THE INTERACTION OF NITROGEN MONOXIDE WITH PYROLYSED POLYACRYLONITRILE

by

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SUMMARY

The object of the work described herein has been to investigate the interaction between nitrogen monoxide (NO) and pyrolysed acrylonitrile copolymer (PAN.P). This interaction has been established and studied in some detail over the temperature range 250 to 700°C. At the same time the feasibility of using PAN.P based catalysts for the removal of small quantities of NO, produced by the internal combustion engine, has been investigated.

The initial work was concerned with depositing a film of polyacrylonitrile from solution onto a pelletised alumina support and converting this into a supported PAN.P catalyst having optimum NO removal activity.

Kinetic studies indicated that at 500°C, $5{,}170 \times 10^{-10}$ moles $s^{-1}m^{-2}$ of NO were removed when using 3,300 ppm NO in nitrogen flowing at 1000 cm^3min^{-1} through 10g of supported PAN.P. The NO removal rate increased with temperature giving activation energies between 33.9 and 39.9 kJ $mole^{-1}$. The reaction appeared to be first order in concentration of NO and in surface area. Surface area measurements which were vital, involved the construction of a semi-micro B.E.T. apparatus.

The activity of PAN.P was examined in the presence of other gases using both dynamic and static conditions. NO was not reduced by carbon monoxide in any significant quantity in the presence of PAN.P. Whilst activity persisted in the presence of oxygen, degradation occurred to an extent which renders the PAN.P in its present form commercially unacceptable.

A detailed analysis of reaction products and an examination of various properties of PAN.P are reported. These results are used in a discussion of possible mechanisms of reaction.

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Finally I should like to thank both the Science Research Council and the University for financial support.

This work was carried out between October 1971 and September 1974 at the University of Aston in Birmingham. It has been done independently and has not been submitted for any other degree.

DCooper

D. R. COOPER

"Any scientist who believes that he and his colleagues are mere tools of discovery whose personal character, ambitions, hopes and doubts are insignificant is guilty of unscientific thinking, for he is disregarding an important, perhaps the decisive, element in scientific experiment - namely his own nature - or labouring under the delusion that he can arbitrarily eliminate that element."

Robert Jungk

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CHAPTER 1

INTRODUCTION

In 1970 the United States Clean Air Amendments Act demanded a progressive reduction in automobile exhaust emissions, including a 90% elimination of oxides of nitrogen after the proposed date of 1976. Unburnt hydrocarbons and nitrogen oxides have been identified as the prime chemical components of "Los Angeles smog", which was first noticed in the late 1940's.

The major source of hydrocarbons, nitrogen oxides and indeed carbon monoxide in the atmosphere is the internal combustion engine.

1.1 Nitrogen monoxide formation in the internal combustion engine

Nitrogen monoxide is formed in the combustion chamber and persists during expansion and exhaust. Upon exposure to additional oxygen in the atmosphere nitrogen dioxide and other oxides of nitrogen may be formed.

The major factors which influence the formation of nitrogen monoxide, hereafter referred to as NO , are flame temperature, reaction time, and fuel to air ratio. Kinetically the two important aspects are that the rate of formation is highly temperature-dependent, and that the extent of formation corresponds nearer to the equilibrium concentration for peak flame temperature than to that for the exhaust condition.

The simple reaction between oxygen and nitrogen:-

$$N_2 + O_2 \underset{}{\overset{K_1}{\rightleftharpoons}} 2NO \qquad 1$$

predicts concentrations much lower than those measured in the combustion engine, because the process is too slow for the NO to reach equilibrium concentration at the peak temperatures and pressures in the cylinders.

This mechanism[1] fails to explain the close parallel found, at a given pressure, between the equilibrium concentrations of both atomic oxygen and NO molecules, where they increase with increasing the temperature, and with leaning the mixture[2]. Glick, Klein and Squires[3] heated air in the range 2000 to 3000 K and showed the rate of formation of NO to be dependent on the square root of the oxygen molecule concentration present, in the pressure range of two to five atmospheres. They also found a much lower temperature dependence than that expected for K_1 which has a large temperature coefficient.

All this evidence supports the Zeldovich mechanism[4], which involves a chain reaction with the reaction of oxygen atoms to produce NO:

$$O_2 \rightleftharpoons 2O \qquad 2$$

$$O + N_2 \rightleftharpoons NO + N \qquad 3$$

$$N + O_2 \rightleftharpoons NO + O \qquad 4$$

The nitrogen atoms do not start the reaction because their equilibrium concentration is relatively low compared to that of atomic oxygen.

Other reactions must also be considered:-

$$O + NO \rightleftharpoons O_2 + N \qquad 5$$

$$N + NO \rightleftharpoons N_2 + O \qquad 6$$

$$O + O + M \longrightarrow O_2 + M \qquad 7$$

$$N + N + M \longrightarrow N_2 + M \qquad 8$$

The above reactions can be used to explain the NO "freezing" phenomena. If chemical equilibrium prevails during the engine cycle, one would expect the NO concentration to drop during the expansion stroke because of a decrease in the gas temperature. Laboratory measurements by Newhall and Starkman[5] showed that no decomposition of the NO, formed at the maximum cycle temperature occurred during the expansion stroke, thus confirming practical observations that although the mixture is suddenly quenched in the exhaust system, the NO remains.

The work of Enschenroeder[6] provides an idea of the likely kinetic events on cooling. The recombination of oxygen and nitrogen atoms in reactions 7 and 8 are not rapid enough to keep equilibrium conditions during expansion so we look at the other interconversion pathways of reactions 3, 4, 5 and 6. Reactions 3 and 5 are found to be characterised by high temperature coefficients, so that on cooling the gas, they rapidly become too slow to be effective in affecting the NO concentration, these are processes removing oxygen atoms. The reactions removing nitrogen atoms, 4 and 6, remain fast to much lower temperatures, so that these "shuffle" reactions will maintain the nitrogen atom/molecule equilibrium to a much later extent in the expansion. Since these last two reactions 4 and 5 produce and remove NO respectively, their relative rates during cooling could be important; but since we are dealing with extremely small concentrations of nitrogen atoms then no change can occur in the NO concentration during expansion.

Several workers[7,8], have shown little correspondence between both NO concentration and the chemical character of organic materials in the exhaust and the type of fuel supplied, all fuels being substantially degraded before exhaust. The effect of the early reaction stages which involves the oxidation of hydrocarbons only, is to reduce the total oxygen available in the later stages. This explains how richer mixtures give lesser concentrations of NO, since at a typical temperature of 2500 K the equilibrium concentration of NO would be near to 40,000 ppm but levels nearer to one tenth of this are found[9]. In conclusion NO equilibrium is only attained, if at all, in the later stages of the heating process after much of the oxygen has been depleted.

Tuteja and Newhall[10], using a laboratory scale vertical coaxial diffusion flame burner, have shown that NO formation is restricted to a very narrow peak in the intense temperature zone external to the fuel rich area i.e. behind the flame front. The peak coincides with that of temperature and approximately with that of CO_2. This work helps to explain how engine design can modify by an order of magnitude the level of NO produced for a given fuel to air ratio; since any change in the geometry of the combustion chamber will affect the temperature profile during the heating process.

1.2 Proposed method for the removal of nitrogen monoxide

The removal of the bulk of hydrocarbons from the atmosphere could feasibly have eliminated the photochemical smog problem. However, any controversy surrounding the need to remove nitrogen oxides was ended following legislation. It is the reduction of the NO_x level which is now receiving most attention since the CO and HC levels can already be adequately reduced.

A variety of methods have been proposed to diminish the concentration of the three main pollutants - these include modifying the composition and/or the injection mechanism of the ingoing fuel mixture, changing the flow path of the fresh exhaust gases, redesigning the construction of the combustion process within the engine, or using a catalyst converter to treat the exhaust gases. The problem is not just technical, but is also one of time restriction and economics, such that the engine modification with its attendant high cost is regarded by many as the least likely alternative, and the use of a catalyst converter the best in the short term. In fact it has been suggested that the catalyst system represents only an interim solution until the ideal new engine appears. The Honda "Compound Vortex Controlled Combustion Engine",already in limited production, looks promising in this respect.

The motor car manufacturers have opted for two physical forms of catalyst, pellets and monoliths, the latter being a continuous bed having an extensive arrangement of narrow channels. The normal practice is to deposit the active component onto the surface of an inert refractory material.

Durability is obviously a major consideration since according to legislation only one change of catalyst is permissible for a 50,000 mile life.

High thermal stability and low heat capacity are common requisites, whilst the pellets should possess adequate resistance to attrition and shrinkage[11], and the monoliths should have good thermal shock and mechanical stress properties[12].

We can now consider the requirements of the ideal catalyst in removing all the offensive exhaust gases from a conventional engine. The most promising has been the use of catalytic after burners to remove the CO and HCs:-

$$2CO + O_2 \longrightarrow 2CO_2 \qquad 9$$

$$C_xH_y + (x + \frac{y}{4})\, O_2 \longrightarrow xCO_2 + \frac{y}{2}\, H_2O \qquad 10$$

The NO can be removed in two ways:-

$$2NO \longrightarrow N_2 + O_2 \qquad 11$$

$$2NO + 2CO \longrightarrow N_2 + 2CO_2 \qquad 12$$

The former reaction (11) is found to be impractical since no known catalysts promote the decomposition reaction at a sufficient rate. The faster reduction process is preferred. This reaction is restricted to a reducing environment, since the reducing agents (CO, HC, H_2 etc.) would be preferentially oxidised by excess oxygen before the NO is reduced. Therefore the trade has opted for a dual bed system whereby the engine is tuned rich to create a reducing atmosphere in which the NO can be removed, and then, with the help of an air pump, a second catalyst accelerates the remaining oxidation processes. At the same time other approaches are being examined, one of which is the all-purpose, or three-way, system. Here a single catalyst is used for all three pollutants simultaneously. An added problem is then to ensure a stoichiometric air:fuel ratio.

Confining our attention to the NO reduction process in the dual bed converter, we must recognise the need for high catalyst specificity. It is no use producing ammonia (14), or dinitrogen oxide (15) in quantity if these are going to be oxidised back to NO downstream. The water-gas shift reaction (13) can supplement any hydrogen emitted in the exhaust.

$$CO + H_2O \longrightarrow CO_2 + H_2 \qquad 13$$

$$2NO + 5H_2 \longrightarrow 2NH_3 + 2H_2O \qquad 14$$

$$2NO + CO \longrightarrow N_2O + CO_2 \qquad 15$$

$$2NO + 2H_2 \longrightarrow N_2 + 2H_2O \qquad 16$$

The catalyst must promote reaction 16 at the expense of reaction 14, and whilst reaction 12 is preferable to reaction 15, the latter could be an acceptable short life intermediate.

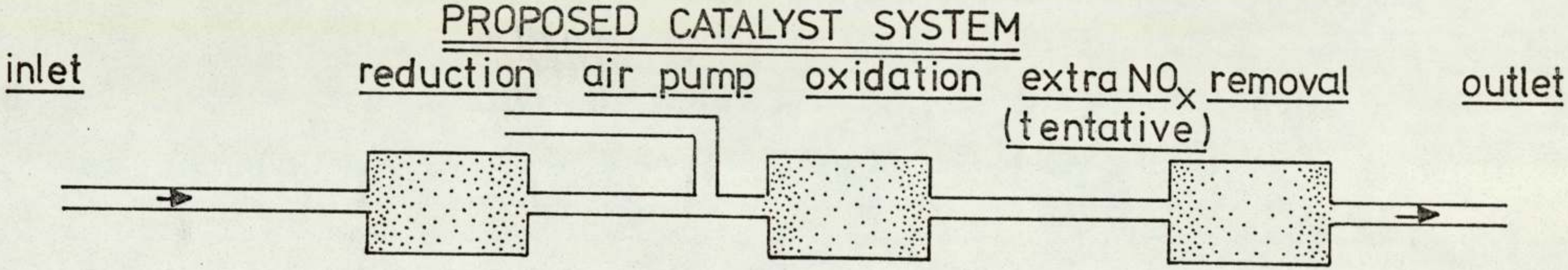
In fact several workers have reported on the production of ammonia by nitrogen oxide removal catalysts such as Rhodium-Platinum[13] and Copper-Vanadia[14]. Iron-based catalysts are said to be very active[15] in assisting the CO/NO reaction, but in the presence of water vapour they favour the water-gas reaction. It has also been shown that platinum catalysts promote the oxidation of sulphur to sulphates and sulphuric acid, thus producing a further health hazard[16]. The overall

Engine Products

HC CO NO_x NH_3 H_2 O_2 N_2 CO_2 H_2O Others;

Ideal Emission Mixture

H_2O CO_2 N_2 O_2:



desired reactions

1. $NO + CO \rightarrow N_2 + CO_2$

$CO + O_2 \rightarrow CO_2$

$HC + O_2 \rightarrow CO_2 + H_2O$

eg 2. $NO \rightarrow N_2 + O_2$

undesired reactions

3. $NO + H_2 \rightarrow NH_3$

4. $NO + HC \rightarrow NH_3$

5. $N_2 + H_2 \rightarrow NH_3$

6. $CO + H_2O \rightarrow H_2 + CO_2$

7. $NO + CO \rightarrow N_2O + CO_2$

$NH_3 + O_2 \rightarrow NO + H_2O$

$N_2O + O_2 \rightarrow NO_x$

FIGURE 1

SCHEMATIC REPRESENTATION OF EXHAUST CATALYST SYSTEM scheme for the proposed catalyst system is summarised in Figure 1.

In addition to these selectivity problems other factors are important. The catalyst, for instance, must have sufficient activity before the engine warms up. The resistance to poisoning by such fuel components as lead and phosphorus must be another objective, whilst concern has been expressed regarding the possible emittance, and then measurement of, metallic particles in the atmosphere[17]. Indeed the position has prompted Shelef, Otto and Gandhi, to conclude that in view of the presently available catalysts the practical application of catalysed decomposition is not promising for the removal of NO from automobile exhausts[18].

Although certain highly conjugated organic polymers have recently been established as efficient heterogenous catalysts, no report could be found on their interaction with NO. Since one school suggests that they owe their activity to a high stable concentration of delocalised electrons, it is reasonable to believe that NO,with its classical electron scavenging properties, may well have a desirable affinity for these polymers. A comprehensive study of the literature dealing with the use of highly conjugated organic polymers as heterogenous catalysts now follows. We have previously published most of this text[19].

1.3 Highly Conjugated Synthetic Organic Polymers as Heterogenous Catalysts

1.3.1 Literature Survey

Since the first independent reports of the catalytic properties of conjugated polymers by Topchiev[21] and Berlin[20] in 1959, many other workers have studied various aspects of these materials. The two initial reports, in which pyrolysed polyacrylonitrile (PAN.P) and polyaminoquinone were used to catalyse the decomposition of hydrogen peroxide were purely qualitative in character. Subsequent reports have often been quantitative and have tried to relate the degree of catalytic activity to certain of the physical properties possessed by the polymer.

In 1960 Nesmeyanov[22] studied the electrical, magnetic and catalytic properties of methyl-(β-chlorovinyl) ketone polymers. These catalyse the oxidation and dehydrogenation of alcohols and the oxidation of toluene. The author also noted that the polymer supported a large concentration of unpaired electron spins.

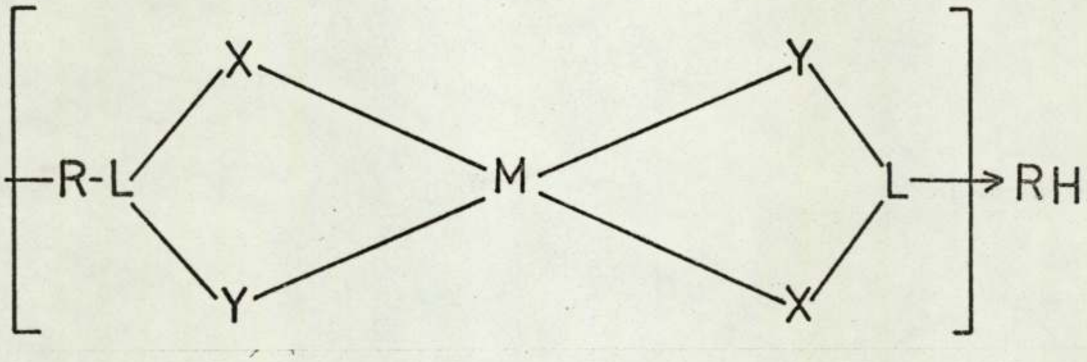
It was subsequently shown by Dokukina[23] that PAN.P, already studied with regard to its semi-conductor properties, was an excellent catalyst for the decomposition of formic acid but that it would not catalyse the decomposition of alcohols or the hydrogenation of ethylene. This observation enabled the hypothesis to be advanced that polymeric catalysts of this type could exhibit selectivity in their action.

In the same year (1961) Kiperman[24], using amongst others poly(vinyl methyl ketone) and poly(p-diethylnyl benzene) pyrolysed in a nitrogen atmosphere, examined the kinetics of the para-ortho hydrogen conversions, and also studied the isotopic exchange reactions between hydrogen and deuterium, and the decomposition of formic acid. He concludes that the para-ortho hydrogen conversion proceeds with a specific magnetic mechanism because of the effect of a heterogenous magnetic field formed by the collection of the polymer electrons.

A substantial advance was made by Keier and co-workers who in a series of four reports on the "catalytic properties of organic polymers" published in 1961 and 1962 include a detailed examination of the use of chelate polymers. Firstly[25] they studied the decomposition of hydrazine on copper, nickel, cobalt, zinc and cadmium bisthiocarbamate complexes. They showed that whilst the zinc and cadmium complexes had practically no catalytic activity, the copper, nickel and cobalt complexes showed high activity which was greater than that found with nickel oxide or nickel sulphide catalysts. The organic portions of the chelate polymers had a strong effect on the electrical conductivity and its activation energy but no correlation could be established between electrical properties and catalytic activity.

In a second paper Keier[26] reports on the catalytic properties of a polymer obtained by dechlorination of poly (vinylidene chloride). She studied this polymer as a heterogeneous catalyst for the decomposition of formic acid, isopropanol, and hydrazine, and for the oxidation of carbon monoxide. The work showed that the specific catalytic activity of the polymer, and of the semiconductors nickel oxide and nickel sulphide are of the same order with respect to the decomposition of hydrazine. The catalytic reaction on the polymer studied proceeds with strong adsorption of hydrogen, ammonia, and hydrazine. They claimed that this is indicative of a high reactability of the unsaturated bonds of the catalyst.

Keier's third paper[27] is concerned with the catalytic properties of chelate polymers having the general structure 1.



STRUCTURE 1

Here X and Y are atoms forming donoracceptor bonds, L and R are organic ligands, and M is the metal atom. The metals used were copper, nickel, cobalt, iron, zinc, cadmium, manganese and palladium. The polychelates were used as catalysts in the decomposition of hydrazine. The~~y~~ authors concluded that the catalytic activity was determined mostly by the atoms forming donor acceptor bonds, for copper chelates activity decreases in the series bis(aza-thia) > bis(dithia) > bis(aza-oxa) > bis(dioxa). For the nickel chelates the bis(dithia) structure is more active than the bis(aza-oxa) structure. They point out that the catalytic activity of the polychelates is considerably higher than that of the corresponding monomeric chelates or metal oxides. Also the selectivity of catalysis is temperature dependent.

The final paper in this series[28] examines their previous range of metal polychelates in their ability to decompose hydrogen peroxide to oxygen and water. Once again they show that the activity of copper polychelates, which are the most active, depends on the structure of the chelate, decreasing in the series bis(dithia)> bis(aza-oxa)> bis(aza-thia)> bis(dioxa). Among the nickel polychelates only those containing the bis(dioxa) structure, and among the cobalt derivatives only poly hexamethylene-bis(dithiocarbamate) are catalytically active. Zinc polychelates were found inactive. They indicate activity to be dependent on the structure of the organic radicals.

Boreskov[29] reiterated the findings of Keier's previous work. He further explained that the copper chelate polymer is twice as active as copper based semi-conductors in the decomposition of hydrazine, and that activity is dependent on the electronic state of the metal in the chelate node and cannot be related to the electroconductivity of the polymer.

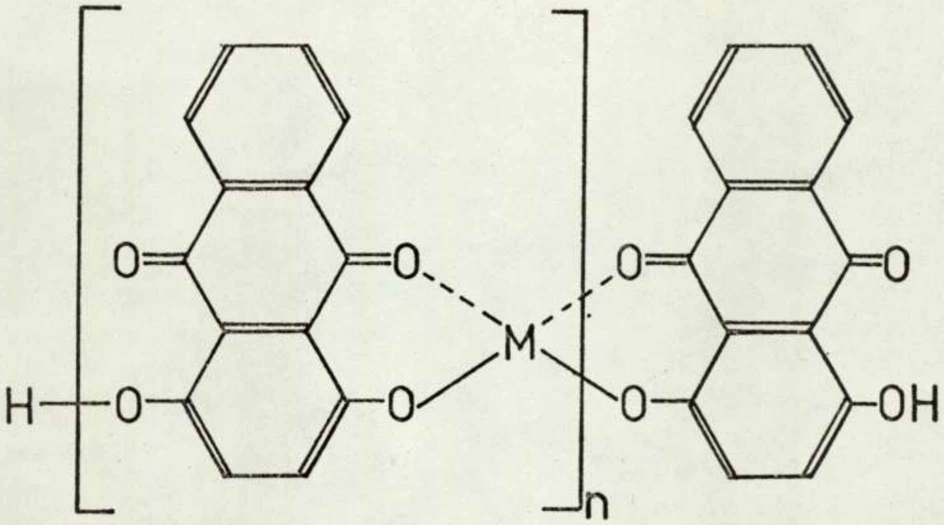
In the first[30] of the four papers, published in 1962 and 1963 by Gallard and co-workers, the catalytic action of PAN.P in the decomposition of dinitrogen oxide is discussed. They note that the PAN.P is paramagnetic giving an electron paramagnetic resonance signal equivalent to approximately 10^{18} spins per g. Only nickel oxide of the semiconductors had a higher decomposition effect on the dinitrogen oxide.

The two subsequent Gallard publications[31, 32] both refer to the use of a variety of highly conjugated polymers mainly as catalysts for the decomposition of dinitrogen oxide.

Phthalocyanines, polyacenequinone, the products of polyisoprene and molten benzoquinone, poly(diphenylacetylene), polymellitimide, aniline black, paramine brown, polyquinoxaline, polyimine, the polycondensate of pyromellitic anhydride and chrysene, the polycondensate of benzidine and chloranil, PAN.P, polybenzimidazole and the product of polyisoprene and chloranil, were examined. The last three were found more active than nickel oxide for the decomposition of dinitrogen oxide. All polymers examined gave e.p.r. signals, and some were semiconductors. The polymers also exhibited catalysis with varying success in the hydrogenation of ethylene, the oxidation of tetralin, the decomposition of alcohols, and formic acid, the isomerisation of but-1-ene, the simultaneous dehydrogenation and hydrogenation of cyclohexanol and isopropanol.

In the last of their earlier papers[33] Gallard's group reports upon the beginning of their work which eventually turns out to show a most fruitful correlation between the properties of the paramagnetic centres in the polymer and its catalytic activity. They note that catalytic activity is proportional to thermal pretreatment and also to the concentration of free spins.

In 1963 Slinkin[34] showed that quinizarin based metal polychelates could be used for the polymerisation of styrene whilst the metal free poly(methyl vinyl ketone) showed very little activity. The chelate polymers had the general structure 2 where M is nickel, cobalt, manganese, copper or zinc. It is interesting that the order of activity varied with the nature of the metal in the same way that Keir had



STRUCTURE 2

found for the decomposition of hydrazine, again the zinc and cobalt complexes were inactive, whilst of the remainder copper was the most active and nickel the least.

From a study of the catalytic activity of a series of polymers Roginskii[35] found electrical conductivity and catalytic activity to vary in a similar fashion. In this work he observed copper polyphthalocyanine, the complex of copper with poly(tetracyanoethylene), and polyvinylenes obtained by the dehydrochlorination of polyvinyl chloride to enhance the reaction of oxygen with cumene, cyclohexane, ethyl benzene, toluene and benzene. Roginskii[36] also reported on the catalytic activity of copper polyphthalocyanines with respect to the decomposition of hydrogen peroxide. The polymer showed the same activity as manganese dioxide in the oxidation. This reaction, carried out in aqueous solution, was not catalysed by the presence of the corresponding monomeric chelate.

A similar piece of work was carried out by Acres[37] in 1964, who reported on a detailed investigation of the activation of hydrogen by copper polyphthalocyanine. The para-ortho hydrogen conversion and the hydrogen-deuterium exchange reactions were studied.

A major advance in the general understanding of the structural requirements of polymers to be catalytically active was made by the research group of Gallard[38] who established a close correlation between catalytic activity and the e.s.r. signal given by polyacrylonitrile (PAN) pyrolysed at different temperatures. They further attempted, without success, to show the free spins to be directly involved in the catalytic process.

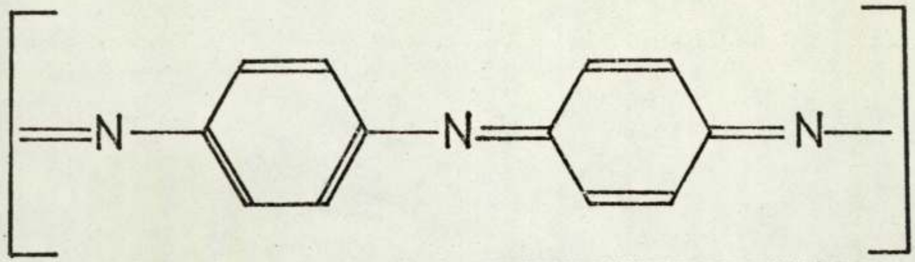
In a paper entitled "Synthesis and properties of poly-(diphenylacetylenes)"[39] Teyssie briefly records that the products exhibit catalytic activity towards the decomposition of dinitrogen oxide.

The Russian worker, Davydova[40] investigated ortho-para hydrogen conversion and the hydrogen-deuterium isotope exchange reactions on activated carbon, pyrolysed poly(vinyl methyl ketone) and pyrolysed poly(p -diethynyl benzene). The isotopic exchange at 312 to 470°C did not proceed at all. The ortho to para hydrogen conversions were catalysed by all three but the para to ortho conversion was not found to be catalysed by the activated carbon.

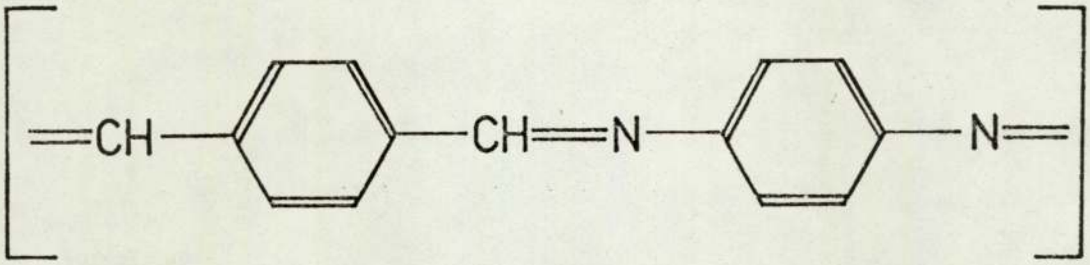
Keier[41] in 1964 described the evaluation of copper, nickel, iron, manganese, cobalt, zinc and cadmium chelates made from sodium dithiocarbamates, α-thioamides, the Schiff bases of 5,5'-methylene bissalicyladehyde, and the latter aldehyde itself. She studied the oxidation of cumene to the hydroperoxide. The most active material of all was the copper chelate of α-thiopicolinamidodiphenyl. Manganese had the maximum activity when chelated through nitrogen and oxygen atoms. Nickel was most active in the bisdiketone series. The chelates of bisdiketones were more active than the corresponding chelates of 5,5'-methylene bissalicyaldehyde.

The Israeli worker Manassen published three papers, between 1965 and 1967, under the general heading "Organic polymers, correlation between their structure and catalytic activity in heterogeneous systems". Although the third paper in this series refers to acid type catalysis and is beyond the scope of this review the others are extremely relevant. Paper I is concerned with PAN.P and polycyanoacetylene[42]. These polymers are strong hydrogen acceptors capable of dehydrogenating olefinic compounds in the vapour phase at elevated temperatures. They become hydrogenated in the process but their catalytic activity can be restored by air oxidation at 140°C. Double bond shifts and the cis/trans isomerisation of olefinic systems are also reported.

In Paper II, "Models for dehydrogenation catalysts", Manassen[43] makes an interesting comparison between two similar polymers. Structure 3 contains quinoid rings and is active, whilst structure 4 is inactive. From this he claims that a material with an extended conjugated system will only



STRUCTURE 3



STRUCTURE 4

be active catalytically in dehydrogenation reactions if the uptake of hydrogen does not destroy the polyconjugation. The polymers show a good correlation between free spins, but a poor correlation for conductance and catalytic activity, which leads them to conclude that chemical units and not electronic properties of solids are responsible for catalytic activity.

In 1966 both Quivoran[44] and Hatano[45] presented the first of several summaries[44-50] and reviews on this subject. In the same year Berlin[51] reported on the activation of the cis/trans isomerisation of dimethyl maleate at 225 to 255°C by polymers with a conjugated system. Black poly(phenylacetylene), polyphenylene, poly(azophenylene), and yellow poly(phenylacetylene) were the polymers he used. Some stable organic radicals were also tried, but these were rapidly deactivated and did not activate the isomerisation. The polymers catalysed the reaction at concentrations corresponding to one unpaired spin per 10^6 to 10^7 moles of dimethyl maleate. Air was without effect on the process. The yellow poly(phenylacetylene) causes an increase in the isomerisation rate and a disappearance of the induction period. It was shown that the concentration of free spins of this polymer decreases initially and then increases again. Berlin proposes that the initial decrease in concentration is due to the existence of trapped electrons and that quasi-radical polymerisation causes the observed increase. The activation energy of isomerisation is lowered by a factor of three when performed in the presence of yellow poly(phenylacetylene).

In a paper[52] on the use of poly(isoindolobenzimidazoles) and their derivatives as catalysts for the decomposition of dinitrogen oxide by Sillion, a concentration of free spins between 10^{16} and 10^{19} spins per g, when heated to 350°C, is reported. The activation energy of decomposition is [illegible] [illegible] dependent on the structure of the thermally stable polymer.

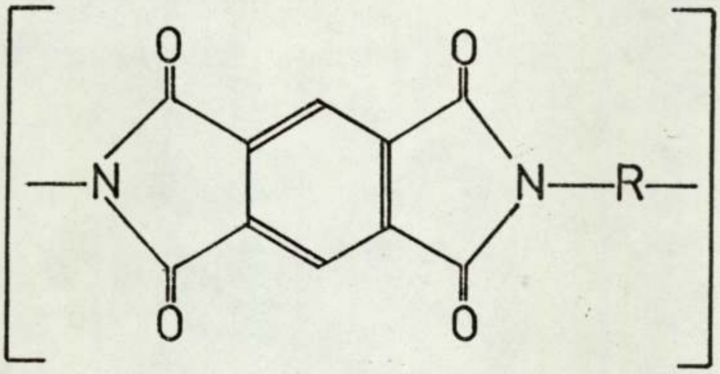
Hanke, in a series of papers entitled "Catalysis on phthalocyanines", attempts to correlate catalytic activity and electrical properties of both the monomeric and polymeric chelates. The first paper is devoted to the decomposition of formic acid vapours on monomeric metal phthalocyanines. The second paper[53] similarly relates to the decomposition of formic acid vapours on polymeric copper phthalocyanines and it describes a relationship existing between catalytic activity and the thermal activation energy of conductivity. This is the first time such a relationship has been recorded.

The final paper[54] which deals with cumene autoxidation in the presence of polymeric copper phthalocyanine points out that the polymer is an "n" type conductor whilst the monomer is a "p" type conductor. No relationship between conductivity and catalytic activity existed when comparing the polymer to the monomer.

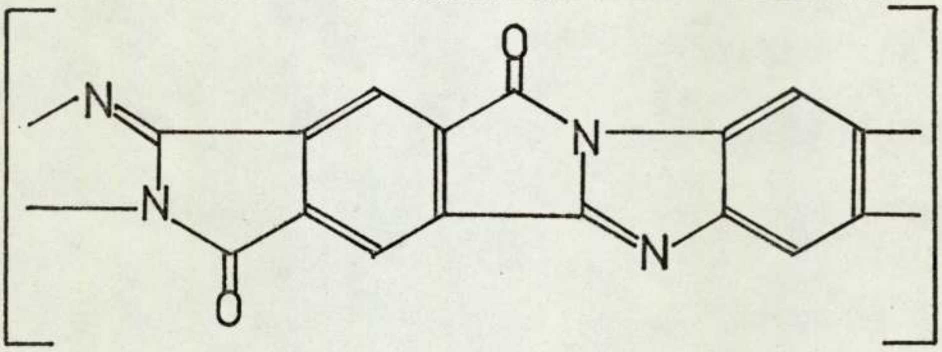
Again in 1966 Hatano[55] published his latest work on semi-conductive high polymers involving the synthesis and catalytic activity of certain polychelates. The copper based polychelates, very active in hydrogen peroxide decomposition, were the most active catalysts of all the ones examined. He suggests that this result infers a contribution of the conjugated double bond structure in the chelate to the increase in its catalytic activity.

A second Japanese worker Inoue[56] reported on the electrical conductivity of vulcanised aniline black and its catalytic action in the decomposition of hydrogen peroxide. He found that catalytic ability was dependent not only on structure but also on electrical conductivity. The nature of the polymer as an electron donor was found important. In 1967, the same author[57] reported on the catalytic action of copper-iron-polyphthalocyanine on the oxidation of acetaldehyde ethylene acetal. He found that the oxygen absorption rates were dependent on the ratio of copper to iron ions involved and to the activation energy of electrical conductivity.

The influence of structure on the catalytic properties of conjugated polymers was investigated by Gallard and co-workers[58]. The polymers used were a series of poly-(pyromellitimides) as in structure 5 and poly(indoloimidazoles) as shown in structure 6. Dinitrogen oxide decomposition was the reaction chosen. They concluded that the catalytic activity of imperfectly conjugated polymers was dependent only on the number of π bonds between the conjugation breaks and, to a lesser degree, on the condensation of the elements. The catalytic activity was essentially independent of other variables such as presence of heteroatoms, chain length and configuration. Catalytic properties of the paramagnetic



STRUCTURE 5



STRUCTURE 6

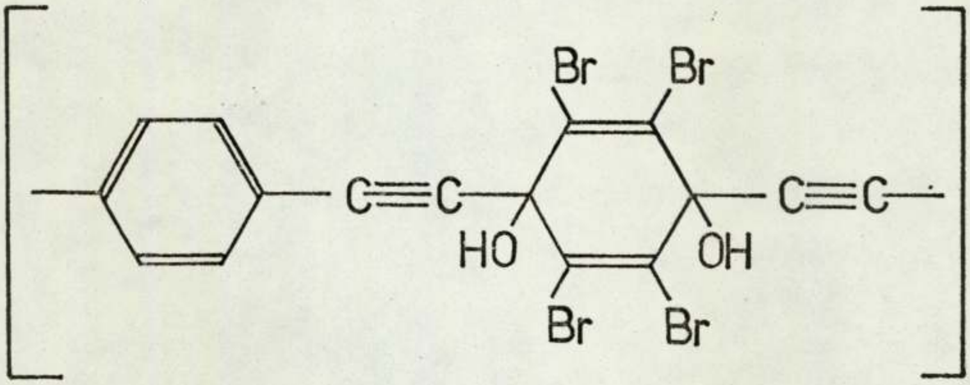
centres in polymers with regular alternating double and single bonds were not related to structural factors but rather to carbon enrichment or the tendency of the structure to order itself in a crystalline manner.

The same school led by Nechtschein[59] studied catalytic activity in relation to the relaxation time of paramagnetic centres in conjugated polymers. They examined the catalytic effects of PAN pyrolysed in an argon atmosphere and several conjugated polycondensates on the decomposition of dinitrogen oxide. Catalytic activity was then found related to spin relaxation time.

M. B. Cutlip[60a] examined the activity of PAN.P in.the tertiary butyl alcohol dehydration reaction producing isobutylene and water. He found the adsorption of the products from this reaction significantly affected the reaction rate and concluded that this adsorption must be accounted for in any reaction mechanism. In a later paper[60b] he produced results which indicated that activity is probably due to the acidity of the catalyst, and that the exact nature of these acidic sites remains unknown because of the uncertain polymer structure.

Paushkin[61], in 1968, published some work designed to examine the use of poly(phenylacetylenes) as catalysts in the conversion of isopropanol and tertiary butanol. The polymers were found to have a high concentration of free electrons and to exhibit more active catalysis at higher temperatures. It is interesting to note that in the previous year Berlin[62] had reported the inhibiting action of the same polymer on the oxidation of cumene by AZBN.

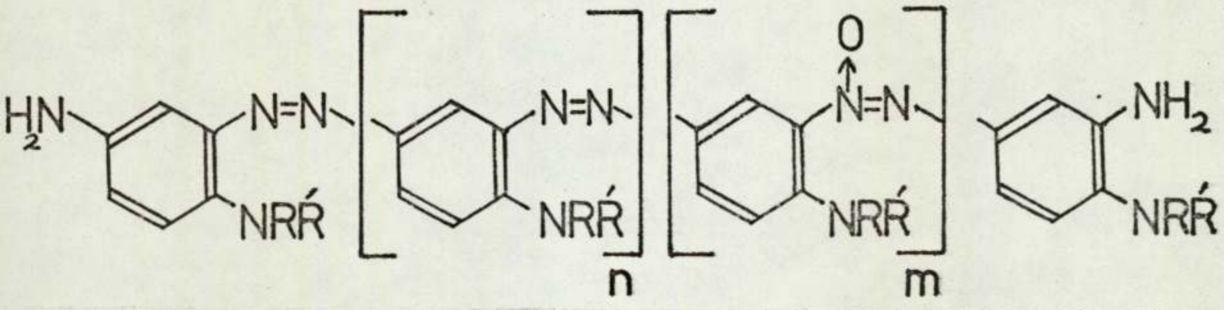
In his second report[63] of the same year, Paushkin described his work to examine the catalytic activity of polymers with ethynyl and cumulative double bond groups in the chain. Thermally stable polymers were prepared by condensing quinone, chloranil, bromanil or anthraquinone with diethynyl benzene bis(MgBr) and the subsequent reduction of polymers to polymeric cumulenes. Structure 7 is typical, this was the most active in the decomposition of isopropanol, since the bromine atoms apparently increase the electron acceptor properties of 7. He showed that polymers having concentrations of paramagnetic particles in excess of 10^{17} spins per g catalyse the reaction whilst diamagnetic polymers are inactive.



STRUCTURE 7

Lescinsky[64], in a study of the properties of PAN, noted that whilst thermal degradation produces a catalytically active polymer, the product obtained by photochemical degradation is inactive. This is because only the thermally treated PAN produced free radicals and a highly conjugated system which exhibits semi-conductivity. He further suggests that laser degradation would be suitable for the production of a catalytically active polymer.

The Russian worker Mazur[65] has described the catalysis of the liquid phase oxidation of cumene using poly(azoarenes) which supports dialky(aryl alkyl) amino groups, see structure 8. Similarly Dabrowski[66] in 1971 published his review and reported on the catalytic properties of some phenylene phthalic polymers in decomposing isopropanol.



STRUCTURE 8

The versatility of catalysts based on polynaphthoquinone was illustrated by Iwasawa and co-workers[67] in 1972. The potassium metal complex of the polymer catalysed the hydrogen, deuterium exchange reactions, ammonia synthesis, propene hydrogenation and isomerisation of cis 2-butene.

In the following year Alt, Binder and Sandstede[68] recognised that a conjugated π electron system is a prerequisite for catalytic activity in the reactions they examined involving the electrocatalytic reduction of the oxygen molecule. They concluded this after finding that catalysis only occurred when the polychelate had a ligand configuration of four nitrogen atoms. The N_2O_2 and N_2S_2 derivatives were inactive.

The highly conjugated organic polymers which have been shown to have catalytic action are catalogued in Table 1.

1.3.2 Factors Affecting Catalyst Efficiency

1.3.2.1 The free spins

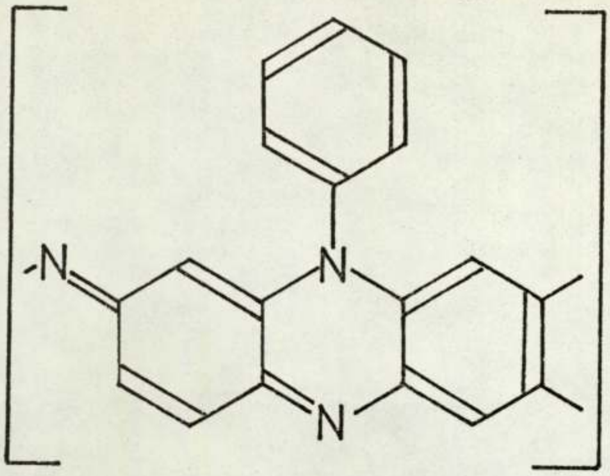
When e.p.r. was first applied to the problems of catalysis using transition metal compounds, catalytic activity was seen to occur wherever a resonance signal was detectable. This observation led to the idea that a correlation between the appearance of paramagnetic centres in a substance and its catalytic properties may exist. In fact this has been found to be the case with highly conjugated organic polymers.

The method of preparation of these polymers designed for use as heterogeneous catalysts, can have a marked influence upon the concentration of paramagnetic particles. Gallard[34], when studying the effect of varying the pyrolysis temperature of PAN on the concentration of free spins and on the catalytic activity in decomposing dinitrogen oxide, found a fairly narrow parallel to exist. Above a pyrolysis temperature of $450^{o}C$ a dramatic fall in the number of spins was observed, this, Nechtschein[69] explained, was due to the appearance of graphitic zones in which recombinations of electrons in doublets with opposite spins can occur.

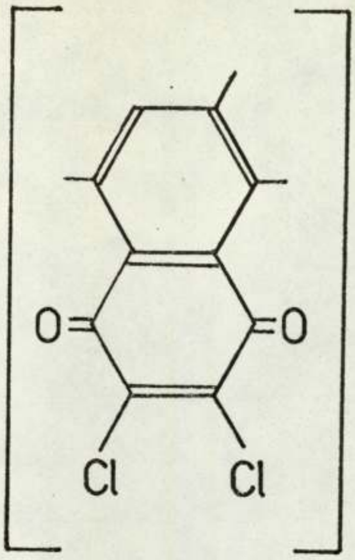
TABLE 1

Polymers which display catalytic activity

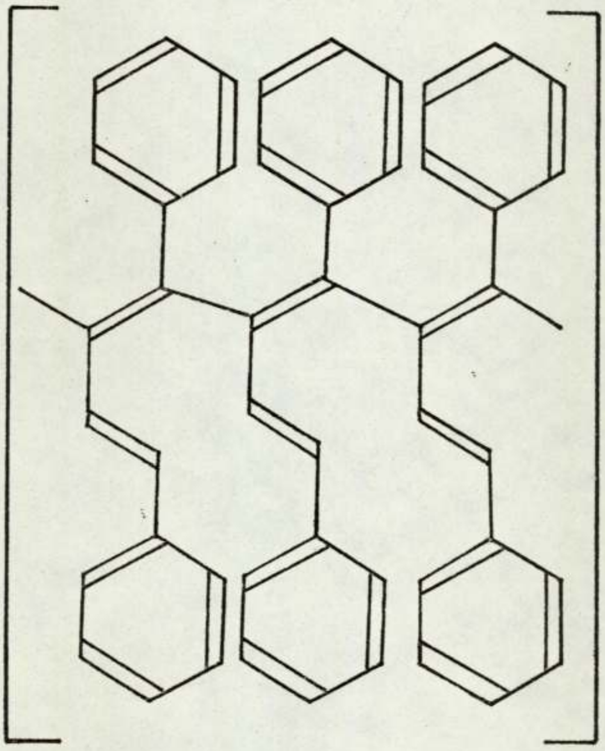
Polymer or precursor	References	Suggested structure
Polyaminoquinone	20	
Pyrolysed polyacrylonitrile (PAN.P)	21,20,23, 30,31,33,38 42,44,59,64 69	20,26
Polymer from methyl-β-chlorovinyl ketone	22,23	19
Pyrolysed poly(vinylmethyl ketone)	24,40	
Pyrolysed poly(p-diethynyl benzene)	24,40	
Polymer from poly(vinylidene chloride)	26	
Polyphthalocyanines	31,32,33	
Polybenzimidazoles	31,33,38,69	13
Polyacenequinones	31,69	
Polyisoprene treated with benzoquinone	31,32,33,38	
Polyisoprene treated with chloranil	31,32,33,38	11
Poly(diphenyldiacetylene)	32,33,38,39 51,61,62	10
Aniline black	32,33,38,39	9
Paramine brown	32,38	
Polyquinoxalines	32,38	14
Polymeric Schiff bases	32,33,38	16
Polycondensates of pyromellitimide	32,33,58,69	5
Benzidine/chloranil polycondensate	32,33,38	12
Polymer from the dehydrochlorination of polyvinyl chloride	33,35	
Mellon	33,38	
Pyrolysed polycyanoacetylene	42	
Paraphenylene diamine polycondensates	43	3,4
Polyphenylene	36	15
Polyazophenylenes	51,65	
Polyisoindolobenzimidazoles	52,58,69	
Polymeric cumulenes and derivatives	63	
Polyquinazolone	69	
Polyarylenequinones	74d	
Phenylenephthalic polymers	66	
Polymeric chelates based on Structure 7	25,27,28,29 34	7
Quinizarin based polychelates	41a,55	2
Polyphthalocyanine/metal complexes	35,36,37,53 54,57	17
Polytetracyanoethylene/metal complexes	35	18
Polychelates of polymers with hydroxamic groups	55	



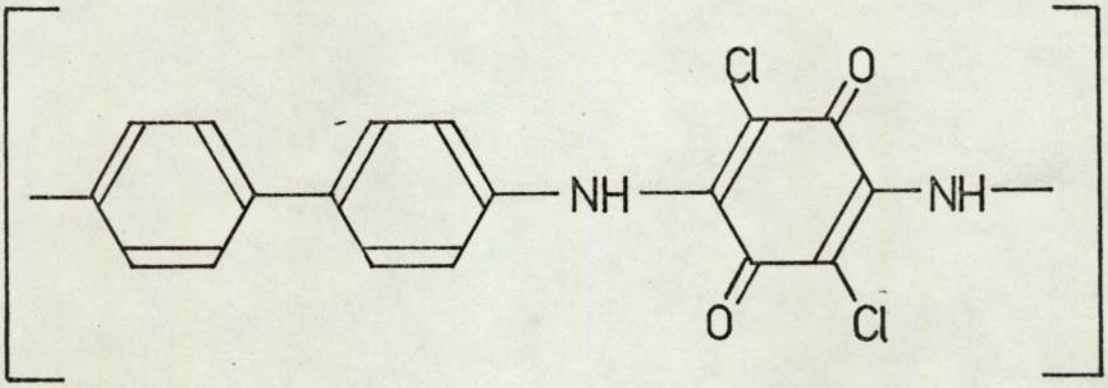
STRUCTURE 9



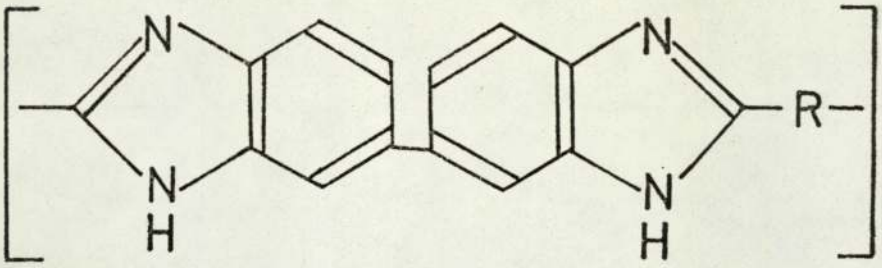
STRUCTURE 11



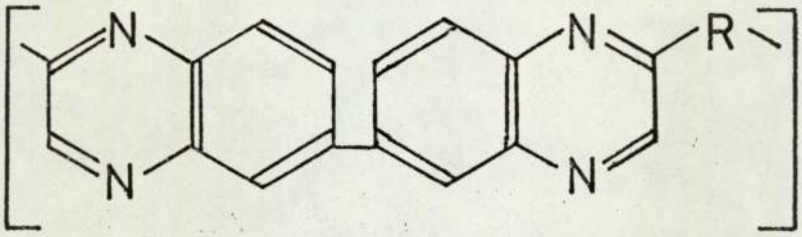
STRUCTURE 10



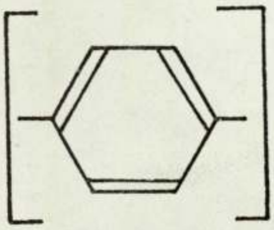
STRUCTURE 12



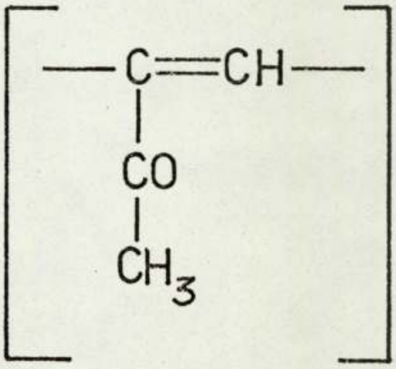
STRUCTURE 13



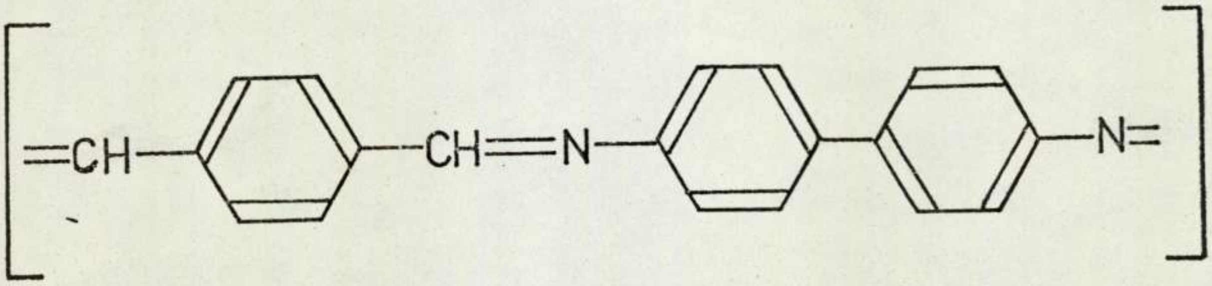
STRUCTURE 14



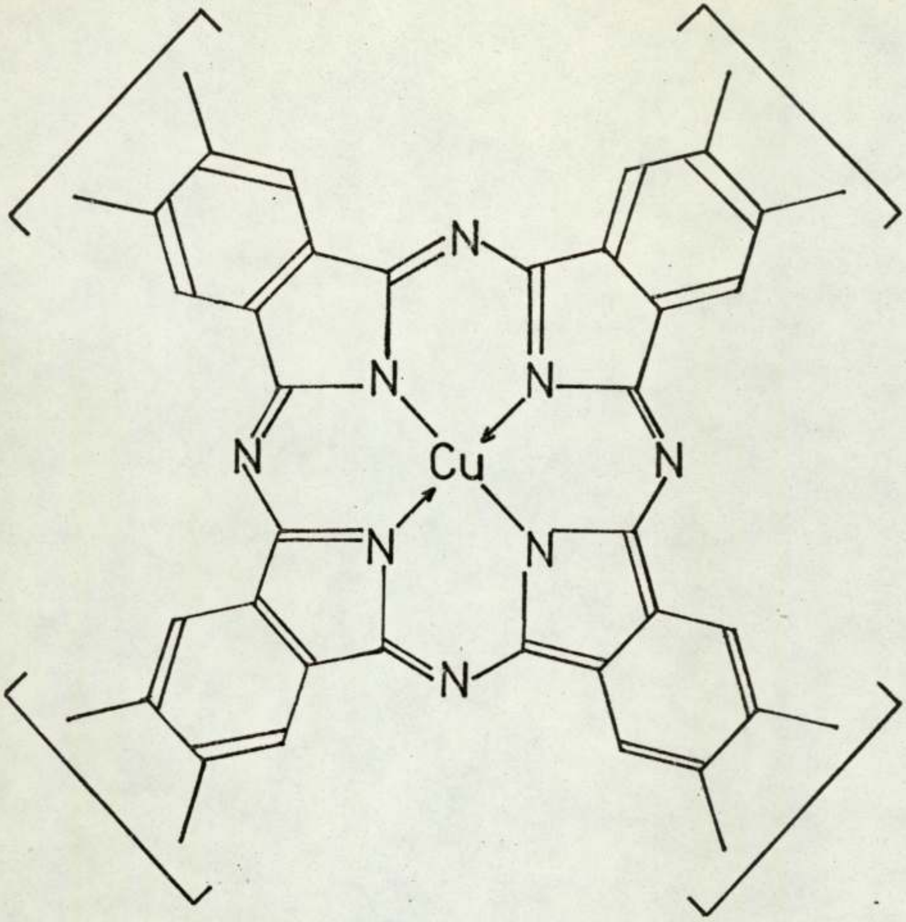
STRUCTURE 15



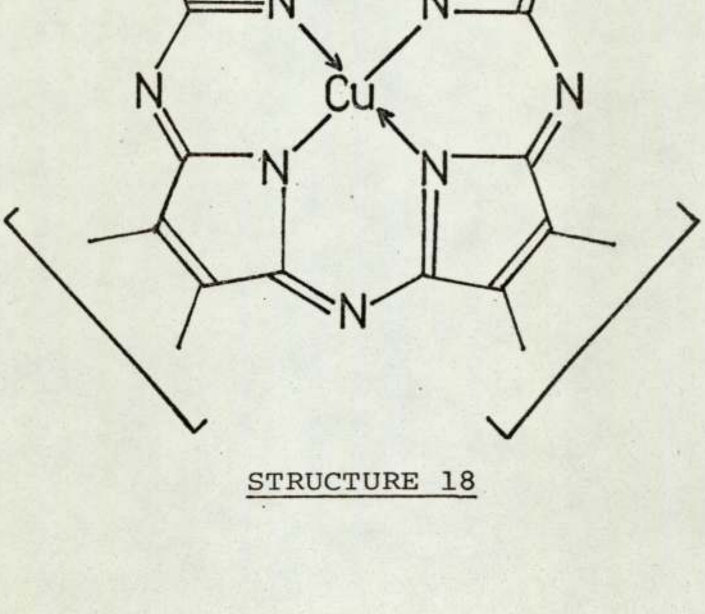
STRUCTURE 19



STRUCTURE 16



STRUCTURE 17



STRUCTURE 18

It can be mentioned in passing that various workers have recorded that certain synthetic organic polymers such as polyethylene and polypropylene, which do not have a conjugated structure, are active in catalysing the autoxidation of tetralin. Nevertheless P.S. Mody[70] and co-workers have attributed this property to surface free radicals caused by the scission of bonds between two carbon atoms.

One of the limitations to the use of e.p.r. as a measure of catalytic activity is that only the free spins on the surface are involved in heterogeneous catalysis but the measured e.p.r. data refer to the spins from the whole sample mass. No work has yet been successful in comparing catalytic activity with concentration of free spins on the polymer surface although the Gallard[38] research group have made such an attempt.

Gallard and co-workers[38,60], noting that the intrinsic catalytic activity of the free spins was not constant, suggest that perhaps not all spins are active in catalysis. Consequently they compared intrinsic catalytic activities to measurements directly related to the specific properties of the spins, namely the width of the e.p.r. line ΔH , and the relaxation time T_1. In the case of PAN.P acting as a catalyst in the decomposition of dinitrogen oxide a very close correlation was found between intrinsic activity and T_i. The same close relationship was found true for several other polymers.

Simionescu and Bulakovschi[49] have pointed out that from an energetic viewpoint the catalytic activity is unlikely to be influenced by the spin relaxation alone. It is more likely that the initial steps in the catalytic reaction are due to some physical process dependent upon the magnetic field found in the vicinity of the paramagnetic centres. This is because the average time during which a local magnetic field is created by a spin has a constant value and depends upon the relaxation times. Kiperman[24] and Berlin[71] have also suggested that similar physical processes exist at the beginning of the catalysis.

1.3.2.2. Structural Considerations

Metal free polymers

Whilst a valuable relationship exists between the concentration of free spins and the catalytic activity of one polymer, it cannot be assumed that different highly conjugated organic polymers having the same concentrations of free spins exert the same catalytic activity. This observation has led to a more detailed study of the structural factors which influence the nature of the free spins and the catalytic properties.

With metal free polymers the primary influential factor has been shown to be the nature of the main chain conjugation. The extent and regularity of conjugation must have a direct bearing on the delocalisation of the paramagnetic centres. The Gallard school[38] have described how the activation energy of the decomposition of dinitrogen oxide is much lower for polymeric catalysts having a regular and uninterrupted alternation of double and single bonds. In fact polymers having regular conjugation were demonstrated to catalyse this reaction with an activation energy much lower than that of polymers from the same chemical family but having main chain conjugation of only intermittent regularity.

We must acknowledge the thesis of Eley[72], as early as 1937, when studying the catalytic properties of phthalocyanine and copper phthalocyanine. He suggested that "the really active catalysts were thermal decomposition products containing numerous condensed rings perhaps, but by no means completely carbonised".

Manassen and Khalif[43], in their work on polymeric catalysts for vapour phase dehydrogenation reactions, report on how one polymer (Structure 3) is active whereas a second polymer of similar structure (4) was inactive. The difference is that during hydrogenation the former can retain uninterrupted conjugation whilst the latter cannot.

In a subsequent publication Gallard and co-workers[68] have established a correlation between the extent of structural heterogenity and the catalytic activity of several polymers. Various members of the polyindoloimidazole family were heat treated and then examined for their activity as heterogeneous catalysts for the decomposition of dinitrogen oxide. The close relationship observed was thought to be due to the role of heteroatoms in hindering graphitisation, hence reducing exchange interactions of the free spins and also the consequent decay in activity. Dokukina[23] and Inoue[56] believe that the nitrogen atom has the central role of chemisorption during catalysis.

Polymeric chelates

Keier et al.[25,29,41] and other workers[34,35,36,45,53,54,55,57,71] have described how the structural features of polymeric chelates play an important role in catalytic processes. The chemical nature of both the metal and the ligand bound directly to the metal, and also of the organic portion of the polymer all have influence on catalytic activity.

Only chelates containing transition metals have been found catalytically active. Keier[29], for example, discusses how for metal polychelates of the general type given as structure 7 the complexes decreased in activity in the order copper, nickel, palladium cobalt, iron the zinc and cadmium complexes were found inactive.

The same authors[27] established that, using the corresponding copper containing polychelates, catalytic activity decreases according to the nature of the ligand atoms in the order (N,S), (S,S), (N,O), (O,O).

Hatano[55] has reported that for a series of copper containing polymeric chelates a conjugated double bond structure in the organic portion of the polymer contributes to a greater catalytic activity during the decomposition of hydrogen peroxide.

1.3.2.3. Electrical considerations

Conductors and semiconductors have been shown to be prominent as heterogeneous catalysts for a series of diverse redox type reactions. Many highly conjugated polymers, whose characteristic large concentration of delocalised π electrons are responsible for a reduced thermal excitation energy of the electrons from the valence to the conduction bands, are classed as intrinsic semiconductors. Complexes involving chelate structures are also characteristic of organic semiconductors. Consequently various workers have published reports referring to the catalytic properties of organic or polymeric semiconductors.

Inoue[57], in a study of the catalytic decomposition of hydrogen peroxide in the presence of a series of vulcanised aniline blacks which vary in the molar ratios of sulphur to nitrogen, describes an impressive parallel between electrical conductivity and rate of catalysis. (The same author[57] found that catalytic activity and electrical conductivity were directly comparable using metal polyphthalocyanines containing differing ratios of copper to iron for the oxidation of acetaldehyde ethylene acetal.). A good relationship between the thermal activation energy of conductivity and activity in the catalysis of formic acid decomposition using polymeric copper phthalocyanines was noted by Hanke[53]. Roginskii[35,36] reports how high catalyst electrical conductivity and low thermal activation energy are necessary parameters for the hydrogen peroxide decomposition and the hydrocarbon oxidation reactions he examined. Paushkin[62] found paramagnetic organic polymers to be catalysts for the decomposition of isopropanol whilst diamagnetic polymers or insulators were inactive.

Other workers have found that no such straightforward comparison exists between electrical conductivity and catalytic activity. Keier[41b] and her co-workers, following an extensive study of the activity of polymeric chelates as catalysts for the decomposition of hydrazine and hydrogen peroxide concluded, in this case, that catalysis was not a function of conductivity. Manassen[43] reported that he could not find any relationship with conductivity when studying various organic polymers for the catalysis of dehydrogenation. Davydova[40] found that when the para-ortho hydrogen conversion was catalysed by a series of metal free organic polymers, an increasing polymer annealing temperature caused a reduction in both the specific rate per unit surface area and the activation energy of electrical conductivity whilst the conductivity increased. No difference in the catalysed rates of autoxidation of cumene were detected by Hanke and Karsch[54] when using copper phthalocyanine monomers which are "p" type semiconductors and the polymers which are "n" type.

1.3.3. Conclusions

Ideally it would be most valuable if the work so far reported on heterogeneous catalysis using highly conjugated organic polymers was extensive and consistent enough to provide evidence that one underlying mechanism influenced their activity and specifity.

Certainly no comprehensive correlation can be found between electrical conductivity (or its thermal activation energy) and catalytic activity, this situation being analogous to that found with inorganic impurity semiconductors. It is apparent that only when polymers of a similar chemical nature and structure are considered that a meaningful relationship can be found. Inoue[57] for instance, discovered a quantitative correlation when using a series of polymers which varied only slightly in structure and chemical composition.

Ample information has been provided to show that organic polymers classed as insulators do not act as heterogeneous catalysts. The unvulcanised polymeric oxidation condensation product of aniline having a resistance of more than 10^{13} ohm cm^{-1} was found by Inoue[57] to have a negligible effect on the rate of catalytic decomposition of hydrogen peroxide, whereas it's semiconducting vulcanised derivatives are very active. Paushkin[62] provides similar evidence when dealing with polymeric cumulenes. During the catalytic hydrogenation of ethylene Gallard[32] showed the semiconducting PAN.P to become inactive, possibly because an insulating polyethylene graft was formed. A more distinct proof of this suspected mechanism would have been rewarding. Although Manassen[43] reports on a series of organic polymers, some catalytically active which should be insulators (having resistances between 10^{10} and 10^{14} ohms cm^{-1} at 21^oC) he includes amongst these PAN pyrolysed at 350^oC which is a known semiconductor. However it must be pointed out that Manassen was more interested in the comparative rather than absolute values of resistivities.

Photoconductivity, or the increase in conductivity when electromagnetic radiation is absorbed by some non metals would be expected to have a major influence on any catalytic reaction sensitive to conductivity. However, outside of biochemistry, no reference could be found concerning the effect of light on catalysis using semiconducting organic polymers.

We may conclude in the light of limited evidence that electrical conductivity seems a necessary but not sufficient condition for catalytic activity. Consequently whilst several workers[25,29,31,43,44] could not find any relationship between electrical conductivity and catalysis it would appear presumptuous to infer that there is no contribution to the mechanism of catalysis by the agents responsible for conductivity. Indeed the involvement of charge carriers (electrons and holes) may well be a prerequisite for catalytic activity. The absence of a universal correlation may be due to the fact that charge carriers need not be involved in the rate determining step of the reaction.

If we now consider the influence that chemical structure and free electrons have on catalytic activity a series of interesting correlations can be observed.

Although several workers[21,38,65] have found that by increasing the polymer pyrolysis temperature an increasing catalytic activity and an increasing concentration of free electrons follow, Davydova[40] has described the opposite effect. He noted that the ortho-para hydrogen conversions, catalysed by pyrolysed poly(vinyl methyl ketone) and pyrolysed poly(p -diethynyl benzene) had reduced rates and lower concentrations of free electrons when higher pyrolysis temperatures were employed. This apparent anomaly may well be explained by the occurrence of graphitic structures at the temperatures of up to 1000°C mentioned, in which the free electrons recombine. This effect was found by the Gallard school with PAN.P at temperatures above 450°C.

Manassen and Khalif[43] have compared the catalytic efficiencies of two polymers based on p-phenylene diamine. One (Structure 4) is a terephthalaldehyde condensation product whilst the other (Structure 3) being condensed with cyclohexane 1,4-dione contains a series of quinoid rings. They conclude, with ample evidence, that chemical structure is the reason for the much greater dehydrogenation capability of structure 3. However they do point out that the pyrolysed polymer having structure 3 has a much higher concentration of free spins than the second polymer.

No reference has been made to the topography of the polymers on a molecular scale. One might reasonably expect a more planar structure to support a higher concentration of free electrons and to have higher conductivity. The conformation of the structure may influence the temperature at which the onset of graphitisation and loss of activity occurs. The presence or absence of steric hindrance to the adsorption of reactants, intermediates or products at a favoured site on the polymer may effect catalytic efficiency.

Only structure 20 (PAN.P) of all the metal-free molecular models constructed displayed extensive planarity. This may well be one reason for the high activity of PAN.P found in dinitrogen oxide decomposition[30], the oxidation of tetralin[31], butene isomerisation[32], and cyclic olefin dehydrogenation[42].

Amongst the metal polychelates investigated the Cu(II) complexes consistently exhibited high activity. This is a possible consequence of the Cu(II) forming square planar complexes so that the whole molecule tends towards being co-planar. Furthermore, electron transport through co-ordinated coplanar metal groups should be enhanced if the ligands have conjugated planar structures. This could account for the observed effects the organic portion of these polymers have on catalytic ability.

In summary, semiconductivity and a high concentration of free electrons are a necessary and seemingly inseparable requisite for catalysis by organic polymers of this type. However it cannot be concluded that either or both conditions alone are sufficient to dictate the mechanism of catalysis. Other factors have been shown to be important, these include chemical structure, regularity, extent and type of conjugation, the nature and concentration of constituent atoms other than carbon and hydrogen. The authors believe that molecular structure and topography must also be considered as having an influence on the catalytic process.

Although the volume of published work on this subject is not inconsiderable it is apparent that the full potential of highly conjugated organic polymers as heterogeneous catalysts has not been realised. Mechanistically, the relative ease of "building in" various properties may lead to a better understanding of catalysis as a whole. Whilst there are no current commercial processes known which involve polymeric catalysts of this type patents[74] do exist, and their exploitation would seem to depend upon the need for particular reactions to be carried out under conditions which enable the high specificity of these catalysts to be exploited.

To honour the objectives of the CAPS award it was decided to direct the project towards some of the problems involved in the removal of NO. Following a careful study into the properties of these synthetic polymers as heterogeneous catalysts, PAN.P was selected for the investigation. This polymer is reported to be typical in displaying all the required physical properties of polymeric catalysts of this typ type.

Several advantages are found in limiting the scope of the work in this way. First and foremost the precursory polymer PAN, unlike most other polymers of this type, is commercially available albeit in copolymer form. This eliminates any immediate need for synthetic work. PAN.P is readily soluble in formdimethylamide and hence easier to deposit on a suitable support. Also a wealth of information is available on both the structure and the specific catalytic properties of the polymer. Finally the expert assistance of the British Leyland Motor Company Pollution Laboratories was available.

A detailed report on some of the work done to elucidate the structure of PAN.P now follows.

1.4 The structure of poly acrylonitrile degraded at low temperatures (PAN.P)

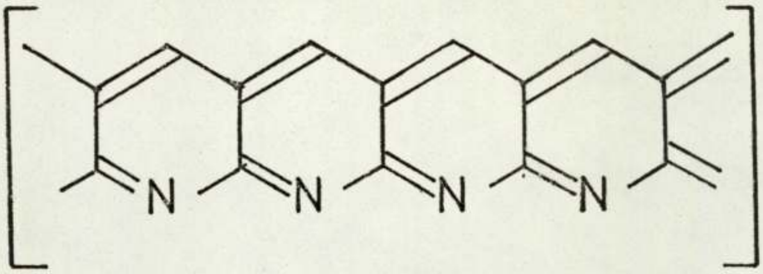
The catalytic properties of PAN.P have been examined more than any other polymer but information on the precise polymer structures involved has often been confusing. The earlier work, mainly on colour formation at low temperatures, was sponsored by the textile industry. The recognition of PAN as a successful precursor to carbon fibre, giving very high modulus and high strength in good yield, has led to more recent work on structure elucidation. The various reports have helped to confirm the presence of a number of structural features which are important from a catalytic viewpoint. These include:-

i. A high extent of conjugation which can support a large concentration of delocalised electrons,

ii. the presence of heteroatoms which are contained in the conjugated main chain, and

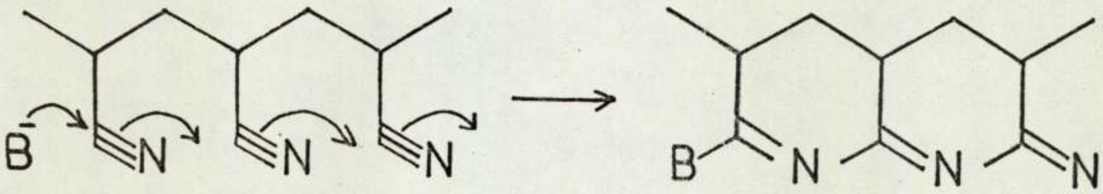
iii. the occurrence of cross linking at higher temperatures giving rise to an extended two dimensional structure.

In 1950 Houtz[73,74,75] proposed a conjugated pyrinoid structure (20) to account for the rate of polymer colouration when heated in oxygen. He found this structure consistent with a constant molecular weight, and the absence of volatile degradation products.



STRUCTURE 20

Following this McCartney[76] suggested the formation of a hydrogenated naphthyridine type structure formed by nucleophilic attack of a base on the nitrile group as outlined in scheme 1. As well as discolouration he also observed an extensive reduction in molecular weight.

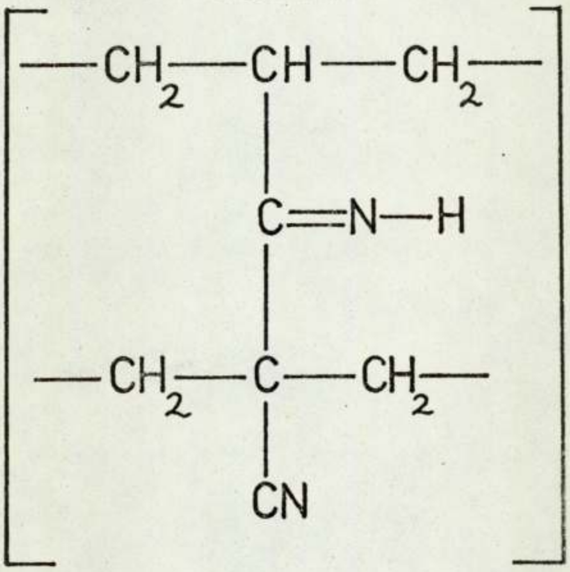


SCHEME 1

Burlant and Parsons[77] related colour formation initially to a McCartney-type structure, which then dehydogenates to form the fully aromatic Houtz structure. They showed good correlation between colour formation and disappearance of the nitrile band in the infra red spectra. Below 200°C, and under inert conditions, no colour change was observed in the polymer, unless a suitable initiator, such as a base, was added. Above this temperature colour change was automatic.

Further support for the naphthyridine structure came from Kennedy and Fontana[78] who noted explosive degradation of polyacrylonitrile at temperatures above 200°C and under inert conditions.

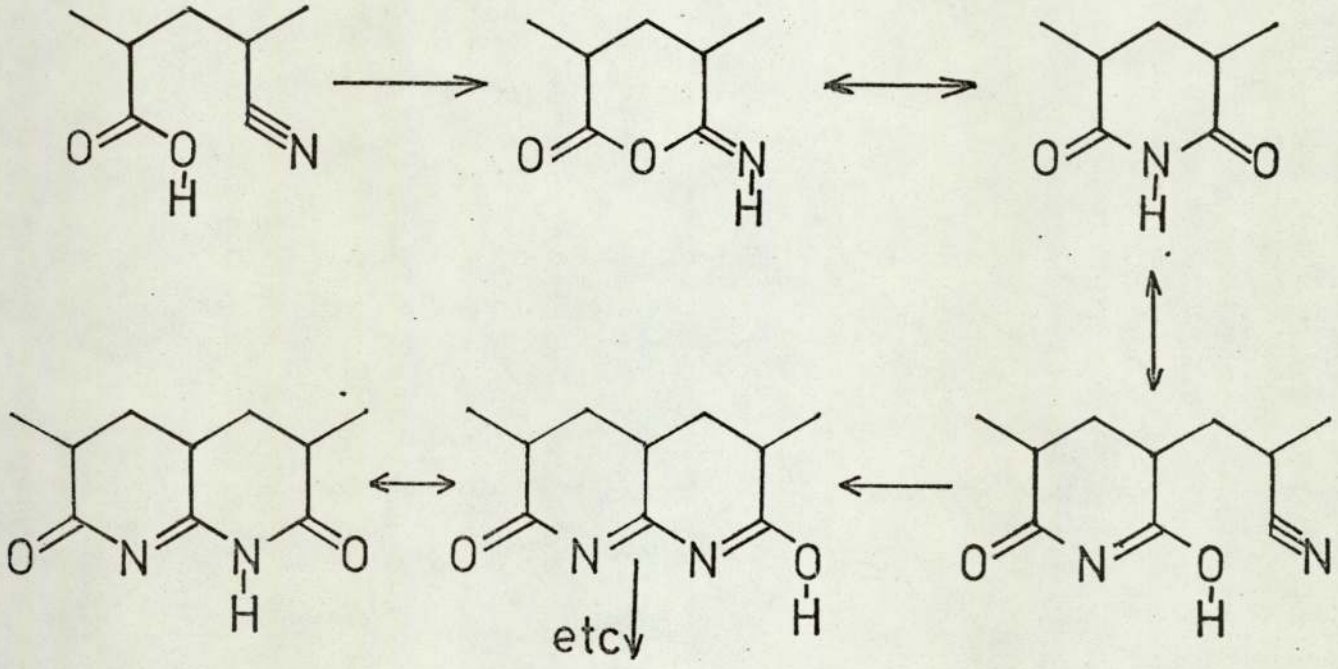
Schurz[79] questioned the pyrinoid structure after studying UV and IR spectra of PAN.P, pyridines and naphthyridines. He concluded that azomethine (Structure 21) cross links are formed.



STRUCTURE 21

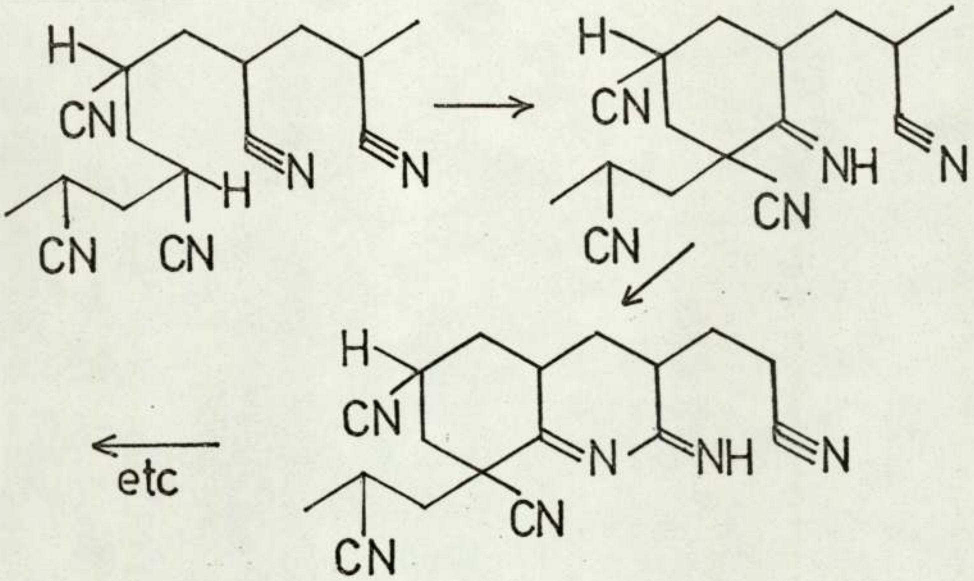
Grassie and McNeill[80] pointed out that this would not explain the intense colour formed, and attributed the difference in U.V. spectra between the degraded polymer and the substituted naphthyridines to incomplete conjugation. They supported the partially hydrogenated structure of McCartney (scheme 1).

Grassie and co-workers[81,82] then proposed a mechanism, Scheme 2, to explain the colouration which can occur below 200°C in the presence of nucleophilic initiators, especially when present as copolymers. They also suggested Scheme 3, a similar process, to explain the self initiated colouration under inert conditions in the absence of nucleophilic species.



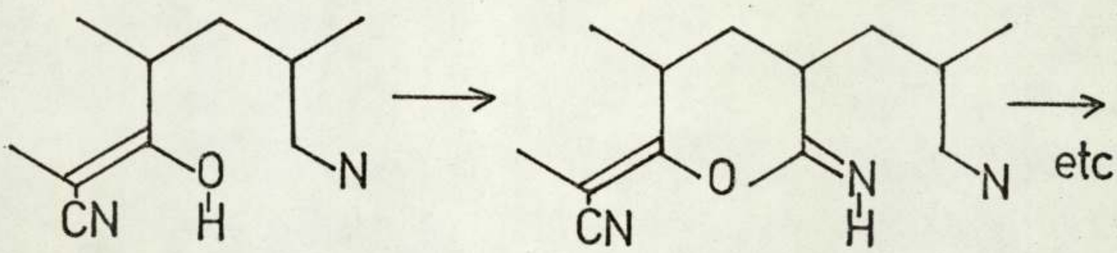
SCHEME 2

It relies on the acidic nature of the hydrogen atom adjacent to the nitrile group to promote cyclisation.



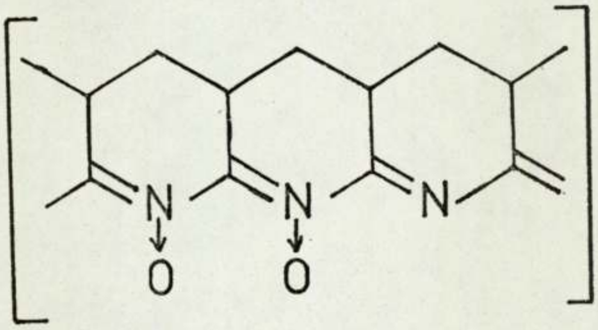
SCHEME 3

Peebles and co-workers[83] have explained the thermal instability of PAN, relative to certain model compounds, in terms of defects present in the polymer, particularly poly β-Keto nitriles. These species can be formed either by hydrolysis of any cyanoenamine groups formed in the polymerisation stage, or by oxidation of the polymer. Their initiation of the discolouration reaction is outlined in Scheme 4 where a hydrogenated naphthyridine structure is eventually formed.



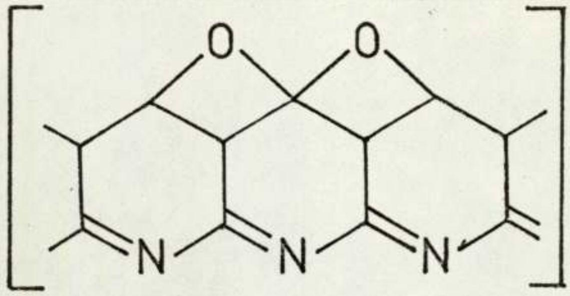
SCHEME 4

The same workers[84] proposed the formation of a structure (22) containing the nitrone group from the hydrogenated naphthyridine polymer to explain the oxygen content of PAN.P when made under oxidative conditions.

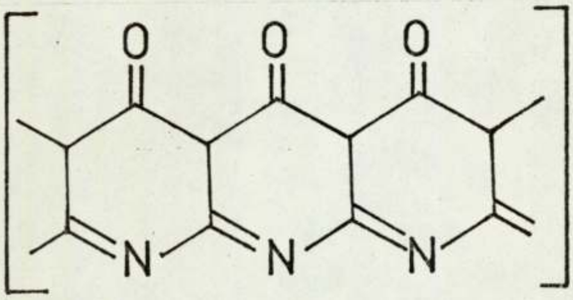


STRUCTURE 22

Standage and Matkowsky[85] decided that oxygen uptake was either through the formation of epoxides (Structure 23) or through carbonyl formation (Structure 24).



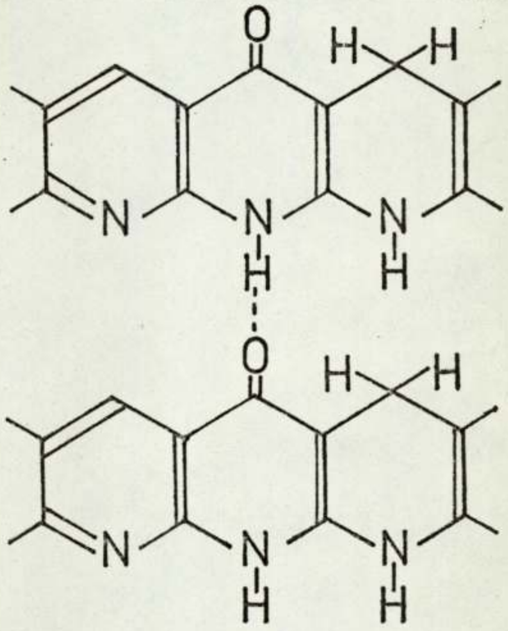
STRUCTURE 23



STRUCTURE 24

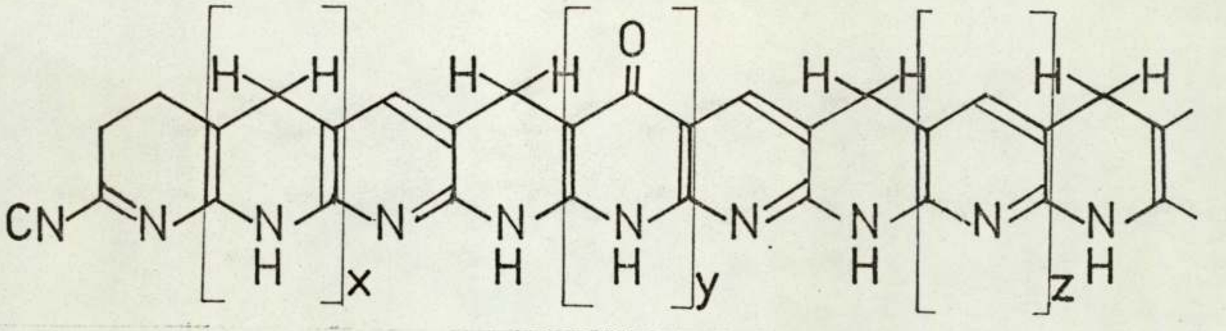
They also[86] showed that PAN fibre, which had been heated under high vacuum at 290°C, subsequently absorbed oxygen from the atmosphere at room temperature. Furthermore when pyrolysed at 335°C for two hours in nitrogen containing less than 50 ppm of oxygen, the end product contained 10% oxygen.

W. Potter[87] and co-workers who examined the extreme sensitivity of PAN.P to oxidation concluded that substantial oxidation does not occur until the polymer has been converted to a ladder structure containing readily oxidisable methylene groups. This is in agreement with the work of Peebles and Brandup[88] who reported that the site of oxidative attack was the methylene hydrogens, and not the tertiary hydrogens as had previously been supposed. Potter believes the development of highly characteristic physical behaviour, notably absence of melting and hydro philicity, is associated with the formation of a strongly hydrogen bonded poly dihydropyrid-4-one structure (25). This acts as an internal restraint to molecular motion and permits the orientation of the parent polymer to be carried through to the higher temperature pyrolysed carbon fibre.



STRUCTURE 25

After extensive work involving model compounds they proposed that the overall structure of the preoxidised fibre may be represented by:-



STRUCTURE 26

CHAPTER 2

EXPERIMENTAL

2.1 Apparatus used in production of catalyst

2.1.1. Rotary Evaporator

The high boiling point solvent (DMF - 143C) was removed from the polyacrylonitrile solution, using vacuum assisted rotary evaporation. The Büchi Rotavapour R apparatus was used in conjunction with a hot water bath.

A pressure of approximately 0.3 mm was employed while the temperature in the water bath slowly increased from approximately 25°C to 90°C over 30 minutes.

2.1.2 Fluidised Bath

A Techne SBL2 fluidised bath was used in conjunction with a Sifam Pyromaxim type TSA temperature control. The heating medium was Alundum powder (small particles of aluminium oxide) which is suitable for the higher polymer pyrolysis temperatures of 550°C.

2.2 Apparatus used in studying catalytic properties

2.2.1 Single Pass Fixed Bed Integral Flow Reactor

2.2.1.1. Apparatus

The catalyst was contained in a cylindrical 18/8 stainless steel vessel, having an internal diameter of 3¼cm and a length of 23 cm see Figure 2. A wire gauze, approximately 3 cm from the bottom, was used to support and suspend the

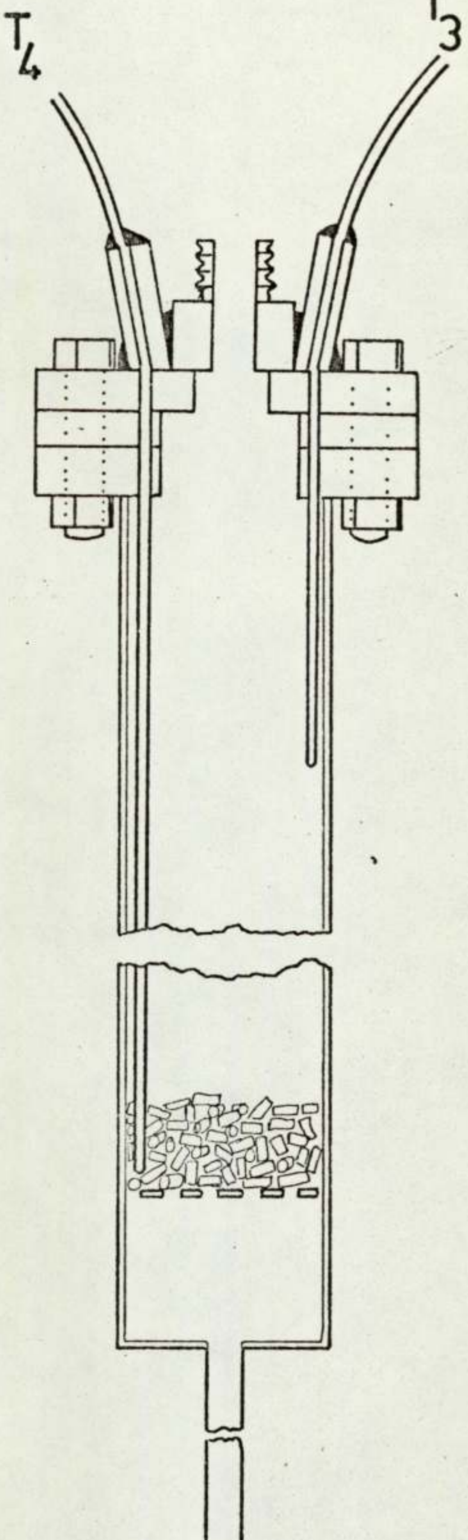


FIGURE 2

STAINLESS STEEL CATALYST VESSEL

catalyst pellets. Two mineral insulated thermocouples probes made by Pyrotenax Ltd. were employed to monitor the temperature of both the incoming gases and the catalyst bed, the latter also being used to control the temperature of the surrounding furnace. A 1½cm wide rim was welded to the top of the vessel, around which six ¼" B.S.F. bolts were evenly placed to secure the matching top. A preshaped 0.6 cm thick "fibrefrax" asbestos gasket was eventually employed to effect an optimum seal. The tap unit was again made out of stainless steel, a leak free "Sif" bronze brazing was applied to secure the two thermocouples, and the ⅜" B.S.P. union for the gas entry path. At the bottom of this vessel an Argon weld was again used to secure a 0.6 cm outside diameter 16 cm long stainless steel tube which directed the outgoing gases.

The preheat chamber was similarly constructed. To assist preheating and dispersion of the incoming gases a bed of 75 gms of inert "Procatalyste SCS 79" pellets was employed.

Beyond the hot furnace area 0.6 cm outside diameter flexible P.T.F.E. tubing was used to transport the gaseous mixture. $\frac{1}{4}$" Drallim brass fittings were used throughout. A Drallim four port, one bank, switch valve was utilised to direct the gas flow on any one of three different routes. Figure 3 is a schematic representation of the full apparatus and conveniently displays the three gas routes. When the gaseous mixture bypasses the furnace system and goes directly from the source to the analysers, this is referred to as route 1. Route 2 is arranged so that the incoming gases pass through the inert preheat chamber only, whilst on route 3, the gases pass over the catalyst.

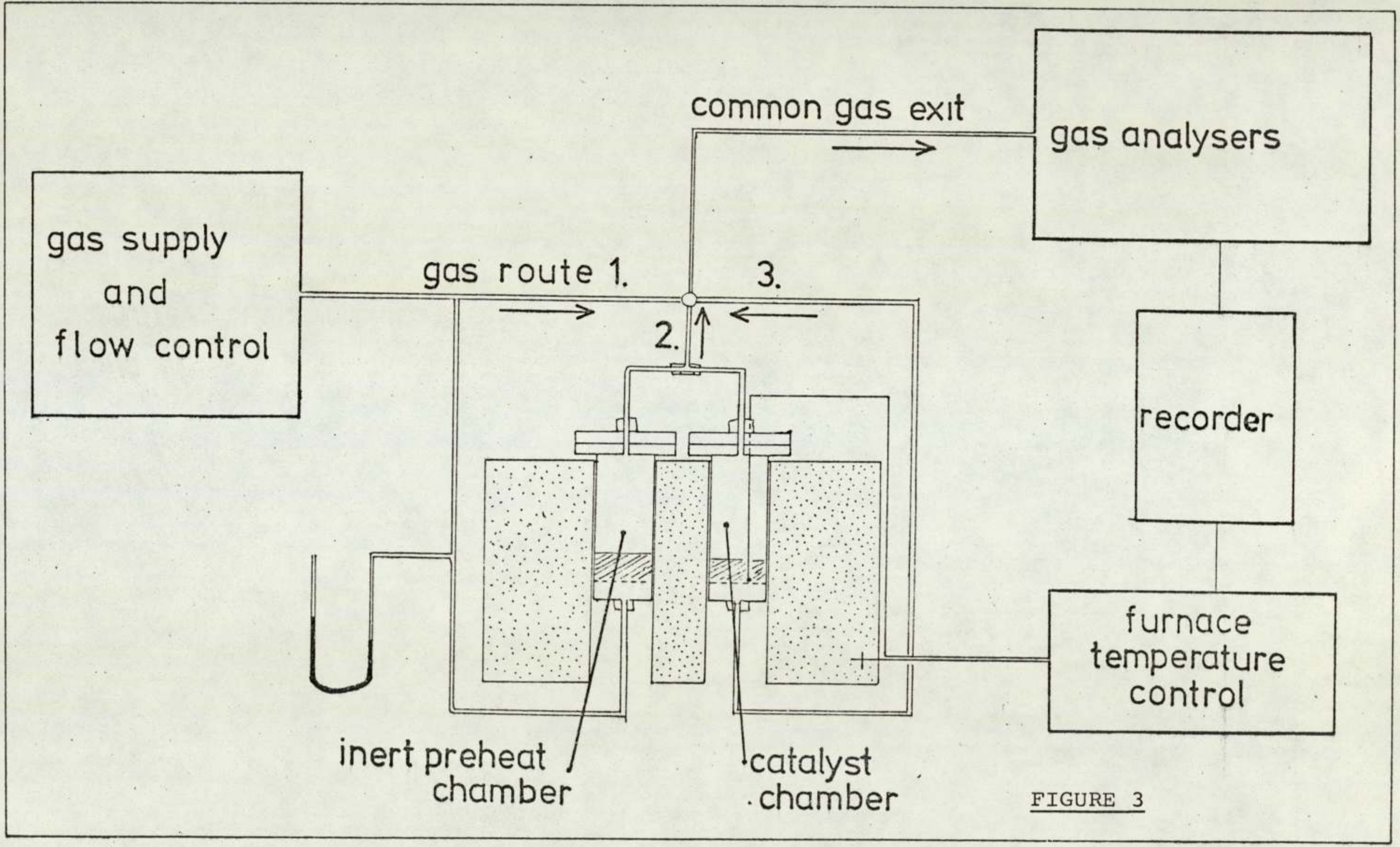


FIGURE 3

SCHEMATIC REPRESENTATION OF FIXED BED INTEGRAL FLOW REACTOR

A mercury manometer was incorporated into the system to monitor the pressure of entering gases. The manometer was also helpful in identifying the occasional accidental blockage.

The Gallenkamp electric furnace was specially modified to fit the two mild steel cylindrical vessels. Its temperature was accurately controlled, using an Ether type 15-98 portable laboratory furnace control, connected to the thermocouple (T_4) embedded in the catalyst pellets.

2.2.1.2 Calibration exercises

2.2.1.2.1 Inlet gas flow rates

The bank of inlet manometers included a series of "Gap meters" capable of controlling flow rates between 0 and 10 dm^3 per minute. They were calibrated by measuring the displacement of water per unit time, at a position downstream from the catalyst and just before the Drallim valve. At the same time the inlet pressure reading on the Beckmann N.D.I.R. gas analyser was recorded. The results showed a good correlation between actual flow rate and pressure on the gas analyser, using a constant outlet gas route.

The effect of varying the inlet flow pressure, registered on the gas bottle control valves, on the eventual flow rate was found to be minimal. However an inlet pressure of 10 p.s.i. was selected for all gas flows.

2.2.1.2.2 Gas Leaks

Gas leakages are inevitable in an apparatus which continually has to be dismantled to add fresh catalyst. The use of a fibrefax asbestos gasket in the catalyst containing vessel greatly eased the problem but the remaining losses are recorded:

Route	1	2	3	
Outlet flow rate	890	850	850	($cm^3\ min^{-1}$)

2.2.1.2.3 Temperature profile through the preheat and catalyst vessels.

The tips of the four thermocouples were positioned as follows:-

T_1 - preheat chamber 10cm from top

T_2 - preheat chamber 19cm from top surrounded by inert pellets

T_3 - catalyst chamber 10cm from top

T_4 - catalyst chamber 19cm from top surrounded by catalyst pellets

Gas flow rate ($cm^3 min^{-1}$)	T_1	T_2	T_3	T_4
200	146	447	146	399
600	176	545	176	497

2.2.2 Gas analysers

2.2.2.1 Continuous infra red gas analysis

The Beckman instrument model 315A infra red analyser was used to monitor Nitrogen monoxide gas concentrations between 0 and 3,300 ppm. This instrument used a double beam optical system to measure the differential absorption of infra red energy and incorporates a Luft type detector described herein.

Two infra red sources are used, one for the sample energy beam and the other for the reference energy beam. The beams are blocked simultaneously ten times per second by the chopper, a two-segmented blade rotating at five revolutions per second. In the unblocked condition each beam passes through the associated cell and into the detector.

The sample cell is a flow-through tube that receives a continuous stream of sample. The reference cell is a sealed tube filled with a reference gas. This gas is selected for minimal absorption of infra red energy of those wave lengths absorbed by NO.

The detector consists of two sealed compartments separated by a flexible metal diaphragm. Each compartment has an infra red transmitting window to permit entry of the corresponding energy beam. Both chambers are filled to the same sub-atomic pressure with NO gas, causing the instrument to respond only to the NO component.

In operation the presence of the infra red absorbing NO in the sample stream, causes a difference in energy levels between the sample and reference sides of the system. This differential energy increment undergoes a certain sequence of transformations, firstly in the sample cell part of the original energy of the sample beam is absorbed by the component of interest. In the reference cell however, absorption of energy from the reference beam is negligible. Then inside the detector each beam heats the gas in the corresponding chamber, the gas in the reference chamber is heated more since energy of the reference beam is greater. The higher temperature of the gas in the reference chamber raises the pressure of this compartment above that of the sample chamber. The gas pressure in the reference chamber distends the diaphragm towards the sample chamber so that the energy increment is thus expended in flexing the diaphragm. This diaphragm, and an adjacent stationary metal button, constitute a two-plate variable capacitor. Distention of the diaphragm away from the button decreases the capacitance.

White spot nitrogen was used to zero all gas analysers used. A series of gaseous mixtures, precalibrated by the suppliers, were used to span the various analysers.

A Grubb Parsons instrument model SB2 infra red gas analyser was used to monitor carbon monoxide gas concentrations between 0 and 25,000 ppm. This analyser operates by a similar mechanism to the Beckman instrument, described in greater detail above.

When using the more common concentrations of up to 2,000 ppm a longer path length cell was used with a higher gain setting. A band pass filter was connected in series to the Servoscribe recorder, to eliminate electrical noise, so that a reduced signal response time of approximately two seconds was given.

A design feature of both the Beckman 315A and Grubb Parson's SB2 instruments is a thermally insulated detector unit. Hence the temperature variation of the sample gases between 15 and 650°C caused only minimal fluctuations in the output signal.

2.2.2.2. Ultraviolet gas analysis

Nitrogen dioxide gas was monitored using the Beckman instrument model 255A ultraviolet analyser. In this instrument a tungsten source lamp directs a beam of near ultraviolet energy to a splitter for division into two equal beams, one each for the sample and reference cells.

A two cell system and rotating beam chopping blade, similar to that described for the infra red gas analysers, are employed.

The two beams, on emerging from the cells, impinge alternately on a beam-combining mirror assembly where they are directed through a band pass colour filter and onto a blue sensitive phototube detector. The phototube receives the alternate pulses of optical energy. The difference between the amounts of energy absorbed from the sample and reference beams during their passage through the associated cells results in the generation of a phototube output signal that is proportional to the concentration of the nitrogen dioxide in the sample cell.

2.2.2.3 Continuous oxygen gas measurement

The Servomex instrument, model OA150, oxygen gas analyser was used. This instrument is based on the Munday[89] cell which uses a platinum ribbon dumb-bell as a freely rotating diamagnetic body. Electromagnetic feed-back is used to maintain the dumb-bell in the zero position, and the current required is a measure of the magnetic susceptibility of the gas present in the cell and hence the oxygen concentration.

The dumb-bell is mounted inside a stainless steel body, having a glass window. Gas inlet and outlet connections are at the rear of the cell.

2.2.2.4 Draeger Equipment

A Draeger-Normalair gas detection system was used to measure 0 - 1,000 ppm quantities of ammonia gas. This involves the use of a special hand operated bellows pump which pulls the sample gases through the Draeger tube causing a characteristic colour change, the extent of which is proportional to the ammonia concentration.

2.2.3 Other catalyst reactor vessels

2.2.3.1 Flow Reactor

Figure 4 shows the glass reactor vessel used. The spiral has a diameter of 15 cm. so that the apparatus can be placed in the fluidised bath. A gas sampling vessel was also

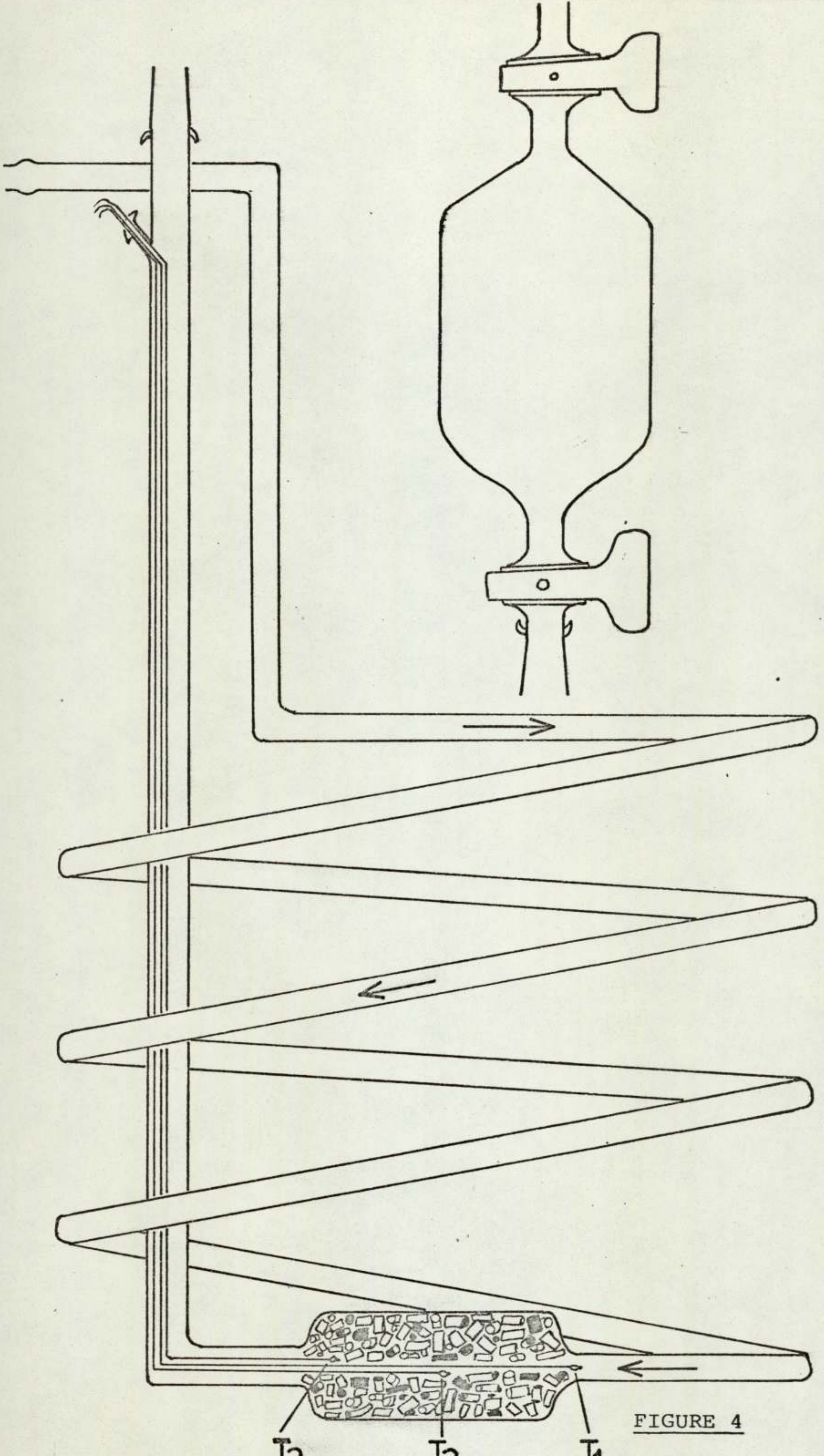


FIGURE 4

GAS FLOW REACTOR VESSEL

constructed.

2.2.3.2 Static Reactor

A glass reactor tube was used having a capacity of about 500 cm^3 and a B34 quick fit assembly with a gas tight tap.

2.3 Surface Area Apparatus

A nitrogen adsorption apparatus had to be constructed in order that reaction rates could be expressed in terms of unit surface area. A modified version of the classical BET apparatus[90] was chosen, similar to the one used by Harris and Sing[91]. A conventional back up vacuum line was first assembled.

2.3.1 Vacuum Apparatus

This was made in borosilicate glass. A diagram drawn to scale only on the vertical axis, (1 : 5) is given in Figure 5. The backing rotary pump used was an NGN type model PSR/2. This was separated from the diffusion pump using a liquid nitrogen trap. A second cold trap was placed between the nitrogen adsorption apparatus and the diffusion pump. The three stage mercury diffusion pump has two condensers, and was heated to 250°C. A Speedivac Pirami type vacuum gauge, model 8/2 was used in conjunction with a G5C-2 head.

2.3.2 Nitrogen Adsorption Apparatus

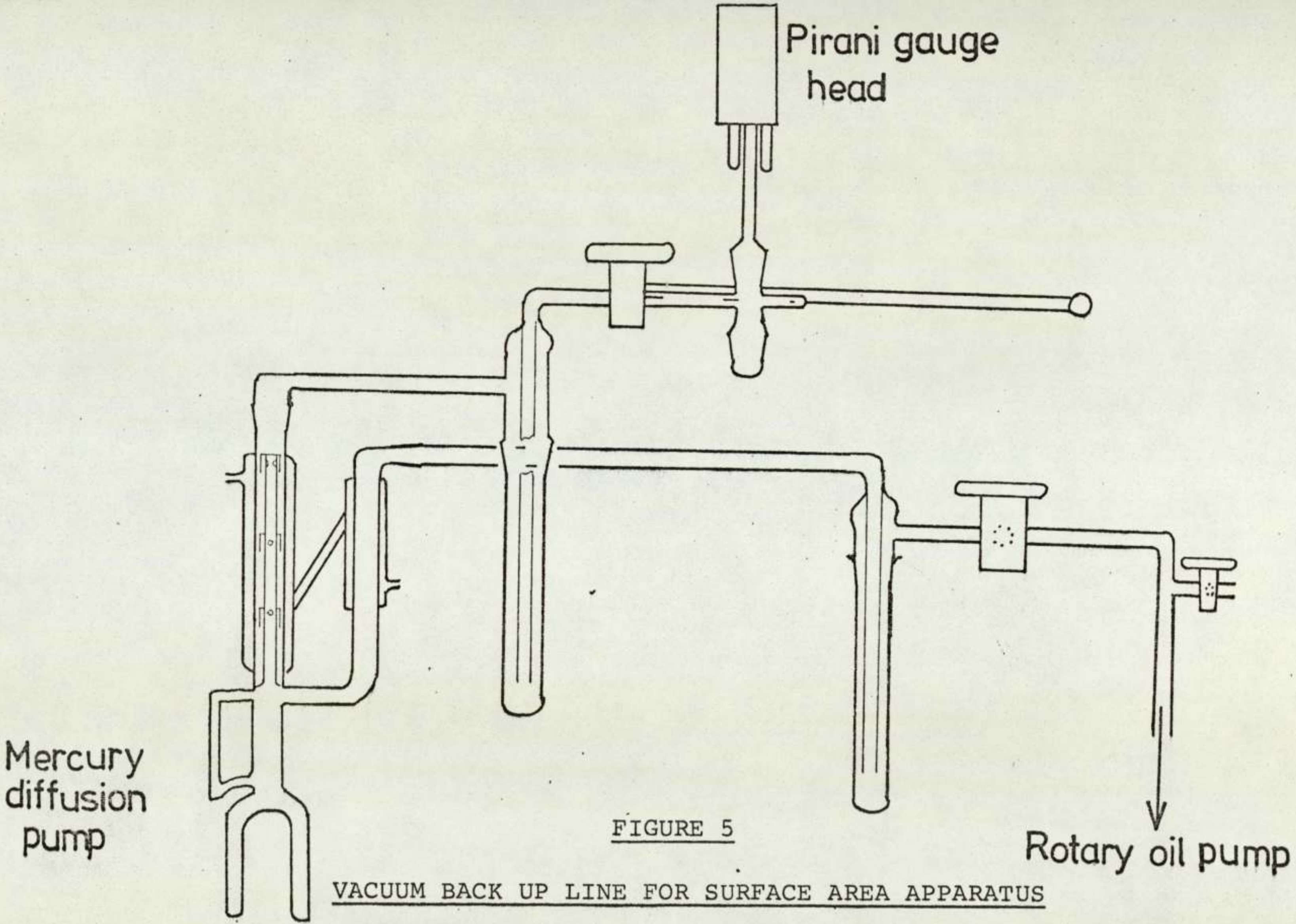


FIGURE 5

VACUUM BACK UP LINE FOR SURFACE AREA APPARATUS

This apparatus, drawn to scale (1 : 2.5) in Figure 6 and further illustrated in Plate 1, was made out of borosilicate glass. The volumes of the four graduated bulbs, the sample holder S, and the dead space were calibrated using a micro gas burette.

The volumes were as follows:-

V_1	1.74 cm^3	all measured at 20°C
V_2	2.58 cm^3	
V_3	5.55 cm^3	
V_4	11.25 cm^3	
S	2.51 cm^3	

Total volume on left hand side of tap T	4.05 cm^3
Total volume on right hand side of tap T with mercury level at lowest graduation	1.35 cm^3
Total volume on right hand side of tap T with mercury level at highest graduation	0.63 cm^3

A sample heating device was constructed using a length of 800 ohm insulated wire wrapped around a 6 cm long, 2 cm diameter glass tube. The heating wire was connected to a variac where a reading of 61% was required to maintain the required degassing temperature at 250°C.

The narrow bore (2 mm) manometer was adjusted using taps A and D so that a difference in mercury levels of 30.0 cm was reached. The three way tap T was turned to allow successive flushes of nitrogen and vacuum, whilst tap C was turned until the mercury level reached the top of the

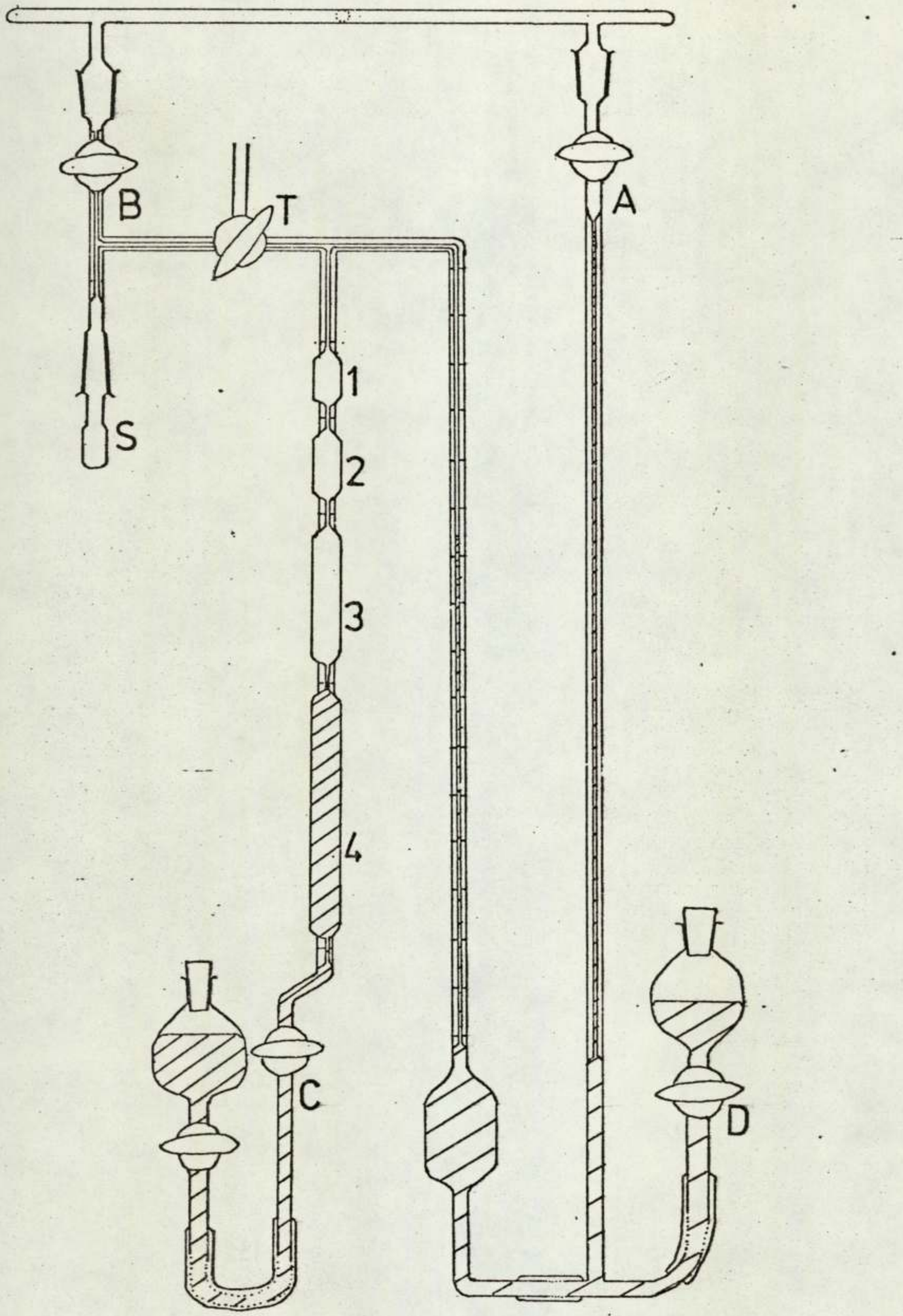


FIGURE 6

NITROGEN ADSORPTION APPARATUS

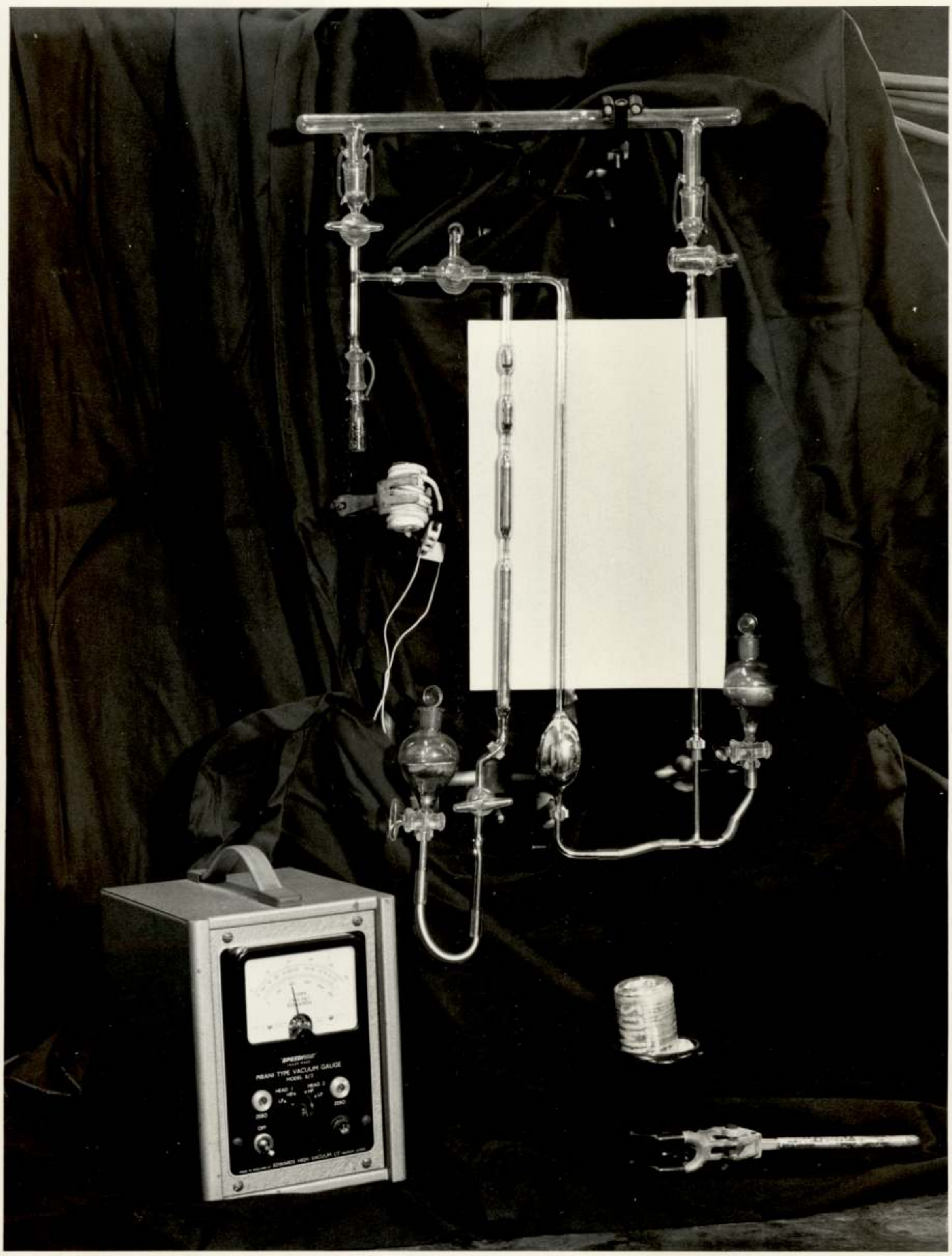


PLATE 1

NITROGEN ADSORPTION SURFACE AREA APPARATUS first graduated bulb. Then, with the preweighed sample in place, tap B was opened, tap T closed, and the sample holder immersed in the heating device. A predetermined degassing time of one hour at 250°C at a pressure of less than 10^{-3}mm was used.

Tap B was then closed and the heating device removed. When the sample cooled to approximately room temperature the vessel S was immersed in a flask of liquid nitrogen so that the liquid level was up to a mark in the narrow bore region. A period of five minutes was given to ensure the sample reached -196°C. Tap T was then turned so that nitrogen gas, at a pressure of one atmosphere, filled the dead space on the righthand side of the apparatus. Bulb 1 was emptied of mercury and tap T turned to isolate the apparatus from the outside nitrogen gas reservoir, and to allow the gas to be adsorbed on the sample. A time of two minutes was usually required for the adsorption to be at equilibrium once bulb 1 was refilled with mercury. The pressure reading was taken and this procedure repeated so that a range of pressure readings, corresponding to adsorbed gas volume, were recorded.

The following represents a typical surface area determination on a sample of catalyst having polymer on its surface which has been pyrolysed at 400°C and used to remove nitric oxide at 500°C.

Weight of catalyst (w) = 3.56 g

Volume of catalyst (vc) = 0.84 cm^3

VB	ΔP	ΣV_2
1.74	0.1	0.025
1.74	0.1	0.025
0	0.1	0.025
0	0.1	0.025
0	0.5	0.125
0	1.5	0.375
0	3.6	0.900
1.74	8.0	1.663
0	10.0	1.985
1.74	15.0	2.775
1.74	19.5	3.219
1.74	23.8	3.572

Where VB represents the volume of nitrogen gas taken via the graduated bulbs. When VB=0 then nitrogen was added from the dead space with all the bulbs full of mercury.

ΔP represents the difference in mercury levels.

ΣV_2 is the calibrated total dead space volume of nitrogen gas for the pressure indicated, under the conditions of adsorption.

This information was fed into a Fortran 1904 series computer using the Algol 60 language. The full programme is given on page 70 .

```
*ALGOL DAVECOOPER,EBS0607

STATEMENT NO.
      0          'BEGIN'
      1          'REAL''ARRAY'
      1          VV2,
      1          ANS,P,VB,V2,PN[1:100];
      2          'REAL'
      2          VC,W;
      3          'INTEGER'
      3          L,
      3          J,K,
      3          I,M;
      4          K:=READ;
      5          'FOR' J:=1 'STEP' 1 'UNTIL' K 'DO'
      5          'BEGIN'
      6          L:=READ;
      7          M:=READ;
      8          VC:=READ;
      9          W:=READ;
     10          'FOR' I:=1 'STEP' 1 'UNTIL' M 'DO'
     10          'BEGIN'
     11          VB[I]:=READ;
     12          P[I]:=READ;
     13          V2[I]:=READ;
     14          'END';
     15          ANS[1]:=(0.045*(30-P[1])+VB[1]-V2[1]-VC)/W;
     16          'FOR' I:=2 'STEP' 1 'UNTIL' M 'DO'
     16          'BEGIN'
     17          VV2[I]:=V2[I]-V2[I-1];
     18          ANS[I]:=ANS[I-1]+(0.045*(30-P[I])+VB[I]-VV2[I])/W;
     19          'END';
     20          'FOR' I:=1 'STEP' 1 'UNTIL' M 'DO'
     20          PN[I]:=P[I]/30;
     21          PAPERTHROW;
     22          NEWLINE(10);
     23          SPACE(30);
     24          WRITETEXT('('TABLE')');
     25          PRINT(L,4,0);
     26          WRITETEXT('('%OF%VOLUME(CM3/G)%FOR%PRESSURE%
     27          NEWLINE(10);                   increment(p/po)')');
     28          SPACE(40);
     29          WRITETEXT('('VOLUME')');
     30          SPACE(13);
     31          WRITETEXT('('PRESSURE%INCREMENT')');
     32          NEWLINE(4);
     33          'FOR' I:=1 'STEP' 1 'UNTIL' M 'DO'
     33          'BEGIN'
     34          SPACE(36);
     35          PRINT(ANS[I],3,6);
     36          SPACE(10);
     37          PRINT(PN[I],3,6);
     38          NEWLINE(2);
     39          'END';
     40          'END';
     41          'END'

EXECUTION STARTED
```

The results were as follows:-

Volume (cm^3g^{-1})	Pressure Increment ($^P/PO$)
0.623736	0.003333
1.490449	0.003333
1.868399	0.003333
2.246348	0.003333
2.591152	0.016667
2.881180	0.050000
3.067416	0.120000
3.619944	0.266667
3.782303	0.333333
4.238764	0.500000
4.735534	0.650000
5.203511	0.793333

Figure 7 was plotted and a point B value of $2.80cm^3g^{-1}$ taken. Assuming one nitrogen molecule to occupy $16.2\mathring{A}^2$ and s.t.p. conditions, then we can calculate the surface area to be 12.2 m^2g^{-1}.

Surface area determinations were carried out on several supports to compare the results (m^2g^{-1}) with those given by the suppliers.

Material		Specification	Quoted	Found
Hydronyl CX0134AA03	(Batch HY446)	10 - 30	10	(10.01 (9.80
" "	(Batch HY381)	10 - 30	19	19.16
Procatalyste SCS 79		95	-	87.08

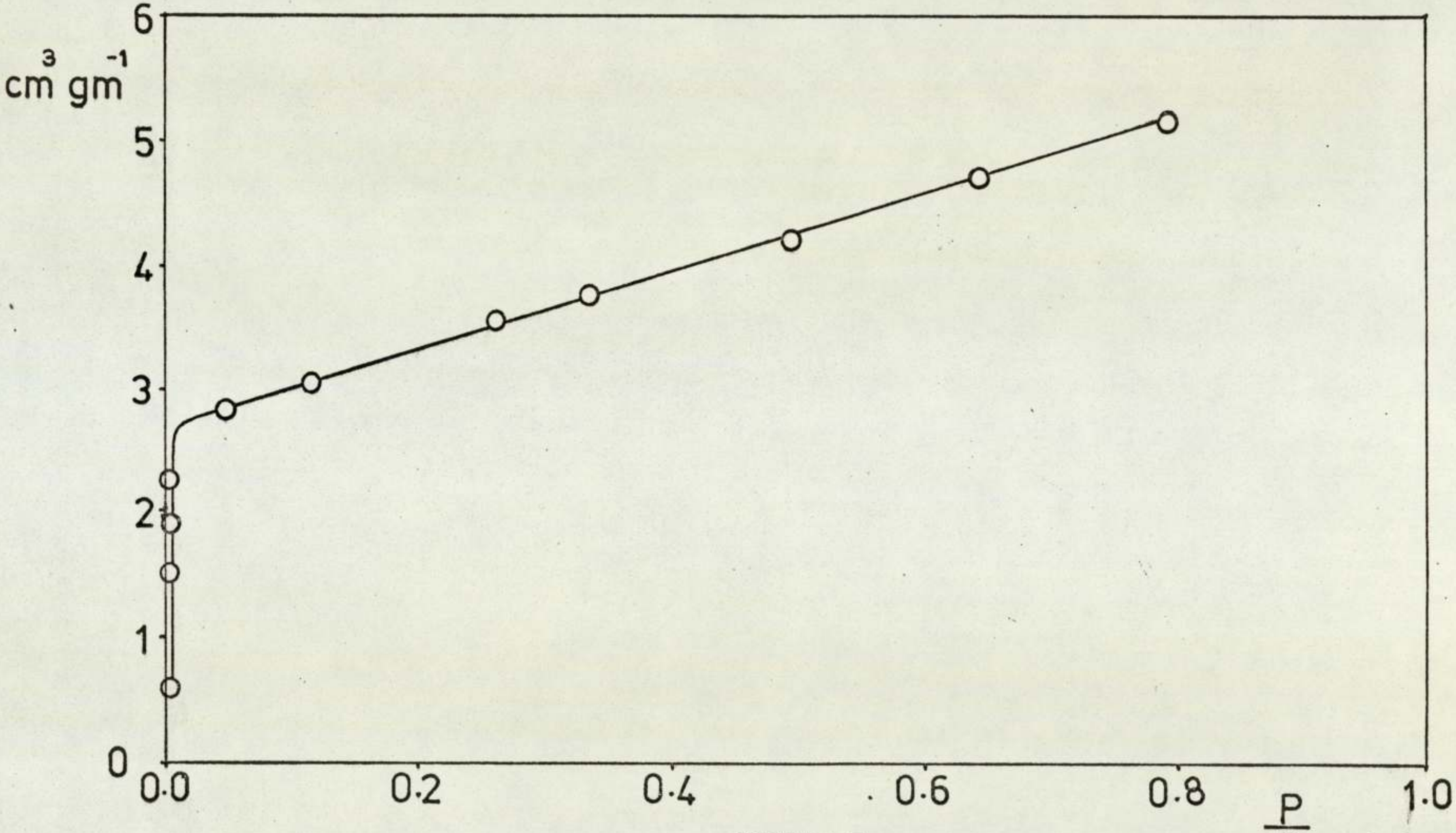


FIGURE 7

NITROGEN ADSORPTION CURVE FOR SUPPORTED PAN.P CATALYST

The encouraging results found eliminated the need to surround parts of the nitrogen adsorption apparatus with constant temperature water jackets. Also any minor correction for s.t.p. conditions was ignored.

2.4 Other Analytical Instruments

The Du Pont 950 Thermogravimetric Analyser.

The Perkin-Elmer model 157 G Grating Infra Red Spectrophotometer.

The AEI MS9 Double Focussing Mass Spectrometer.

The electron spin resonance spectrometer was a Hilger and Watts microspin ESR 3 instrument with an X band A.F.C. accessory.

2.5 Materials

2.5.1 General Chemicals

"Acrilan" Polyacrylonitrile powder	Monsanto Textiles Ltd. Coleraine, Northern Ireland.	Copolymer of undisclosed composition
Polyacrylonitrile powder	Polymer Consultants Ltd. 3-4 Fox Court, London, E.C.1.	Homopolymer

"Vespel" polymide	E.I. Du Pont De Nemours and Company, Wilmington, Delaware, U.S.A.	Precise chemical structure not released
Iron-Chrome catalyst/3572	ICI Ltd., Agricultural Division, Billingham, Teeside.	
Formdimethylamide	BDH Chemicals Ltd. Poole, England.	More than 99% pure

2.5.2 Gases

All the following gases were obtained from the British Oxygen Company Ltd. who quoted an accurate analysis on all mixtures.

Nitrogen	99.9%, oxygen free (white spot)
Nitrogen monoxide/ nitrogen mixtures	between 500 ppm and 3,300 ppm of nitrogen monoxide
Carbon monoxide/ Carbon dioxide/ nitrogen mixtures	0.3% CO, 2.35% CO_2;and 8.5% CO, 13.5% CO_2

Hydrogen/nitrogen mixtures	40% purified hydrogen
Hydrocarbon/ nitrogen mixtures	0.15% propane

The following gases were obtained in lecture bottle sizes from B.D.H. Ltd., Poole.

Nitrogen	99.999%
Nitrogen monoxide	99%

2.5.3 Catalyst Carrier Materials

2.5.3 Catalyst Carrier Materials

Trade Name And Grade	Source	Chemical Assay	Shape and Size	Surface area m^2g^{-1}	Attrition Loss	Maximum Temperature
Activated alumina pellets	Hopkin and Williams, Chadwell Heath, Essex	Alumina	cylinders 5/16" diameter, 5/16" long	not known	not known	not known
"Sorbsil" silica gel. A quality	Joseph Crosfield Warrington, Lancashire.	Silica	Grains 3mm x 6mm	850	not known	600°C
"Celite" 408	Johns-Manville GB Ltd., Richmond, Surrey.	Diatomite silica	Cylinder 4mm diameter	3 - 10	not known	1000°C
"Hydronyl" CX0134AA03	Hydronyl Ltd., Fenton, Staffordshire.	More than 99% Alpha AI_2O_3 less than 0.02% SiO_2	Cylinder 2.8mm diameter, 7.9mm average length	10 - 30	0.64%	above 900°C
"Hydronyl" CX0136AA03	"	"	Cylinder 2.8mm diameter, 7.9mm average length	80 - 120	2.2%	above 900°C
"Procatalyste" SCS 79	Pechiney, Saint Gobain.	"	Sphere 3-4mm diameter	95	less than 1%	high but not known exactly
Harshaw Al 0104T	Harshaw Chemicals Ltd., Daventry Northamptonshire	99% aluminium oxide	Cylinder	80 - 100	not known	not known

CHAPTER 3

THE SELECTION OF A SUITABLE CATALYST CARRIER

It was decided to survey the possibilities of using an inorganic support for the polymeric catalyst. Such carriers have a well developed resistance to attrition and provide a high surface area base for the more expensive polymer component. No attempt was made to produce inorganic supports, instead the project was confined to the use of commercial materials.

In this work acrylonitrile copolymer in powder form has been used as the precursor to the catalytically active component. The polymer used was "Acrilan".

3.1 The requirements of a catalyst for exhaust pollution control

The choice between catalysts in the monolith (corrugated ceramic) or pellet form has already been mentioned in the introductory chapter. In this work only supports in the pellet form have been examined because of several advantageous factors. Firstly the pellet supports were, at the time of the search, available in a greater number of grades. Only small quantities of support were required in the deposition experiments. Finally the end properties such as extent of coverage and polymer adhesion could more easily be assessed using pelletised supports.

In fact from the point of view of catalyst efficiency pellet shape is not as important as size in the present work. Small cylinders, spheres and grains were examined. The spheres of 3 or 4 mm diameter, and cylinders of 3mm diameter and 6mm length were recommended by the suppliers.

In the case of this project it is preferred that the support is catalytically inert when in contact with exhaust gases. The loss of small particles of polymer, or support, may affect the zero control on the gas analyser and in addition would be emitted into the atmosphere as particulate matter during use. Polymer adhesion to the support must therefore be at a maximum.

3.2 Methods of Polymer Deposition

3.2.1 Dry Polymer

In two separate experiments 20g each of Hopkins and Williams activated alumina pellets, and Harshaw Al0104T pellets, were subjected to a pressure of approximately 2mm Hg. in a wide flange, vacuum tight, resin flask. 10g of the powdered polymer was also placed in the flask and the dry mixture shaken for ten minutes, whilst under vacuum. The pressure in the vessel was allowed to reach one atmosphere by admitting air, and this procedure was repeated five times. The idea was that the powder would block some of the evacuated carrier pores, eventually to form a continuous layer which could then be pyrolysed.

3.2.2 Precipitation Methods

It was thought possible that under suitable conditions the polymer could be preferentially precipitated from solution with formdimethylamide, (hereafter referred to as D.M.F.), onto the support. A 5% solution was prepared.

Sorbsil silica gel was the first support examined but this disappointingly shattered into very small pieces when immersed in the solution, this is shown in Plate 2. The Harshaw Al0104T, and Hydronyl CX0134AA03 pellets, were found to be inert and stable.

Two methods were tried, one by immersing the pellets in the polymer solution and adding methyl alcohol as the precipitant, and secondly by presoaking the pellets in methyl alcohol. In the former case uniform precipitation resulted throughout the solution, with no preference for the surface of the pellet. Whilst the prewetting technique failed to bring about the required local precipitation.

3.2.3 Solvent Evaporation Methods

The slow removal of solvent from a polymer solution which surrounded a continually rotating batch of immersed pellets, eventually furnished a suitable technique for polymer deposition. A pressure of approximately 0.3mm was used during evaporation whilst the water bath slowly increased from approximately 25°C to 90°C over a period of 30 minutes.

A variety of grades of pellet, and of formulations were chosen to select the process giving the optimum in coverage and adhesion properties. In order to minimise the number of variables a solution concentration of 2.22g of polymer and 25 or 50g of D.M.F. was used throughout. This represented the arbitrary first levels used. The material was then heated for 24 hours at 250°C under vacuum.

PLATE 2

FRAGMENTATION OF SORBSIL GRADE A SILICA GEL AFTER TREATMENT WITH D.M.F.

3.3 Results

An empirical adhesion rating from 1 to 10 was used, where a higher figure indicates better adhesion. A small knife was used in the estimation. The coverage figures were obtained by taking a random 100 pellet sample and rating each pellet as 1.00, 0.90, 0.75, 0.50, 0.25, 0.10 or 0 coverage of black pyrolysed polymer. The eventual coverage figure was given to the nearest 5%.

In practice it was established that the grade of pellet had the major influence on eventual properties. The conditions of preparation of the catalyst, before the evaporation stage, were also found to be important. The experiments are reported in full in tables 2 to 5.

Some of the more promising compositions were further pyrolysed, under vacuum, for two hours at 400°C, and their properties were assessed. Several of these were then exposed to a nitrogen purge for 45 minutes at 500°C using a flow rate of $500 cm^3 min^{-1}$. The coverage and adhesion properties are recorded in table 6.

3.4 Discussion of Results

3.4.1 The Support

Commercial catalyst carriers are based on silicon

CODE	PELLET GRADE	FORMULA WEIGHT (g)				PREPARATION PROCEDURE				PHYSICAL PROPERTIES	
						PELLET PRETREATMENT CONDITIONS		SOLUTION/PELLET CONTACT CONDITIONS		(250^{o}C Pyrolysis)	
		PELLETS	DMF	PAN	DMF	PELLET PREWET TIME (Hours)	PELLET UNDER VACUUM?	CONTACT TIME BEFORE EVAPORATION (Hours)	SOLUTION TEMPERATURE (^{o}C)	% COVERAGE	ADHESION RATING
A1	(	25	25	2.22	25	2	NO	16	20	30	2
A2	Celite 408 (	25	25	2.22	25	2	NO	16	50	25	2
A3	(	25	25	2.22	25	2	NO	16	80	25	2
B1	Harshaw (	25	25	2.22	25	2	NO	16	20	25	2
B2	A10104T (	25	25	2.22	25	2	NO	16	50	20	2
B3	(	25	25	2.22	25	2	NO	16	80	20	2
C1	Hydronyl (	25	25	2.22	25	2	NO	16	20	80	9
C2	CX0134AA03 (	25	25	2.22	25	2	NO	16	80	85	9

TABLE 2

FORMULAE, PREPARATION AND PROPERTIES OF SOME EXPERIMENTAL SUPPORTED PAN.P CATALYSTS

CODE	PELLET GRADE	FORMULA WEIGHT (g)				PREPARATION PROCEDURE				PHYSICAL PROPERTIES	
						PELLET PRETREATMENT CONDITIONS		SOLUTION/PELLET CONTACT CONDITIONS		(250°C Pyrolysis)	
		PELLETS	DMF	PAN	DMF	PELLET PREWET TIME (Hours)	PELLET UNDER VACUUM? (Hours)	CONTACT TIME BEFORE EVAPORATION (Hours)	SOLUTION TEMPERA-TURE (°C)	% COVERAGE	ADHESION RATING
D	Celite 408	25	0	2.22	50	0	0	46	20	20	3
E	Harshaw A10104T	25	0	2.22	50	0	0	21	20	30	2
F1	Hydronyl (	25	0	2.22	50	0	0	21	20	95	9
F2	CX0134AA03 (	25	0	2.22	50	0	0	46	20	85	9
G1	Hydronyl (	25	0	2.22	50	0	0	21	20	40	5
G2	CX0136AA03 (	25	0	2.22	50	0	0	46	20	90	7
H	Celite 408	25	0	2.22	50	0	1	2	20	40	3
J	Harshaw A10104T	25	0	2.22	50	0	1	2	20	60	2

TABLE 3.

FORMULAE, PREPARATION AND PROPERTIES OF SOME EXPERIMENTAL SUPPORTED PAN.P CATALYSTS

CODE	PELLET GRADE	FORMULA WEIGHT (g)				PREPARATION PROCEDURE				PHYSICAL PROPERTIES	
						PELLET PRETREATMENT CONDITIONS		SOLUTION/PELLET CONTACT CONDITIONS		(250^{o}C Pyrolysis)	
		PELLETS	DMF	PAN	DMF	PELLET PREWET TIME (Hours)	PELLET UNDER VACUUM? (Hours)	CONTACT TIME BEFORE EVAPORATION (Hours)	SOLUTION TEMPERATURE (^{o}C)	% COVERAGE	ADHESION RATING
K.	Hydronyl 0136AA03	25	0	2.22	50	0	1	28	20	90	7
L	Hydronyl 0134AA03	25	0	2.22	50	0	1	28	20	100	9
M	Hydronyl 0134AA03	25	0	2.22	50	0	1	0	-	85	9
N	Hydronyl 0136AA03	25	0	2.22	50	0	1	0	-	90	8
P	Celite 408	25	0	2.22	50	0	1	0	-	20	3
Q	Harshaw A10104T	25	0	2.22	50	0	1	0	-	50	2
R1	Procatalyste (	25	0	2.22	50	0	1	0	-	80	5
R2	SCS (	25	0	2.22	50	0	NO	16	20	70	5
R3	79 (	25	0	2.22	50	2	NO	16	20	80	5

TABLE 4
FORMULAE, PREPARATION AND PROPERTIES OF SOME EXPERIMENTAL SUPPORTED PAN.P CATALYSTS

		FORMULA WEIGHT (g)				PREPARATION PROCEDURE				PHYSICAL PROPERTIES	
						PELLET PRETREATMENT CONDITIONS		SOLUTION/PELLET CONTACT CONDITIONS		(250°C Pyrolysis)	
CODE	PELLET GRADE	PELLETS	DMF	PAN	DMF	PELLET PREWET TIME (Hours)	PELLET UNDER VACUUM?	CONTACT TIME BEFORE EVAPORATION (Hours)	SOLUTION TEMPERATURE ($^{\circ}$C)	% COVERAGE	ADHESION RATING
S1	Hydronyl CX0134AA03	25	0	2.22	50	0	NO	0	-	70	5
S2		25	0	2.22	50	0	NO	2	20	100	9
S3		25	0	2.22	25	0	NO	2	20	100	9
S4		25	0	2.22	20	0	NO	2	20	95	9
S5		25	0	2.22	10	0	NO	2	20	100	9
S6		25	0	2.22	15	0	NO	2	20	95	9
S7		25	0	2.22	10	0	NO	2	20	100	9
S8		25	0	2.00	10	0	NO	2	20	50	6
S9		25	0	1.00	10	0	NO	2	20	30	5

TABLE 5

FORMULAE, PREPARATION AND PROPERTIES OF SOME EXPERIMENTAL SUPPORTED PAN.P CATALYSTS

CODE	PELLET GRADE	PHYSICAL PROPERTIES					
		250°C PYROLYSIS		400°C PYROLYSIS (Fresh)		400°C PYROLYSIS (Gas Purged)	
		% Coverage	Adhesion Rating	% Coverage	Adhesion Rating	% Coverage	Adhesion Rating
C1	Hydronyl 0134AA03	80	9	100	10	100	9
F1	Hydronyl 0134AA03	95	9	100	10	100	10
G2	Hydronyl 0136AA03	90	7	100	10	100	8
J	Harshaw Al0104T	60	2	70	6	70	3
M	Hydronyl 0134AA03	85	9	100	9	100	10
N	Hydronyl 0136AA03	90	8	100	9	100	7
R1	Procatalyste SCS 79	80	5	95	6	95	4
S1)	Hydronyl CX0134AA03	70	5	100	10	100	9
S2)		100	9	100	9		
S5)		100	9	100	9		
S6)		95	9	100	9		
S7)		100	9	100	10		
S8)		50	6	70	7		
S9)		30	5	40	7		

TABLE 6

FURTHER PROPERTIES OF FORMULAE DESCRIBED IN TABLES 2, 3, 4, AND 5 dioxide or aluminium oxide.

3.4.1.1 Silicon dioxide based supports

The silica gel carrier Sorbsil grade A was ruled out because of excessive fragmentation when in contact with D.M.F. solvent. This effect is recorded in Plate 2. The synthetic silica gels are, in common, of high pore volume. Sorbsil grade A has a specific surface area of 850 m^2g^{-1}. They are also highly organophilic, so that when in contact with organic liquids such as D.M.F. a high heat of adsorption results. This causes local expansion and fragmentation.

A gel having a pore size above the normal 20 Angstroms diameter could have been examined. This would have had the effect of diminishing the localised rapid expansion. However a lower attrition resistance is one consequence of a greater pore diameter, and since high attrition resistance is a prime objective, this approach was not pursued.

Alternatively consideration was given to using a silica gel of a higher macro particle size. This may then shatter to particles of more acceptable dimensions. The problems of control of this process seemed to be too great, an even distribution of macro particle size, and of surface area per particle, was desired. Consequently it was decided to abandon any further work involving synthetic silica gel supports.

To overcome fragmentation processes a natural silica, Celite 408 diatomaceous silica, in pellet form was examined.

This has a low specific surface area between 3 and $10m^2g^{-1}$. Tables 2, 3 and 4 contain information on the properties of catalyst composites, based on this support. These are formulations A1, A2, A3, D, M and P; Plate 3 shows formula A1.

In each of the six formulations based on Celite 408 the "keying" of the polymer to the silica was unsatisfactory. Hence relatively low coverage and adhesion ratings were common, and on these grounds the carrier was rejected.

3.4.1.2 Aluminium Oxide based supports

Four Alumina supports were obtained and examined in detail. These were Hydronyl CX0134AA03 and CX0136AA03, Harshaw Al0104T and Procatalyste SCS79. The latter is in spherical form, all have diameters of approximately 3mm. The CX0134AA03 has a specific area between 10 and $20m^2g^{-1}$ and the remainder are around 100 m^2g^{-1}. It is claimed that they will all withstand temperatures up to 900°C.

As a group they consistently displayed adhesion and coverage properties which were superior to those found for Celite 408 based composites (Tables 2 to 6). Plate 3 illustrates the end composite of the SCS 79 (R1), Al0104T (B1), CX0136AA03 (K), and CX0134AA03 (S2) respectively. One reason for this difference may be related to the affinities the supports have for the polymer solution. It was noticed during the rotary evaporation stage that the solution wetted out the alumina pellets much easier than was the case with Celite 408.

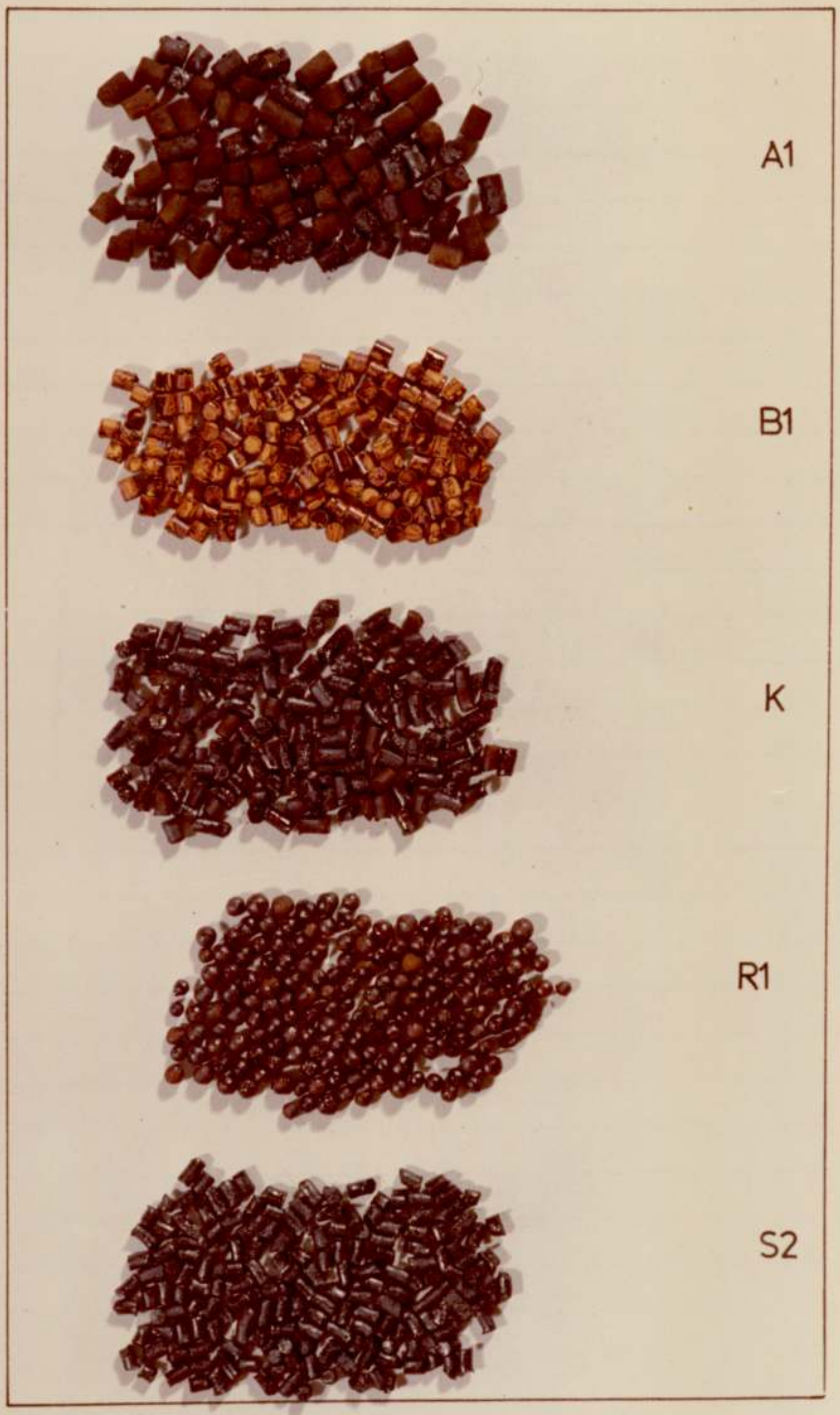


PLATE 3 PAN·P on various supports

Within this group the Hydronyl products supported the PAN.P in higher coverages than the SCS 79 and the A10104T. This is shown in the series F1, G1, E and R2 and in the series M, N, Q and R1. Moreover Hydronyl CX0134AA03 was consistently found to be the best support, and was subsequently used for all the catalytic experiments.

One reason for the superior polymer adhesion to the CX0134AA03 is probably related to surface area. The higher surface area supports have a weaker structure just under the polymer surface than the more dense CX0134AA03. Hence adhesion failure and consequent lower coverage were probably due to surface breakdown within the pellet, as opposed to polymer/alumina adhesion failure.

It is more difficult to propose the reason for the superiority of both of the Hydronyl products, especially since more information on the other two supports was not divulged. Since the Hydronyl products contain more than 99.9% of Alumina having the single alpha crystal phase, the answer could well be related to this.

3.4.2 Pellet Treatment

The pellet/polymer solution mixture prior to rotary evaporation was prepared in several ways, in order to optimise the end properties of the catalysts. The pellets were either taken straight from the container, subjected to vacuum or presoaked in D.M.F. before adding a freshly prepared PAN solution. This mixture was then left for various lengths of time at a variety of temperatures before solvent evaporation.

3.4.2.1 Prewetting and Vacuum Treatment

The possibility exists that a dry pellet, when exposed to a polymer solution, may extract the solvent locally to deposit the polymer. Therefore the method of prewetting the pellet to enhance maximum diffusion of the solution into the pores was investigated.

The comparison of the properties of the following pairs of formulations shows that there are no advantages to be gained in prewetting the pellets: C1, F1; B1, E; R2 and R3.

Similarly the pellets were subjected to vacuum so that the solution, when added, may flow well into the pores once the mixture was brought to atmospheric pressure. By confining our attention to the CX0134AA03 support (L compared to F1), we can find little or no advantages in this extra step.

3.4.2.2 Pellet/Solution Contact Time and Temperature

If the diffusion of the polymer solution into the pellet has any bearing on the end properties of the composite then contact time and temperature may in turn be expected to influence these properties. In fact it was shown (A1, A2, A3, B1, B2, C1, C2) that the extra effort in keeping the mixture at temperatures above 20°C could not be justified.

It was observed that mixtures, which were given no contact time before evaporation gave end products having lower coverage than those given two hours or more (L, M). The difference caused by having contact times of between two and fortysix hours were negligible. A convenient contact time of twenty-one hours was chosen.

3.4.2.3 Solvent and Polymer Levels

Once it was decided to use Hydronyl CX0134AA03 as the catalyst carrier, several formulae were tried to test the effect of varying the polymer and solvent concentrations.

D.M.F. levels of 50, 25, 20 and 10g per 25g pellets (S2, S3, S4 and S5) indicated that the solvent level played only a minor role in influencing coverage properties. The 25g level was selected because the 10g and 20g level formulae were of high viscosity.

The arbitrary polymer level of 2.22g per 25g of pellets was surprisingly better than the 2.0g or 1.0g levels (S7, S8 and S9).

3.5 The Final Formulation

Weights

Hydronyl CX0134AA03	75.00 g
PAN (Acrilan, powder)	6.66 g
D.M.F.	75.00 g

The pellets were vacuum dried for 30 minutes at 250°C before use. The D.M.F. was distilled and stored over molecular sieve.

The PAN was dissolved in the solvent for 2 hours and then poured over the pellets which were contained throughout the experiment in the bottom of a glass vessel 35 cm deep and having an internal diameter of 4cm.

The mixture was left at room temperature for 21 hours before evaporation.

Solvent Evaporation

The Bϋchi Rotavapour was used at speed 5 (approximately 60 r.p.m.) with a 45° angle for 30 minutes. A progressively increasing water bath temperature from 25°C to 90°C was always employed, along with a reduced pressure of approximately 0.3 mm Hg.

Pyrolysis

All samples were pyrolysed using a fluidised bath for 24 hours at 250°C at a pressure of 0.1 to 0.3 mm Hg. Unless otherwise stated further pyrolysis under vacuum at 400°C was given for two hours.

Other Information

The pyrolysed sample was freed of any excess polymer through a sieve having 10 mesh holes per linear inch.

On a random analysis an average of 20g of D.M.F. was retained by the composite per formula weight after evaporation, and an average of 2.4g of excess polymer was found following pyrolysis.

CHAPTER 4

SOME PRELIMINARY STUDIES OF THE INTERACTION BETWEEN NO AND PAN.P USING A FIXED BED INTEGRAL FLOW TECHNIQUE

4.1 Reactions involving NO only

The initial work was concerned with the activity towards the removal of NO alone. The apparatus used was a conventional fixed bed flow reactor in conjunction with a continuous gas analyser. These are fully described in sections 2.2.1 and 2.2.2 respectively. The flow reactor consisted of a cylindrical stainless steel vessel in which the catalyst is seated on a wire gauze (Figure 2). A temperature controlled furnace surrounded the catalytic reactor and the preheat vessel. A gas valve directed the incoming gases over the catalyst or through the preheat chamber. In this way an examination of the interaction of NO with PAN.P was undertaken.

4.1.1 Initial Experiments

Initially the NO removal activity was examined using conditions randomly selected on the basis of the characteristics of PAN.P. The polymer was pyrolysed for 12 hours at 250° C under vacuum and then for 1½ hours at 375°C again under vacuum. It was supported on Sorbsil grade A silica granules and 35 g were used. An input gas flow rate of 1000 $cm^3 min^{-1}$ and a NO concentration of 6,000 ppm in nitrogen were chosen.

It was found that between 90 and 100% of the NO was removed at temperatures above 585°C. In contrast a commercially available iron oxide/chromium oxide NO removal catalyst exhibited no activity when tested under similar conditions up to 700°C in the absence of carbon monoxide.

Having demonstrated this previously unobserved reaction between PAN.P and NO, more work was carried out to establish the exact nature of the reaction, with pollution control in mind. The normal kinetic variables such as flow rates, temperature of reaction, concentration of gases and preparation conditions of the polymer were examined.

4.1.2 Reaction Profiles and Rate Calculations

Throughout the work the recorder trace was used to calculate the amount of reactant gas removed as well as to record the reaction temperature. In the first instance the gas analysers were precalibrated using a series of standard gas mixtures. NO, for example, was spanned up to 3,900 ppm in nitrogen using the 10 mv recorder range. The concentration/recorder signal relationship is illustrated in Figure 8. All analysers were checked immediately before each series of experiments by separately guiding both nitrogen and the reactant gas, of known concentration, directly into the analyser (Route 1, Figure 3).

When the catalyst was admitted to the steel vessel the furnace was allowed to reach the required temperature whilst nitrogen gas was passed over the catalyst at the desired flow rate. Once the temperature was reached and the recorder was switched on at a chart speed of 1 cm per minute, the nitrogen flow was stopped. Then the reactant gases were allowed through the preheat chamber (route 2) at predetermined flow rates. The analyser signal now represents the concentration of gases which would emerge if the catalyst has zero activity. The reactant gases were then directed over the catalyst for several minutes (route 3) and finally the gases were switched back on route 2 to check the zero removal concentration. This sequence of events is shown in terms of the recorder trace in Figure 9. It is a simulation of an actual run involving 10g of standard PAN.P catalyst at 400°C using a flow of 500 $cm^3 min^{-1}$ of 500 ppm NO in nitrogen and 500 $cm^3 min^{-1}$ of nitrogen, a 2 mv recorder range was used.

From a kinetic viewpoint the initial reaction rate is a most important parameter. Consequently the response time of the analyser and recorder need to be at a minimum as does the dead space volume of the apparatus downstream to the catalyst. This volume was approximately 50 cm^3, up to the Beckmann NO analyser. Furthermore the overall time for equilibration should be known for each flow rate. Figure 9 in fact shows this full response time to be in the region of 20 seconds when changing from route 2 to route 3 for the 1000 $cm^3 min^{-1}$ flow rate used.

During the course of the work the isothermal NO removal curves displayed several shapes. Those given in Figures 9, 10 and 11 were most common. Figures 10 and 11 illustrate a decrease in activity with time, the former being more pronounced.

In another series of comparative experiments, catalytic activity was monitored continuously during a programmed temperature increase. This is shown in Figure 12, described in detail in section 4.1.4.

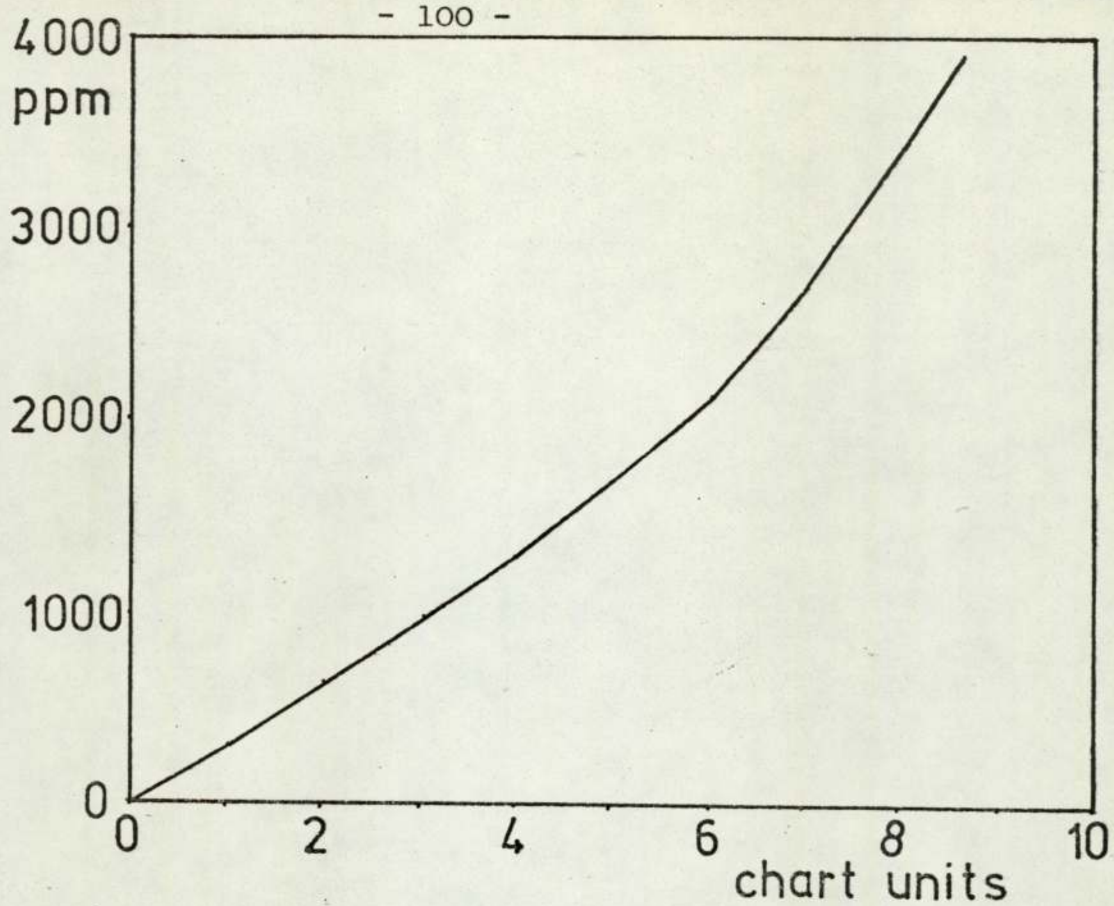


FIGURE 8 - NO calibration

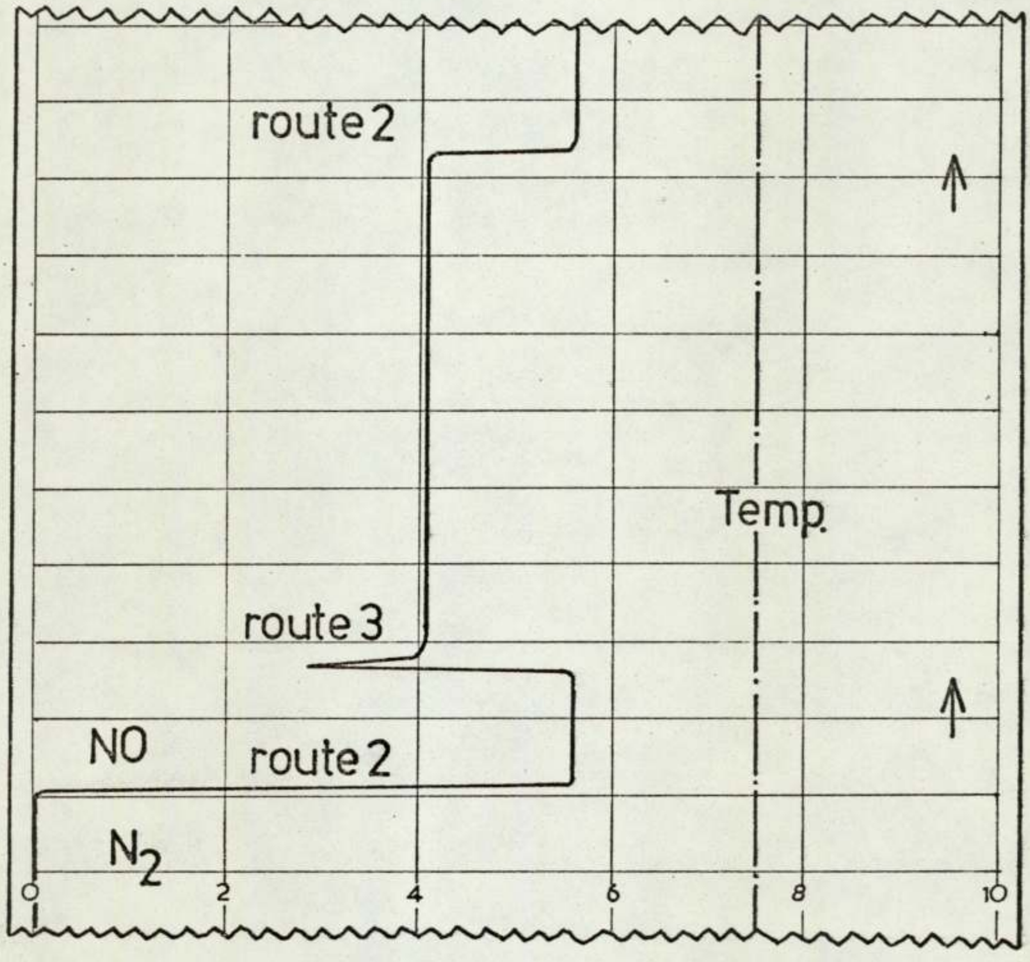


FIGURE 9 - Reaction profile showing a constant removal of NO by catalyst

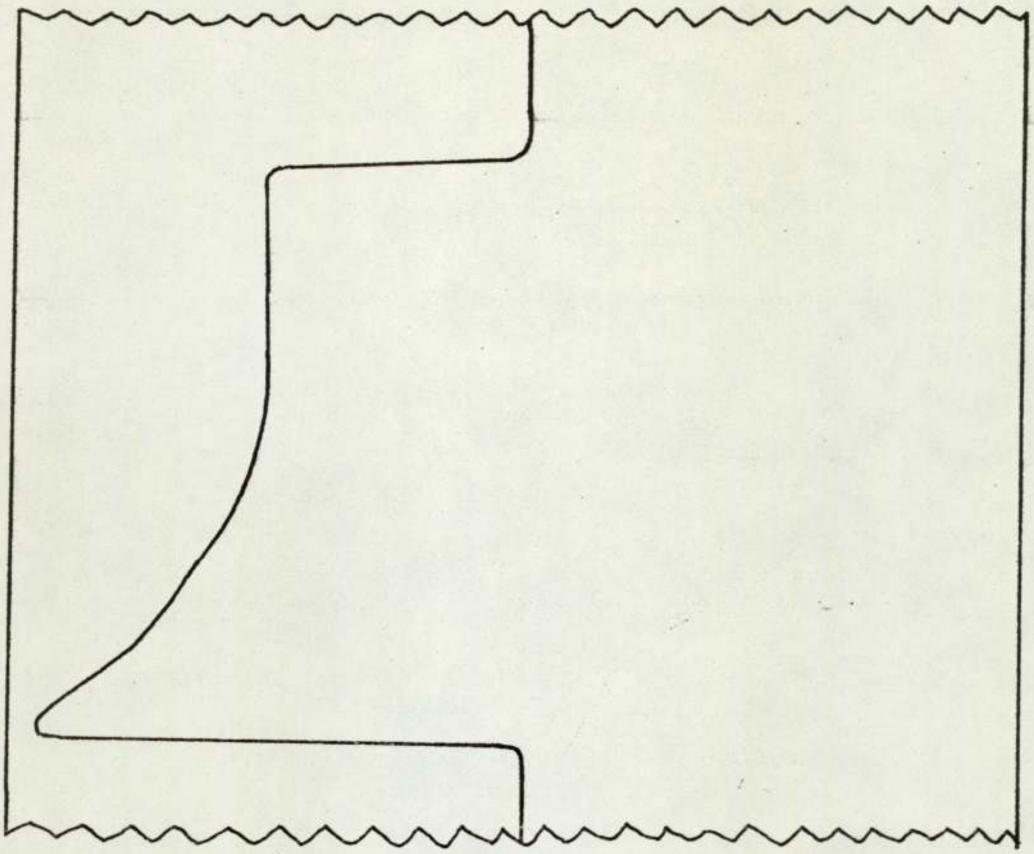


FIGURE 10

Reaction profile showing rapid decay in initial rate of removal of NO

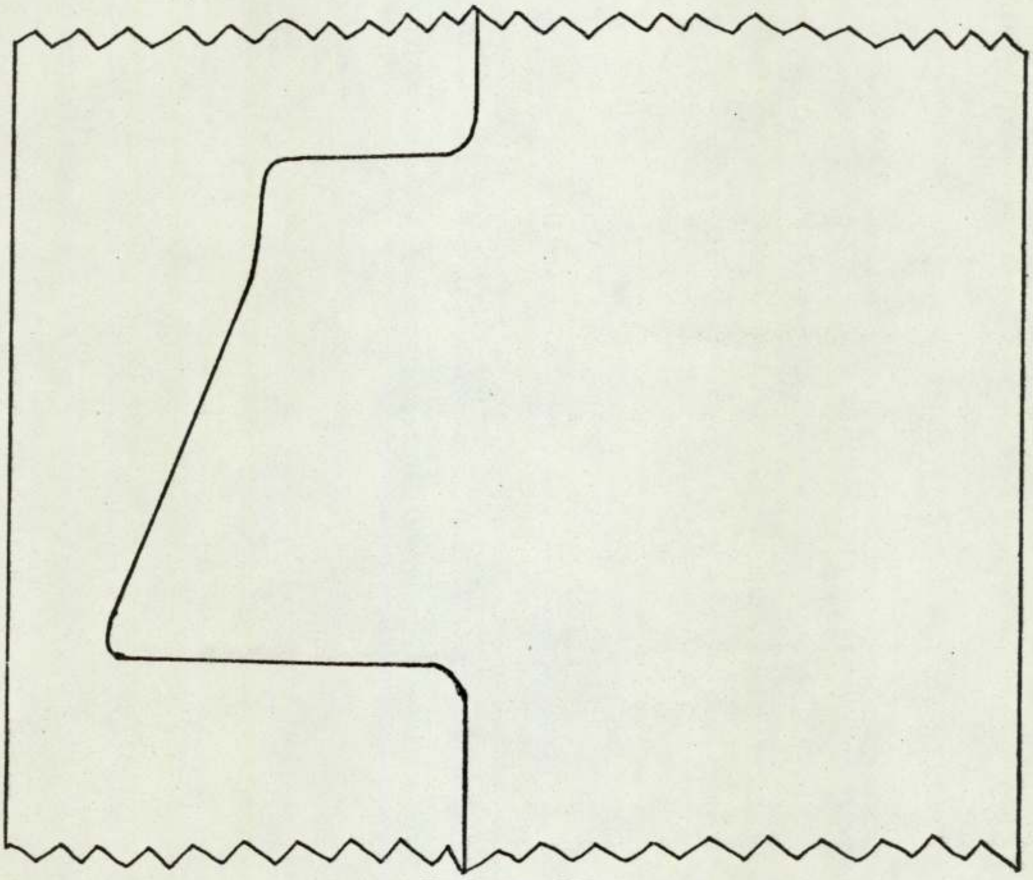


FIGURE 11

Reaction profile showing linear decay in initial rate of removal of NO

The concentrations of NO in nitrogen selected were between 250 and 6000 ppm whilst the reaction temperatures were from 250 to 650°C. In converting ppm of NO removed at any one time to moles $\text{second}^{-1}\text{metre}^{-2}$ (moles s^{-1} m^{-2}) of catalyst it was taken that the full surface area of the catalyst, as determined by the nitrogen adsorption method described previously, consisted of polymer.

It was observed quite consistently that the surface areas of polymers increased during NO removal reactions. This was a combined time/temperature effect and one which occurred independently of polymer pyrolysis temperature. The most important consequence of this was that for non-isothermal runs surface area values for intermediate temperatures had to be calculated rather than measured directly. Examples of this are given where appropriate in the text.

$$\text{Rate of removal} = \frac{\text{ppm removed}}{10^6} \times \text{total flow rate}(\text{cm}^3\text{min}^{-1})$$

$$= \frac{\text{ppm x flow rate}}{10^6 \times 60 \times 22{,}400} \quad \text{moles } s^{-1}$$

$$= \frac{\text{ppm x flow rate}}{10^6 \times 60 \times 22{,}400 \times \text{s.area } (m^2)} \quad \text{moles } s^{-1}m^{-2}$$

and for a 10g catalyst charge

$$\text{Rate of removal} = \frac{\text{ppm x flow rate}}{10^6 \times 60 \times 22{,}400 \times 10 \times \text{s.area}(m^2g^{-1})} \quad \text{moles } s^{-1}m^{-2}$$

$$= \frac{\text{ppm x flow rate}}{1.344 \times 10^{13} \times \text{s.area of 1g}} \quad \text{moles } s^{-1}m^{-2}$$

4.1.3 The weight of catalyst

To eliminate any variation caused by having different charges of catalyst it was decided to examine this effect in the early stages of the work. A range of catalyst weights between 10g and 40g was chosen. The importance of ensuring a maximum of gas/catalyst contact was recognised, whilst at the same time the lowest weight was experimentally most convenient. Table 7 lists the initial rates of NO removal determined at various weights of catalyst and compares these to the rates obtained when a 10g charge was used at the temperatures given.

TABLE 7

The influence of the weight of PAN.P catalyst on rate of removal of NO

Reaction Conditions

Input gas mixture:

NO (1500 ppm in nitrogen)	500 $cm^3 min^{-1}$
Nitrogen	500 $cm^3 min^{-1}$

Results

Catalyst weight	Isothermal reaction temperature	Initial rate of NO removal moles $s^{-1} m^{-2} \times 10^{10}$	
g	^oC		(10 g charge)
20	515	19.54	(22.00)
20	472	15.09	(15.20)
30	475	15.60	(15.20)
30	447	15.06	(11.50)
40	430	9.45	(9.80)

The NO removal rate is shown to be linearly proportional to the surface area of the catalyst. The work also supports the decision to use 10g quantities of catalyst in all subsequent runs. This approximately corresponds to a pellet depth of 1.2 cm.

However, it must be stressed that the choice of a 10g mass of catalyst can only be regarded as sufficient for flow rates of 1,000 cm^3 min^{-1} or less.

4.1.4 Pyrolysis temperature

The effect of the polymer pyrolysis temperature on NO removal activity was investigated. This was to test whether the 400°C pyrolysis temperature of the standard catalyst produces activity close to the maximum possible. Furthermore it would provide a good comparison with the work of Gallard and colleagues[69] who found the temperature of maximum activity of PAN.P for the decomposition of dinitrogen oxide to be 400°C.

In this series of experiments the polymer was deposited onto the support and prepyrolysed under vacuum at 250°C for 24 hours as described in section 3.5. Then six different batches were treated for two hours under vacuum at temperatures of 300, 350, 400, 450, 500 and 550°C respectively. This pyrolysis time was selected on the basis of the observation of Ph. Traynard [74(c)] who stated that heating beyond 30 minutes appears to have no substantial influence on the activity. The full results are displayed in Figure 12, a selection of results at 350 and 500°C are given in Table 8.

Variation of initial rate of removal of NO with polymer pyrolysis temperature

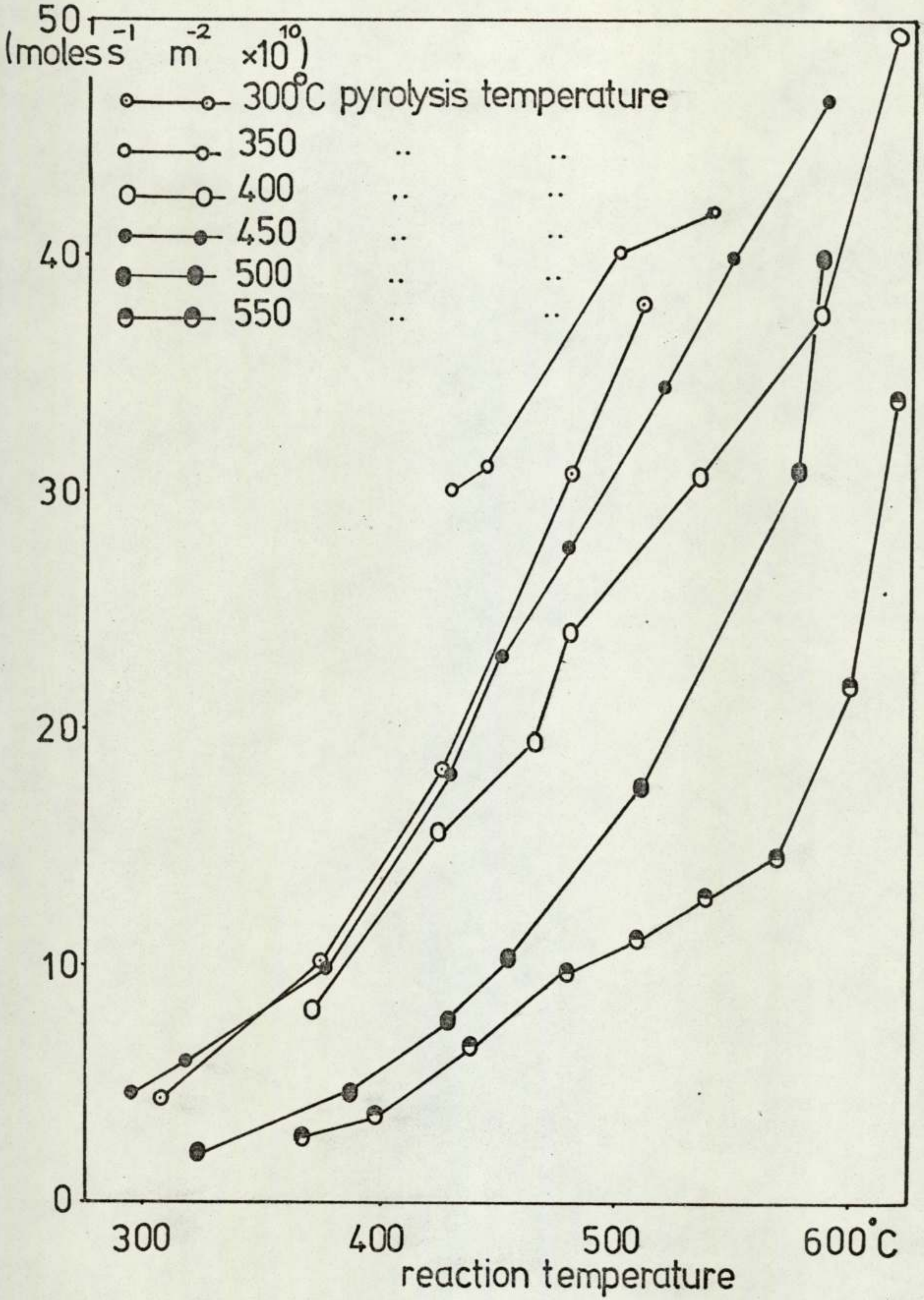


FIGURE 12

TABLE 8

The effect of varying polymer pyrolysis temperature on the initial rate of removal of NO at the reaction temperatures of 350 and 500°C

Reaction conditions

Temperature: linear rise of 12°C min^{-1} from 290 to 630°C

Catalyst weight: 10g

Input gas mixture:

NO (1500 ppm in nitrogen)	500 $cm^3 min^{-1}$
Nitrogen	500 $cm^3 min^{-1}$

Results

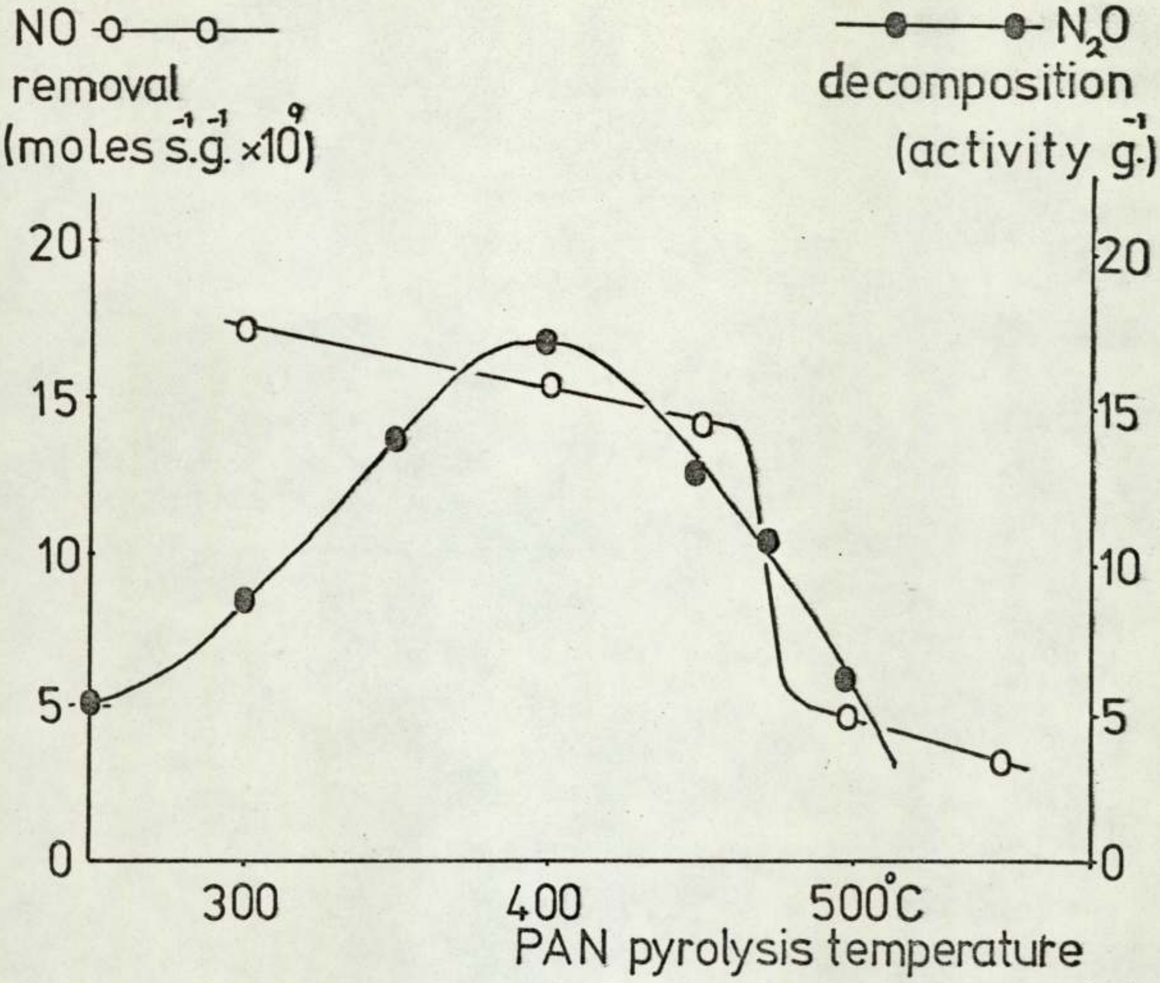
Polymer pyrolysis temperature (°C)	NO removal activity (moles $s^{-1} m^{-2} \times 10^{10}$) reaction at 350°C	reaction at 500°C
300	8.1	35.8
350	-	40.1
400	-	26.7
450	8.0	31.1
500	3.0	16.4
550	-	10.4

The results indicate that at a given pyrolysis temperature the NO removal rates increase with increasing reaction temperature. Furthermore the rates are shown to remain high until the pyrolysis temperature of the polymer exceeds 450°C. this is the case for the reactions carried out at temperatures between 300 and 550°C. The use of a pyrolysis temperature of 400°C in the standard formulation (section 3.5) is therefore confirmed as being in the temperature range which provides the optimum in NO removal activity for this polymer.

Figure 12 illustrates that a more rapid increase in activity is observed at reaction temperatures above that of the pyrolysis temperature. This is especially noticeable with the sample which was pyrolysed at 550°C. Any postulated (overall) reaction mechanism must account for this observation.

It is interesting to compare this work with the findings of Gallard[69] who examined the catalytic decomposition of dinitrogen oxide using PAN.P. In one study they followed the effect of pyrolysis temperature on activity at a particular reaction temperature (400°C). They expressed their results in arbitrary units of activity per gram of polymer.

Figure 13 represents an attempt to correlate the two sets of results. To do this the NO removal rates given in Figure 12 were converted from moles $s^{-1}m^{-2}$ to units of moles $s^{-1}g^{-1}$. The rates of removal at 400°C were calculated from non-isothermal experiments using the surface area estimation previously referred to. The variation of surface area with respect to pyrolysis temperature and reaction conditions are



Comparison of initial rate of removal of NO and decomposition of N_2O for PAN pyrolysed at several temperatures. (reaction temperature 400°C.)

FIGURE 13

Pyrolysis temperature °C	Surface Areas $m^2 g^{-1}$			Final Reaction temperature °C
	Fresh catalyst	400°C (estimated)	Used catalyst	
300	6.09	8.7	11.70	510
350	6.53	-	10.30	540
400	7.55	8.0	12.00	620
450	8.05	9.7	12.62	590
500	10.01	10.7	12.55	590
550	9.80	10.1	12.30	620

The variation in surface area of the PAN.P catalyst with pyrolysis temperature and reaction temperature.

TABLE 9

listed in Table 9 along with the appropriate values for the reaction temperature of 400°C.

The comparison can only be to a first approximation since there are too many differences involved. One of these is that Gallard has used unsupported homopolymer whereas alumina supported copolymer was used with NO. Gallard used static and isothermal conditions for each experiment.

In both sets of results (Gallard and the present work) some values relate to polymer pyrolysis at temperatures below the reaction temperature (400°C). This is a factor which has already been shown to cause complications. Nevertheless this criticism does not apply to samples pyrolysed at 400°C and above. In this region a most striking similarity is the drastic reduction in activity once a pyrolysis temperature of 500°C is reached. Gallard explains this phenomena in terms of the properties of the free spins supported by the PAN.P. For instance a reduction in their concentration was measured for pyrolysis temperatures above 450°C.

The results obtained at the reaction temperature of 400°C have been presented in this comparison to maintain the greatest similarity to the reaction conditions of Gallard. However the NO removal rates follow the distribution of the Gallard results more closely at reaction temperatures of 450°C. In other words an initial increase and final decrease in activity with respect to pyrolysis temperature is evident.

4.1.5 Comparison between Homopolymer and Copolymer

A small sample of powdered acrylonitrile homopolymer was secured and its activity compared to the Acrilan copolymer in the form of supported catalysts prepared according to the standard formulation. The NO removal results appear in Table 10.

TABLE 10

The comparison between polyacrylonitrile homopolymer and copolymer, pyrolysed at 400°C, on their initial rates of NO removal.

Reaction Conditions

Temperature: linear rise of 12°C min^{-1} from 315 to 585°C

Catalyst weight: 10g

Input gas mixture:

NO (1500 ppm in nitrogen)	500 $\text{cm}^3\ \text{min}^{-1}$
Nitrogen	500 $\text{cm}^3\ \text{min}^{-1}$

Results

Reaction Temperature (°C)	Rate of NO removal (moles $\text{s}^{-1}\text{m}^{-2} \times 10^{10}$) Copolymer	Homopolymer
315	-	4.99
370	8.18	-
395	-	9.08
425	15.84	-
430	-	17.75
440	-	20.10
465	19.74	-
480	24.23	31.86
535	30.97	-
570	-	43.60
585	37.53	-

It can be seen that the two polymers have activities of the same order.

4.1.6 The effect of separately varying the flow rates and input gas concentrations

The effect of varying the flow rate and the input concentration of the reactant gas was studied. A series of experiments were conducted using the standard catalyst under isothermal conditions.

Concentrations of 250, 500, 750 and 3,300 ppm of NO in nitrogen were used at a common flow rate of 1000 $cm^3\ min^{-1}$. The reaction profiles were of the same form as Figures 9 and 11 so that no problems were encountered in identifying the initial removal rates. The results are represented in Figure 14.

In a second series of experiments a NO gas concentration of 500 ppm in nitrogen was used at flow rates of 75, 150, 500 and 1000 $cm^3\ min^{-1}$. Again the initial removal rates were easily derived and the results are illustrated in Figure 15.

A second way of representing the removal rates would be to express them as a fraction of the maximum rate, derived from the amount of NO introduced and from the surface area, at one reaction temperature. This would account for the variation in surface area encountered during the experiments. The results, in terms of the initial rate divided by the maximum rate possible, are given in Table 11 for the lowest

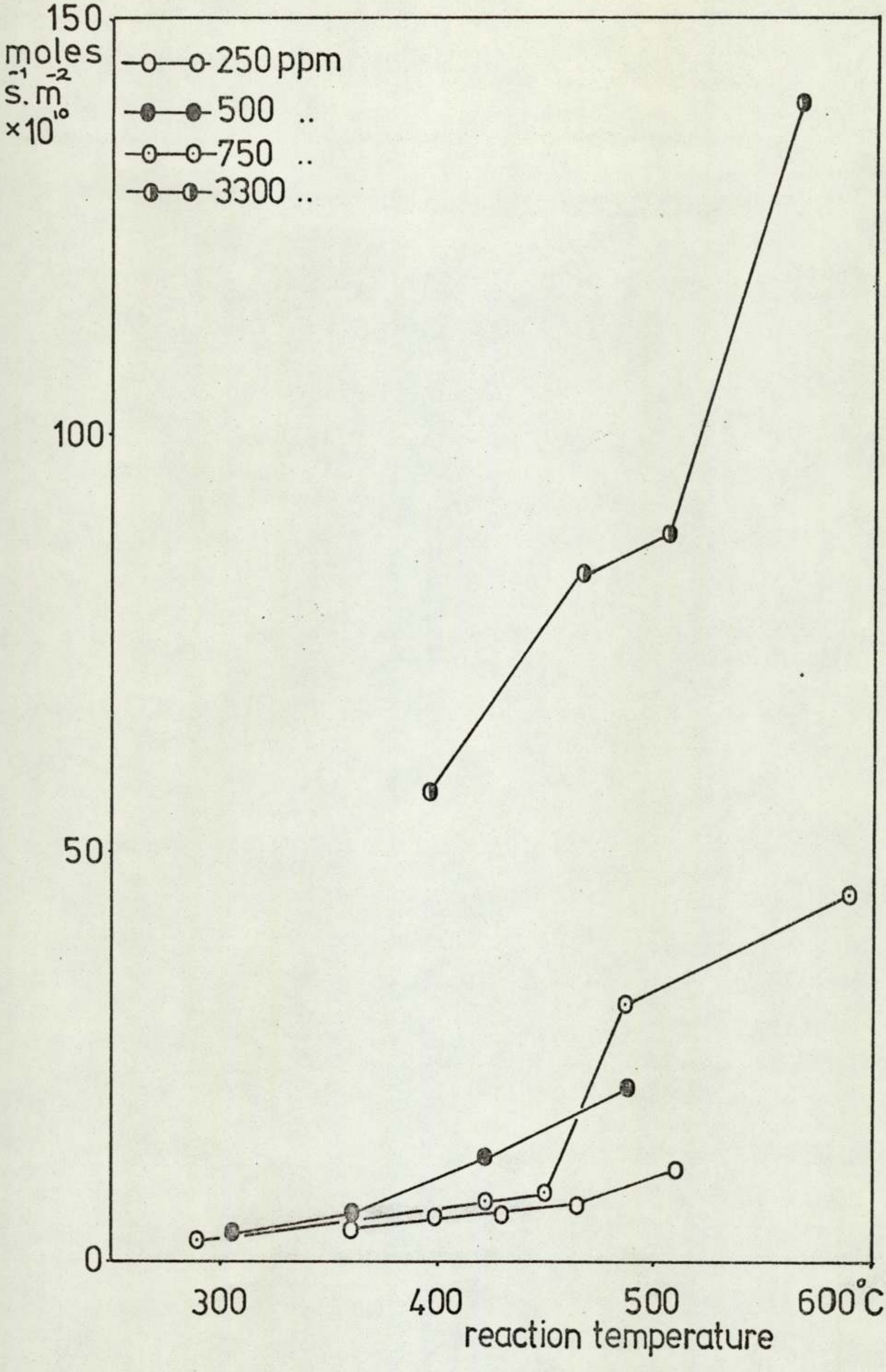


FIGURE 14

Variation of initial rate of NO removal with concentration of inlet gas (1000cm^{3}min^{-1} NO in nitrogen)

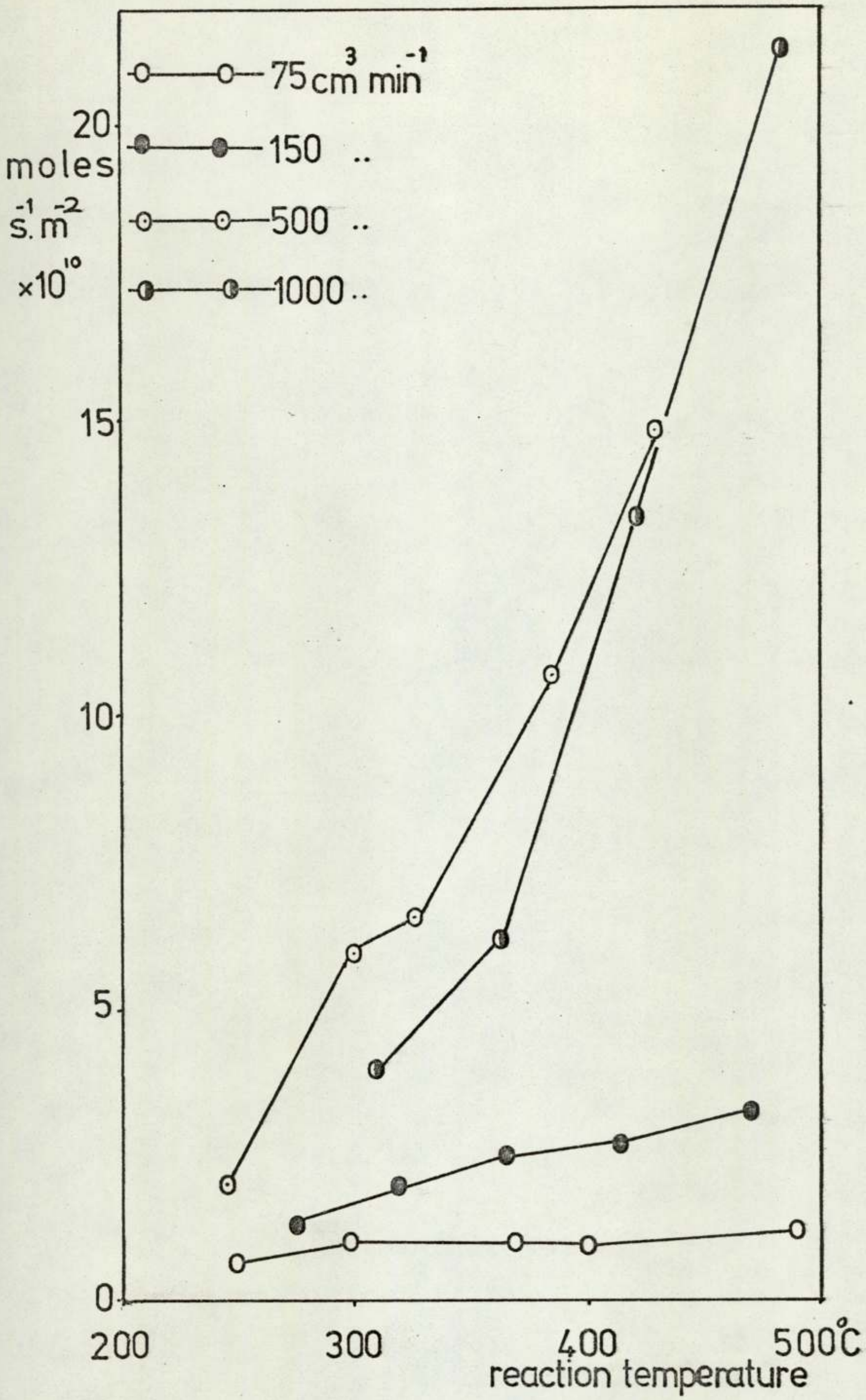


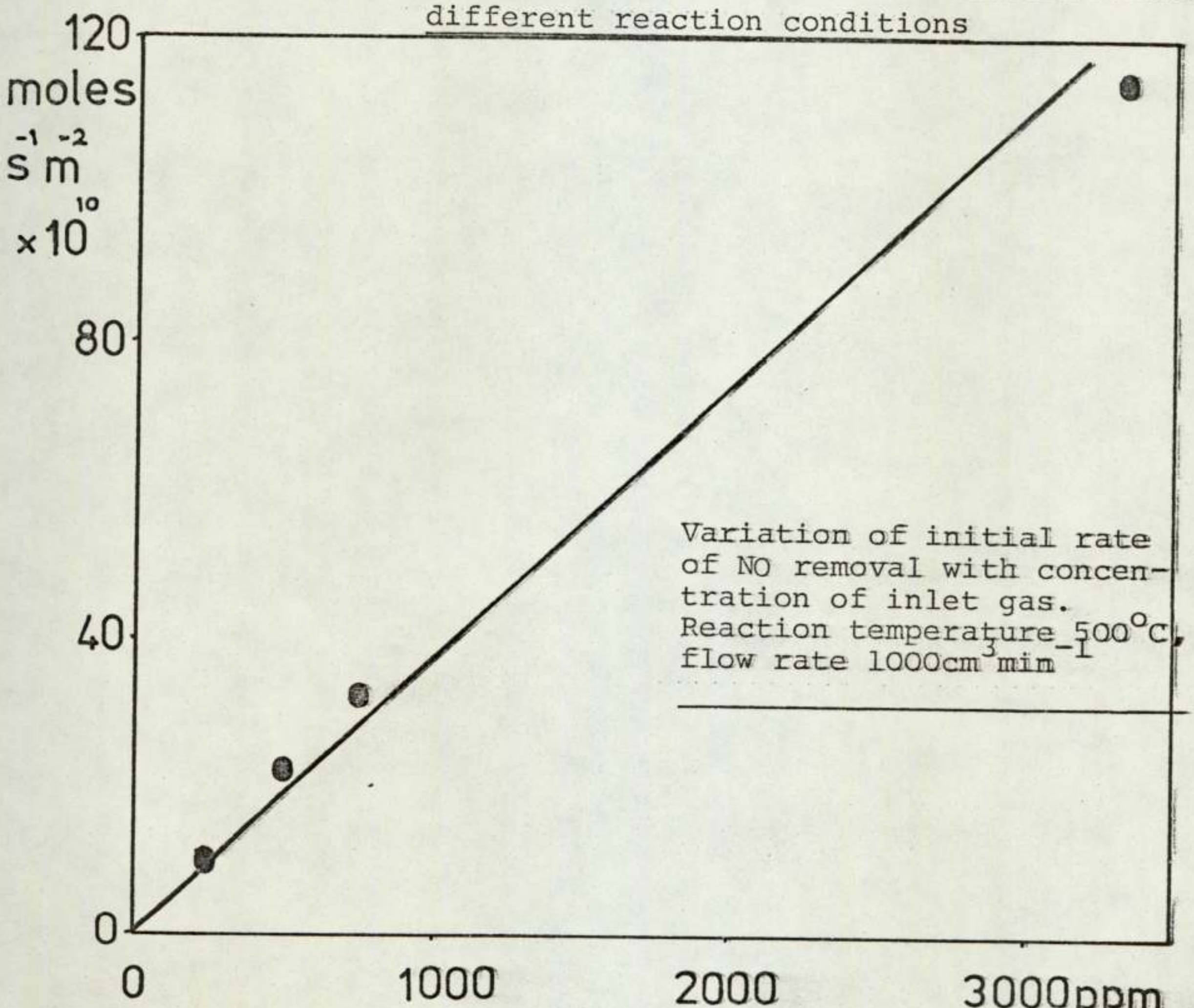
FIGURE 15

Variation of initial rate of NO removal with flow rate of inlet gas (500 ppm NO in nitrogen)

TABLE 11

	Flow Rate $cm^3 min^{-1}$	Temp. ^oC	$\frac{\text{rate}}{\text{max rate}}$	Temp. ^oC	$\frac{\text{rate}}{\text{max rate}}$
common inlet gas concentration of 500ppm NO in nitrogen	75	250	0.45	490	1.00
	150	275	0.23	470	0.91
	500	245	0.08	430	0.90
	1000	305	0.42	485	0.78
	(ppm)				
common flow rate of 1000 $cm^3 min^{-1}$	250	360	0.17	510	0.77
	500	305	0.10	485	0.78
	750	290	0.04	580	1.00
	3300	395	0.25	565	0.87

The relationship between the actual rate of removal of NO and the maximum possible rate of the PAN.P catalyst using different reaction conditions



Variation of initial rate of NO removal with concentration of inlet gas.
Reaction temperature 500°C, flow rate 1000$cm^3 min^{-1}$

FIGURE 16

and highest reaction temperature.

Examination of both sets of results shows two distinct regions. One is around 500°C where high activity is found and the rates of removal suggest a first order relationship as in Figure 16. Whereas at lower temperatures of less than 400°C, the activity is much less and no simple kinetic dependences are observed. Instead, a relationship that implies the saturation of total surface or of some specific active sites, at intermediate or higher concentrations.

Two conclusions can be drawn:-

1. The qualitative idea of some type of reaction "triggering temperature", first discernible in Figure 12, seems to be confirmed in more specific terms by these results.

2. There is no evidence that might support a reaction which is kinetically second order with respect to NO, as might be expected.

Alternatively these results (Figure 16) and the results relating to the variation in mass of catalyst, in section 4.1.3, strongly suggest a reaction which is first order in surface and in concentration of NO. That is: Rate = R [S] [NO]. However the term involving the catalyst surface may more specifically be related to the concentration of certain reaction sites which are as yet undefined.

It is important to realise that these conclusions may apply only to the limits of concentrations used in these experiments and that they apply to rates of removal or disappearance of nitric oxide and not necessarily to the rates of formation of any specific products. Nevertheless the results provide an interesting and unexpected insight into the nature of the reaction even though it was never intended to set the reactions in this way.

A worthwhile comparison can be made between the activity of the PAN.P catalyst and the series of inorganic catalysts listed by Shelef and Kummer[92]. The results for PAN are extrapolated to 500°C from Figure 14.

TABLE 12

NO removal rates for a series of inorganic catalysts and the PAN.P catalyst

	Decomposition rate at 500°C moles m^{-2} min^{-1} x 10^{10}
An assortment of 10 catalysts	2.67 to 74.8
Copper chromite derivative	116
UOP commercial catalyst	147
Unsupported Co_3O_4	954.2
PAN.P (250 ppm)	580
PAN.P (750 ppm)	1,920
PAN.P (3,300 ppm)	5,170

As Shelef points out these are the maximum rates available and with the exception of Co_3O_4 (which is stated to be a material unsuitable for practical application) they are too low to be of any utility in NO decomposition reactions. In contrast the PAN.P results do not represent maximum rates although the value at 3300 ppm may be approaching that figure.

It is interesting to note that Shelef found that the reaction order in NO on all tested catalysts was close to 1 with the exception of one noble metal catalyst where it was less than 0.5.

4.1.7 Cleaning the PAN.P surface

During thermal degradation, polyacrylonitrile is known to evolve a series of products which can include hydrogen cyanide, ammonia, acrylonitrile monomer, acetonitrile and methacrylonitrile[93]. A check was made on whether partial removal of any degradation product retained by the polymer influenced activity or diminished the objectionable odours. The presence of such reactive low molecular weight compounds at the high reaction temperatures involved could reasonably be expected to affect the extent of interaction between NO and PAN.P. In addition, the catalyst had emitted certain characteristic odours which would be offensive to the automobile engineer.

Consequently a search was made amongst common laboratory solvents to clean up the catalyst surface. Boiling acetone was found to be the most effective, extracting more colour. The final procedure was to extract approximately 150g of catalyst with two lots of acetone boiling under reflux for a total of 20 minutes and then to dry under vacuum at 100°C for 30 minutes.

The effect was to considerably reduce the odour at normal reaction temperatures. Flow rates of 1000 $cm^3 min^{-1}$ were employed to evaluate the treated catalyst. The reaction temperature was increased at a linear rate of 12°C min^{-1} whilst the activity was measured. Figure 17 represents the results obtained, a marginal change in activity is noted.

The results provide additional information in confirming the conclusions of the previous section (4.1.6). The extracted sample has, above 500°C, removal properties which reflect the two concentrations of input gas. That is the 750 ppm mixture gives a threefold difference in removal rate when compared to the mixture at 250 ppm. It is interesting to note that in this respect the temperature programmed runs compare with the isothermal runs of section 4.1.6.

4.2 Reactions involving NO in the presence of other gases

The NO removal activity of PAN.P was examined in the presence of several other gases. Activity in the presence of oxygen and the reducing species carbon monoxide, hydrogen and hydrocarbons, is of particular importance in the automobile pollution problem. Work of this kind may also provide information on the reaction mechanism.

Throughout the experiments reactant gases were generally carried in nitrogen. This enables the use of mixtures which were conveniently analysed and which were closer in concentration to exhaust gases. The nitrogen was always assumed

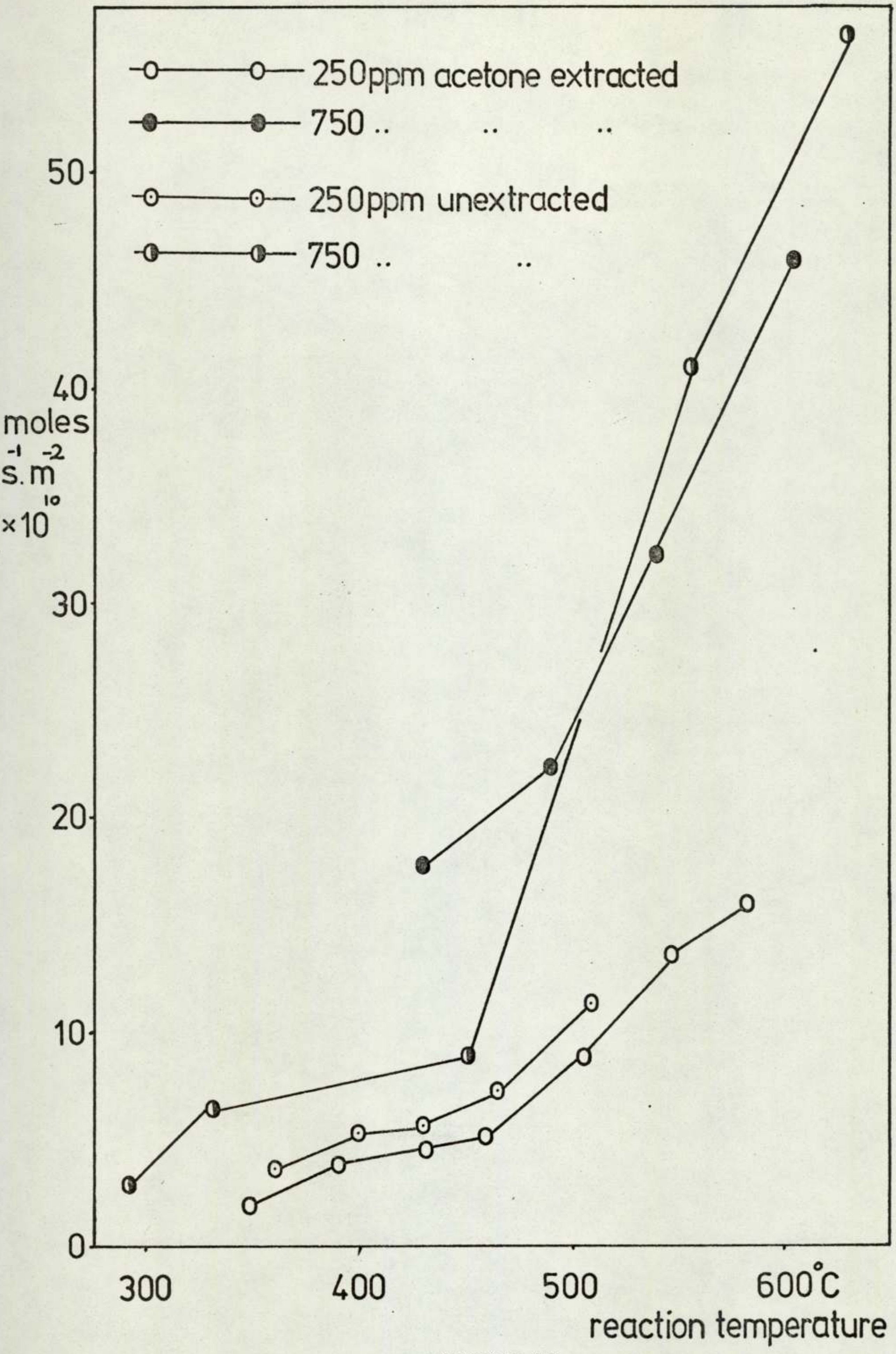


FIGURE 17

Effect of extracting PAN.P with acetone on initial rate of removal of NO using different concentrations of inlet gas to be inactive towards PAN.P.

4.2.1 Carbon Monoxide

It is commonly believed that NO in exhaust gas will be removed by reaction with the constituent carbon monoxide (hereafter referred to as CO). Shelef[18] has noted that reactions of this type are usually several orders of magnitude faster than straightforward decomposition. The work described in this section is concerned with the CO/NO reaction in the presence of the PAN.P catalyst.

In the first instance the reaction was followed using the normal flow apparatus which holds the catalyst in a steel vessel as described in section 2.2.1.1. However, it was realised that at the reaction temperatures involved (250 to 700°C) the stainless steel vessel itself becomes active as a catalyst for this reaction. This confirms the work of Jenkins and Voisey[94,95] who studied the CO/NO reaction when catalysed by various iron based materials including 18/8 stainless steel. Consequently a series of correction factors had to be determined to account for the activity of the apparatus over the range of input gas mixtures and temperatures used.

A commercially approved catalyst, based on oxides of iron and chromium was studied as a reference for the PAN.P work. Gas flow rates of 500 cm^3min^{-1} for the NO in nitrogen (1500 ppm) and 500 cm^3min^{-1} for the CO in nitrogen (2000 ppm) were used. Catalytic activity was followed continuously during a linear reaction temperature increase of 12^{o}C min^{-1}. The results, corrected for the activity of the apparatus, appear in Figure 18 in which the theoretical maximum removal rates are included.

Under these reaction conditions it can be seen that this catalyst displays only activity for CO in the early stages. It is not active towards NO until over 80% of the CO is being removed. This pattern of events may be indicative of the need to convert the surface of this catalyst to the reduced state before reaching optimum activity for NO.

The PAN.P catalyst was examined for NO removal activity in the presence of CO using a variety of input gas concentrations and a range of reaction temperatures. Throughout the work the polymer remained active to NO but no decrease in the concentration of inlet CO could be detected. The results obtained for the removal of NO are reported in Figure 19. This shows that at temperatures above 500°C a progressive decrease in the rate of NO removal occurs for increasing ratios of pure CO to NO. This ratio seems to be a controlling factor since the decreased activity of the catalyst to NO does not correspond directly to the changes in input concentration of pure NO.

In calibrating the Grubb Parsons infra red analyser for such unusually low concentrations of CO, a pronounced eletrical noise effect was apparent. Consequently any minimal change in the levels of CO may not have been noticeable. However the activity of the PAN.P was certainly not as high, with respect to CO, as the commercial inorganic catalyst.

A further experiment was carried out using the PAN.P

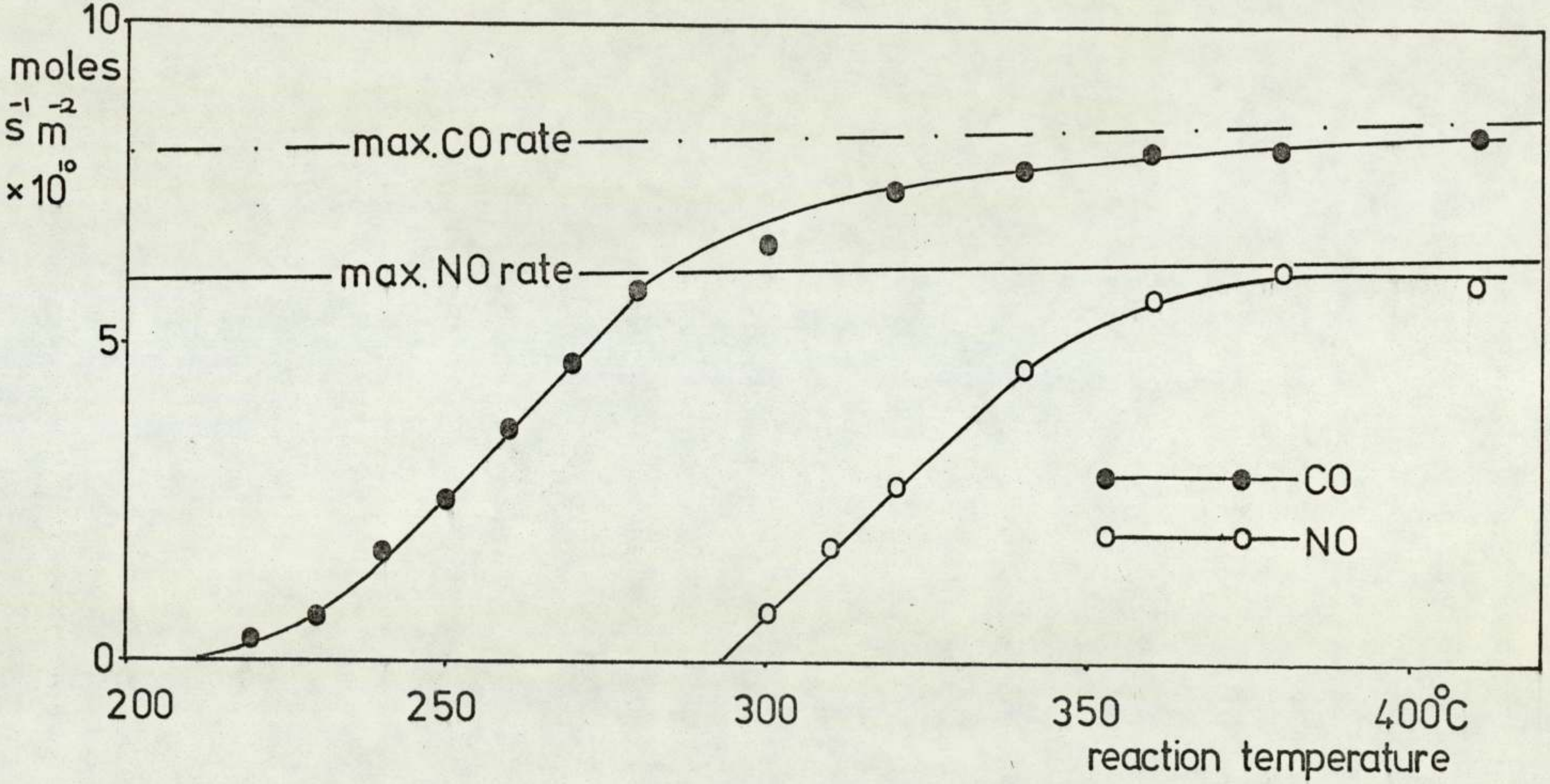


FIGURE 18

Removal rate of NO and CO with commercial inorganic catalyst for mixtures of CO and NO in nitrogen (1.0 and 0.75 cm^3min^{-1} respectively, 1000 cm^3min^{-1} total flow rate)

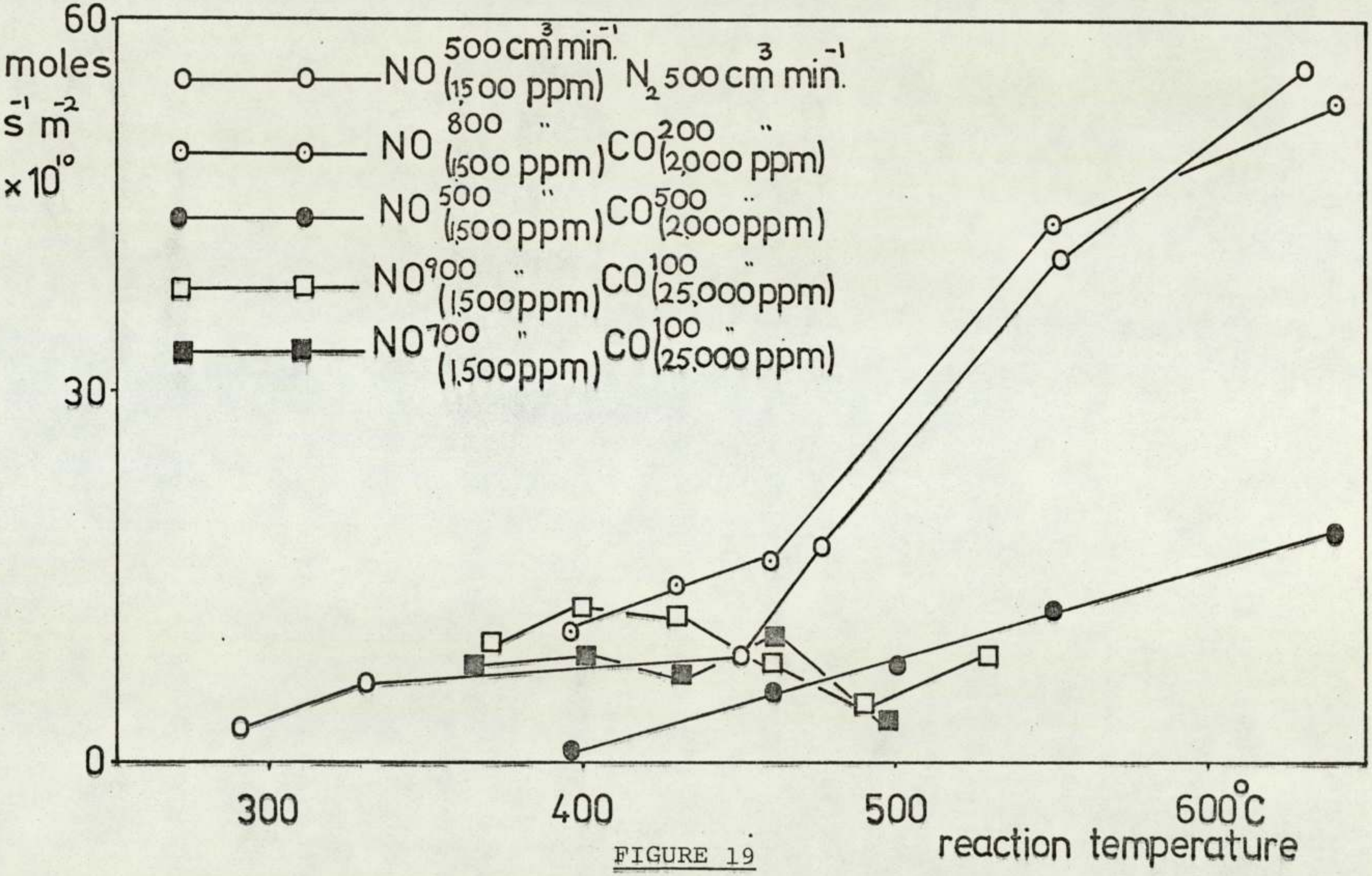


FIGURE 19

Effect of CO on the initial rate of NO removal (total flow rate 1000 $cm^3 min^{-1}$ for all runs) catalyst, where the normal alumina support was replaced by the iron oxide/chromia catalyst. This was in an effort to improve the CO removal properties of a PAN.P based catalyst. The reaction conditions used were the same as those used for the commercial catalyst. A small CO activity was established, beginning at 400°C, but this was short lived. The results for this catalyst are given in Figure 20 along with results found for the normal PAN.P/alumina catalyst, tested under the same reaction conditions.

Since the PAN.P based catalysts displayed no continuous catalytic activity to CO, these results are not subjectable to a straightforward kinetic interpretation. It may be possible, however, to reconsider them at a later stage.

4.2.2 Other gases

4.2.2.1 Hydrogen

The need for catalyst selectivity when removing NO in the presence of hydrogen, a common constituent of exhaust gas, was mentioned in section 1.2. If hydrogen is to take any part in the NO reduction stage then it is important that ammonia or dinitrogen oxide are not the final products:-

$$2NO + 5H_2 \longrightarrow 2NH_3 + 2H_2O$$

$$2NO + H_2 \longrightarrow N_2O + H_2O$$

On the other hand the complete reduction process would be acceptable:

$$2NO + 2H_2 \longrightarrow N_2 + 2H_2O$$

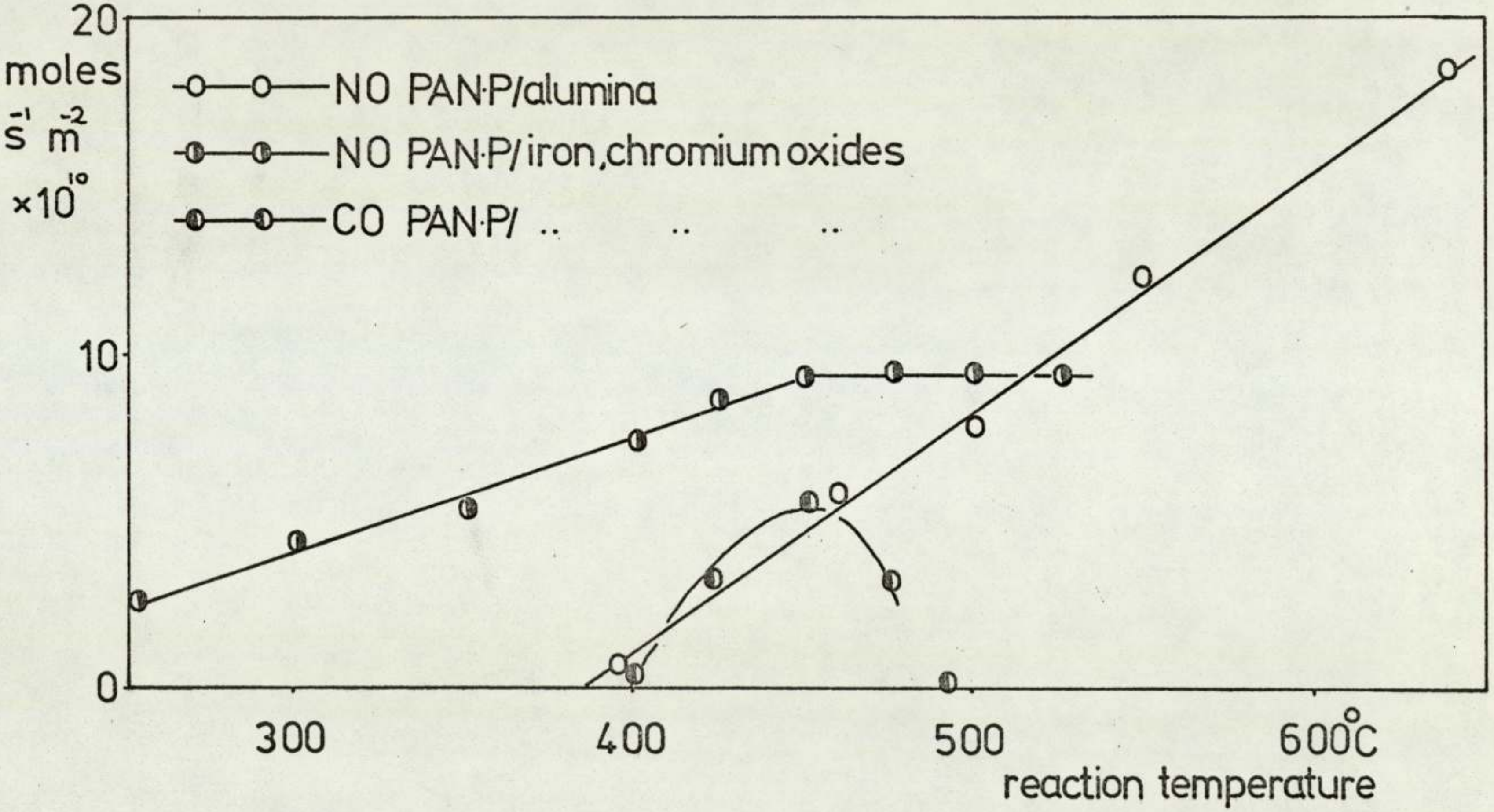


FIGURE 20

Removal rates of NO and CO with two PAN.P based catalysts

The work to establish the characteristics of any reaction between hydrogen and NO in the presence of PAN.P under dynamic conditions is described in this section. A more detailed investigation of reaction products, using static conditions, is reported in Chapter 5.

As in the case of the CO/NO reaction, the steel vessel itself was an active catalyst for the reaction between NO and hydrogen. Table 13 shows the quantity of NO removed by the reaction vessel in the presence of hydrogen. Large amounts of ammonia (above 500 ppm) were detected by Draeger analysis after a time of 3 minutes from the start of the reaction.

TABLE 13

Effect of the 18/8 stainless steel reaction vessel on the rate of NO removal in the presence of hydrogen

Reaction conditions:

Temperature	500^{o}C
NO (1500 ppm in nitrogen)	900 cm^{3}min^{-1}
Hydrogen (40% in nitrogen)	100 cm^{3}min^{-1}

Results

Reaction time (minutes)	Quantity of NO removed (ppm)
0	0
0.5	80
1	310
1.5	560
2	805
2.5	1060
3	1225

Consequently the characteristics of the interaction between PAN.P and NO in the presence of hydrogen could not be established using the standard flow apparatus. Therefore this reaction was studied using the glass apparatus described in section 2.2.3.1 and Figure 4.

A temperature of 529°C was obtained by immersing the glass vessel in a fluidised bath. Flow rates of 150 cm^3min^{-1} of NO in nitrogen (3,300 ppm) and 50 cm^3min^{-1} of hydrogen (100%) were used with approximately 16g of PAN.P catalyst. Samples of the output gas were taken after 3 and 5 minutes. It is interesting to note in passing that no reaction exotherm could be detected by comparing the temperature at the position of the front thermocouple (T_1) to that at the rear (T_3).

The gas samples were analysed by mass spectometry in order to identify reaction products in a qualitative sense. The spectra provided no evidence of the presence of species having mass peaks at 44 (characteristic of N_2O), 32 (O_2), 30 (NO), or 18 (H_2O). The highest peak corresponded to the nitrogen carrier gas at 28. Small peaks associated with ammonia at 16 and 17 were visible. Some idea of the quantity of ammonia produced was gained by experiments carried out under static conditions where the ratio of mass peaks 30 (input NO) to 16 (output NH_2^+) was 271 to 4.

In conclusion it must be recorded that whilst small quantities of ammonia were produced under these reaction conditions no evidence of the production of dinitrogen oxide was found. Any change in the activity between NO and PAN.P in the presence of hydrogen could not be deduced from the work carried out. A more detailed account of the products of this reaction appears in Chapter 5.

4.2.2.2 Hydrocarbons

Unburnt hydrocarbons, like hydrogen, are constituents of exhaust gases. Consequently the catalyst selectivity requirements outlined in section 4.2.2.1 for hydrogen also apply to hydrocarbons. The work carried out to assess the effect of hydrocarbons, in the form of propane, on the PAN.P/NO activity is described in this section.

The normal flow reactor, with its steel catalyst container, was used in this investigation. Only small quantities of ammonia (35ppm) were detected by Draeger analysis and this enabled a more meaningful comparison of activity to be made. The quantities of NO removed in both the absence and presence of hydrocarbons are given in Table 14.

Table 14 shows a decay in initial NO removal activity which reaches a constant value after a short time. This reaction profile (Figure 11) is quite common for NO-only experiments. Therefore in the light of this limited evidence it is probably that hydrocarbons have negligible, if any, effect on the rate of removal of NO.

4.2.2.3 Oxygen

Although the NO removal catalyst in the exahust stage

TABLE 14

The effect of propane on the rate of interaction between NO and PAN.P

Reaction conditions

Temperature	500°C
Catalyst weight	10g
Input gas mixture 1:	
NO (1,500 ppm in nitrogen)	500 $cm^3 min^{-1}$
Nitrogen	500 $cm^3 min^{-1}$
Input gas mixture 2:	
NO (1,500 ppm in nitrogen)	500 $cm^3 min^{-1}$
Hydrocarbon (1,400 ppm propane in nitrogen)	500 $cm^3 min^{-1}$

Results

Reaction time (minutes)	Quantity of NO removed (ppm)	
0	300	input mixture 1 (no hydrocarbon)
4	215	
10	200	
12	165	input mixture 2 (with hydrocarbon)
16	180	
22	180	

is designed to operate under petrol rich or reducing conditions, a residual oxygen content of 0.1 to 1.0% is normal[95, 96,97]. Consequently it is important that any such catalyst remains active in the presence of oxygen. The problem appears to be so serious that it is unlikely that the tentative idea of a "NO mop-up" bed, as shown in Figure 1, could ever succeed when placed downstream to the air pump.

Many workers have shown the detrimental effect that oxygen has on the NO decomposition properties of conventional inorganic catalysts[18,95,98,99]. In these cases oxygen is said to be chemisorbed onto the catalyst surface in preference to NO, so that subsequent CO oxidation can occur at the expense of NO decomposition. In our case the PAN.P may exhibit NO adsorption properties more in line with that of freshly cleaved graphite as reported by Zarifyants[100]. He showed that NO adsorption inhibits the subsequent adsorption of oxygen whilst NO can still adsorb on an oxidised surface. The work in this section examines the effect that oxygen has on the NO/PAN.P interaction.

Initial experiments were carried out using the normal gas flow apparatus. Oxygen, in the form of synthetic air, was passed over the catalyst with NO gas under isothermal conditions. Table 15 gives the quantities of NO removed.

It was found that the PAN.P had been completely removed from the support. This was the first time when using the finalised method for catalyst preparation that any polymer had broken away to expose the white surface of the support. The catalyst was in the reaction vessel for approximately

TABLE 15

The effect of oxygen on the rate of interaction between NO and PAN.P

Reaction conditions

Temperature	500°C
Catalyst weight	10g
Input gas mixture 1:	
NO (3,300 ppm in nitrogen)	600 cm^3min^{-1}
nitrogen	400 cm^3min^{-1}
Input gas mixture 2:	
NO (3,300 ppm in nitrogen)	600 cm^3min^{-1}
Oxygen (21% in nitrogen)	400 cm^3min^{-1}

Results

Reaction time (minutes)	Quantity of NO removed (ppm)	
0	830	input mixture 1 (no oxygen)
4	555	
10	490	
15	530	input mixture 2 (with oxygen)
19	680	
25	540	
30	435	input mixture 1
34	380	
40	300	
45	205	input mixture 2
49	205	
55	205	

two hours. This experiment was repeated giving the same result.

The results in Table 15 seem to confirm that the PAN.P/NO activity remains in the presence of oxygen. A further study was carried out along these lines involving the saturation of one catalyst sample with oxygen at 500°C and a subsequent comparison in NO removal activity between the "oxidised" and untreated catalysts. The results are given in Table 16.

This work confirms the results of Table 15 in showing NO activity to persist in the presence of oxygen or oxygen pretreatment. In fact the reaction seems to be more closely aligned to that found for freshly cleaved graphite than for inorganic catalysts, with the added advantage of having higher removal rates than many of the latter. Nevertheless the problem of durability of the PAN.P catalyst in the presence of oxygen remains. In relation to oxygen stability it was noted that the "preoxidised" sample retained its full coverage of PAN.P during the NO removal runs at 500°C. A more detailed study of the effect of oxygen on PAN.P appears in Chapter 5.

4.3 The effect of temperature on NO removal rate

Since the velocity of a chemical reaction between reactants X and Y can be expressed as:

$$- \frac{d(X)}{dt} = k\ (X)^n\ (Y)^m$$

TABLE 16

Comparison between fresh and "preoxidised" PAN.P catalyst on the initial removal of NO

Reaction conditions

Temperature	Isothermal runs between 260 and 630°C
Catalyst weight	10g
Input gas mixture:	
NO (1,500 ppm in nitrogen)	500 $cm^3 min^{-1}$
Nitrogen	500 $cm^3 min^{-1}$

Results

Reaction temperature (°C)	Initial rate of NO removal ($moles\ s^{-1} m^{-2} \times 10^{10}$)	
	Untreated PAN.P	"Oxidised" PAN.P
260	-	2.18
290	2.72	-
320	-	2.68
330	2.90	-
360	-	1.88
375	2.30	-
410	-	4.23
425	6.32	-
450	8.60	7.11
485	17.53	-
500	-	23.2
555	40.89	-
560	-	52.0
580	23.04	-
610	-	47.0
630	56.32	-

where k is related to the absolute temperature T by the expression Aexp (- Ea/RT), then the reaction rate at a given temperature will be defined by the values of the frequency factor, A, and the energy of activation, Ea. A reduction in Ea or an increase in A will bring about an increase in reaction rate at a given temperature. In catalysis the system may follow a new reaction path with a lower Ea. Consequently the energy of activation of the present reaction is an important parameter.

In this section the various NO removal rates are collated in order to derive the activation energy of the process. Arrhenius plots of log k vs $\frac{1}{T}$ are used so that the slope = Ea/2.303R. A selection of results were treated in this way so that the energy of activation for the different reaction conditions could be derived (see Figures 21, 22, 23 and 24).

Figure 21 corresponds to Figure 12 in showing the effect of temperature on NO activity for a series of different polymer pyrolysis temperatures. This work has been described in greater detail in section 4.1.4. In Figure 21 the numerous results are contained by two lines which have slopes which are similar in value to those found at individual pyrolysis temperatures. On e exception to this generalisation is found for the polymer which was pyrolysed at 350^{o}C, but this might be the result of using too narrow a temperature range.

Figure 22 is related to the work described in section 4.1.7 which is illustrated in Figure 17. Again two slopes,

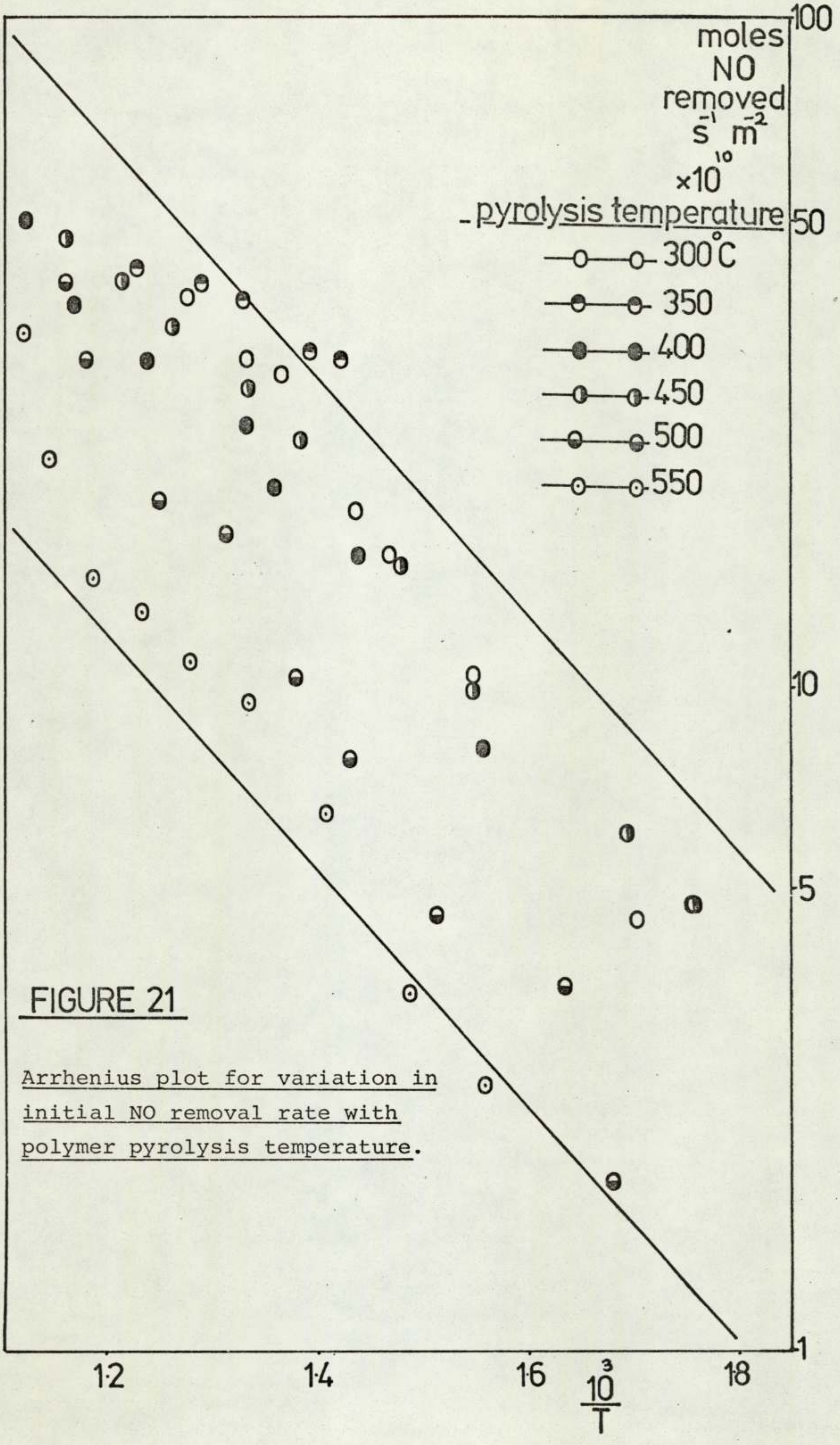


FIGURE 21

Arrhenius plot for variation in initial NO removal rate with polymer pyrolysis temperature.

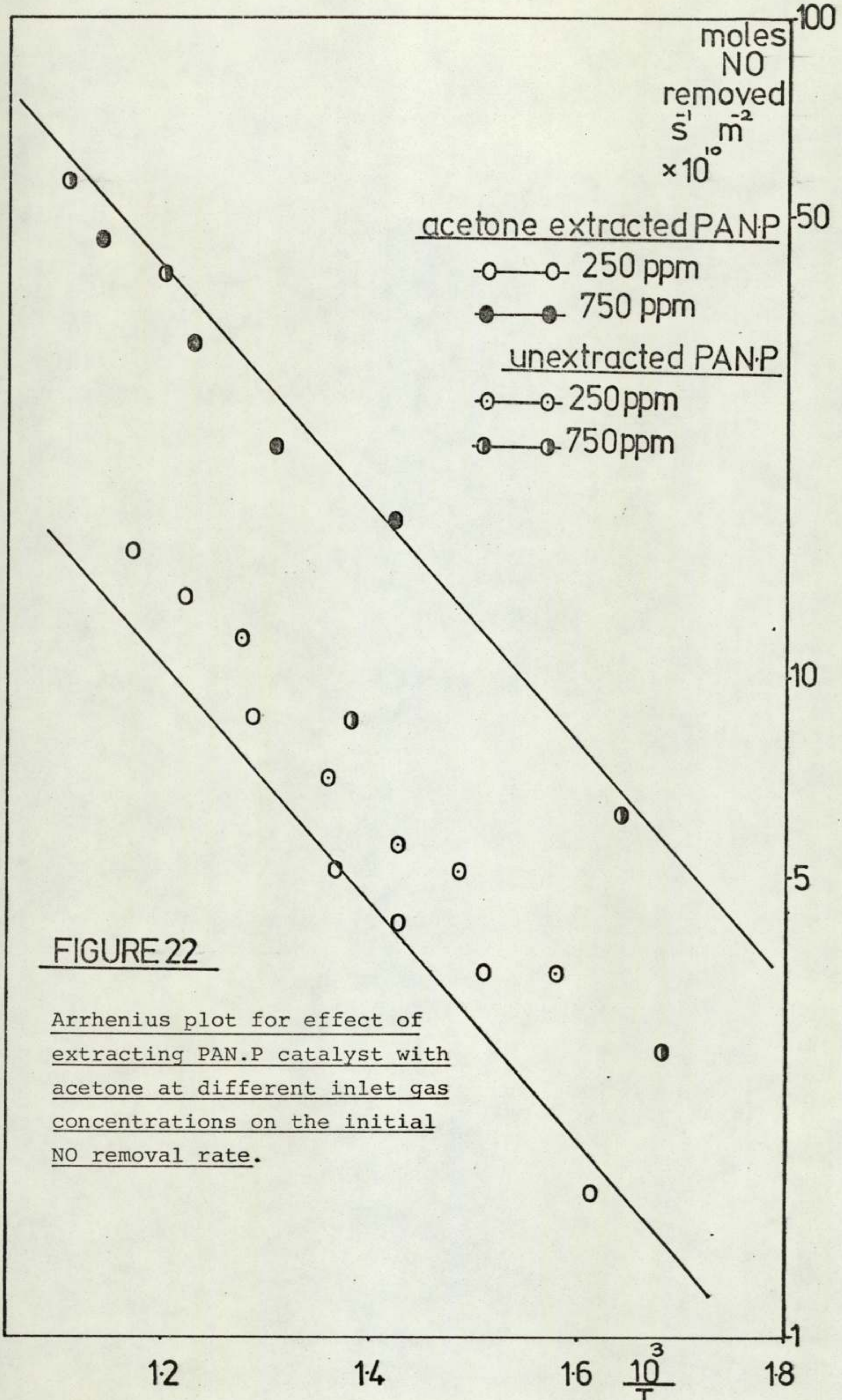


FIGURE 22

Arrhenius plot for effect of extracting PAN.P catalyst with acetone at different inlet gas concentrations on the initial NO removal rate.

representing the higher and lower ends of NO removal activity, have been drawn. In this study the effect of using different inlet concentrations of NO is seen to be more significant than that of acetone extraction.

Figure 23 can be compared to Figure 15 since both represent the work discussed in section 4.1.6. It can be seen that in the case of the two highest flow rates, 500 and 1000 cm^3min^{-1}, the gradients are similar in magnitude to those from Figures 21 and 22. However, NO activity recorded for the lower flow rate of 150 cm^3min^{-1} shows a lesser temperature dependence. This difference is illustrated in Table 17 where the activation energies are reported.

The final Arrhenius plot is given in Figure 24. This corresponds to the results presented in Figure 20 where the NO removal activity was followed in the presence of CO (section 4.2.1). Slopes are drawn for the two cases having the highest ratios of NO to CO and these appear typical of previous gradients. When the NO/CO ratio was much lower no meaningful gradients were apparent since both process seem to be independent of temperature.

Energies of activation have been derived from the four Arrhenius plots and these are presented in Table 17.

The majority of results presented here show that there is an increase in NO removal activity with temperature. At the same time the narrow range of activation energies, in the region of 33.9 to 39.9 kJ $mole^{-1}$ (8.10 to 9.57 K cal $mole^{-1}$),

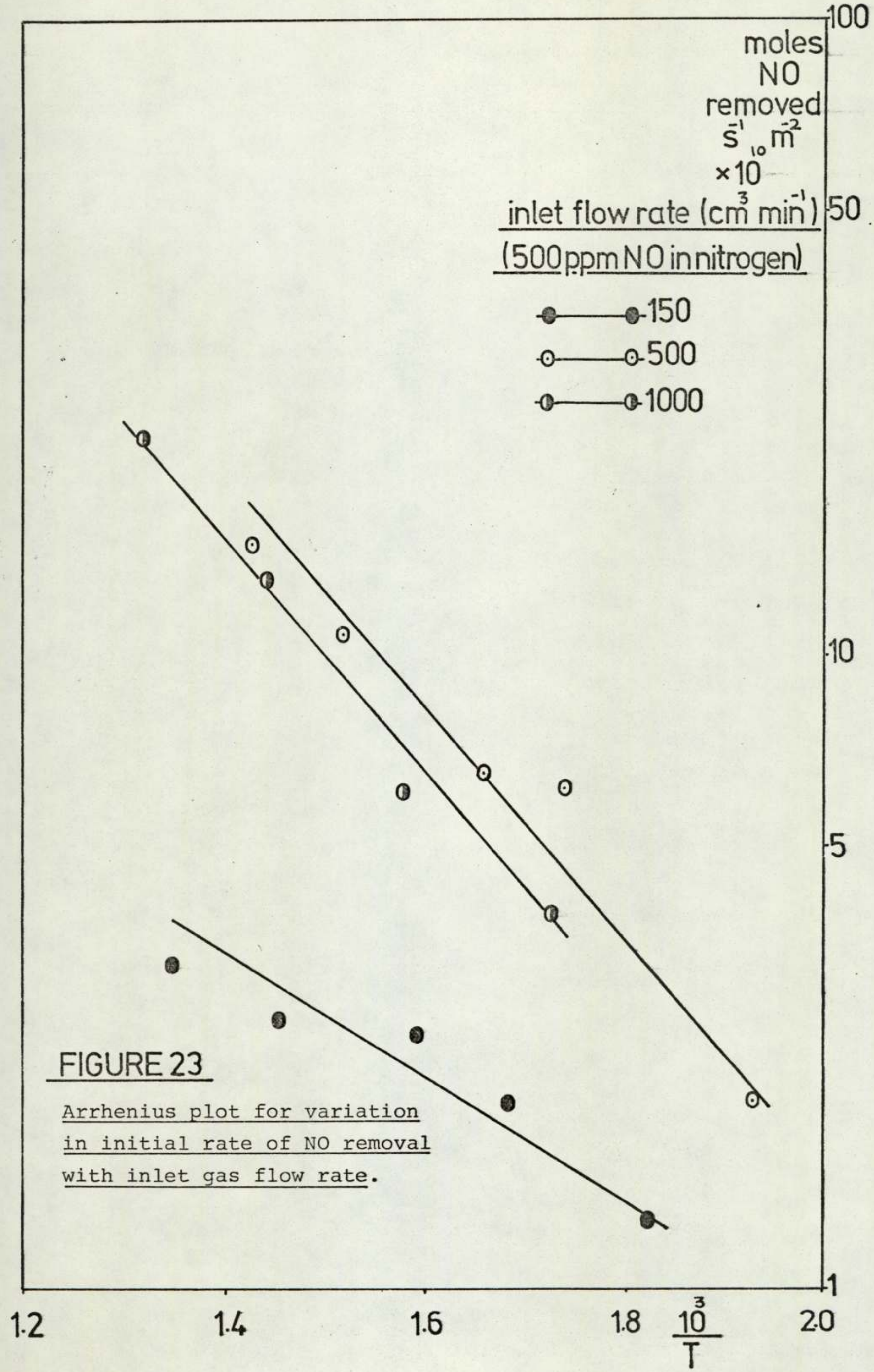


FIGURE 23

Arrhenius plot for variation in initial rate of NO removal with inlet gas flow rate.

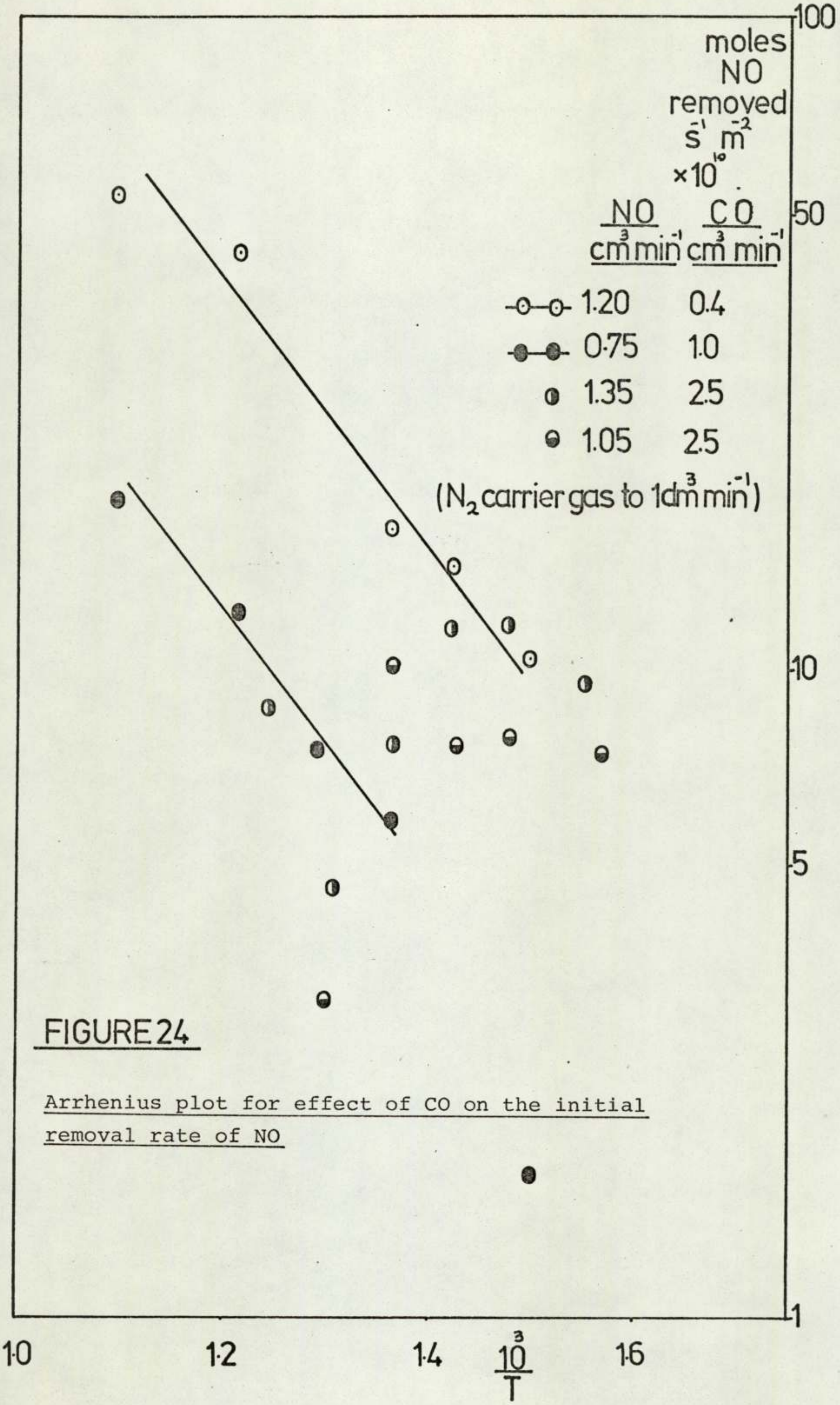


FIGURE 24

Arrhenius plot for effect of CO on the initial removal rate of NO

TABLE 17

Activation energies for the interaction between NO and the PAN.P catalyst for a variety of reaction conditions

FIGURE	GRADIENT	Ea(kJ $mole^{-1}$)
21	top	33.9
21	bottom	33.9
22	top	34.6
22	bottom	34.9
23	1000 $cm^3 min^{-1}$	35.5
23	500 $cm^3 min^{-1}$	35.5
23	150 $cm^3 min^{-1}$	19.4
24	1.20:0.4, NO:CO	39.9
24	0.75:1.0, NO:CO	39.9

is indicative of the reaction proceeding by the same mechanism for all the conditions used.

CHAPTER 5

SOME STUDIES OF THE PROPERTIES OF PAN.P AND THE PRODUCTS OF ITS REACTION WITH NO AND OTHER GASES

5.1 Properties of PAN.P

5.1.1 Thermogravimetric analysis

The thermal degradation properties of polyacrylonitrile and some of its pyrolysed derivatives have been examined.

Figure 25 shows the weight loss of the acrylonitrile copolymer under isothermal conditions. Whilst the thermogram illustrates the expected increase in degradation rate at higher temperatures, two other features are found significant in the context of the present work. One is that at 250°C under nitrogen, the polymer ceases to lose weight after several hours, a fact that has been reported by many previous workers[82,87]. An initial pyrolysis time of 24 hours at 250°C in vacuo has been consistently used throughout the current work. This represents a time at which a thermally stable structure has become well established. It is presumed that some of the polymer cyclises to form a ladder structure as discussed in Chapter 1.

The second feature is that at the two highest temperatures of degradation only a small difference in weight loss is evident for the oxygen and nitrogen environments. This contrasts sharply with the well known behaviour of the pyrolysed derivatives of polyacrylonitrile which show much faster degradation in oxygen (Figures 26 and 27).

Potter[87] and Brandrup[88] have independently concluded that this substantial oxidation cannot occur until the polymer has been converted to a ladder structure containing readily oxidisable methylene groups. Potter suggests the formation

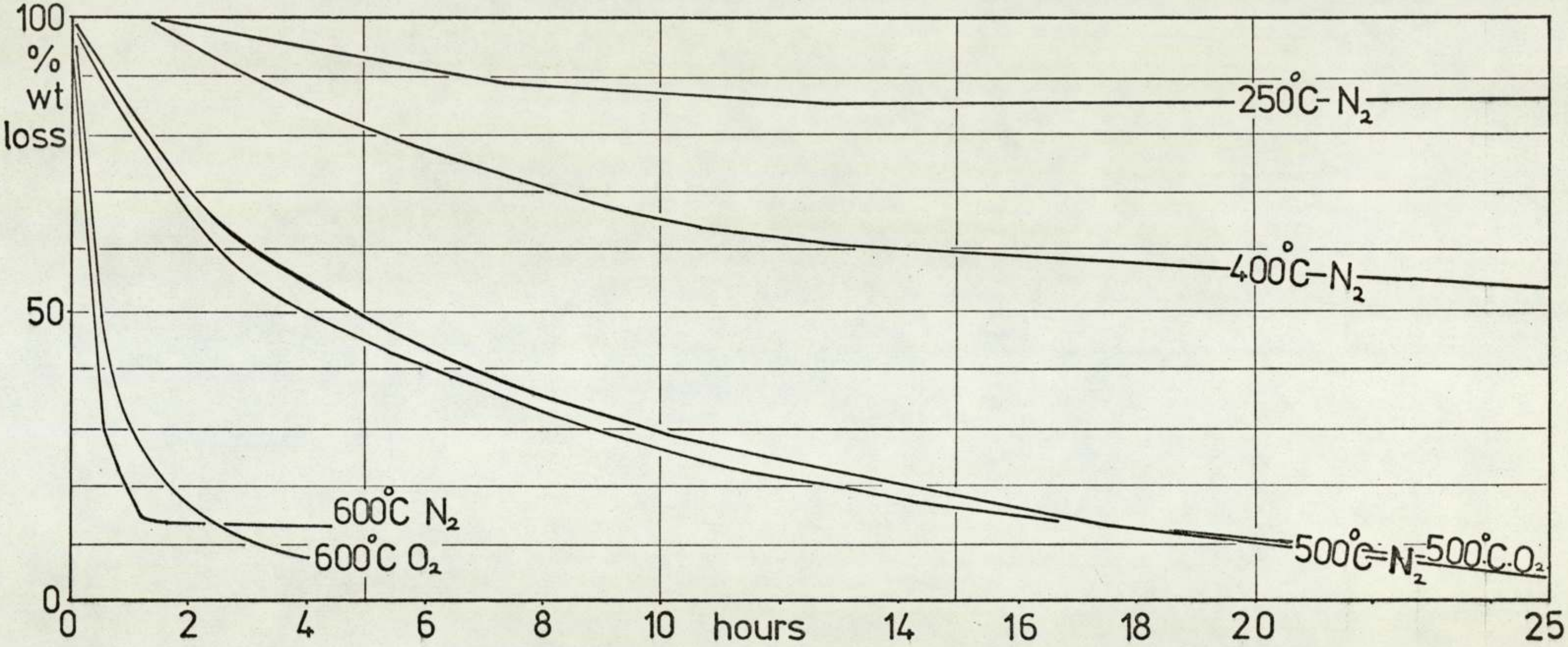


FIGURE 25

ISOTHERMAL TGA ON POLYACRYLONITRILE IN ATMOSPHERES OF OXYGEN (O_2) AND NITROGEN (N_2)

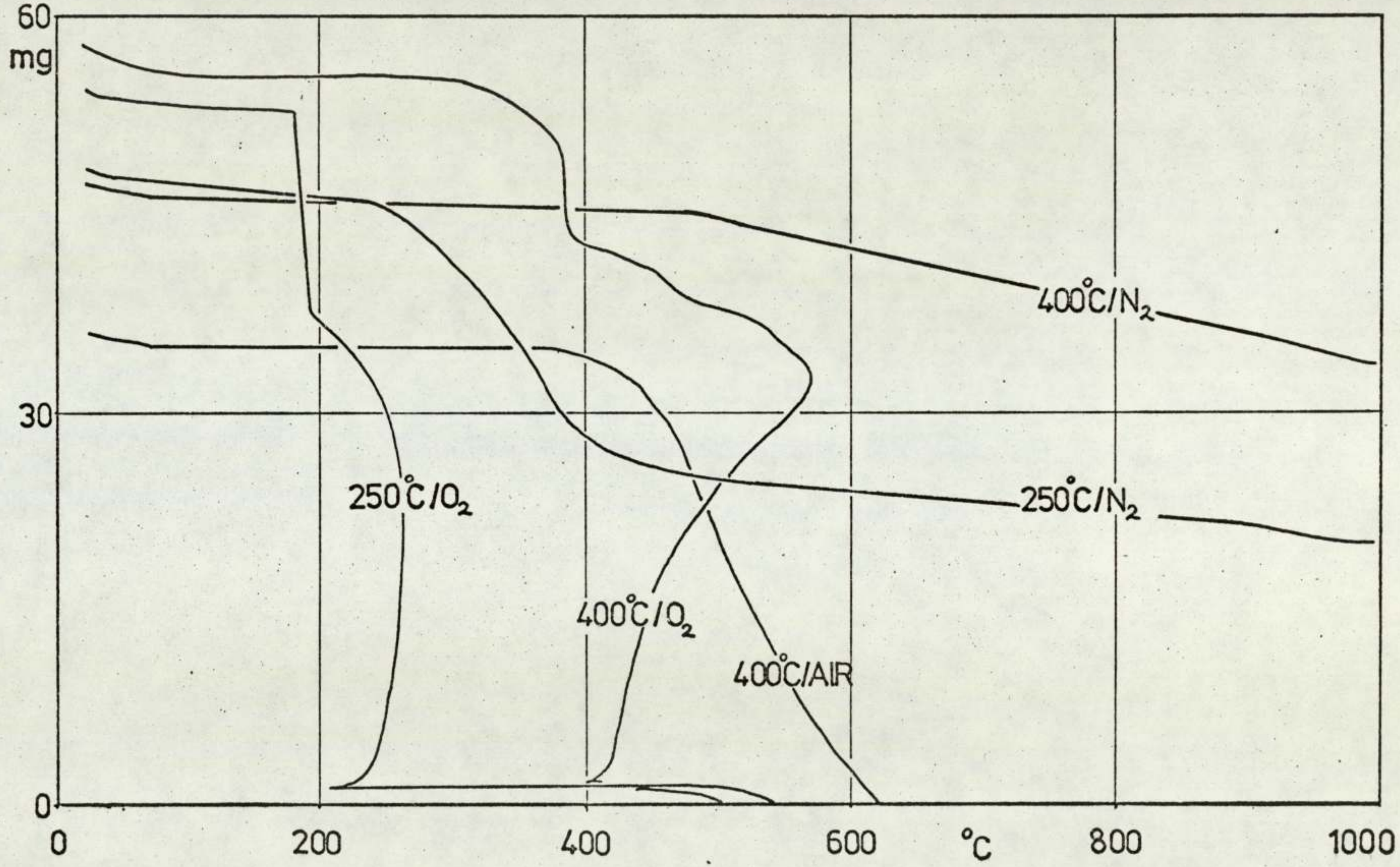


FIGURE 26

TEMPERATURE PROGRAMMED TGA ON POLYACRYLONITRILE PYROLYSED AT 250 AND 400°C. ATMOSPHERES OF OXYGEN (/O_2) AND NITROGEN (/N_2)

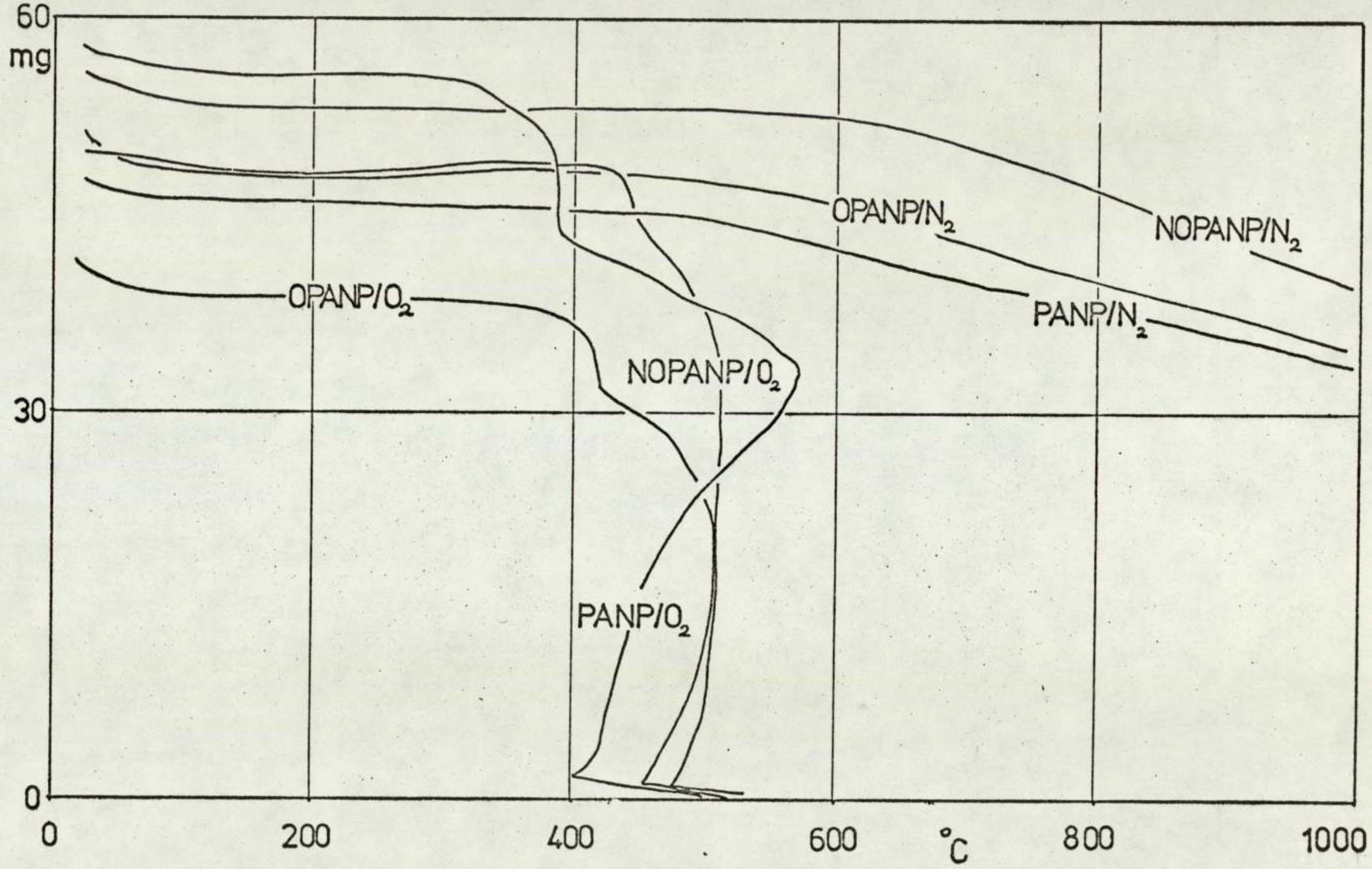
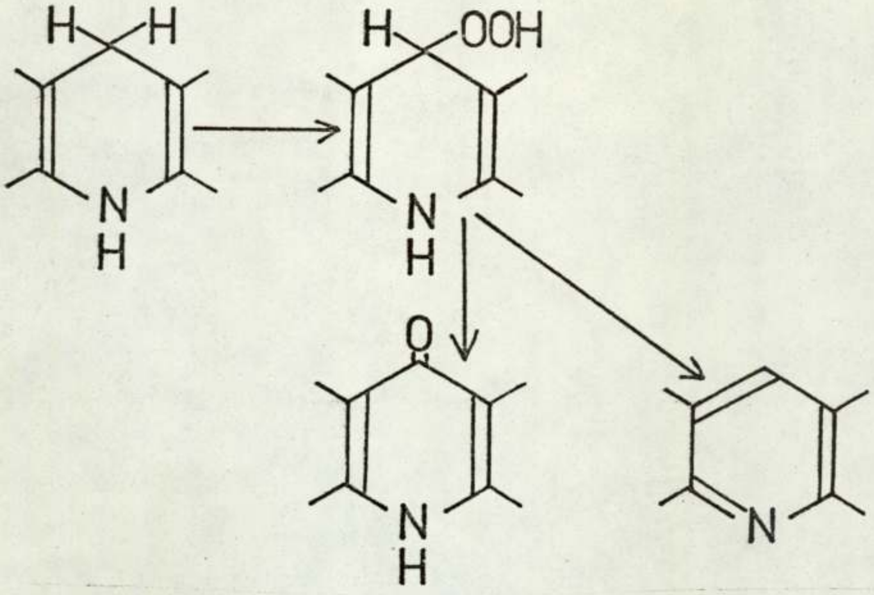


FIGURE 27

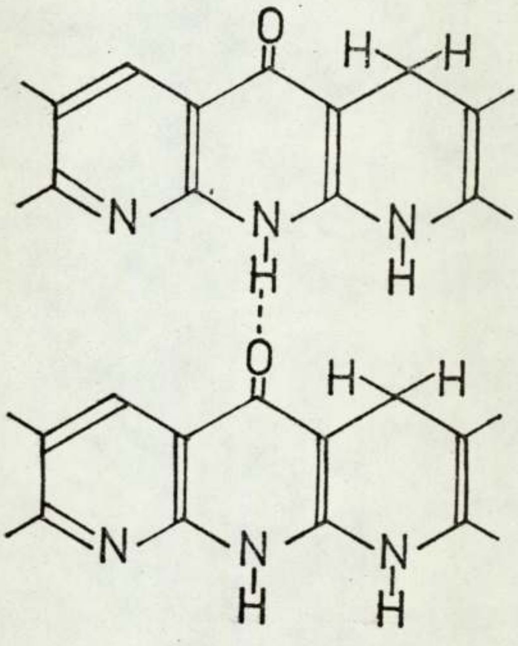
TEMPERATURE PROGRAMMED TGA ON FRESH PAN.P AND PAN.P PREREACTED WITH OXYGEN (OPAN.P) AND WITH NO (NOPAN.P). ATMOSPHERES OF OXYGEN (/O_2) AND NITROGEN (/N_2)

of Ketonic and aromatic structures according to Scheme 5.



SCHEME 5

He then attributes the powerful stabilising effect of oxygen to the formation of a strongly hydrogen bonded structure (25).



STRUCTURE 25

In section 4.2.2.3 the effect of oxygen on the interaction between NO and PAN.P has been reported and although the activity was seen to remain, a side effect of the "cleaning away" of the PAN.P from the alumina support was observed. A separate series of experiments were carried out to examine the effect of oxygen, in the form of synthetic air, on polymer stability using the normal flow reactor.

TABLE 18

THE EFFECT OF OXYGEN ON THE DURABILITY OF THE PAN.P BASED SUPPORTED CATALYST UNDER NORMAL FLOW CONDITIONS

Reaction Conditions

Temperature	500°C
Weights of catalyst	10g
Input gas flow rate (21% oxygen in nitrogen or "white spot" nitrogen)	1,000 $cm^3 min^{-1}$

Results

SYNTHETIC AIR		NITROGEN	
Reaction time (minutes)	% Coverage	Reaction time (minutes)	% Coverage
0	100	0	100
5	8	120	100
15	5		
30	3		
60	0		

The results in Table 18 show that oxygen is clearly responsible for polymer removal. Furthermore the TGA results indicate that a process of rapid oxidative degradation would occur at reaction temperatures of 500°C.

The thermograms presented in Figure 27 show the results obtained for polyacrylonitrile pyrolysed for 24 hours at 250°C and 2 hours at 400°C whilst under vacuum. A PAN.P sample was treated with NO, and another with oxygen at 500°C and their thermal properties are reported along with those of the untreated sample. It can be seen that under nitrogen the three samples behave in the same way. In oxygen, however, the thermal stability of the PAN.P is improved by oxygen pre-treatment and even more so by NO pre-treatment. All three samples degraded in oxygen in an exothermic manner but the extent of the exotherm was less for the pre-treated PAN.P samples. The comparative results from Figure 27 for the polymers degraded in oxygen are given in Table 19.

TABLE 19

THE EFFECT OF PRE-TREATING PAN.P WITH NO AND OXYGEN ON DEGRADATION CHARACTERISTICS

Degradation Conditions

Heating rate	$20^{\circ}C\ min^{-1}$
Environment	Oxygen

Results

Pre-treatment	Weight Loss		Exotherm
	Commences at (°C)	Finishes at (°C)	°C per g of initial sample
None	300	385	320
Oxygen	350	420	220
NO	400	440	130

The effect of oxygen pretreatment may well be to remove or neutralise a proportion of the reactive sites available and so the exothermic reaction during degradation will be reduced. In addition, the higher thermal oxidative stability of the oxygen pretreated PAN.P could be explained by the presence of a greater proportion of hydrogen bonding as suggested by Potter (Structure 25). Exposure of the freshly prepared PAN.P to the atmosphere was hard to avoid and so it was assumed that some uptake of oxygen had occurred. A colour change from brown to black was observed when the PAN.P was exposed to the atmosphere. This effect is reported by Standage[86] who noted a relationship between colour and oxygen absorption at room temperature.

When one compares the pretreatment of PAN.P with oxygen to that with NO, then the latter is seen to be more active in improving the thermal oxidative stability. It is interesting to note that the use of NO as a rapid "carbonising" agent for polyacrylonitrile is preferred by Morita[101]. He claims that this treatment gives high yields of carbon fibre having high strength and elastic modulus.

This degradation work provides further evidence of NO/PAN.P interaction and shows the modified polymer to have properties which are similar to those found with oxygen. This observation is consistent with the results obtained by analysis of the gaseous products from the reaction of NO with PAN.P in Section 5.2.2.2.1. The product was mainly nitrogen, the oxygen must have been removed by the polymer. Some N_2O was also produced. However, when the PAN.P was "preoxidised" the NO was still completely removed but oxygen was produced along with N_2O and nitrogen.

5.1.2 Electron spin resonance studies

Ample evidence of a close relationship between catalytic activity and properties of the free spins for highly conjugated organic polymers has been provided by Gallard and coworkers[34,38,60,69]. This has been discussed in greater detail in section 1.3.2.1.

In the current work an attempt was made to quantify the ESR signals so that the effect of preparation and storage conditions on spin concentration could be examined. A solution of Copper II Chloride was used as a standard throughout the work. Figure 28 is a simulation of an actual result with the peak from the copper standard on the left and that from the PAN.P on the right. The experimental details are as follows:-

Weight of 4M $CuCl_2 \cdot 4H_2O$ (used in all experiments) = 0.0125g
Weight of PAN.P = 0.0109g
PAN.P prepared via 24 hours/250°C and 2 hours/ 400°C, under vacuum - extracted by boiling acetone and oven dried - aged for 90 days in vacuum.
ESR instrument settings -

modulation current	0.19 amps
gain setting	0.2
field strength	1000 gauss

The variation of the peak height ratio, expressed in terms of PAN.P/Cu II ratios, was calibrated using the same

28

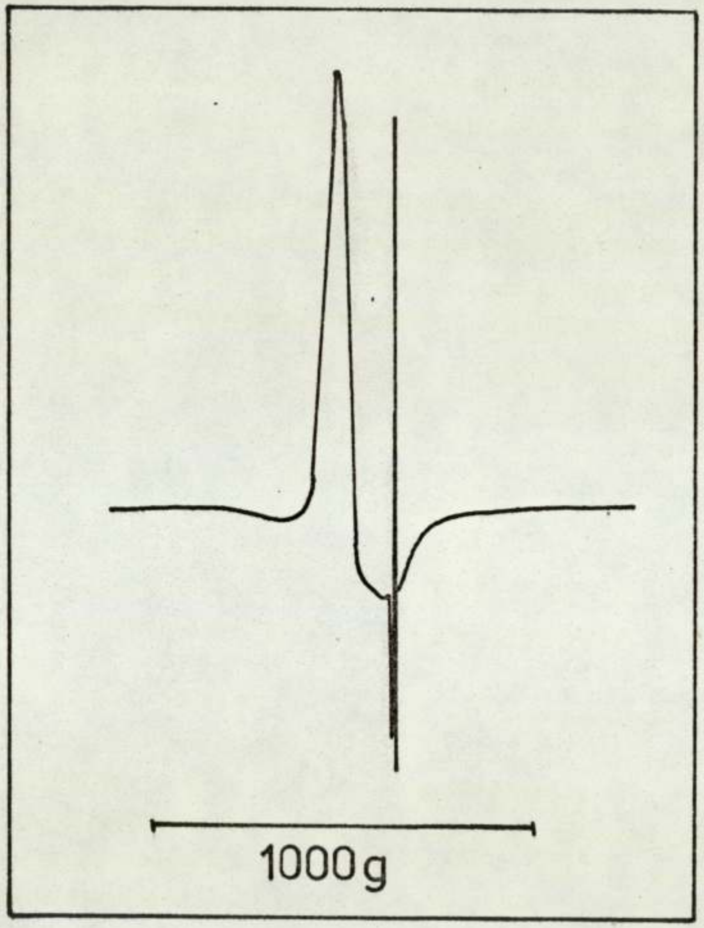


FIGURE 28

ESR SIGNAL FROM BOTH PAN.P (RIGHT HAND SIDE) AND COPPER II STANDARD

29

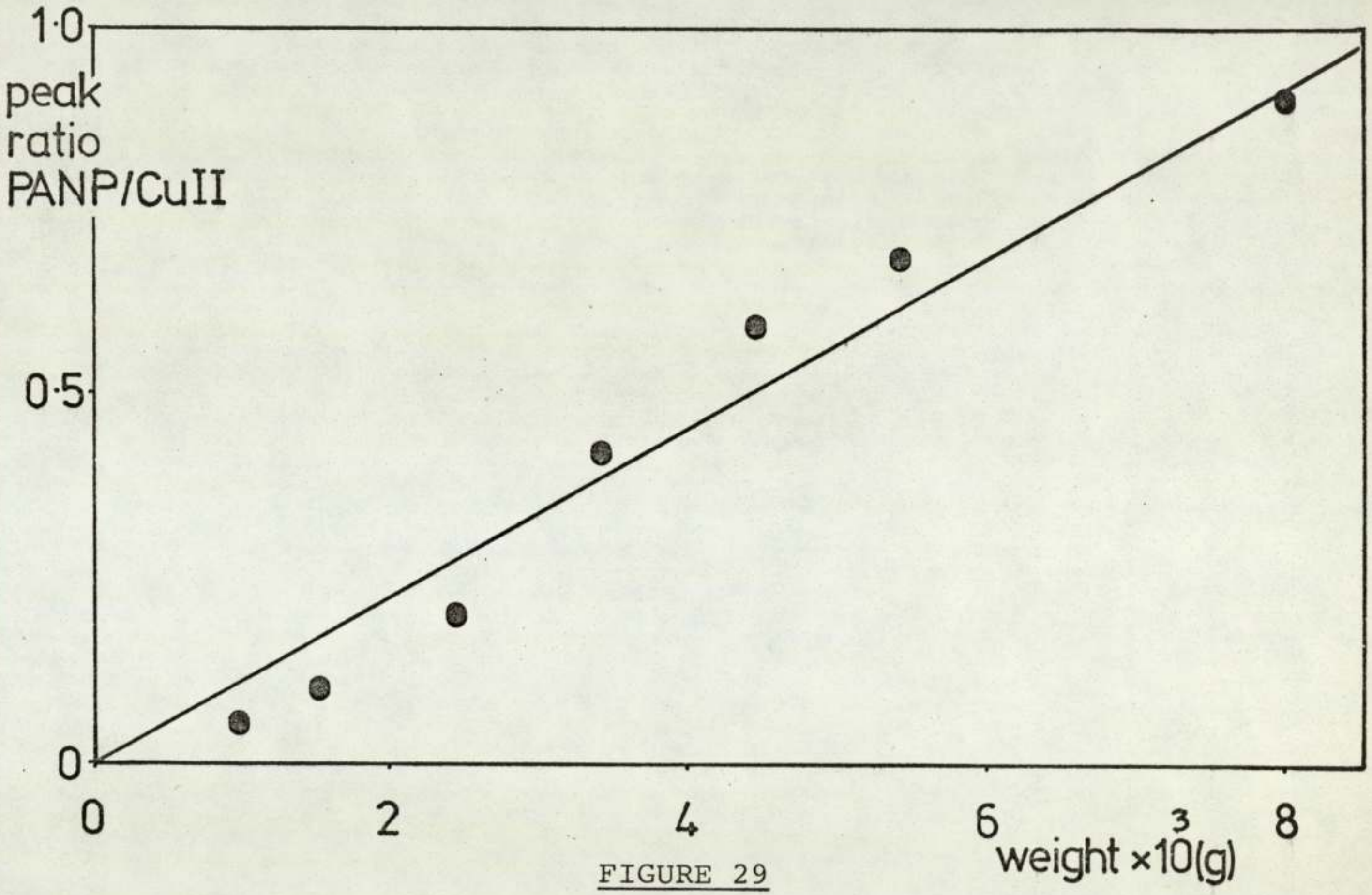


FIGURE 29

RELATIONSHIP BETWEEN RATIOS OF PEAK HEIGHTS FROM ESR SPECTRA, PAN.P/COPPER II, FOR VARIOUS WEIGHTS OF PAN.P weight of the Cu II standard. The results are given in Figure 29 where a near-linear relationship is found.

It was difficult to get each sample to the same weight consequently an assumption was made that all PAN.P samples under examination had peak height ratios which varied linearly with sample weight according to the relationship given in Figure 29. In this way results have been expressed for sample weights of 0.010g. In practice polymer weights of between 0.075 and 0.105 were used.

5.1.2.1 The effect of ageing on the size of the ESR signal

In the following work polyacrylonitrile (Acrilan) was pyrolysed for 24 hours at 250°C and 2 hours at 400°C whilst under vacuum.

TABLE 20

EFFECT OF AGEING ON THE SIZE OF THE ESR SIGNAL

Acetone Extracted?	Fresh Sample peak height ratio	Aged Sample (90 days at room temperature)	
		environment	peak height ratio
NO	0.75	vacuum	0.80
		air	0.73
YES	1.20	vacuum	1.27
		air	0.98

These results show that the PAN.P samples support a stable concentration of free spins even when aged in air. The reason for the difference between the acetone extracted and unextracted sample is not clear at this moment in time.

5.1.2.2 The effect of the temperature of pyrolysis on the size of the ESR signal

In these experiments the polyacrylonitrile was pyrolysed under vacuum for 24 hours at 250°C and for 2 hours at the temperatures quoted in Table 21. The samples were aged for 18 days in air before testing.

TABLE 21

EFFECT OF PYROLYSIS TEMPERATURE ON THE SIZE OF THE ESR SIGNAL

Final Pyrolysis Temperature (°C)	Peak Height Ratio
250	0.02
375	0.56
400	0.74
425	0.92
450	0.86
475	1.83
500	2.18

In a more detailed study than this, Gallard and Nechtschein noted a dramatic fall in the number of spins of PAN.P above a pyrolysis temperature of 450°C. The results quoted in Table 21 fail to show any reduction in spin concentration with increasing pyrolysis temperatures. One may have expected a similar relationship between the free spin concentration and pyrolysis temperature as that found by

Gallard, especially since a decay in NO activity is found with pyrolysis temperatures above 450°C (Figure 13).

5.1.2.3 The effect of NO on the size of the ESR signal

One reason for investigating the interaction between NO and PAN.P is that they should show a mutual affinity. This is because of the odd electron behaviour of NO and the high concentration of free spins associated with the PAN.P. It is reasonable to expect that when a sample of PAN.P is exposed to NO the subsequent combination will cause a reduction in the number of free spins on the PAN.P. In this work polyacrylonitrile pyrolysed for 24 hours at 250°C and 2 hours at 400°C under vacuum and then extracted by hot acetone, was tested when fresh and after saturation with NO at 400°C for 5 minutes. Another sample was saturated with oxygen under the same conditions.

TABLE 22

EFFECT OF NO ON THE SIZE OF THE ESR SIGNAL

	Peak Height Ratio
Freshly prepared PAN.P	1.20
PAN.P exposed to NO	1.30
PAN.P exposed to O_2	0.75

Contrary to expectations, the NO did not bring about a decrease in the number of free spins. It may change the structural characteristics of the polymer enabling an even greater number of delocalised electrons to be supported. The effect of oxygen was to reduce the size of the signal given by the virgin PAN.P.

5.1.3 Carbon Hydrogen and Nitrogen Analysis

Samples of PAN.P were analysed for the elements carbon, hydrogen and nitrogen using the Hewlett Packard 185 C, H, N Analyser. Freshly prepared PAN.P was obtained by heating polyacrylonitrile for 24 hours at 250°C and 2 hours at 400°C whilst under vacuum, and this was examined for C, H and N content. The same material was saturated at 500°C with both NO and oxygen and these derivatives were analysed. The results appear in Table 23.

TABLE 23

C, H, AND N ANALYSIS OF PAN.P AND ITS DERIVATIVES

SAMPLE	C (%)	H (%)	N (%)
Freshly prepared PAN.P	47.95	3.26	18.90
	45.29	3.34	18.90
	41.86	3.86	18.22
	35.77	3.04	16.85
PAN.P saturated with oxygen	44.53	2.35	19.13
	44.53	1.80	18.67
	43.99	1.86	18.90
	42.08	1.86	19.59
PAN.P saturated with NO	48.97	1.86	21.18
	48.97	1.86	20.50
	35.77	1.88	19.36
	30.06	1.84	17.76

The technique involves the oxidisation of sample to gaseous products which are then characterised by chromatographic methods. A sample weight of 0.5 mg is heated at

1100°C for 45 seconds in helium carrier gas. Consequently substances which are difficult to pyrolyse in inert atmospheres may give results of poor reproduceability. The TGA work has shown that a significant quantity of PAN.P can remain at 1000°C in a nitrogen environment (Figure 27). Hence, although only a small sample weight is taken for elemental analysis, the poor reproduceability found in Table 23 must be attributed to the incomplete combustion of the polymer. It was impossible to draw any conclusions from the results.

5.1.4 Infra Red analysis

Infra red analysis was carried out in an attempt to identify any change in the chemical structure of PAN.P which would be caused by reaction with NO. The acrylonitrile copolymer was pyrolysed for 24 hours at 250°C and for 2 hours at 400°C whilst under vacuum. A 2g portion of this PAN.P was then ground up and reacted with NO (3,300 ppm in nitrogen) having a flow rate of 1000 $cm^3 min^{-1}$ at 440°C for 3 hours. The PAN.P was suspended between two glass wool plugs in the stem of a U tube whilst the gas mixture was passed through the vessel. The U tube was heated in a fluidised bed.

In the initial experiments freshly prepared PAN.P and its NO saturated derivative, were ground in nujol and also with K Br. The resulting spectra had poor resolution presumably because the particle size of the two polymer samples was too high.

The spectra represented in Figure 30 were obtained by a method of predispersing the polymer samples in formdimethylamide. A mixture of KBr and polymer were ground in a mortar and pestle for 5 minutes in a medium of DMF. The solvent was slowly removed using a rotary evaporator, with the sample contained in an extended glass tube which was immersed in a water bath so that the temperature was allowed to increase from room temperature to 90^{o}C. The drying process was completed by heating the mixture to 250^{o}C for 30 minutes under vacuum. The product was then further ground with more KBr and a disc made for infra red analysis.

In Figure 30 the unpyrolysed polymer is seen to give the spectrum having the most detail. The spectrum of the PAN.P/NO product shows the least detail, probably because of the difficulty in getting the particle size low enough.

The differences in absorption characteristics caused by the pyrolysis of polyacrylonitrile have been the subject of more detailed studied than this[80,81,87]. Consequently we are more concerned with the differences in spectra of the PAN.P and its NO derivative. In the double band region (1550 - 1760 cm^{-1}) the characteristic maxima of the PAN.P at 1595 is replaced by one at 1630 cm^{-1} after reaction with NO. Absorption at 1380 cm^{-1} seems to be reduced by the NO reaction although absorption at 800 cm^{-1}, which has been attributed to the same species ($- C = C - H$), is increased.

Reference could not be found for the infra red absorption of NO when adsorbed on organic substrates. In a study

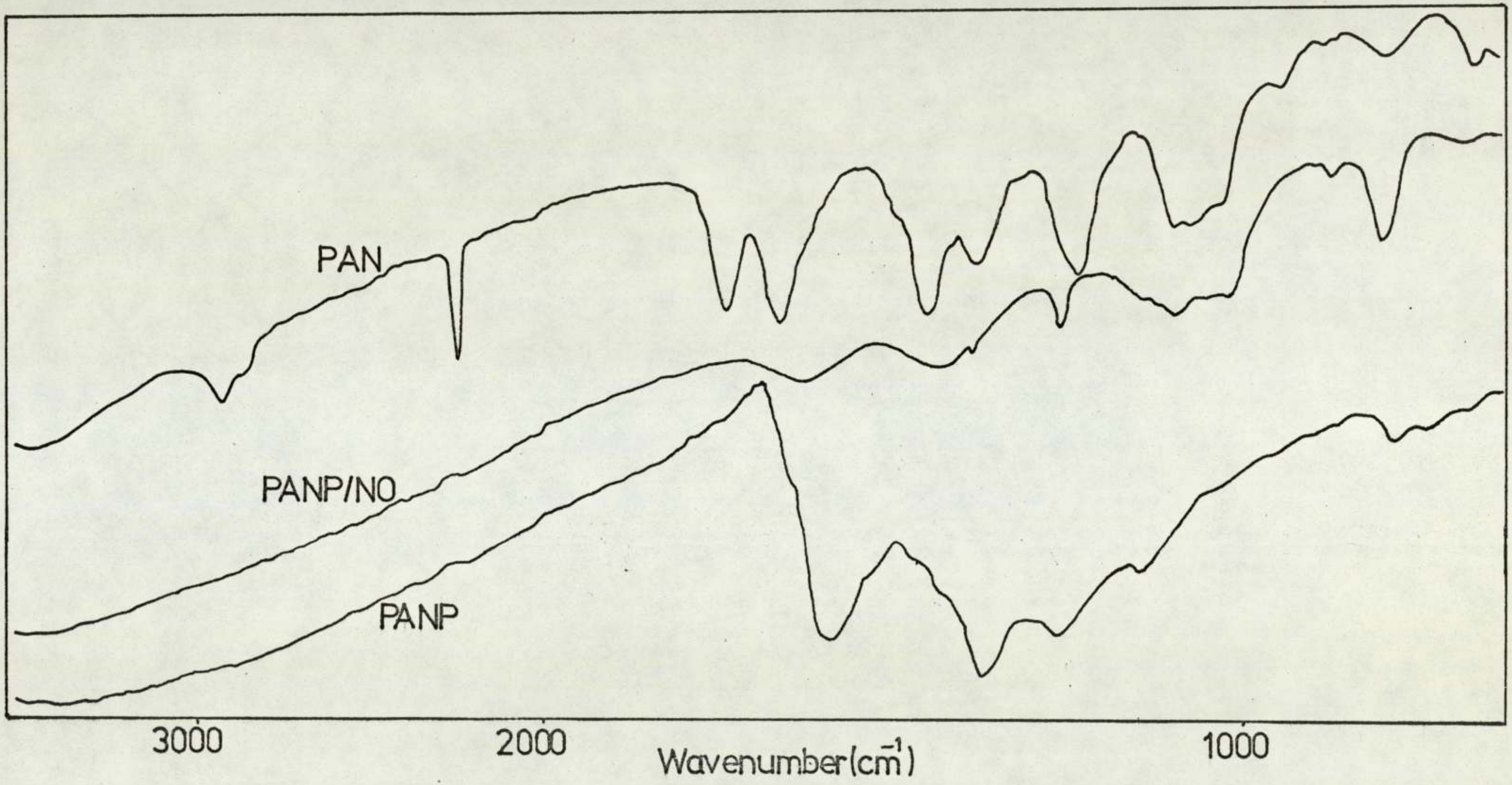


FIGURE 30

INFRA RED SPECTRA ON ACRYLONITRILE COPOLYMER (PAN), PAN.P AND PAN.P WHICH HAS BEEN PREREACTED WITH NO (PAN.P/NO) of NO on the surfaces of noble metal catalysts, Unland[102] lists the characteristic bands to be between 1715 and 1882 cm^{-1}. Absorption in this region is certainly not shown in the current work. However the lack of detail has made any further interpretation difficult.

5.2 A detailed examination of the gaseous products of the reaction of NO with PAN.P

Although catalytic activity can be assessed by monitoring the appearance of reaction products, the disappearance of reactants was followed in this study. The convenience of having well serviced, continuous NO and CO analysers which were readily available, was the sole reason for this choice. As a consequence only a minimum of information was collected regarding the concentration and identity of the products of reaction. The work described herein serves to characterise these products in order than an overall reaction mechanism can be proposed.

A series of experiments were carried out to establish the chemical nature of gaseous products of the interaction between NO and PAN.P, both in isolation and in the presence of other reactant gases. The majority of the tests were run under static conditions, but some involved the use of the normal flow reactor apparatus. Whilst the properties of freshly prepared PAN.P catalyst were examined in most cases, a few experiemnts were conducted using PAN.P and a metal oxide catalyst which had been previously reacted with oxygen. Reaction products were analysed using the MS9 mass spectrometer unless otherwise stated.

5.2.1 Examination of products from experiments carried out under dynamic conditions

An occasional product analysis was carried out during the various experiments to assess PAN.P/NO activity when using the normal flow apparatus described in section 2.2.1. Quantitative assessments of oxygen, nitrogen dioxide and ammonia were made.

5.2.1.1 NO-only reactions

5.2.1.1.1 Oxygen production

A Servomex continuous oxygen gas analyser was used to record the quantity of oxygen produced. Allowances have to be made, with this instrument, because NO is one of the few gases which has a magnetic susceptibility approaching that of oxygen. In fact a gaseous mixture of 2.32% NO in nitrogen will give the same result as a 1% mixture of oxygen in nitrogen at a given temperature. For example if NO at a concentration of 2,320 ppm in nitrogen is fully decomposed by a suitable catalyst according to the equation:

$$2NO \longrightarrow N_2 + O_2$$

then 1,160 ppm of oxygen would be produced. This in turn would cause an increased Servomex reading of 16% above that for the value of the NO at 2,320 ppm.

However, in practice a reduction in the Servomex reading was found, and this closely corresponded to the quantity of NO removed and not to the formation of any oxygen. The results of a typical experiment are given in Table 24.

TABLE 24

SERVOMEX ANALYSIS FOR OXYGEN IN PRODUCTS OF THE REACTION BETWEEN NO AND PAN.P UNDER DYNAMIC CONDITIONS

Reaction conditions

Temperature	450^{o}C
Catalyst weight	10g
Input gas mixture:	
NO (3,300 ppm in nitrogen)	1000 cm^{3}min^{-1}

Servomex calibration

19 units equivalent to 0.33% NO in nitrogen

Results

Reaction time (minutes)	Quantity of NO removed (ppm)	(%)	Servomex reading	Calculated Servomex reading for quantitive production of oxygen	Calculated Servomex reading for NO removal only
0	655	20	15	19.6	15.2
5	465	14	16	19.5	16.3
10	395	12	16½	19.4	16.7
15	360	11	16½	19.4	16.9

The results show the initial Servomex reading to change from 19 to 15 when the inlet NO gas route is switched from the preheat vessel to go through the vessel containing the catalyst. Calculations based on the previous discussion give results which compare more favourably with the expected Servomex value for the complete adsorption of NO rather than quantitive NO decomposition as in the above reaction. These observations were confirmed when studying similar reactions under static conditions (Section 5.2.2.2.1).

5.2.1.1.2 Nitrogen Dioxide production

The Beckmann continuous ultra violet analyser was used to identify any nitrogen dioxide produced. From a pollution viewpoint catalysis of NO to nitrogen dioxide is unacceptable.

Several attempts to find nitrogen dioxide in the gas stream proved unsuccessful. Tests were made during the NO removal runs carried out between the temperatures of 310 and 500°C. Inlet NO concentrations were 1,500 and 3,300 ppm in nitrogen, and a flow rate of 1000 $cm^3 min^{-1}$ was used.

5.2.1.2 NO - hydrogen and NO - hydrocarbon reactions

Draeger analysis was used to measure the concentration of any ammonia produced in these reactions. The results, previously discussed in Section 4.2.2, were inconclusive because of the over-riding effect of the activity of the steel vessel in producing ammonia. A more meaningful evaluation is described in Section 5.2.2.4 for reactions carried out in a glass apparatus under static conditions.

5.2.2 Examination of the reaction products from experiments carried out under static conditions

A series of experiments were carried out in order to characterise the products of reactions between NO and PAN.P. A simple cylinder shaped glass apparatus was used which is described in Section 2.2.3.2. After reaction, the gaseous mixtures were analysed on the MS9 Spectrometer.

All reactions were investigated, both with and without the catalyst, using the same conditions of time, temperature and reactant concentrations. In this way the reaction due only to the catalyst could be assessed.

The values of the heights of mass peaks were corrected to account for background signal on all spectra. High resolution and peak matching techniques were used to differentiate between the pairs of ions having mass numbers which are very close. In particular dinitrogen oxide (N_2O) and carbon dioxide (CO_2) both occurring at 44, and nitrogen (N_2) and carbon monoxide (CO) visible at 28. Table 25 lists the mass numbers, accurate to six decimal places, of the main species involved.

TABLE 25

PARENT PEAK MASS NUMBERS OF SOME GASEOUS REACTION PRODUCTS

H_2	2.015649	
NH_3	17.026549	(NH_2 16.018723)
H_2O	18.010563	
CO	31.994914	
N_2	28.006148	
NO	29.997988	
O_2	31.989828	
CO_2	43.989828	
N_2O	44.001062	
NO_2	45.992902	

The results from the spectra are purely qualitative in nature. However, in a few cases it was convenient to take ratios of peak heights as an approximate measure of concentrations. When a more precise quantitative relationship was required between two components a conversion factor was derived by use of a calibration run involving the two gases at several known input concentrations. In this way the conversion factor for mixtures of N_2O and NO has been evaluated in Section 5.2.2.1.

Any quantitative assessment of the products from the static reaction cannot be taken as typical of reactions under flow conditions, nevertheless the results must be valid in a qualitative sense for dynamic systems.

In practice the instrument resolved the spectra into three traces representing different magnifications, so that peak heights at both high and low concentrations can be accurately determined. The factors for expressing peak heights in terms of the most sensitive trace were found to be 47.2 and 5.22 (Figure 31). In the current work the values for peak heights are expressed in mm and some values have been converted to what they would be on the most sensitive scale. Figure 31 shows a typical spectrum which is obtained from analysis of the products of the reaction between pure NO and PAN.P. The results of this particular investigation are given in greater detail in sections 4.1 and 5.2.2.2.

The first results presented were obtained in an attempt to compare actual relative concentrations of N_2O and NO to the ratios indicated by the heights of the parent peaks.

5.2.2.1 Analysis of mixtures of NO and N_2O

Any interpretation of spectra for quantitative analysis must involve a calibration factor C so that for mixtures of NO and N_2O:-

$$\frac{i_{44}}{i_{30}} = C \frac{p\ N_2O}{p\ NO}$$

where i is the current or peak height and p the partial pressure. In fact C is the product of two other factors:-

$$C = \left[\frac{IE\ N_2O}{IE\ NO}\right] \left[\frac{f\ N_2O}{f\ NO}\right]$$

where IE is the ionisation efficiency and f is a fragmentation factor.

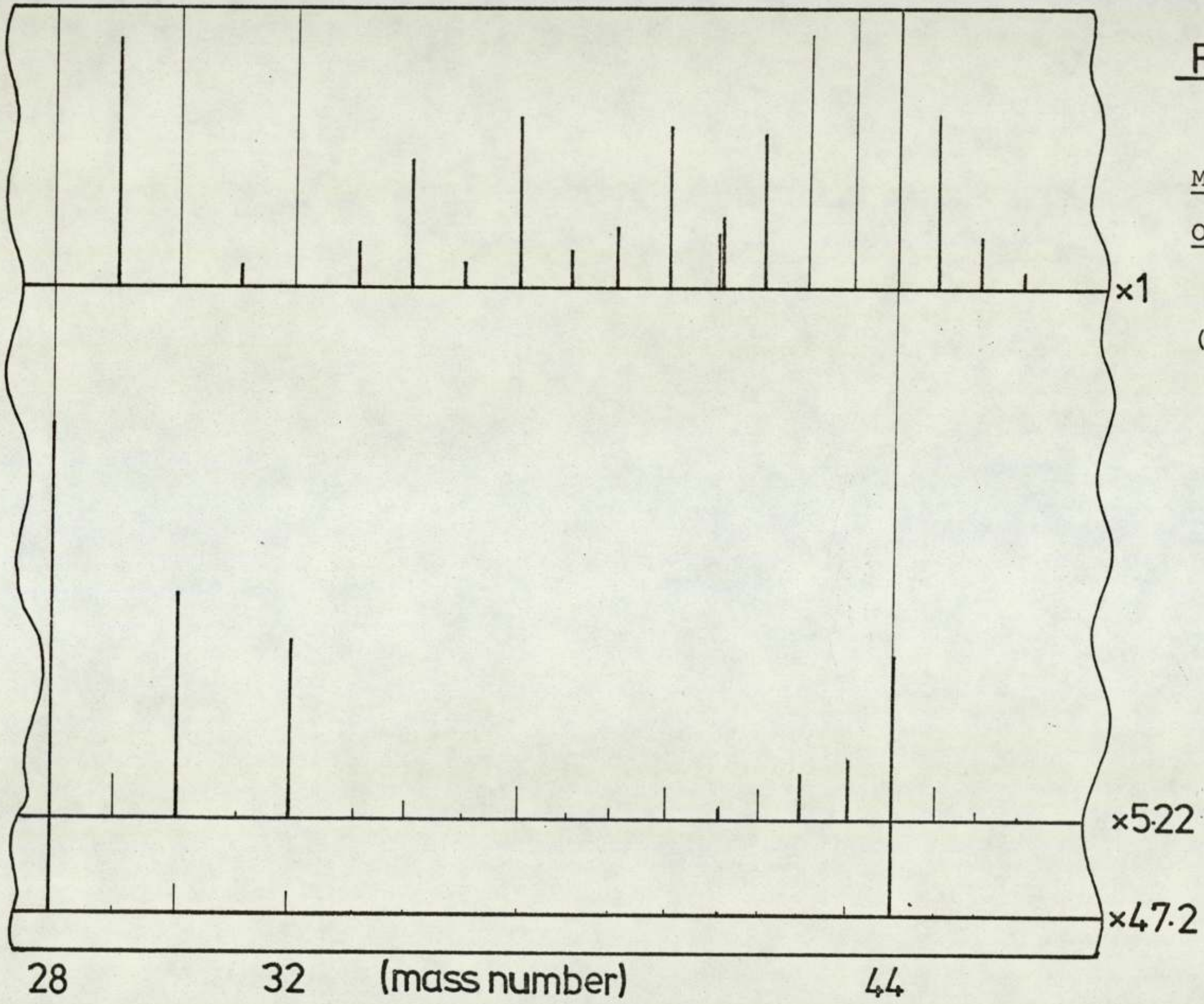


FIGURE 31

MASS SPECTRUM FROM REACTION OF PURE NO AND PAN.P

(conversion factors are given and the heavier lined peaks are those which were measured)

In this work C was established by using three mixtures having different concentrations of NO and N_2O. The results are given in Table 26.

TABLE 26

MASS SPECTOMETRIC ANALYSIS OF MIXTURES OF NO AND N_2O

Reaction conditions

Pure NO and N_2O were added to the evacuated glass reaction vessel in various concentrations at room temperature.

Results

All spectra results are expressed in terms of peak height in mm. Some values have been scaled up so that all results are based on the most sensitive scale.

$\frac{N_2O}{NO}$ (mm Hg)	46 (NO_2)	44 (N_2O)	32 (O_2)	30 (NO)	28 (N_2)	$\frac{iN_2O}{iNO}$	C
$\frac{300}{300}$	5	1680	0	3050	300	0.552	1.81
$\frac{400}{200}$	4	2832	0	2500	380	1.140	1.75
$\frac{500}{100}$	10	5390	0	2080	520	2.595	1.93

The average calibration factor C = 1.83.

5.2.2.2 Reaction with pure NO

In this series of experiments a study was made of the products from the reaction between NO and the virgin PAN.P catalyst, a "preoxidised" PAN.P sample and a commercial inorganic catalyst in a "preoxidised" state. Each experiment was carried out in the presence and absence of catalyst using the same conditions. The term catalyst refers to PAN.P supported on alumina pellets and prepared as described in Section3.5.

5.2.2.2.1 Freshly prepared PAN.P catalyst

TABLE 27

A STUDY OF THE PRODUCTS OF THE REACTION BETWEEN NO AND THE VIRGIN PAN.P CATALYST

Reaction conditions

Temperature	500°C
Time	20 minutes
Catalyst weight	20g
Volume of reaction vessel	500 cm^3
Pressure of input NO (pure) at room temperature	300 mm

Results

Mass number Species	46 NO_2	44 N_2O	32 O_2	30 NO	28 N_2
Without catalyst	0	80	20	5,370	260
With catalyst	8	410	10	190	2,925
Difference *	+8	+320	-10	-5,180	+2,665

* A negative sign infers a removal and a positive sign infers the production of that species by the catalyst.

The outstanding feature of these results is the absence of any oxygen. If the NO, which is shown to be almost completely removed, decomposes quantitatively to nitrogen and oxygen one would expect their peaks to have heights of the same order. These results seem to confirm previous work on the flow system, where the Servomex continuous analyser failed to detect any oxygen in the outlet stream, (section 5.2.1.1.1).

A study was made of the gases evolved during the heating under vacuum of a sample of PAN.P catalyst which had been exposed to a flow of NO.

TABLE 28

A STUDY OF THE "DEGASSED" PRODUCTS OF PAN.P PRETREATED WITH NO

Reaction conditions

NO (2,500 ppm in nitrogen) was passed over 20g of freshly prepared PAN.P catalyst for five hours at 500°C.

The pretreated PAN.P was allowed to cool and stored in a small tube positioned at the bottom of a 100 cm^3 glass vessel. The vessel was evacuated to a pressure of 0.001 mm Hg and the catalyst heated for one hour at a temperature of 250°C.

Results

Mass number	46	44	32	30	28
Species	NO_2	N_2O	O_2	NO	N_2
Peak height	15	3,900	0	2	725

The main product, N_2O, is in fact reported to be a common intermediate in many NO reduction reactions[92,103]. Nitrogen is also produced but once again oxygen was absent.

The effect of prereacting the PAN.P with oxygen has been mentioned in section 4.2.2.3 where no significant reduction in the rate of removal of NO was found compared to the virgin catalyst. A study was made of the identity of the products of the NO/"preoxidised" PAN.P catalyst reaction.

5.2.2.2.2 "Preoxidised" PAN.P catalyst

TABLE 29

A STUDY OF THE PRODUCTS OF REACTION BETWEEN NO AND A "PREOXIDISED" PAN.P CATALYST

Reaction conditions

Preoxidation-by treating the virgin PAN.P catalyst with oxygen at 500°C until no further removal of oxygen occurred.

Reaction temperature	500°C
Time	20 minutes
Catalyst weight	20g
Volume of reaction vessel	500 cm^3
Pressure of input NO (pure) at room temperature	300 mm

Results

Mass number Species	46 NO_2	44 N_2O	32 O_2	30 NO	28 N_2
Without catalyst	0	80	20	5,370	260
With catalyst	0	4,500	2,110	0	2,070
Difference	0	+4,420	+2,090	-5,370	+1,810

Oxygen is now produced in quantities which are of the same order as the nitrogen. Table 27 confirms the results of other workers[104] in showing that any formation of oxygen by the fragmentation of N_2O, under these conditions of reaction and analysis, can be ignored. Consequently oxygen can only be formed by the decomposition of NO, or in other words by the dissociative adsorption of NO, so that true catalysis is displayed.

5.2.2.2.3 Preoxidised metal oxide catalyst

A comparison was made between the "preoxidised" PAN.P material and the "preoxidised" iron oxide/chromia catalyst in the nature of the products of their reaction with NO.

TABLE 30

A STUDY OF THE PRODUCTS OF THE REACTION BETWEEN NO AND A "PREOXIDISED" IRON OXIDE/CHROMIA CATALYST

Reaction conditions

Preoxidation-by treating the inorganic catalyst with oxygen at 500°C until no further removal of oxygen occurred.

Reaction temperature	500°C
Time	20 minutes
Catalyst weight	20g
Volume of reaction vessel	500 cm^3
Pressure of input NO (pure) at room temperature	300 mm

Results

Mass number Species	46 NO_2	44 N_2O	32 O_2	30 NO	28 N_2
Without catalyst	0	80	20	5,370	260
With catalyst	0	1,600	0	2,030	565
Difference	0	+1,520	-20	-3,3340	+305

The first difference was found in the oxygen uptake measured at room temperature during the preoxidation process. The PAN.P accounted for a reduction in the oxygen pressure of 120 mm whilst a reduction of only approximately 20mm was evident with the oxide catalyst.

The preoxidised PAN.P was more active towards NO, removing it completely under these reaction conditions. In the absence of any reducing species the inorganic catalyst was not as effective in decomposing NO as was the PAN.P. The latter produced large amounts of oxygen and nitrogen whereas no oxygen was detected in the case of the inorganic catalyst.

5.2.2.3 Reactions with NO in the presence of CO

In this experiment a study was made of the products of the reaction between freshly prepared PAN.P and NO in the presence of CO gas. The reaction was carried out in the presence and absence of catalyst using the same conditions.

TABLE 31

A STUDY OF THE PRODUCTS OF THE NO/PAN.P INTERACTION IN THE PRESENCE OF CO

Reaction conditions

Temperature	500°C
Time	20 minutes
Catalyst weight	20g
Volume of reaction vessel	500 cm^3
Pressure of input NO (pure) at room temperature	200 mm
Pressure of input CO (pure) at room temperature	150 mm

(NOTE: CO added first)

Results

Mass number	46	44		32	30	28	
Species	NO_2	N_2O	CO_2	O_2	NO	N_2	CO
Without catalyst	0	30	160	45	5,900	485	5,010
With catalyst	0	15	885	45	105	1,400	1,650
Difference	0	-15	+725	0	-5,795	+ 915	-3,360

The outstanding feature of this reaction is the disappearance of a large proportion of the reactant gas CO, with only a minimum of CO_2 produced. In view of the failure to record any CO activity during the flow reactions described in section 4.2.1, this result was unexpected. It may, however, be meaningful in relation to the trend of the decreasing rate of NO removal for higher ratios of CO to NO, illustrated in figure 20.

Whilst a high activity for NO remains, there is no evidence of any accompanying production of N_2O. In fact a significant difference in heights of the N_2O parent peaks is found in going from NO only to NO/CO reactions with PAN.P. This may be due to a reaction between N_2O and CO:

$$N_2O \quad + \quad CO \longrightarrow N_2 \quad + \quad CO_2$$

5.2.2.4 Reactions with NO in the presence of hydrogen

If the PAN.P is an active catalyst for reactions between

NO and hydrogen then nitrogen and water are preferred as products to ammonia or N_2O:

$$NO \quad + \quad H_2 \begin{array}{l} \nearrow N_2 \quad + \quad H_2O \\ \longrightarrow N_2O \quad + \quad H_2O \\ \searrow NH_3 \quad + \quad H_2O \end{array}$$

work is described in this section to identify the appearance of any of these products.

TABLE 32

A STUDY OF THE PRODUCTS OF REACTIONS BETWEEN NO AND PAN.P IN THE PRESENCE OF HYDROGEN

Reaction conditions

Temperature	500°C
Time	20 minutes
Catalyst weight	20g
Volume of reaction vessel	500 cm^3
Pressure of input NO (pure) at room temperature	100 mm
Pressure of input hydrogen (pure) at room temperature	250 mm

(NOTE: hydrogen added first)

Results

Mass number	46	44	32	30	28	18	17	16	2
Species	NO_2	N_2O	O_2	NO	N_2	H_2O	NH_3	NH_2	H_2
Without catalyst	1	240	15	2,710	800	5	3	10	130
With catalyst	2	520	0	10	4,910	15	0	50	205
Difference	+1	+280	-15	-2,700	+4,110	+10	-3	+40	+75

The results show that only small quantities of ammonia are formed. If any of the other two reactions between NO and hydrogen are catalysed then the small peak for water is indicative of the reactions occurring only to a limited extent.

The reaction shows the characteristics of previous experiments in that the great majority of NO is removed, oxygen is not released, and a large amount of N_2O is produced. In addition a greater ammount of nitrogen than usual was found.

5.2.2.5 The water gas shift reaction

The composition of the exhaust gas, especially under petrol rich conditions, is well on the left of the water gas shift equilibrium:-

$$CO + H_2O \rightleftharpoons H_2 + CO_2$$

Gross[105] has described how a large number of catalysts are effective in shifting this equilibrium to the far right. The hydrogen on the catalyst surface is then an active reducing agent for NO. Consequently any promotion of the water gas shift reaction is regarded as advantageous providing the subsequent NO reduction yields nitrogen and not ammonia or N_2O. This section deals with the reaction of CO and H_2O in the presence of the PAN.P catalyst.

TABLE 33

A STUDY OF THE PRODUCTS OF THE REACTION BETWEEN CO AND HYDROGEN IN THE PRESENCE OF PAN.P

Reaction conditions

Temperature	500°C
Time	20 minutes
Catalyst weight	20g
Volume of reaction vessel	500 cm^3
Pressure of input CO (pure) at room temperature	150 mm
Weight of water	0.793g

Results

Mass number Species	44 CO_2	28 CO	18 H_2O	2 H_2
Without catalyst	20	6,850	7	0
With catalyst	650	2,620	5	35
Difference	+630	-4,230	-2	+35

The water gas shift reaction seems to be promoted to quite a significant extent. Previous work has shown that the low peak heights for hydrogen correspond to relatively high concentrations. For example, in section 5.2.2.4 a peak height of 130 mm was caused by a pressure of hydrogen of approximately 250 mm. Although no precise quantitative relationship can apply it is probably that hydrogen is formed in quite large amounts. This factor could also account for the large quantity of CO_2 produced.

A major reduction in the concentration of the reactant CO was once again evident.

CHAPTER 6

DISCUSSION OF RESULTS

The purpose of this chapter is to correlate the results presented in previous sections with selected reports from other workers. In this way an attempt will be made to derive the possible mechanisms involved in the NO/PAN.P interaction. One difficulty is to decide which of the many structures proposed, are valid for PAN.P when prepared according to the method previously described in this work. Furthermore the mechanism of NO decomposition and the structure of the catalyst surface required for maximum activity are not too well understood with inorganic catalysts, in spite of the extensive practical data available. Consequently it is unlikely that one underlying mechanism can be derived which will account for all the results and their trends reported in Chapters 4 and 5.

It has often been convenient to give brief comment on the more striking inferences of the various groups of results in the respective sections. In this context the conclusions presented in the work to deposit polymer onto a suitable support (Chapter 3) are regarded as sufficient and we have confined our attentions to those results presented in Chapters 4 and 5.

6.1 The information required to define the general reaction mechanism

If catalysis occurs in the classical sense then the NO will adsorb on the PAN.P surface, react with a second molecule and the products will desorb to expose the surface in its original form. The first problem is to decide what proportion, if any, of the reacting NO is decomposed by catalysis. In addition the answers to several related questions would be valuable in determining the overall reaction mechanism. These questions are as follows:-

i. What structurally related features of the PAN.P are important in attracting NO in the initial stages and if there are any changes in the polymer structure before or during reaction, what bearing do they have on this attraction?

ii. What is the nature of the bonding between NO and PAN.P?

iii. What is the composition of the desorption products and what happens to the remainder of the NO which has been adsorbed on the catalyst?

6.2 The nature of NO adsorption on PAN.P

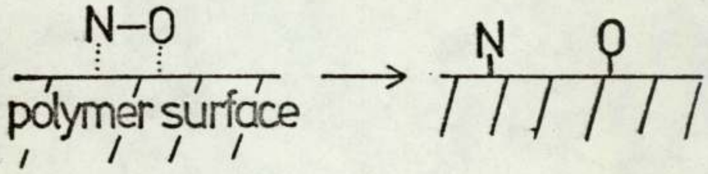
The most common feature of the NO/PAN.P interaction is that activity increases with increasing reaction temperature (section 4.1). This can be taken as evidence for the predominance of a chemisorption process. In addition, a purely physical adsorption process is highly reversible, so that NO would be the only desorption product. The results given in section 5.2.2.2.1 show that dinitrogen oxide (N_2O) is the main desorption product of PAN.P which had been reacted with NO at 500°C, small amounts of nitrogen were also found along with a negligible quantity of NO.

The products of the PAN.P/NO interaction given throughout section 5.2.2.2. provide further support for the occurrence of an irreversible chemisorption process. In each of the reactions described the removal of NO was almost complete. Moreover, all reactions carried out in the presence of freshly prepared PAN.P displayed one outstanding feature - a disappearance of oxygen in the gaseous products. For example in the reaction between pure NO and PAN.P under static conditions at 500°C, nitrogen was the major product and smaller amounts of N_2O were also detected.

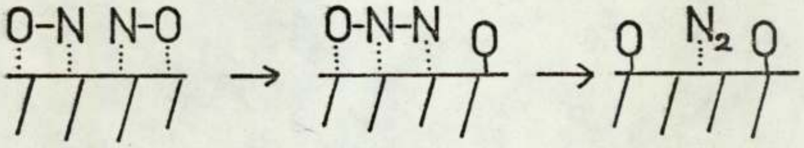
6.3 The "missing oxygen"

The phenomenon of oxygen-deficient products has been well established in other reactions involving NO. In one case Shelef[92] has shown that in the irreversible desorption of NO from a Platinum catalyst between 250 and 421°C, 18.2% of NO reappears along with 6.0% of N_2O and 75.8% of nitrogen. Whilst a similar effect was noted by Watts[106] in the reaction of NO with freshly outgassed charcoal.

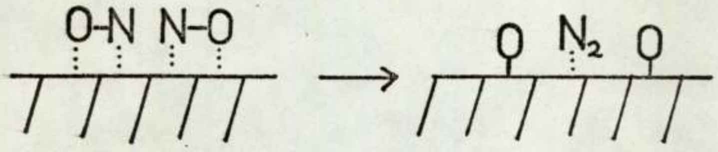
It is reasonable to assume that the NO molecule could attach itself to the polymer surface through the nitrogen atom since Dousmanis[107] has shown that the odd electron is 65% localised on the nitrogen and 35% on the oxygen atom. However, this does not account for the missing oxygen. The three mechanisms used by Watts to explain how an adsorbed NO molecule could give up its oxygen to the surface are more likely to apply. These are presented in schemes 6, 7 and 8.



SCHEME 6



SCHEME 7



SCHEME 8

It is unlikely that the reaction according to scheme 6 can predominate since molecular nitrogen and N_2O were consistently found as reaction products. Scheme 7 would account for the formation of N_2O if this reaction intermediate was desorbed, and both schemes 7 and 8 account for molecular nitrogen. In fact if schemes 7 and 8 run concurrently it would be difficult to assess their relative contributions.

6.4 The effect of separately prereacting the PAN.P with oxygen and NO

In scheme 7 if some of the sites at which the oxygen atoms can be chemisorbed are removed or saturated then one would expect an increase in the production of N_2O since its decomposition would be inhibited. Therefore by neutralising or blocking a proportion of these "O-seeking" sites then the products of the NO/PAN.P interaction may provide a measure of the extent to which scheme 7 predominates. In sections 5.2.2.2.1 and 5.2.2.2.2 experiments are reported concerning the nature of the products from the NO/PAN.P interaction where the polymer has been prereacted with NO and molecular oxygen respectively. In the former case, where the desorption products of PAN.P which has been exposed to large quantities of NO at 500°C have been identified by mass spectrometry, peak heights of 3,900 mm for N_2O and 725 mm for molecular nitrogen are reported. In the case of the "preoxidised" PAN.P the N_2O peak was equivalent to 4,420 mm and the nitrogen peak 1,810 mm, oxygen was a third product. Although both schemes 7 and 8 can account for the formation of nitrogen it would seem that a mechanism involving N_2O as an intermediate occurs to the major extent.

Thermogravimetric studies have revealed a greater oxidative stability for PAN.P which had been pre-reacted with NO and oxygen compared to the freshly prepared material (Figure 27). Results presented in Table 19 show that PAN.P which was prereacted with NO, commenced weight loss at 400°C whilst the oxygen pretreated polymer was 50°C lower and the virgin material 100°C lower. In addition the degradation exotherm was much less for NO prereaction (130°C g^{-1}) than for the unreacted material (320°C g^{-1}) and the oxygen pretreated polymer was in between (220°C g^{-1}).

It is difficult to understand how pretreatment with NO and oxygen can increase the temperature at which the onset of PAN.P weight loss appears, especially since the mechanism of oxidative degradation is not yet fully resolved. One explanation which may be related to the previous discussion is that the pretreated polymer will have more sites with chemisorbed oxygen on them. Consequently, when heated in an oxygen environment, the extent of the exotherm should be reduced since less sites can be available for the chemisorption of more oxygen. Chemisorption reactions are usually characterised by high heats of reaction. If thermal oxidative degradation of PAN.P is influenced by localised build up of heat then one would expect the fresh PAN.P to start losing weight at an earlier stage than the pretreated sample. In the one attempt to monitor exotherm from the NO/PAN.P interaction (section 4.2.2.1) no temperature change was detected but the reason may be related to the low concentration of NO used (3,300 ppm in nitrogen).

Several of the results described in previous work are relevant to the thermal oxidative degradation properties of pretreated PAN.P. Firstly oxygen pretreatment at 500°C did not bring about visible degradation even though pure oxygen was admitted in stages to the static reaction vessel until no further reduction in concentration was found. In contrast, freshly prepared PAN.P degrades completely between the temperatures of 300 and 385°C in an unlimited supply of oxygen (Table 19). An equilibrium process can be envisaged in the case of oxidation under static conditions where molecular oxygen is both adsorbed and desorbed so that the amount of oxygen attached to the polymer may never be high enough to cause decomposition. The ability of one PAN.P derivative to desorb some of the oxygen present on its surface has also been shown in section 5.2.2.2. In this case near stoichiometric decomposition of NO is catalysed under static conditions by preoxidised PAN.P.

The second feature is that pretreating the polymer with NO gave a product which has different degradation properties to the preoxidised polymer even though we have discussed how NO can dissociate on the polymer surface to denote atomic oxygen. One reason for this could be that during pretreatment under static conditions, the NO may be more effective in depositing oxygen on the polymer because N_2O or N_2 can be desorbed to provide an equilibrium with the adsorption processes. Alternatively oxygen and NO may bring about different changes in the polymer structure.

It is unlikely that oxygen chemisorption occurs on one site only of the polymer. In section 1.4 some account has been given of the extensive work which has been carried out to elucidate the structure of PAN.P. If any conclusion can be drawn from this work, it is that the polymer is probably composed of a diversity of structural species. Consequently there would be many different sites available for oxygen chemisorption and it is possible that some of these sites have more affinity for NO than oxygen and vice versa. For instance molecular oxygen may be more effective in producing hydroperoxides with the methylene groups of any segments of the polymer which has not been cyclised during pyrolysis.

6.5 The removal of oxygen-seeking sites on the polymer

If, in catalysis, a reactant gas is irreversibly chemisorbed and one or more dissociation products is not quantitatively desorbed, then the catalyst may eventually become "poisoned". The majority of NO/PAN.P interaction studies have been run under dynamic conditions (flowing reactant gases) to establish an initial rate of NO removal. The reactions were followed for an average of only 10 minutes each. Consequently separate experiments were carried out to evaluate any loss in activity with time. Both "preoxidised" and freshly prepared supported catalysts were examined:

TABLE 34

Study on the decay in NO removal activity of supported PAN.P and its preoxidised derivative over prolonged periods

Preoxidation procedure

20g of supported PAN.P were placed in a gas tight cylindrical glass vessel. This was evacuated and then pure oxygen admitted until a pressure of 300 mm at room temperature was reached. The vessel was then heated at 500°C for 10 minutes, allowed to cool to room temperature and replenished with oxygen to a pressure of 300 mm. The procedure was repeated until no further reaction occurred.

Reaction conditions

Temperature	500°C
Weight of catalyst	10g
Input gas mixture	
NO (1,500 ppm in nitrogen)	500 $cm^3 min^{-1}$
Nitrogen	500 $cm^3 min^{-1}$

Results

FRESH CATALYST		PREOXIDISED CATALYST	
time (minutes)	NO removed (ppm)	time (minutes)	NO removed (ppm)
0	363	0	160
20	182	12	129
40	100	24	113
60	50	36	97
80	25	48	89
100	25	60	81
120	16	90	60
140	0	120	49
160	0	150	33
		180	16
		210	0
		240	0

	FRESH CATALYST	PREOXIDISED CATALYST
Total volume of pure NO removed	11.46 cm^3	8.85 cm^3
Surface area: before	8.35 m^2g^{-1}	8.20 m^2g^{-1}
after	not tested	14.0 m^2g^{-1}

The results show a complete loss in apparent activity after 2½ to 3½ hours. Furthermore the lower total volume of pure NO removed by the preoxidised polymer may be a consequence of a lesser number of sites available for oxygen chemisorption. In other words dissociation of NO at the polymer surface is limited by the "blocking" of some of the oxygen-seeking species.

If it is assumed that the reduction in NO removal ability with time is the result of the loss of oxygen-seeking sites on the polymer, then more than one process may be involved. Obviously saturation of these sites by oxygen atoms from NO dissociation is one process but this would not explain how activity can diminish when the virgin PAN.P catalyst is heated at 500°C in an inert atmosphere. Such an experiment is reported in Table 35.

TABLE 35

STUDY OF THE RETENTION OF NO ACTIVITY OF FRESHLY PREPARED SUPPORTED PAN.P CATALYST WHEN HEATED UNDER INERT CONDITIONS

Reaction conditions		
Temperature	400°C	500°C
Catalyst weight	10g	10g
Input gas mixture		
1,500 ppm NO in nitrogen	500 $cm^3 min^{-1}$	700 $cm^3 min^{-1}$
Nitrogen	500 $cm^3 min^{-1}$	300 $cm^3 min^{-1}$
Inert gas		
500 $cm^3 min^{-1}$ white spot nitrogen	19 hours	17 hours

Results

Results

	Time (minutes)	NO removed (ppm)	NO removed (ppm)
Fresh catalyst	0	165	507
	4	168	411
	10	168	379
Catalyst aged in nitrogen	0	90	16
	4	74	8
	10	82	8

It would appear that the structural changes which occur by heating the polymer in nitrogen at 500°C cause a corresponding reduction in the number of sites available for oxygen chemisorption. A similar reduction in activity is noted at 400°C.

6.6 The effect of polymer surface area on NO removal activity

Table 7 reports the effect that increasing catalyst surface area has on initial removal rate of NO at several reaction temperatures. The results show the reaction rate to be dependent on surface area only and not catalyst weight. For example at a reaction temperature of 430°C, 40g of freshly prepared supported PAN.P removed NO at the rate of 9.45 moles $s^{-1}m^{-2} \times 10^{10}$ whilst 10g of the same material provide a removal rate of 9.80 moles $s^{-1}m^{-2} \times 10^{10}$. Therefore we can regard the initial NO removal reaction to be first order in surface for PAN.P which has been prepared under precisely the same conditions of pyrolysis. Plates 4 and 5 are provided to give some idea of the appearance of the surface for conjugated sequences of PAN.P. Plate 4 shows a model of the conjugated pyrinoid structure as first proposed by Houtz[67] (structure 20). Plate 5 represents the hydrogenated napthyridine structure outlined in scheme 1.

6.7 The "triggering temperature"phenomena

In section 4.1.6 it has been shown that the initial reaction rates around 500°C suggest a relationship which is first order in concentration of NO (figure 16). Below the reaction temperature of 400°C no simple kinetic dependencies are observed (figures 14 and 17). In the same text it was concluded that no evidence was provided which might support an NO removal reaction which is kinetically second order in NO. Also the "triggering temperature" phenomena was noted where an increase in the rate of change of NO activity occurred above a characteristic reaction temperature. It is interesting to note that in many cases this "triggering temperature" occurs at reaction temperatures above the temperature at which the polymer was finally pyrolysed. This is especially displayed in Figure 12 by samples pyrolysed at 500 and 550°C. Furthermore the first order relationship in NO found at reaction temperatures around 500°C was for polymer which had been pyrolysed at 400°C, that is below the "triggering temperature".

It is probable, in view of the current studies, that the species responsible for high NO activity above the "triggering

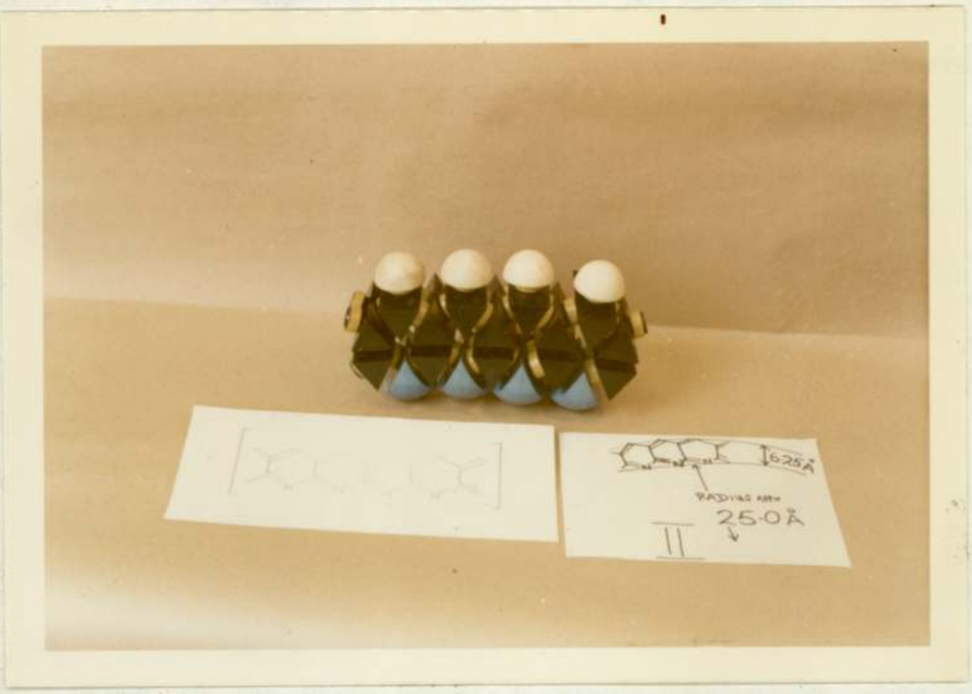


PLATE 4

MOLECULAR MODEL OF THE CONJUGATED PYRINOID STRUCTURE

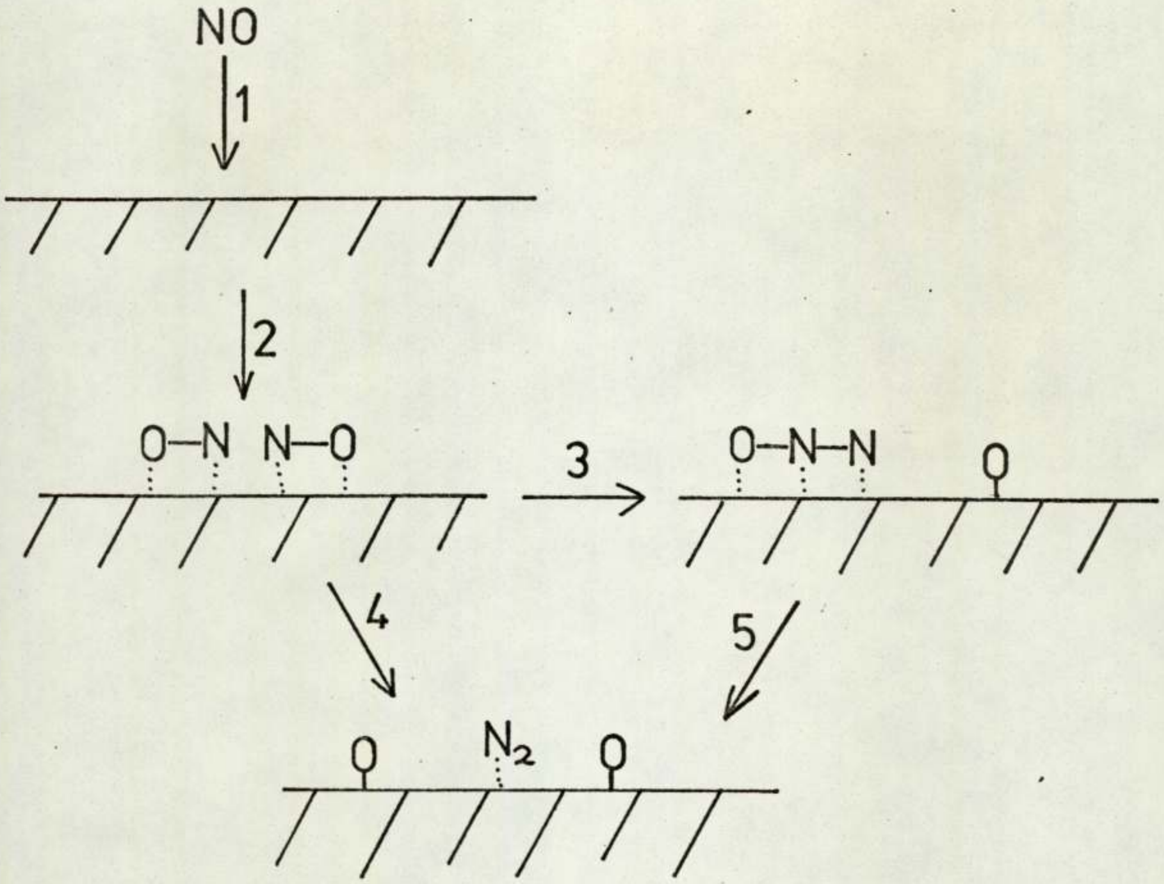
PLATE 5

THE HYDROGENATED NAPHTHYRIDINE STRUCTURE temperature" are a consequence of structural rearrangements within the polymer. Below the pyrolysis temperature it is reasonable to assume that only a minimum of structural alteration occurs, which may be one reason for the low activity observed. In addition, exposure of the catalyst to the atmosphere was unavoidable and Standage[86] has reported that oxidation of PAN.P occurs even at room temperature. Therefore, if the process of preoxidation has some bearing on the reaction at temperatures below the pyrolysis temperatures then activity would be dependent, to a lesser or greater extent, on the history of the catalyst before use. However, above the pyrolysis temperature any reactive sites freshly generated on the polymer can be immediately accounted for by NO. This may well be the reason for the more quantitative relationship between activity and NO concentration at 500°C illustrated in figure 16.

Schemes 7 and 8 can provide a general reaction mechanism for the NO/PAN.P interaction at temperatures above the "triggering temperature".

Firstly the NO decomposition reaction can only occur when sites are available for oxygen chemisorption. Above the "triggering temperature" these can be freshly generated by the polymer. If reaction 1 then becomes rate controlling then the observed first order dependence on NO concentration would be the outcome.

In section 4.3 activation energies have been calculated, for the PAN.P/NO interaction, to be between 33.9 and 39.9 kJ mole^{-1}. These low values are consistent with those

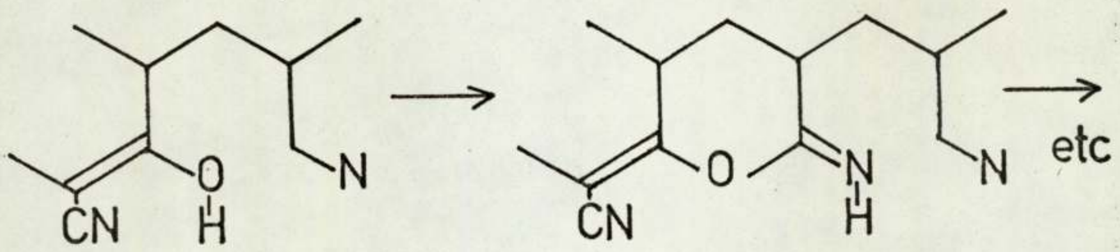


SCHEMES 7 AND 8

reported by Flory[108] for organic reactions involving polymer chain free radicals and unsaturated monomer units. If, in the case of the PAN.P/NO reaction, activation energy is a function of reaction 1 only, then this reaction could be assumed to proceed by some free radical type mechanism, or more likely via the odd electron on the NO and the unpaired electrons on the polymer.

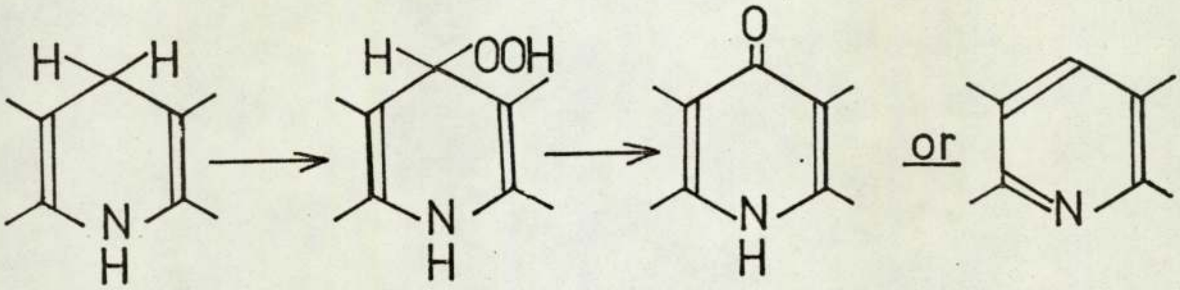
6.8 Possible sites for the chemisorption of oxygen

It has already been mentioned that oxygen chemisorption can probably occur at several different sites on the polymer structure. For example Peebles[83] and co-workers have suggested that hydroperoxides can be formed at the methylene group in the uncyclised polymer. These in turn can form poly β-ketonitriles which can then cyclise according to scheme 4:



SCHEME 4

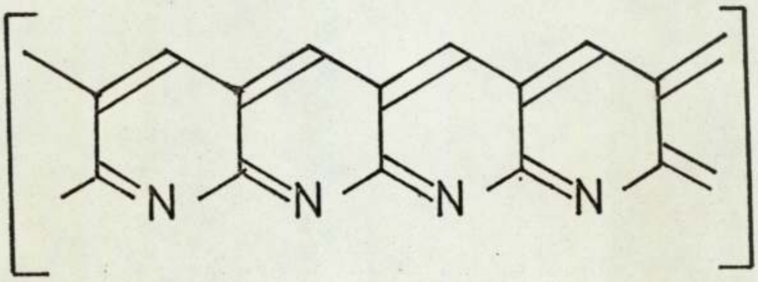
Potter[87] has shown that any cyclised polyacrylonitrile in the dihydropyridine form can accept oxygen according to scheme 5:



SCHEME 5

If cyclisation occurs, forming dihydropyridine or hydrogenated naphthyridine (scheme 1) structures, by heating the polymer above the temperature of pyrolysis, then oxygen accepting sites would be freshly generated. The mechanism might be the one in scheme 5 or even one leading to the products in structures 23 and 24 as predicted by Standage and Matkowsky[85].

On the other hand the loss in activity caused by heating the PAN.P in nitrogen at 500°C (Table 35) could be accounted for by the absence of oxygen accepting structures. One such possibility is the predominance of a conjugated pyrinoid structure as proposed by Houtz[75].



STRUCTURE 20

The loss of activity also reported by heating PAN.P under nitrogen at 400°C could also be explained by a reduction in the number of oxygen accepting groups. It appears that oxygen seeking sites are generated on the PAN.P which is freshly heated above its pyrolysis temperature, but that these sites are lost after a longer period of heating.

6.9 The effect of carbon monoxide (CO) on the PAN.P/NO interaction

The NO/PAN.P interaction in the presence of CO provides some insight into the nature of oxygen chemisorption on the polymer. In conventional catalysis the atomic oxygen bound on the surface would probably be exposed to attack by CO. As a result the reaction to produce CO_2 would have the effect of replenishing the oxygen-seeking sites and more NO could be dissociated. In this way an increase in the NO removal rate could be caused. The results presented in figure 18 for the NO/CO reaction in the presence of inorganic catalyst confirm this mechanism. The CO was observed to be removed first, from the stream of reactant gases, to reduce the metal oxide surface so that oxygen seeking sites then become available for the subsequent removal of NO.

In the case of PAN.P, however, the opposite trend was observed where an increase in the ratio of input CO to NO brought about a decrease in the rate of removal of NO. This effect is independent of the input concentration of NO, even though previous work has shown the reaction rate to be highly dependent on NO concentration at temperatures of around 500°C. This effect is shown in Figure 20 from which the results presented in Table 36 are derived.

In the study of the products of the water gas shift reaction (Table 33) reported earlier, a large proportion of the reactant CO was removed when in contact with PAN.P at 500°C.

TABLE 36

THE EFFECT OF CO ON THE RATE OF REMOVAL OF NO ON SUPPORTED PAN.P AT 500°C

Reaction conditions

Temperature	500°C
Catalyst weight	10g

Input gas mixture

As given, made up with nitrogen to	1000 $cm^3 min^{-1}$

Results

Pure NO $cm^3 min^{-1}$	Pure CO $cm^3 min^{-1}$	Fraction of NO	Rate of removal of NO moles $s^{-1} m^{-2}$ x.10^{10}
0.75	0	1.0	25.0
1.20	0.4	0.75	28.5
0.75	1.0	0.43	8.3
1.35	2.5	0.35	5.0
1.05	2.5	0.30	3.5

This cannot be wholly accounted for by reaction with hydrogen or the level of CO_2 produced. Therefore the CO is being absorbed and not desorbed by the polymer. Similarly in the presence of NO, the concentration of reacting CO was shown to be reduced and only a small quantity of CO_2 was produced (Table 31).

Although CO was not seen to remove chemisorbed atomic oxygen in significant quantities it does appear to react with

N_2O. A mass spectrum peak height of 320mm was found when PAN.P was reacted with pure NO (Table 27) whereas no N_2O could be detected in the presence of CO. This may be related to a process whereby N_2O sits exposed on the polymer surface but atomic oxygen is removed from the surface by some reaction with the polymer.

Large quantities of CO were not removed in the flow experiments (section 4.2.1). Consequently any mechanism involving a competitive adsorption on the polymer surface between NO and CO cannot solely be responsible for the reduction in NO activity.

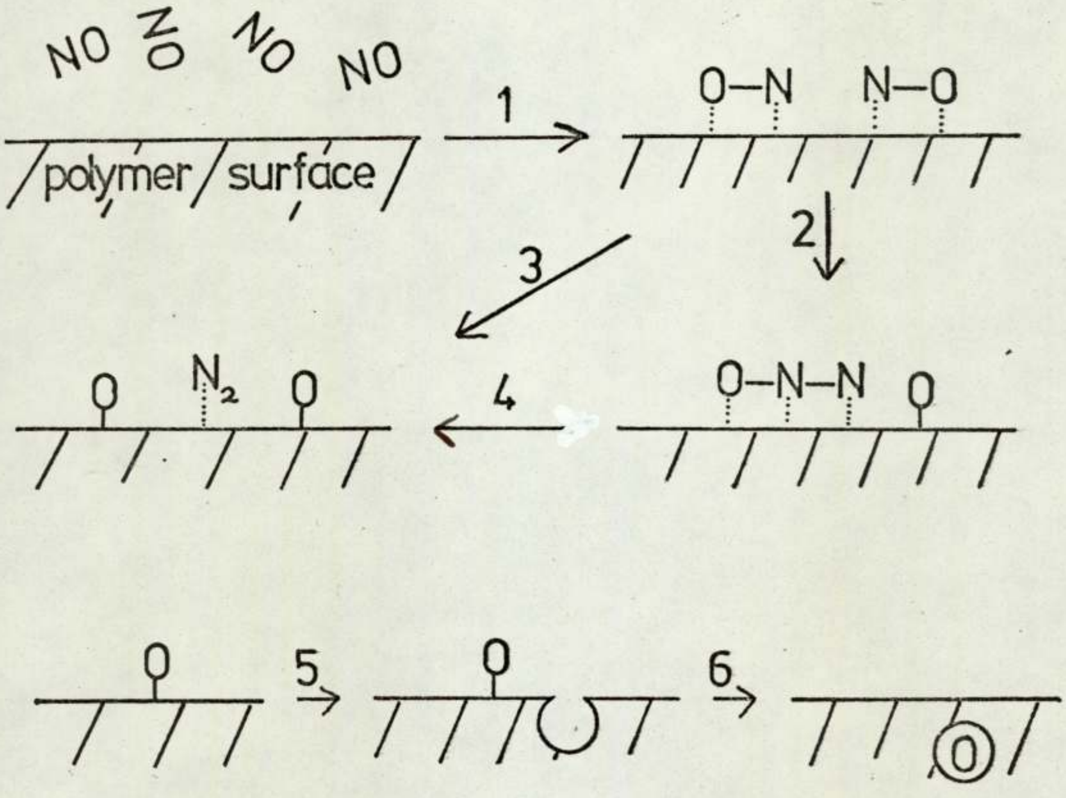
It is more likely that CO associates itself in some way with the oxygen seeking sites on the PAN.P thus blocking the way for the previously uninhibited decomposition of NO. As more fresh sites are generated at this reaction temperature, they are competed for by CO and the oxygen atoms from the NO. However when an increased proportion of CO is present in the reactant gas stream then the availability of sites for the dissociation of NO may be greatly reduced. A mechanism of this type would explain the results in Table 36.

In the absence of CO, the NO removal rate has been shown to increase with increasing reaction temperature (Figures 12, 14, 15, 21, 22 and 23). It has been proposed that at higher reaction temperatures PAN.P generates more sites for oxygen atom removal and a higher NO removal rate is the result. However, in the presence of large proportions of CO then the oxygen-seeking sites can be swamped with CO so that any effect that increasing the reaction temperature has on NO removal activity is lost. This would then account for the limited temperature response illustrated for some reaction mixtures of CO and NO in figures 20 and 24.

CONCLUSIONS

CONCLUSIONS

In conclusion, a generalised mechanism can be proposed for the PAN.P/NO interaction. This mechanism can account for many of the observations reported in this thesis.



Reaction 1	-	Adsorption of NO molecules onto polymer surface.
Reaction 2	-	Chemisorption of one oxygen atom onto polymer surface for every two molecules of NO.
Reaction 3	-	Chemisorption of two oxygen atoms onto polymer surface for every two molecules of NO.

Reaction 4 - Chemisorption of one oxygen atom onto polymer surface for every one molecule of N_2O.

Reaction 5 - The appearance of an oxygen-seeking site under the polymer surface. In reality these sites are more likely to react in a chemical sense with the atomic oxygen. The oxygen then becomes part of the polymer structure.

Reaction 6 - The removal of an exposed chemisorbed oxygen atom from the polymer surface.

The characteristics which can be expected for a reaction proceeding by this mechanism can be listed as follows:-

1. If reaction 1 is rate controlling then a first order dependence in both surface area and NO concentration would be found. One way of ensuring this is to promote reaction 5 by heating the polymer above its original pyrolysis temperature.

2. If reaction 1 is solely responsible for the activation energy of the overall process then a low value, i.e. approximately 37 kJmole^{-1}, compared with 45 to 120 kJmole^{-1} for NO decomposition on metal oxide catalysts, would be consistent with interaction between the odd electron of the NO and the delocalised odd electrons on the polymer.

3. The overall rate of reaction will increase with

increasing temperatures because chemisorption processes are involved. Furthermore reactions evolving heat will be observed.

4. Any treatment of the polymer which inhibits reactions 2 and 3 will reduce the overall rate of reaction. For example, pretreatment of the polymer with NO or oxygen will reduce the number of sites on which atomic oxygen, from the dissociation of NO, can be chemisorbed. Alternatively heating the polymer for prolonged periods in nitrogen will reduce the number of sites at which oxygen chemisorption can occur.

5. In contrast with point 4, any method of increasing the number of oxygen-seeking sites under the polymer surface will bring about an increase in the overall rate of reaction. One way of doing this is to increase the reaction temperature. It is believed that most of the oxygen which reacts with the polymer is removed from the exposed sites to a position under the surface (in reality most of the oxygen reacts to become an integral part of the structure).

6. The products of NO reacting with freshly prepared polymer will be N_2, N_2O and little, if any, oxygen. If the polymer is pretreated so that some of the potential oxygen chemisorption sites are saturated then the products should show an increase in N_2O at the expense of N_2.

7. Oxygen can be chemisorbed in two ways. One is by sitting exposed on the polymer surface and the other is by being included in the polymer structure according to reaction 6. If the polymer is pre-treated so that the supply of oxygen-seeking sites under the polymer surface is exhausted, then some oxygen will sit on the surface. If the preoxidised polymer is then allowed to react with NO under static conditions the surface chemisorbed atomic oxygen can appear in the reaction products as molecular oxygen. This is because under static conditions a desorption process will be promoted to a state of equilibrium with the adsorption process.

   For the same reasons, reaction with oxygen under static conditions will deposit less oxygen onto the polymer than when under dynamic conditions at the same temperature, where the desorption processes are at a minimum. Consequently the extent of oxidative degradation will probably be less under static conditions.

8. The presence of carbon monoxide (CO) can alter the characteristics of the NO/polymer reaction. Firstly CO is effective in reacting with any N_2O which is produced on the polymer surface to give N_2 and CO_2. Secondly the CO can compete with oxygen for the sites which appear under the surface according to reaction 5. In this way, if the concentration of CO is high enough then the rate of NO removal can be reduced (see point 5).

All the above points, which are predicted by the generalised mechanism given, are in agreement with the observations for the reaction of NO with PAN.P. Unfortunately, the precise chemical nature of the oxygen-seeking sites, which are represented as being under the polymer surface, has not been established. The nature of some of the possible sites has been given in Chapter 6.

It would seem that the features which promote the well known oxidative instability of PAN.P are also effective in causing a high NO removal activity. Whilst catalysis is more evident under static conditions because of the adsorption/desorption equilibria, the PAN.P soon becomes inactive under dynamic conditions. Consequently the realtively poor oxidative stability and capacity limit the practical utility of PAN.P based catalysts with the gaseous systems studied. Additional reactant gases (hydrogen, steam etc.) may, however, facilitate more efficient NO removal. An additional potential difficulty is to be expected in that any method of improving the oxidative stability of PAN.P will cause a corresponding loss in NO removal activity. The effective balancing of these various factors will govern the successful commercial use of catalysts of this type.

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SUGGESTIONS FOR FURTHER WORK

1. An examination of NO removal activity of other highly conjugated synthetic organic polymers would, of course, provide the basis for an extensive research programme. If any of the polymers show appreciable activity then the effect of oxygen on structural stability should be checked in order that the mechanism proposed herein can be substantiated or disproved.

2. A more detailed study of electron spin resonance spectra of the products of the PAN.P/NO interaction would be worthwhile since it may provide more evidence of the reaction mechanism involved.

3. An accurate C, H and N analysis would be useful in showing the quantity of oxygen present in fresh PAN.P, when stored in air at room temperature, and when reacted with NO, oxygen or carbon monoxide. The results would be useful in further elucidation of the overall reaction mechanism previously described.

4. The oxidative stability of the PAN.P which is treated at 500°C with nitrogen, according to the conditions given in Table 35, could be examined. This polymer which is rendered inactive towards NO by this treatment, may have improved stability.

5. In view of the well established degradation characteristics of PAN.P in oxygen, the influence of the magnitude of the reaction exotherm on polymer stability could be followed. It has been mentioned in section 6.4 that localised build

up of heat, from chemisorption processes, may have some influence on polymer stability.

6. A further series of experiments could be carried out under static conditions to check the proposed mechanism for the PAN.P/NO reaction.

    i. A supported PAN.P sample could be preoxidised at a temperature above that used for pyrolysis. The products of the reaction with NO between a series of reaction temperatures from, for example, 100 to 600°C could then show a greater deficiency in oxygen content above the "triggering temperature".

    ii. The products of NO reacting with freshly prepared PAN.P at one temperature above that chosen for polymer pyrolysis could be compared to those found with the same polymer which had been progressively saturated with small quantities of NO. An increase in the amount of oxygen in the products would be expected from the proposed mechanism.

    iii. A quantitative interpretation would be useful to show if the nitrogen removed from the reactant NO was equal in quantity to the nitrogen found in the products, either in the molecular form or when combined.

    iv. An indication of the proportion of oxygen chemisorbed onto the PAN.P surface (reactions 2, 3 and 4) to that under the surface (reaction 6) in the reaction with NO would be useful since the mechanism proposes that only a minimum of oxygen remains in the former mode. The method would be to measure the quantity of oxygen removed from saturation of the PAN.P with the reactant NO for a range of surface areas. If surface oxygen chemisorption is the predominant mode then a direct proportionality should be found.

v. A study could be made of the role of carbon monoxide in inhibiting the rate of NO removal (section 4.2.1). Experiments could be carried out under static conditions to determine the products of the reaction of CO on PAN.P which is presaturated separately with NO and oxygen. Also the products could be examined for the reaction between NO and fresh PAN.P, as well as with PAN.P which is presaturated with CO.

The characterisation of any reaction of CO with the holes within the polymer structure would be valuable in terms of one of the suggestions in the overall reaction mechanism. Initial experiments could be carried out to establish a relationship between the quantity of reactant CO removed and the rate of appearance of these sites.

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