysts (Patterson and Kemball, 1963; Otto and Montreuil, 1976). In the case of hydrogen bromide, the loss in activity was the same as that observed for 1,2-dibromoethylene but high temperatures and reactant gas mixtures which contained high levels of oxygen

were used for these experiments which may encourage removal of carbon-halogen deposits. However, bromocarbon-inhibited catalysts studied by XPS also exhibited a shoulder on the $C_{1s\frac{1}{2}}$ peak as did the chlorocarbon-inhibited catalysts. The fact that this inhibition was reversible may also point to slow oxidation of the carbon as a recovery step, but it is more likely that chlorine, which was also observed by XPS, was the major inhibitor.

The interaction of chlorocarbons with precious metal surfaces therefore produced a surface residue rich in chloride ions which caused loss in activity for methane oxidation. The degree to which these chloride ions were formed must control both the rate and the extent of deactivation of the catalyst. Increasing the work function of the surface will increase the activation energy necessary for negative ion formation. The work functions of the precious metals used for this investigation increased in the order:

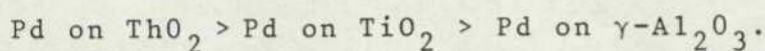


The degree of deactivation of the precious metals by trichloromethane increased in the order:



Thus rhodium is out of step. When oxygen is adsorbed on the catalyst, however, the work function may be altered and the presence of oxygen (an electron acceptor) on the surface raises the work function and may decrease the ability of the precious metal to form Cl^- . Although adsorbed oxygen had little effect on the adsorption of

chlorine by silver, the Ag-O bond strength is only 138 kJ mol⁻¹ while that of Pd-O is 331 kJ mol⁻¹ and that of Pt-O is 317 kJ mol⁻¹ (Myerson, 1965) and the displacement of this oxygen of high bonding strength may occur less readily on palladium and platinum than on silver. Supported palladium catalysts showed rates of deactivation which increased in the order of their lack of ability to adsorb O₂ viz.



Bromocarbons would be expected to form a more covalent compound with precious metals, the formation of which is encouraged by large electron exit work functions, large positive values of electron density at the highest occupied energy levels and the presence of unfilled d-orbitals.

The agglomeration of palladium and rhodium particles observed under the transmission electron microscope after exposure to chlorocarbons was not extensive (Table 4:2). Both these catalysts underwent a considerable loss in activity and both showed an increase in particle size distribution which was not observed for platinum catalysts. Particle size was shown to have a negligible effect on methane oxidation over palladium catalysts supported on γ -aluminium (III) oxide under methane-rich conditions (see Section 3:6). In addition, if agglomeration was responsible for loss in activity, then this loss would not be expected to be reversible. Redispersion of palladium particles is thermodynamically unlikely on passage of methane/oxygen mixtures through the catalyst. Some confirmation of this lack of

Catalyst/support.	Inhibitor	Temperature of exposure of catalyst to inhibitor. (K)	Mean precious metal particle diameter. (nm)
2.7% Pd on γ -Al ₂ O ₃	-	-	16.1
2.7% Pd on γ -Al ₂ O ₃	CHCl ₃	580-730	20.5
2.7% Pd on γ -Al ₂ O ₃	CHCl ₃	625	17.3
2.7% Pd on γ -Al ₂ O ₃	CHCl ₃	650	19.8
2.7% Pd on γ -Al ₂ O ₃	CHCl ₃	700	16.7
2.7% Pd on γ -Al ₂ O ₃	CHCl ₃	730	18.6
2.7% Pt on γ -Al ₂ O ₃	-	-	2.8
2.7% Pt on γ -Al ₂ O ₃	CHCl ₃	650	3.18
2.7% Pt on γ -Al ₂ O ₃	CH ₂ Br ₂	650	2.8
2.7% Rh on TiO ₂	-	-	6.65
2.7% Rh on TiO ₂	CHCl ₃	650	8.38

Table 4:2 Effect of halogenated hydrocarbon on the particle sizes of some supported precious metal catalysts.

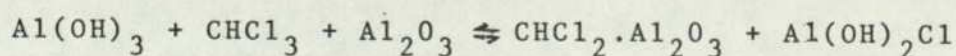
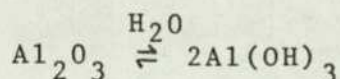
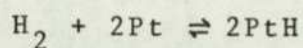
particle size effect was obtained from the observation that the loading of palladium on γ -aluminium (III) oxide had little effect on the degree of inhibition. Both 2.7% Pd on γ -Al₂O₃ and 25% Pd on γ -Al₂O₃ underwent a 60% loss in their initial activity on exposure to dibromomethane at 650K. No recovery was observed for either catalyst. A larger palladium particle size would be expected for the catalyst with a high loading but these particles showed the same susceptibility to poisoning as the smaller particles found on catalysts with lower palladium loadings.

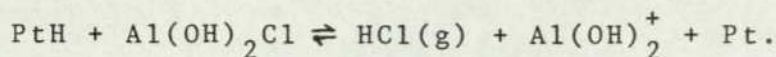
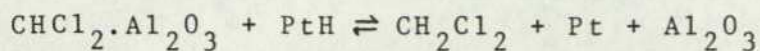
4:5:3 Recovery.

Recovery of catalysts inhibited by halocarbons was effected most readily either by raising the temperature or by passage of methane/oxygen pulses through the catalyst bed. The use of helium alone did not produce appreciable recovery in most cases. Pulses of oxygen were not as effective as methane/oxygen, indicating that the oxidation of palladium was not rate-determining in the recovery process, although there was an initial change in oxidation state of the palladium surface from Pd⁰ to Pd². The slow step in the recovery process is probably that of removal of halogen from the precious metal surface. Thus a similarity may exist between the conditioning of a catalyst prepared from a precious metal-halogen salt and recovery from halogen-induced inhibition. The effect of the atmosphere present during conditioning suggested that hydrogen was more effective than helium which in turn was more effective than oxygen in activating the catalyst (Section 3:3:6). Hydrogen would be expected to be effective in

removing chlorine in the form of hydrogen chloride.

Recovery from halocarbon inhibition was slower than conditioning which may have been due to carbonaceous residues being present as well as chlorine. Methane/oxygen pulses will produce water and, in some cases, hydrogen on reaction over a palladium catalyst, both of which may accelerate the desorption of chlorine. A more rapid recovery was observed using methane-rich pulses. This may be attributed to the high levels of water relative to carbon dioxide and the production of hydrogen from pyrolysis of methane on the palladium surface that occurred when the methane:oxygen ratio of the reactant mixture was high. Water has been found to prevent coking when reforming catalysts (Pt on Al_2O_3 and Pt-Re on Al_2O_3) have been used for dehydrochlorination of chlorocarbons (Noelke and Rase, 1979). Aluminium (III) oxide will, itself, catalyse the conversion of chloromethane to methylene chloride, carbon monoxide and water. The reaction was self-poisoning, however, and water was necessary to restore activity lost by chloride formation on the aluminium (III) oxide surface (Mochida, Uchino, Fujitsu and Takeshita, 1978). In the case of platinum on aluminium (III) oxide exposed to trichloromethane in the presence of hydrogen and water, the following reaction scheme was suggested:





The aluminium (III) oxide surface thus plays an active role in the maintenance of activity. Platinum alone is not as good at removing chlorine as are the basic sites on the aluminium (III) oxide surface, the formation of which are aided by hydration. The retention of chlorine on aluminium (III) oxide was also observed by Sivasanker, Ramaswamy and Ratnasamy (1979). Platinum supported on ϵ -aluminium (III) oxide adsorbed and retained more chlorine than platinum on γ -aluminium (III) oxide. Chlorine had ion-exchanged with hydroxyl groups on the alumina surface. The water content of the air/hydrogen atmosphere used and the temperature of calcination/reduction were the factors that controlled the rate of chlorine loss.

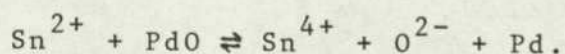
An investigation into the effect of chlorocarbons on palladium supported on metal oxides other than γ -aluminium (III) oxide indicated that the support had a significant effect on the inhibition of methane oxidation over precious metals. Supports for which strong precious metal-support interactions were likely to occur (e.g. tin (IV) oxide or titanium (IV) oxide) tended to show a rapid loss in activity followed by a more rapid recovery than that obtained for catalysts in which these interactions were weaker (e.g. palladium on thorium (IV) oxide). Slow inhibition with no recovery was obtained with 2.7% Pd on ThO_2 . The stability of palladium (II) chloride was found by Bozon-Verduraz, Tardy, Bugli and Pannetier (1976) to be

greater on γ -aluminium (III) oxide than on titanium (IV) oxide in a hydrogen atmosphere. After being dried at 393K, the palladium was in the form of PdCl_4^{2-} on aluminium (III) oxide, while on titanium (IV) oxide only a small part of the palladium (II) chloride formed PdCl_4^{2-} and the remainder formed a layer of PdCl_2 . In this case, the stability of the palladium (II) chloride may be assigned to the interaction between the precious metal salt and γ -aluminium (III) oxide.

Palladium supported on tin (IV) oxide showed some anomalies in behaviour when its performance towards methane oxidation was compared with that of other supports (e.g. γ -aluminium (III) oxide, thorium (IV) oxide or titanium (IV) oxide). Hydrated tin (IV) oxide, unlike these other supports, will undergo extensive ion-exchange with metal ions (Fuller and Warwick, 1974) and the resultant fine dispersion of palladium, as well as the strong metal-support interactions may well explain the absence of palladium particles observed under the transmission electron microscope (Section 3:6). Further evidence for interaction between the palladium and tin (IV) oxide was obtained from the fact that the activation energy for methane oxidation over 2.7% Pd on SnO_2 was 55 kJ mol^{-1} , while that for 20% Pd on SnO_2 was 75 kJ mol^{-1} . Furthermore, the temperature range over which the rate of methane oxidation was measurable and was controlled by true chemical kinetics was 588-714K for the higher loaded catalyst and 714-833K for the catalyst of lower loading. The activation energy for methane oxidation over tin (IV) oxide was found to be

57 kJ mol⁻¹ and methane oxidation took place at relatively low temperatures over this support. It thus appeared that, for 2.7% Pd on SnO₂, the palladium was shielded by tin (IV) oxide. Enrichment of the surface of tin-palladium alloys by tin has been observed before (Verbeek and Sachtler, 1976). Hughes and McNicol (1979) observed platinum crystallites on a 20% Pt on SnO₂ catalyst only when reduction temperatures of greater than 773K in hydrogen were used. This was attributed to reduction of Sn⁴⁺ to Sn⁰, a reaction accelerated by the platinum. After calcination in air, however, it proved difficult to reduce the platinum due to interaction between the precious metal and the tin (IV) oxide with formation of a PtO₂/SnO₂ alloy.

Similar behaviour was observed with the catalysts used in the present work. XPS revealed that the palladium on tin (IV) oxide remained as Pd²⁺ during inhibition by chlorinated hydrocarbons unlike palladium on other supports where Pd⁰ was formed. Oxygen may be transferred from palladium on to tin (IV) oxide (Bond, Fuller and Molloy, 1977) by a "spillover" mechanism:



The reverse reaction has also been observed (Bacaud, Bussiere, Figueras and Mathieu, 1976). The rapid decrease in activity observed in the presence of chlorocarbons may be explained by a combination of the inhibiting effect of chlorocarbons and of the interaction between palladium and tin (IV) oxide, whereby palladium may be incorporated into the tin (IV) oxide structure. The equally rapid recovery may be attributed to a spillover mechanism whereby a reser-

voir of oxygen is available in the tin (IV) oxide which can be used to replenish the oxygen lost from palladium (II) oxide during inhibition which may prevent deposition of carbon. In addition, it is conceivable that chlorine may spillover from the palladium onto the tin (IV) oxide, hastening the recovery of the palladium.

4:6 Inhibition and poisoning of hydrocarbon oxidation by organosiloxanes.

Inhibition of the oxidation of methane over a 2.7% Pd on $\gamma\text{-Al}_2\text{O}_3$ catalyst by hexamethyldisiloxane showed some differences when compared with the inhibition of a similar catalyst by chlorocarbons. Total deactivation with some recovery on removal of the inhibitor occurred with hexamethyldisiloxane, whereas only partial deactivation occurred with trichloromethane with little recovery, (Section 3:8:2).

Catalytic beads, on the other hand, showed no recovery for methane oxidation after exposure to hexamethyldisiloxane but inhibition of n-butane oxidation was almost totally reversed, in some cases, on removal of the inhibitor. The recovery appeared to be dependent on the concentration of and the time of exposure to the inhibitor. The difference in the behaviour of the powder catalysts and the catalytic beads towards hexamethyldisiloxane may be due to the short contact time (0.5s) of the pulse flow technique used for the powder catalysts. Beads were exposed to organosiloxanes for relatively long periods (ca. 1.5h). In addition, the

surface temperature of the catalytic bead (ca. 800K) was higher than that of the powder catalysts (650K) and the decomposition process undergone by the organosiloxanes is temperature dependent and provides a range of reaction products.

Transition metal compounds catalyse the cleavage of silicon-alkyl bonds in organosiloxanes and polymerisation to polyorganosiloxanes may occur (Akhrem, Chistovalova, Mysov and Vol'pin, 1972). The methane produced in our experiments was presumably formed by rearrangement of the molecule during the loss of methyl groups with concurrent hydrogen abstraction. Polydimethylsiloxanes decompose twice as fast in a nitrogen atmosphere as in an oxygen atmosphere (Sobolevskii and Andrianov, 1959). Thus, adsorption with demethylation initially occurs on the precious metal surface. Polymerisation of hexamethyldisiloxane by thermal degradation is a slow reaction even at temperatures above 673K and the products are numerous (Kuz'minskii, Goldovskii, Dudenkova, Sunitsa and Orlov, 1965). Using platinum (as hydrogen hexachloroplatinate (IV) hydrate) as a catalyst, the reaction occurs slowly at 473K. If the temperature is sufficiently high, however, silicon (IV) oxide would be expected to form in an oxygen atmosphere. Hence deactivation by hexamethyldisiloxane could occur via the formation of adsorbed polyorganosiloxanes and silicon (IV) oxide which prevents the adsorption of the reactants. The temperature and time of exposure to inhibition would be expected to control the volatility of the inhibiting species on the surface.

The penetration of both silicon and carbon below the surface of the Pd on $\text{ThO}_2/\text{Al}_2\text{O}_3$ beads exposed to hexamethyldisiloxane was not observed for the Pd on SnO_2 bead. The concentration of palladium remained the same, however, after argon ion etching of the surface layers of both beads. Thus the palladium present on tin (IV) oxide was more effective in removing the silicon from its surface before penetration into the bulk occurred. The 20% Pd on SnO_2 powder catalyst, too, showed little penetration of the silicon into the palladium. The chlorine obtained from chlorocarbons was not observed below the palladium surface (Hucknall, Willatt and Hockham, 1979). Hence the ability of the catalyst to resist deactivation may be reflected in its ability to adsorb the inhibitor into its bulk. (A similar effect has been observed for lead-poisoned palladium films (Williams and Baron, 1975)).

Penetration of silicon into the bulk of the palladium may explain the lack of recovery observed for catalytic beads. Decomposition of hexamethyldisiloxane is slow (see above) and the short contact times and low temperatures (650K) in the microreactor may prevent bulk penetration by the silicon so that irreversible poisoning is prevented. Palladium on thorium (IV) oxide/aluminium (III) oxide beads underwent irreversible poisoning probably due to bulk diffusion by the silicon, whereas the palladium on tin (IV) oxide bead showed little bulk penetration by silicon and carbon. The interaction between palladium and tin and the ability of the tin (IV) oxide to retain palladium in the oxide form (see previous section) is probably responsible

for this behaviour.

Inhibition of the oxidation of n-butane over catalytic beads (Pd on $\text{ThO}_2/\text{Al}_2\text{O}_3$) by hexamethyldisiloxane was in most cases only temporary. The activity of the catalyst recovered on removal of the inhibitor from the reactant gases. This may reflect the relative abilities of the palladium to oxidise n-butane and methane (Section 1:7:3). Lead also selectively poisons the oxidation of methane relative to that of higher hydrocarbons (Shelef et al, 1973). The high energy sites necessary for methane oxidation are thus more susceptible to poisoning than the lower energy n-butane oxidation sites that are only irreversibly poisoned after exposure to high concentrations of hexamethyldisiloxane.

Examination of the stability of the output obtained from catalytic beads operated in methane and n-butane revealed that a decrease in activity with time was observed during methane oxidation which was not found for n-butane oxidation. This may be due partially to consumption of the reactants, but self-inhibition by the reaction products probably accounts for most of the loss in activity. As oxygen is present in excess, preventing coking, it is probably inhibition by water vapour which is detrimental only to the oxidation of methane.

4:7 Conclusions.

The oxidation of methane over supported palladium

catalysts was found to occur by a Langmuir-Hinshelwood mechanism whereby both methane and oxygen are adsorbed on the palladium surface before they undergo chemical reaction with one another. The ability of the catalyst to adsorb oxygen at low temperatures plays an important part in the oxidation of methane. Palladium catalysts are more active than platinum catalysts and their superior activity is ascribed to their ability to form oxides. At high temperatures, however, adsorbed oxygen appreciably inhibits the adsorption of methane.

Three possible causes of the observed decrease in activity of supported precious metal catalysts, viz. thermal deactivation, self-poisoning and chemical deactivation, were studied. Of these, chemical deactivation is responsible for the greatest loss in activity. Thermal deactivation, although irreversible, occurs to a significant extent only at very high temperatures. As regards self-poisoning, coking is almost non-existent at high oxygen:methane ratios, while water vapour has only a transient effect on activity.

Platinum proved to be more resistant than palladium to poisoning by chlorocarbons. In addition, palladium supported on metal oxides for which strong precious metal-support interactions have been observed (e.g. Pd on SnO_2 or TiO_2) appeared to recover its activity more rapidly than palladium on those supports for which interactions are weaker (e.g. Pd on ThO_2). High temperatures, too, encourage

the restoration of catalytic activity, the rate-determining step for recovery being removal of carbon and chlorine from the precious metal surface.

Organosiloxanes cause permanent deactivation of catalytic beads for the oxidation of methane. The degree of deactivation depends on the extent of penetration of silicon and carbon into the precious metal, which, in turn, depends on the nature of the support. Although palladium catalysts poisoned by hexamethyldisiloxane showed no recovery towards methane oxidation, the same catalysts when used for the oxidation of butane underwent poisoning which was less extensive and reversible.

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