CATALYTIC REACTIONS OF HIGHLY CONJUGATED POLYMERS: THE REMOVAL OF NITROGEN MONOXIDE FROM GAS STREAMS USING PYROLYSED POLYACRYLONITRILE

by

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SUMMARY

This work is concerned with the use of pyrolysed polyacrylonitrile, a highly conjugated organic polymer, as a heterogeneous catalyst for the removal of nitrogen monoxide from motor vehicle exhaust gas. Previous work had shown that the polymer was capable of removing nitrogen monoxide from gas streams and it was intended to optimise the activity of the polymer and to investigate the nature of the reaction.

Although attempts were made to maximise the surface area of the polymer by coating it on to high surface area inorganic supports prior to pyrolysis, the bulk of the experimental work was carried out using pyrolysed polyacrylonitrile fibre as the catalyst. BET nitrogen adsorption measurements, infrared spectroscopy, electron spin resonance spectroscopy and electron microscopy were used to characterise the catalyst samples.

Kinetic studies showed that the removal of nitrogen monoxide by pyrolysed polyacrylonitrile commenced at about 200°C and increased in rate with increasing temperature. At 500°C the initial nitrogen monoxide removal rate by the polymer was 2.4×10^{-5} mol min^{-1} g^{-1}. The rate of nitrogen monoxide removal decreased with time due to the formation of oxides on the polymer surface. Nitrogen was believed to be the other main product of the reaction. At temperatures above 720°C continuous oxidation of the polymer by nitrogen monoxide took place. Oxygen also reacted readily with the polymer at temperatures above 200°C. Electron spin resonance studies indicated that unpaired electrons in the polymer structure were involved in the reactions with nitrogen monoxide and oxygen. An activation energy of 10.8 kJ mol^{-1} was measured for the reaction between nitrogen monoxide and the 'clean' polymer surface. A mechanism is proposed for the reaction between nitrogen monoxide and pyrolysed polyacrylonitrile and a critical survey is given of the use of the polymer for the removal of nitrogen monoxide from motor vehicle exhaust gas.

Key words: polyacrylonitrile, nitrogen monoxide, polymer,
catalyst, pyrolysis

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CHAPTER 1

INTRODUCTION

This work is concerned with the nature and practical utilisation of the interaction between nitrogen monoxide and a highly conjugated organic polymer. Increasing use of the internal combustion engine has caused air pollution problems and the use of conventional catalysts has not been entirely successful in controlling the levels of these pollutants. Nitrogen monoxide has proved one of the more difficult gases to eliminate and methods of doing so efficiently and cheaply are of continuing interest and importance to the motor industry.

1.1 Motor vehicle emissions and air pollution

In recent years there has been increasing concern about the adverse effect of industry and technology on the natural environment. This is reflected in the anti-pollution controls now in force in many countries, and in the vast amount of research which is being carried out on the effects of pollution by different substances.

The problems caused by large numbers of motor vehicles became apparent in California as long ago as the late 1940's. Los Angeles suffered regular mid-afternoon smogs which had an irritant effect on the eyes and lungs of the population and also caused plant damage. It was found that exhaust fumes from vehicles used during the morning rush hour were, in the presence of the strong sunlight, undergoing a photochemical chain reaction which produced the smog. Nitrogen oxides and hydrocarbons were the two constituents of vehicle exhaust emissions involved in the reaction.

In 1970 in an Amendment to the Clean Air Act the United States government introduced legislation limiting the levels of carbon monoxide, hydrocarbons and nitrogen oxides in motor vehicle exhaust emissions. This stimulated a great deal of research into methods of eliminating these gases from exhaust emissions. In the long term it seems likely that modifications to the design of the internal combustion engine will provide the most satisfactory answer to the problem. However until that has been achieved most motor manufacturers are relying on catalytic conversion of the exhaust gases into an acceptable form before emission into the atmosphere.

1.2 Catalytic conversion of exhaust gases

Table 1 shows the levels of the three specified gases in the exhaust from an untreated vehicle under various driving conditions. Also shown are the maximum levels permitted if the vehicle is to comply with the limits originally stipulated for a vehicle manufactured in 1975.

Table 1

Exhaust gas composition for a 4,000 lb vehicle[1]

		Hydrocarbons /ppm	Carbon monoxide /%	Nitrogen oxides /ppm
Untreated Vehicle	Idle	750	5.2	30
	Cruise	300	0.8	1,500
	Acceleration	400	5.2	3,000
	Deceleration	4,000	4.2	60
Limits for 1975 vehicle		40	0.5	225

Carbon monoxide and hydrocarbons are produced by incomplete combustion of the petroleum fuel. Their production is favoured by a rich fuel/air mixture and low engine temperatures. They can be removed by catalytic oxidation to carbon dioxide using a supported platinum group metal catalyst.

Nitrogen monoxide is produced by reaction between atmospheric oxygen and nitrogen at the high temperatures achieved during combustion. Its production is favoured by high engine temperatures and a lean fuel/air mixture. Thus the conditions which produce the least carbon monoxide and hydrocarbon produce the greatest amount of nitrogen monoxide.

Removal of nitrogen oxides (NO_x) is more difficult. Ideally the NO_x must be converted to harmless nitrogen and either oxygen or carbon dioxide. This can be achieved by decomposition of the NO_x into its elements or by its reduction to nitrogen by one or more of the other exhaust gas components.

Table 2

Change of equilibrium constant and equilibrium nitric oxide[3] concentration with temperature

T K	$K = \frac{P_{N_2}^{\frac{1}{2}} P_{O_2}^{\frac{1}{2}}}{P_{NO}}$	Equilibrium NO concentration/ppm
298	1.549×10^{15}	5.6×10^{-11}
1,000	1.208×10^{4}	7.23
1,500	3.236×10^{2}	269
2,000	5.297×10	1,640

The data in Table 2 shows that nitrogen monoxide (NO) is thermodynamically very unstable with respect to nitrogen and oxygen. At temperatures below 1000 K the thermal decomposition of NO is almost complete. However, NO is kinetically very stable to homogeneous decomposition at these temperatures in accordance with the high energy of activation (268–359 kJ mol^{-1}) measured for this reaction.[3]

Heterogeneous decomposition of NO is also rather slow although the activation energy for the reaction (42 – 125 kJ mol^{-1}) is much reduced. Shelef[2] tested the best catalysts quoted in the literature and found that at 500°C and 1 atmosphere NO pressure the rate of decomposition was in the range 1.5×10^{-9} to 1.5×10^{-8} mol m^{-2} min^{-1} which was far too slow to be of any practical use for the removal of NO in combustion processes.

The reduction reactions of NO shown in Table 3 are thermodynamically very favourable at exhaust temperatures as indicated by the equilibrium constants.

Table 3

Equilibrium constants for some reduction reactions of[3] nitrogen monoxide

(1) $NO + CO = \frac{1}{2}N_2 + CO_2$

(2) $2NO + 2H_2 = N_2 + 2H_2O$

$\log K_p$

T K	600	700	800	900
(1)	27.3	22.6	19.7	16.5
(2)	51.7	43.4	37.1	32.2

Thus, research has concentrated on the reduction of NO by the carbon monoxide and other reducing gases already present in the exhaust stream in the presence of a suitable catalyst. This requires a chemically reducing atmosphere as the carbon monoxide reacts preferentially with any oxygen present.

The catalyst must be selective as undesirable reactions are also possible.

$$2NO + CO = N_2O + CO_2$$

$$2NO + 5H_2 = 2NH_3 + 2H_2O$$

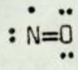
Ammonia is a toxic gas in its own right. Dinitrogen oxide is less harmful but in a dual bed catalytic converter, where reduction of NO is followed by oxidation of the carbon monoxide and hydrocarbon, it would be oxidised back to NO.

Various catalysts have been found which promote the reduction of NO. These include supported precious metals and supported transition metal oxides. However, problems associated with catalyst selectivity and durability have resulted in the United States government relaxing the NO_x emission standard set in 1970. Thus the chemical behaviour of NO and of catalysts capable of promoting its removal from gas streams is of continuing interest and importance.

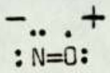
1.3 Properties of nitrogen monoxide

Nitrogen monoxide has eleven valency electrons and is paramagnetic at ambient temperatures.

In terms of the valence bond theory its structure may be considered as a resonance hybrid of structures (i) and (ii) below, with (i) predominating as shown by the very small dipole moment of 0.16 Debye.



(i)



(ii)

Analysis of the hyperfine structure of the microwave spectrum of NO indicates that the odd electron is 65% localised on the N atom and 35% on the O atom.[4]

The molecular orbital scheme for the electronic structure of NO is shown below.

N	NO	O
	$\pi^{*}2py^{1}$	
	$\pi 2py^{2}$ $\pi 2px^{2}$	
$2px^{1}$ $2py^{1}$ $2pz^{1}$	$\sigma 2pz^{2}$	$2px^{1}$ $2py^{1}$ $2pz^{2}$
$2s^{2}$	$\sigma^{*}2s^{2}$	$2s^{2}$
	$\sigma 2s^{2}$	

The eleventh electron goes into a π^{*} anti-bonding orbital giving a total bond order of 2.5. This is confirmed by the N–O bond distance for nitrogen monoxide of 0.115 nm compared with 0.119 nm for a double and 0.106 nm for a triple nitrogen-oxygen bond. The ionisation potential for the process $NO \rightarrow NO^{+} + e^{-}$ is only 9.5 V and the nitrosyl cation thus formed has a bond dissociation energy of 1,045 kJ mol^{-1} compared with 631 kJ mol^{-1} for NO.

Chemically nitrogen monoxide behaves as a stable free radical. It does not readily combine with itself but is well known for its ability to combine with other free radicals. In all cases NO associates initially with the radical at the nitrogen end.

$$R\cdot + \cdot NO \longrightarrow R\text{–}NO$$

There is no recorded evidence for the initial association occurring at the oxygen atom.[5]

Due to the low ionisation potential the NO molecule is easily converted to the nitrosyl cation. Conversely it can accept an electron to form the nitrosyl anion $(N{=}O)^{-}$.

NO can also coordinate as a neutral entity by donating a lone pair of electrons, by donating three electrons, or by accepting an electron from a metal site to form an electron pair bond.

Examples of the various types of bonding are shown in Table 4 below.

Table 4

Types of nitrogen monoxide bonding in inorganic compounds[3]

Bond type	Nature of bonding	Example
NO–X	Sharing of electron pair	NOCl
NO^+X^-	Donation of one electron	$NO^+ClO_4^-$
M^+NO^-	Acceptance of one electron	Na^+NO^-
M –NO	An electron pair donated to a metal atom	A few metal coordination complexes
M –N=O	Three electrons donated to a metal atom	Most coordination complexes
M –N=O	Electron pair bond but one electron also donated by metal to NO group	A few metal coordination complexes

By surveying the elements which coordinate the NO group it is possible to select those most likely to chemisorb NO and prove active as catalysts. Ruthenium is the element giving the largest variety of NO complexes and it is a very active reduction catalyst. In the same way materials which support a large concentration of unpaired electrons are likely to have an affinity for the NO molecule with its unpaired electron. Certain organic polymers have this property and have already been shown to be active heterogeneous catalysts for a variety of chemical reactions. It is possible that they will be very effective in catalysing nitrogen monoxide reactions.

1.4 Organic polymers as heterogeneous catalysts

There is no certain way of predicting whether a substance will act as a catalyst. Heterogeneous catalysis is generally concerned with the reaction of molecules adsorbed at the surface of the catalyst. The type of molecules that are adsorbed and the nature of the reaction will depend on the chemical structure of the surface. Semi-conducting metal oxides make good catalysts for redox reactions because of the electronic properties of their surfaces. Similarly, it was first suggested that highly conjugated organic polymers might make good heterogeneous catalysts because they possess a large number of delocalised electrons which could take part in redox or radical reactions.[6]

Since then numerous polymers have been used to catalyse a wide variety of chemical reactions. In a comprehensive review of the work carried out up to 1973 Tighe et al[7] found that, although an understanding of the use of organic polymers as heterogeneous catalysts was incomplete, certain underlying features appear to influence their efficiency and selectivity. Prime among these is chemical structure.

Successful polymeric heterogeneous catalysts generally possess highly conjugated structures which can support a large concentration of delocalised TT electrons along the conjugated chain. This gives rise to paramagnetism and a decrease in the internal energy of the system. Lowering of the excitation energy of the triplet state and the decrease in ionisation potential for long conjugated systems gives rise to semi-conductivity.

Although paramagnetism and semi-conductivity appear to be necessary, the presence of these two factors alone is not sufficient to ensure catalytic activity. Regularity of structure, extent and type of conjugation and the presence of heteroatoms in the polymer chain have also been shown to be important.

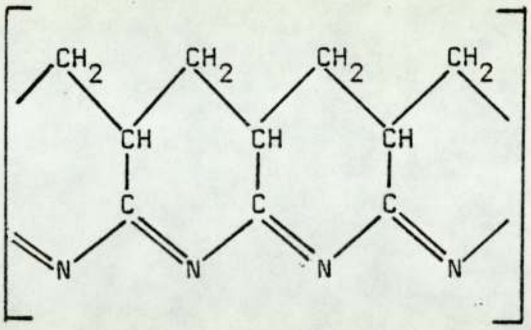
Pyrolysed polyacrylonitrile (PAN.P) was chosen as the polymer to be used in this work as it has all the features of a typical polymeric heterogeneous catalyst. It has the advantage that its structure has been extensively studied. It also possesses very good thermal stability which will be necessary if it is to function at the elevated temperatures encountered in exhaust systems.

Polyacrylonitrile (PAN) is produced commercially containing a small quantity of copolymer and is therefore available at a reasonable price. The catalytically active PAN.P is readily obtained from the polymer by heating the latter to the required temperature in an inert atmosphere.

1.5 The structure of pyrolysed polyacrylonitrile

The mechanism of the thermal degradation of polyacrylonitrile and the structure of PAN.P have received much attention recently due to the use of PAN polymers in the production of carbon fibres. Most of this work has concentrated on the pyrolysis of PAN under inert conditions although the presence of oxygen is known to have a significant effect on the reaction.

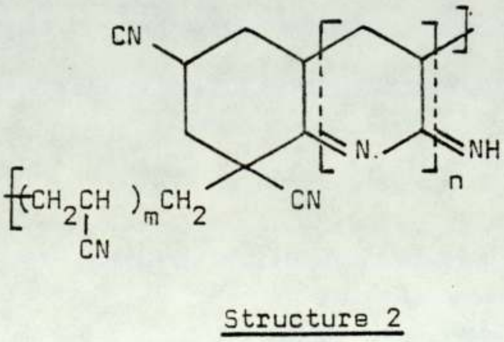
When PAN is heated in an inert atmosphere under temperature programmed conditions it starts to discolour at temperatures above 150°C, going from yellow to brown. The polymer becomes insoluble in its normal solvents with onset of colo ration. At about 260°C the PAN undergoes a very exothermic reaction. This coincides with a decrease in the nitrile content of the polymer as measured by infrared absorption. There is also an increase in the torsional modulus, but not tensile strength, of PAN fibres which suggests a strengthening of the molecular skeleton or ladder formation.[8] It is generally agreed that oligomerisation of the nitrile groups has resulted in the formation of a conjugated polyimine[9] as shown in Structure 1.



Structure 1

The same species is believed to be responsible for colouration of the polymer.

The PAN undergoes considerable weight loss during the exothermic reaction due principally to the evolution of polymer chain fragments. Ammonia and hydrogen cyanide are also produced. It has been proposed[11] that the oligomerisation reaction is a radical process initiated by abnormal structures formed during polymerisation and distributed at random throughout the polymer molecules. The zip length of the nitrile oligomerisation is believed to be fairly short but the kinetic chain length of the overall process is long, being maintained by transfer reactions. This produces a polymer chain consisting of short cyclised segments linked by segments of unchanged monomer units as shown in Structure 2.[11]

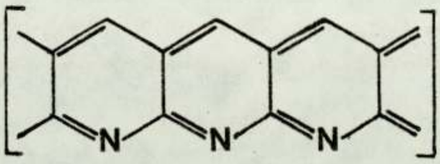


n = 0 to 5
m = 0 to 2

Structure 2

Scission can occur at these latter structures to produce the volatile chain fragments. It has been estimated that up to 80% of the nitrile groups participate in the oligomerisation reaction.

As the temperature of the polymer is raised further the weight loss continues but it gradually decreases at about 450°C.[12] At temperatures above 350°C hydrogen is evolved which is thought to indicate aromatisation of the cyclic structures as shown in Structure 3.



Structure 3

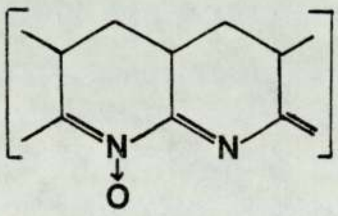
This process continues up to at least 700°C. Finally, above 900°C the polymer begins to lose nitrogen indicating breakdown of the heterocyclic ring and rearrangement to give pure carbon.

PAN which has been pyrolysed under inert conditions reacts readily with oxygen on exposure to the atmosphere at room temperature. The PAN.P darkens in colour and its mass increases by up to 2%.[12]

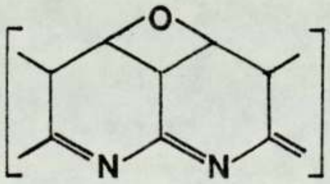
Temperature programmed pyrolysis of PAN in air produces the same oligomerisation of the nitrile groups as under inert conditions. However onset of colouration occurs at lower temperatures and the colour is more intense for the same decrease in nitrile absorbtion. The exothermic reaction occurs at about 50°C higher than it does under inert conditions and is spread over a greater temperature range. This suggests that oxygen inhibits the oligomerisation reaction, possibly by reaction with the initiating centres. Heating to higher temperatures in air results in progressive oxidation of the polymer which is completely consumed, leaving no residue, by 600°C.

Prolonged heating of the polymer in air at temperatures below the exotherm temperature leads to increased structural stability and virtually eliminates weight loss during the exothermic reaction. In carbon fibre production the preferred process is to preheat PAN fibres for two hours at 210°C in air before raising the temperature further. Fibres which have not been treated in this way fuse together on heating above 260°C and the ultimate pyrolysed product is weak and brittle.[8]

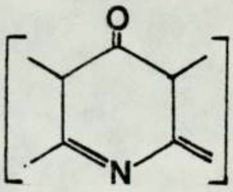
The precise structure of the oxidised polymer is not certain. The basic reaction occurring during pyrolysis in air is still oligomerisation of the nitrile groups initiated by abnormal structures. It has been suggested that the polyimine structure (Structure 1) reacts with oxygen to give nitrones[10] (Structure 4) or, via the methylene hydrogens to give hydroperoxides. The latter then break down to give epoxides[13] (Structure 5) or carbonyl groups[8] (Structure 6).



Structure 4



Structure 5



Structure 6

Aromatisation of the polymer structure has also been proposed.[8,14] The increased conjugation thus produced would explain the deeper colours obtained and would lead to stabilisation of the methylene bridges at which chain scission normally occurs. Crosslinking reactions[14] or hydrogen bonding[8] have also been proposed to explain the increased stability to fragmentation.

Most commercially produced samples of polyacrylonitrile are copolymers, containing small quantities of carboxylic acid or ester groups in addition to the nitrile groups. The effect of various comonomers on the pyrolysis of PAN has been investigated by Grassie and McGuchan.[15] They found that carboxylic acid comonomers acted as initiators for the oligomerisation reaction as indicated by a reduced temperature of colouration, decreased exotherm temperature, and a broader, less intense exotherm.

They have also shown that because the comonomer unit is an integral part of the polymer molecule it may block the passage of the cyclisation reaction along the polymer chain. Styrene was found to act in this way. It greatly reduced the extent of nitrile oligomerisation while increasing the amount of chain scission. On the other hand some comonomers, such as methyl acrylate, take part in the reaction and merely act as diluents.

1.6 Pyrolysed polyacrylonitrile as a catalyst

The catalytic properties of PAN.P were first demonstrated by Topchiev et al[16] who used the polymer to decompose hydrogen peroxide. They also noted the electrical conductivity of the polymer and the presence of 10^{18}-10^{19} unpaired electrons per gramme of catalyst.

Dokukina[17] used two samples of PAN.P, one of which had been treated with copper(II)chloride before pyrolysis. The samples had surface areas of 0.06 m^2g^{-1} and 0.04 m^2g^{-1} respectively. They were active in the decomposition of methanoic acid and the presence of the copper had no effect on the activity. The PAN.P did not catalyse the hydration of hydrazine, the hydrogenation of ethylene or the dehydration of alcohols and it was therefore suggested that PAN.P was a selective catalyst.

In a series of papers concerning heterogeneous polymeric catalysts Gallard and her co-workers studied a variety of polymers including PAN.P. In the first paper[18] she describes how PAN.P which had been pyrolysed to 400°C easily decomposed hydrogen peroxide and also decomposed dinitrogen oxide over the temperature range 150 - 350°C. The PAN.P had a surface area of 18 m^2g^{-1} and gave an electron paramagnetic resonance signal corresponding to approximately 10^{18} spin centres g^{-1}. Gallard also mentions that PAN.P had been found to promote certain isomerisation reactions and she claims that it is not as selective a catalyst as Dokukina had thought. She suggests that the very small surface area of Dokukina's samples may have reduced their effect as catalysts in certain reactions.

Later work[19] showed that PAN.P catalysed the dehydrogenation and dehydration of alcohols, the isomerisation of butene and the oxidation of tetralin. Gallard also found that PAN.P which had been pyrolysed to 350°C in argon decomposed the dinitrogen oxide much better than a similar sample which had been pyrolysed in air.[20] The argon sample also proved superior to a nickel(II)oxide catalyst for this reaction.

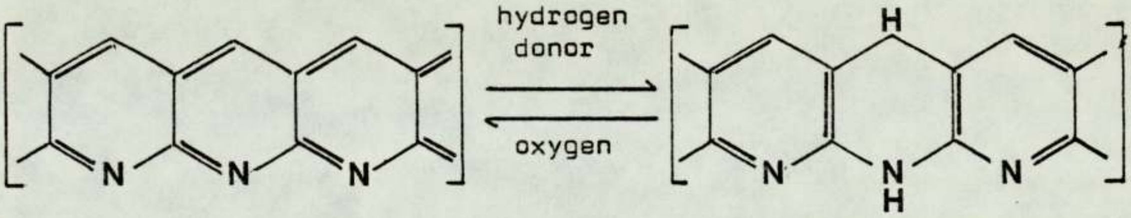
Gallard went on to study the effect of the paramagnetic centres on catalytic activity.[21] She found that the free spin concentration, as measured by electron paramagnetic resonance, varied with pyrolysis temperature for PAN.P and certain other pyrolysed polymers. In each case the concentration of free spins increased with increasing pyrolysis temperature until it reached a maximum value after which it decreased. The maximum spin concentration for PAN.P was obtained at a pyrolysis temperature of 450°C. She also found a close correlation between free spin concentration and the rate of decomposition of dinitrogen oxide. However, the pyrolysis temperature which gave optimum catalytic activity (400°C for PAN.P) was slightly lower than that for maximum free spin concentration. Gallard also carried out experiments with PAN.P and dinitrogen oxide in the sample cavity of the e.p.r. instrument to see if there was any change in the free spin concentration of the polymer during the reaction.[22] Under these conditions it was not possible to detect any change in the e.p.r. signal. Further work by the same team found a close relationship between the activity of PAN.P in catalysing the decomposition of dinitrogen oxide and the spin relaxation time.[23]

Manassen[24] found that PAN.P, pyrolysed to 450°C in nitrogen, was capable of dehydrogenating alcohols and olefininic compounds in the vapour phase at elevated temperatures.

Propan-2-ol and cyclohexanol were converted to their respective alkanones at 250°C. No hydrogen was produced and the PAN.P was gradually deactivated. Subsequent heating of the catalyst to 340°C in nitrogen had no effect but heating in air to 140°C restored the PAN.P to its original activity. Water was produced during this latter treatment indicating that the missing hydrogen was bound to the catalyst surface.

In a further reaction PAN.P at 350°C converted cyclohexene to benzene giving a 50% yield. No cyclohexane or hydrogen was produced although charcoal, graphite and palladium catalysts all gave cyclohexane. Again the PAN.P was rapidly deactivated but passage of air restored activity. The passage of cyclohexene and air simultaneously gave a higher yield of benzene and slowed down the deactivation.

Treatment of PAN.P with hydrogen at 350°C did not deactivate the polymer suggesting that gaseous hydrogen is not an intermediate in these reactions. The model compound 5-ethyl-5-methly-1,3-cyclohexadiene was used to differentiate between hydrogen atom, hydride ion and proton abstraction by the catalyst. It was found that H / H-were removed in the ratio 2.2/1 with only a trace of proton removal. This showed that PAN.P is a good hydrogen atom acceptor. The hydrogen is retained chemically bound to the polymer until it is removed during regeneration by oxygen under very mild conditions. Manassen explained this property by suggesting that the accepted PAN.P structure of annularly condensed pyridine rings gains aromaticity by being hydrogenated, as shown below in Structure 7.



Structure 7

Cutlip and Peters[25] studied the dehydration of t-butyl alcohol to isobutylene and water over PAN.P. The catalyst was prepared by pyrolysing PAN in air to 230°C and then in stages to 350°C under nitrogen. The PAN.P had a surface area of 17.7 m^2g^{-1}. The reaction was carried out at temperatures between 240 - 280°C. The polymer deactivated gradually but could be restored by heating in a stream of nitrogen or by passing a small amount of oxygen. The activity of the PAN.P was twenty times less than for an alumina catalyst.

Cutlip and Bhatt[26] carried out further experiments in which the PAN.P was agitated with varying quantities of sodium hydroxide solution prior to the reaction. They found that the rate of dehydration of the t-butyl alcohol decreased as the quantity of alkali increased. These results indicated that the catalytic activity of PAN.P for alcohol dehydration is probably due to the acidity of this catalyst.

All the reactions described thus far have involved the use of 100% PAN.P in powder or pellet form. However a patent produced by the Compagnie Francaise de Raffinage[27] describes the use of supported PAN.P samples. These, it is claimed, have the advantage of a very much greater surface area and thus a greater catalytic activity than the unsupported polymer. Solid inorganic supports of a suitable porosity gave catalyst surface areas in excess of 100 m^2g^{-1} compared to 2 - 6 m^2g^{-1} for unsupported PAN.P. It is also stated that the optimum catalytic activity of the PAN.P was produced by pyrolysis to 500°C in an inert atmosphere. Pyrolysis beyond 30 minutes had no effect on catalytic activity.

As mentioned earlier Gallard had found a close relationship between free spin concentration and catalytic activity for PAN.P. Cooper[28] noted that the nitrogen monoxide molecule had an unpaired electron which may interact with the free spins on PAN.P. He went on to investigate the efficiency of PAN.P as a catalyst for reactions involving NO. He found that PAN.P removed NO from gas streams at temperatures above 200°C. The products of the reaction were nitrogen and small quantities of dinitrogen oxide. Oxygen was retained by the polymer. The PAN.P did not promote any reaction between NO and carbon monoxide when the two gases were passed over the polymer together. In fact an excess of carbon monoxide was found to inhibit the reaction between the NO and PAN.P.

In recent years the interest in PAN.P as a heterogeneous catalyst has decreased as shown by the very small number of papers published on this subject. Dini[29] investigated the properties of catalysts containing platinum on polymeric supports including PAN.P Similar work was carried out by Tyurenkova et al[30] using palladium on a PAN.P support. Several patents have been published citing the use of PAN.P as a catalyst.[31] There is one covering the work of Gallard[31a] and another the work of Cooper.[31b] Two Japanese patents are concerned with the production of activated carbon from PAN. In the first case[31c] PAN is carbonised to above 500°C in an inert atmosphere. The second[31d] concerns the production of activated high surface area carbon by the oxidation of a PAN + zinc chloride fibre.

In conclusion it has been found that PAN.P which has been pyrolysed to temperatures between 300 - 600°C catalyses a wide variety of reactions. The structure of PAN.P produced between these temperatures is thought to consist of annularly condensed pyridine rings as shown in Structure 3, Page 11. This structure has associated with it a large concentration of free spins which are believed to play an important part in the catalytic activity of the polymer.

1.7 Aims of the work

It was intended to investigate further the reaction between PAN.P and NO first noted by Cooper with a view to using this reaction to remove small concentrations of NO from motor vehicle exhaust gas.

The original intention was to use supported PAN.P catalyst samples as Cooper had done but to maximise the PAN.P surface area, and therefore activity, by using supports of greater surface area. However, after some preliminary investigations most of this work was carried out using PAN.P fibre as the catalyst.

PAN.P catalyst preparation and reaction conditions were to be investigated in order to optimise activity to NO. The fundamental nature of the PAN.P–NO interaction was also of interest and spectroscopic studies were to be carried out on the polymer and the products of its reaction with NO. Motor vehicle exhaust gas contains several other gases besides NO and it was intended to find out how these reacted with PAN.P both individually and in the presence of NO.

CHAPTER 2

EXPERIMENTAL

2.1 Apparatus used in the preparation of the catalyst

2.1.1 The rotary evaporator

A Buchi Rotavapour R apparatus was used to remove formdi-methylamide (DMF) solvent from a solution of polyacrylonitrile during the preparation of supported catalyst samples. A water bath was used to heat the solution while the apparatus was maintained under reduced pressure using a water vacuum line.

2.1.2 Fluidised bath

All the catalyst samples were pyrolysed using a Techne SBL2 fluidised bath in conjunction with a Sifam Pyromaxim TSA temperature controller. The bath was filled with Alundum powder (small particles of aluminium oxide) which was suitable for use at temperatures up to 700°C.

2.2 Apparatus used in studying catalytic properties

2.2.1 Fixed bed catalytic reactor

The catalytic reactor, shown in Plate 1, consisted of two identical stainless steel vessels, one of which contained the catalyst sample while the other served as a preheat chamber. A diagram of a vessel is shown in Figure 1. It measured 23 cm in length by $3\frac{1}{4}$ cm in internal diameter, and had a detachable lid which was held in place by six bolts. An asbestos gasket was placed between the lid and body of the vessel to prevent leaks. A chromel/alumel thermocouple was attached to the lid and positioned so as to measure the temperature of the catalyst sample inside the vessel. A wire gauze placed 3 cm from the outlet was used to support the catalyst pellets. At the outlet a 0.6 cm diameter stainless steel was welded to the body of the vessel.

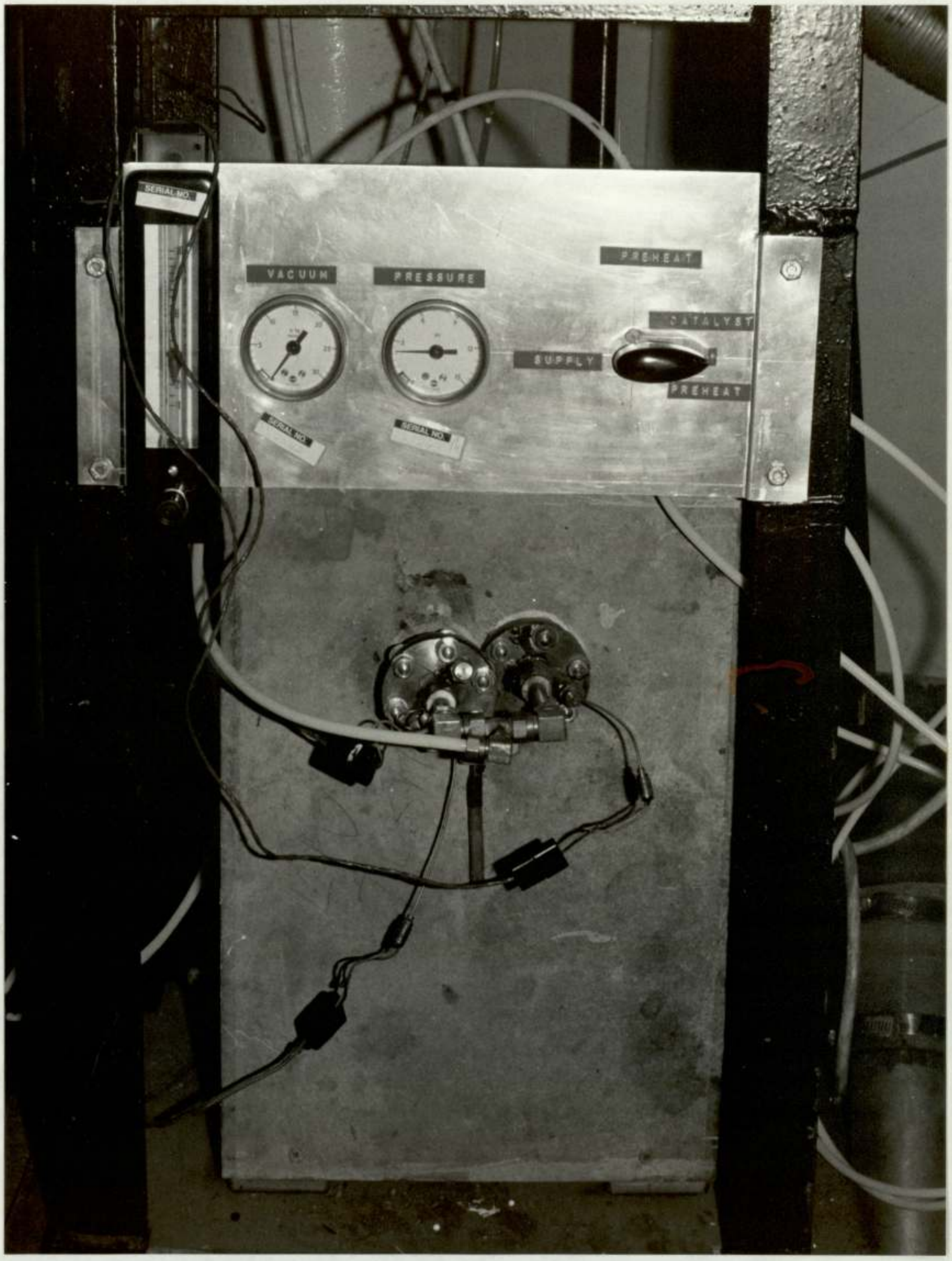
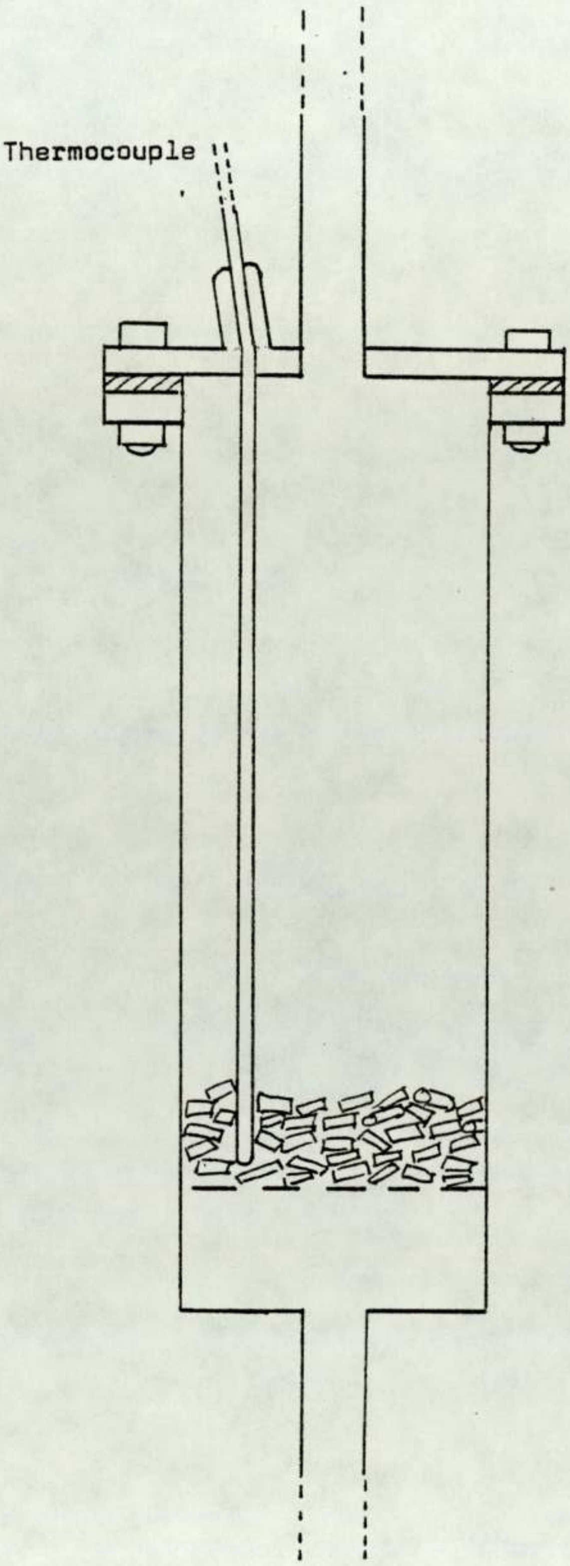


PLATE 1

THE CATALYTIC REACTOR

FIGURE 1

STAINLESS STEEL CATALYST VESSEL



The preheat vessel was filled with Procatalyse SCS 79 alumina pellets. These pellets were 3 mm diameter spheres and were considered to be inert to the gases used in these experiments. The same pellets were also used to fill up the catalyst chamber after the catalyst sample had been added.

The lids of the two vessels were connected by a 0.6 cm diameter stainless steel pipe. Both vessels were housed in a specially modified Gallenkamp electric furnace capable of temperatures of up to 1000^{0}C. The furnace temperature was controlled by a Eurotherm controller connected to a thermocouple inside the furnace.

Figure 2 shows a diagram of the whole apparatus. Outside the hot furnace area 0.6 cm diameter P.T.F.E. tubing, with $\frac{1}{4}$ inch Drallim fittings was used to transport the gases. A Drallim 4-port, 3-way valve was used to direct the gases along three different routes.

Route 1 - The gases passed directly from the supply cylinders to the analysers.

Route 2 - The gases passed through the preheat chamber and then to the analysers.

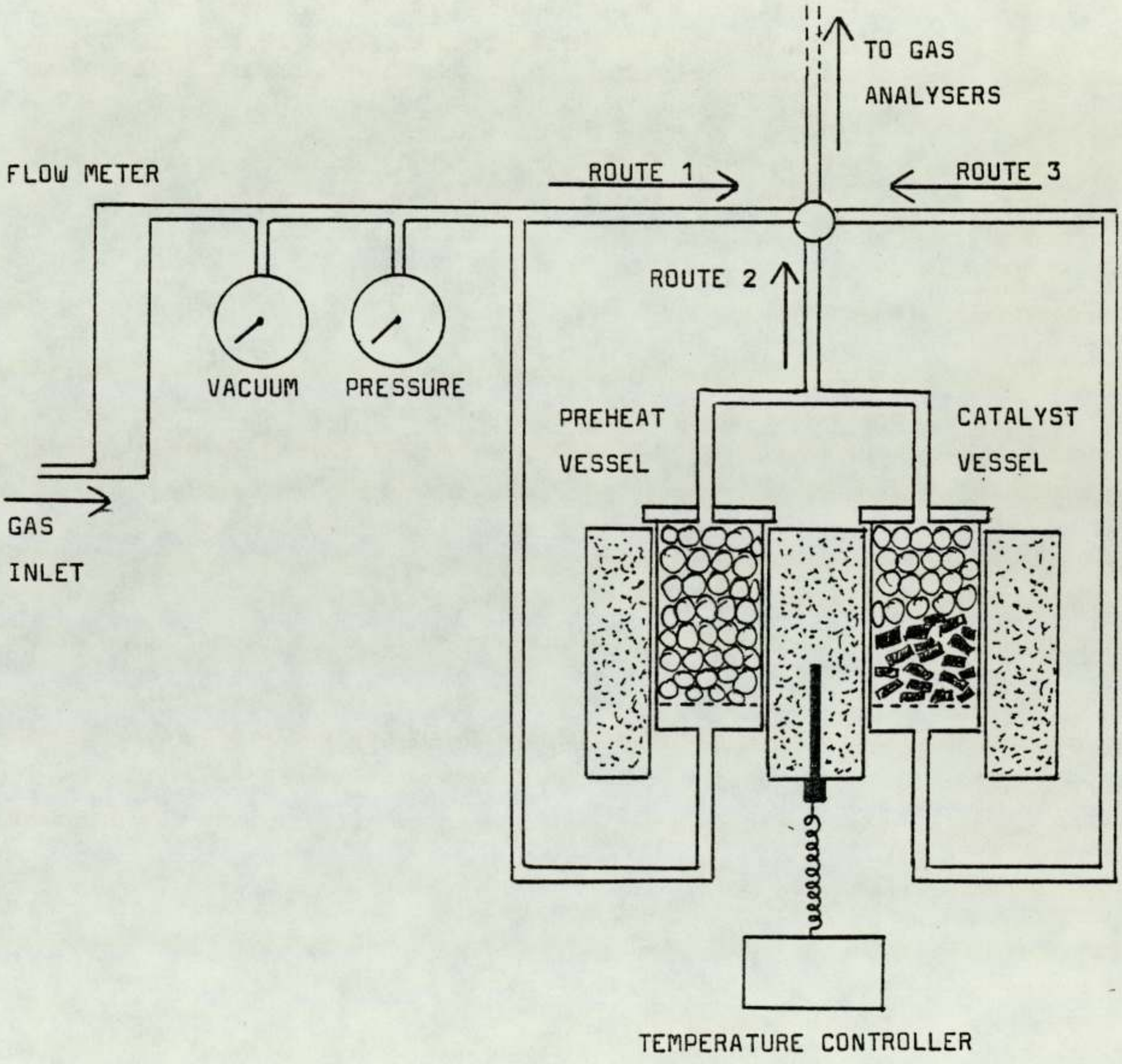
Route 3 - The gases passed through the preheat chamber and the catalyst chamber before going on to the analysers.

Comparison of the gas analysis results for routes 1 and 2 allowed any effect of the stainless steel vessel to be monitored.

Gas flow rates through the apparatus were measured on a flow meter on the inlet to the reactor. Gases were drawn to the analysers by a pump on the analyser trolley. By adjusting the pump by-pass valve and the gas supply pressure the gas pressure inside the apparatus was maintained at just above atmospheric. A pressure and a vacuum gauge were attached to the gas inlet pipe on the apparatus. The gases were maintained at a pressure above atmospheric to avoid air being sucked into the apparatus. However, too high a pressure was undesirable as toxic gases may have

FIGURE 2

DIAGRAM OF THE FIXED BED CATALYTIC REACTOR



leaked out of the apparatus.

By closing the flow meter inlet valve the apparatus could be partially evacuated using the analyser pump. The reading then obtained on the vacuum gauge gave a useful indication of any leaks which may have developed after dismantling and reassembly of the catalyst vessel.

The thermocouples inside the catalyst and preheat vessels were connected to a recorder which gave a continuous trace of the respective temperatures.

2.2.2 Gas analysers

2.2.2.1 Beckman gas analysis trolley

The gas analysers used to monitor the gases after their passage through the catalytic reactor were mounted together on a single moveable trolley; the whole unit being manufactured by Beckman. The unit was designed specially for the continuous analysis of car exhaust gases and this is reflected in the nature of the gases which could be detected and in the concentration ranges over which the instruments operated. This information is listed in Table 5. The sample gas was fed to the analysers by two electric pumps and could be simultaneously analysed for all the gases mentioned. The various instruments were connected to a six channel Mitsubushi pen recorder which provided a continuous record of the gas concentrations in the sample. It was also possible to operate each analyser independently.

2.2.2.2 NO/NO_x analyser

The Beckman model 951 NO/NO_x analyser operated by the chemiluminescent method of detection. This method is based upon the principle that NO reacts with ozone(O_3) to give oxygen and nitrogen dioxide (NO_2). About 10% of the nitrogen dioxide is in an electronically excited state (NO_2^*) and emits light when it reverts to its ground state. The intensity of this emission is proportional to the mass flow rate of

Table 5

Gas analysers used in conjunction with the fixed bed catalytic reactor

Manufacturer	Analyser	Gas monitored	Mode of operation	Concentration Range
Beckman	Model 951	NO/NO_x	Chemiluminescent	0 -2500 vpm
Beckman	Model 864	CO_2	N.D.I.R.*	0 - 4%
Beckman	Model 865	CO	N.D.I.R.	0 - 2%
Beckman	Model 400	Hydrocarbon	Flame ionisation detector	0 - 1000 vpm
Beckman	Model 715	Oxygen	Polaragraphic sensor	0 - 5%
Analytical Development Company Ltd.		CO	N.D.I.R.	0 - 0.2%
C.R. Laboratory Services		CO	N.D.I.R.	0 - 500 vpm

* N.D.I.R. = Non dispersive infrared

NO into the reaction chamber. The light emission is measured by a photomultiplier tube and associated electronics.

Ozone for the reaction is generated by passing oxygen over an ultraviolet light source.

NO_x analysis ($NO + NO_2$) is optional and is obtained by passing the gases over a hot reduction catalyst which converts NO_2 to NO.

2.2.2.3 CO/CO_2 gas analysis

Carbon dioxide (CO_2) was monitored using a Beckman model 864 Process Infrared Analyser while carbon monoxide was monitored using the 865 model of the same instrument. Both instruments operate in the same way. Infrared radiation is produced from two separate sources and passes through a chopper which interrupts both beams ten times per second. The infrared beams pass through two cells; one a reference cell containing a non-absorbing background gas, the other a sample cell containing a continuous flowing sample. The infrared beams then pass into the detector unit. This consists of two sealed chambers, each with an infrared transmitting window, separated by a flexible metal diaphragm. Each chamber is filled to the same pressure with the particular gas selected for analysis. This enclosed gas absorbs energy from the infrared beam, heats up, and expands. The gas only absorbs its characteristic wavelengths of radiation. If the same gas is present in the sample these wavelengths will be reduced in intensity in the sample beam in proportion to the concentration of the gas in the sample. The gas on the sample beam side of the detector unit will be heated less than that on the reference side. The resulting pressure difference in the two cells causes distension of the diaphragm which forms part of a variable capacitor. The capacitance change, equivalent to component concentration, is amplified and transmitted to a meter and a recorder.

2.2.2.4 Hydrocarbon analysis

Hydrocarbons in the gas stream were monitored using the Beckman Model 400 Hydrocarbon Analyser. This instrument uses the flame ionisation method to determine the concentration of hydrocarbons present in the gas stream. The flame formed when hydrogen burns contains a negligible number of ions. Introduction of traces of hydrocarbons into the flame results in a complex ionisation, producing a large number of ions. A polarising voltage applied between the burner jet and the collector produces an electrostatic field in the vicinity of the flame. The electrostatic field results in an ion migration whereby the positive ions are attracted to the collector and the negative ions to the burner jet. Thus a small current is established between the two electrodes. This current is measured by an electrometer amplifier circuit and is directly proportional to the hydrocarbon concentration in the flame.

2.2.2.5 Oxygen analysis

Oxygen was analysed using a Beckman Model 715 Process Oxygen Monitor. This instrument consists of a polarographic oxygen sensor and a solid state battery powered amplifier. The sensor contains a silver anode and a gold cathode that are isolated from the sample by a thin membrane of P.T.F.E.. An aqueous solution of potassium chloride which serves as an electrolyte is retained inside the sensor by the membrane. As P.T.F.E. is permeable to gases, oxygen from the sample diffuses through the membrane into the sensor and takes part in the following redox reaction :-

Cathode reaction $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

Anode reaction $4Ag + 4Cl^- \rightarrow 4AgCl + 4e^-$

With a D.C. voltage applied across the electrodes, oxygen in the sample will be reduced at the cathode, causing a current to flow. The magnitude of this current is proportional to the amount of oxygen present in the sample.

2.2.2.6 Instrument calibration

Calibration of the instruments was carried out using specially prepared mixtures of the appropriate gases in the required concentrations in nitrogen. A full list of the gases and their concentrations is given in section 2.7.2. The mixtures were calibrated by the suppliers and then rechecked against standard mixtures in the laboratory. White spot nitrogen was used to zero all the instruments.

2.2.2.7 Calculation of gas supply and removal rates

The recorder attached to the gas analysers provided a continuous trace of the gas concentrations in parts per million by volume (vpm) or in percent by volume of the total gas stream. The gas flow rate was measured in litres min^{-1} by a flow meter attached to the catalyst apparatus. By assuming that 1 mole of a gas occupies 24 litres at 20°C the gas flow rate in moles second^{-1} was calculated using the following formula :-

$$\text{Gas flow rate/mol s}^{-1} = \frac{\text{gas conc./vpm}}{10^6} \times \frac{\text{flow rate/l min}^{-1}}{60} \times \frac{1}{24}$$

Calculation of the rate of removal of a gas , in moles second^{-1}, was obtained by substituting the difference between the supply and outlet concentrations, in parts per million, into the above equation.

2.3 Surface Area Measurements

2.3.1 Apparatus

The nitrogen adsorption apparatus used was originally constructed by Cooper.[28] It was a modified version of the classical BET apparatus[32] similar to one used by Harris and Sing.[33]

The vacuum part of the apparatus consisted of a mercury diffusion pump and an NGN type model PSR/8 rotary backing pump. A liquid nitrogen trap was placed between the rotary and diffusion pumps. A second trap was placed between the mercury diffusion pump and the nitrogen adsorption apparatus.

In order to measure the pressure inside the nitrogen adsorption apparatus a speedivac Pirami vacuum gauge model 8/2 was used in conjunction with a G5C-2 head.

The nitrogen adsorption apparatus is illustrated in Figure 3. It was made out of borosilicate glass. Slight modifications were made to Cooper's apparatus in that the mercury manometer tube was extended to a height of 80 cm and connected directly to the vacuum line.

The volumes of the four bulbs were obtained from the mass of mercury held by each bulb at 20°C. The volume of the dead space in the apparatus on the right hand side of tap T was obtained using the bulb volumes and application of the gas laws. The dead space was filled with nitrogen at atmospheric pressure. The gas was then allowed to expand into one or more of the bulbs by lowering the mercury level. From the change in pressure the dead space volume could be calculated.

The volume of the sample holder and the dead space on the left hand side of tap T was obtained in a similar manner to that above except that helium gas was used to fill the space. The sample holder was immersed in liquid nitrogen during the measurements.

Volumes were as follows :-

Volume of bulb 1 (V_1) = 1.74 cm^3

V_2 = 2.58 cm^3

V_3 = 5.55 cm^3

V_4 = 11.25 cm^3

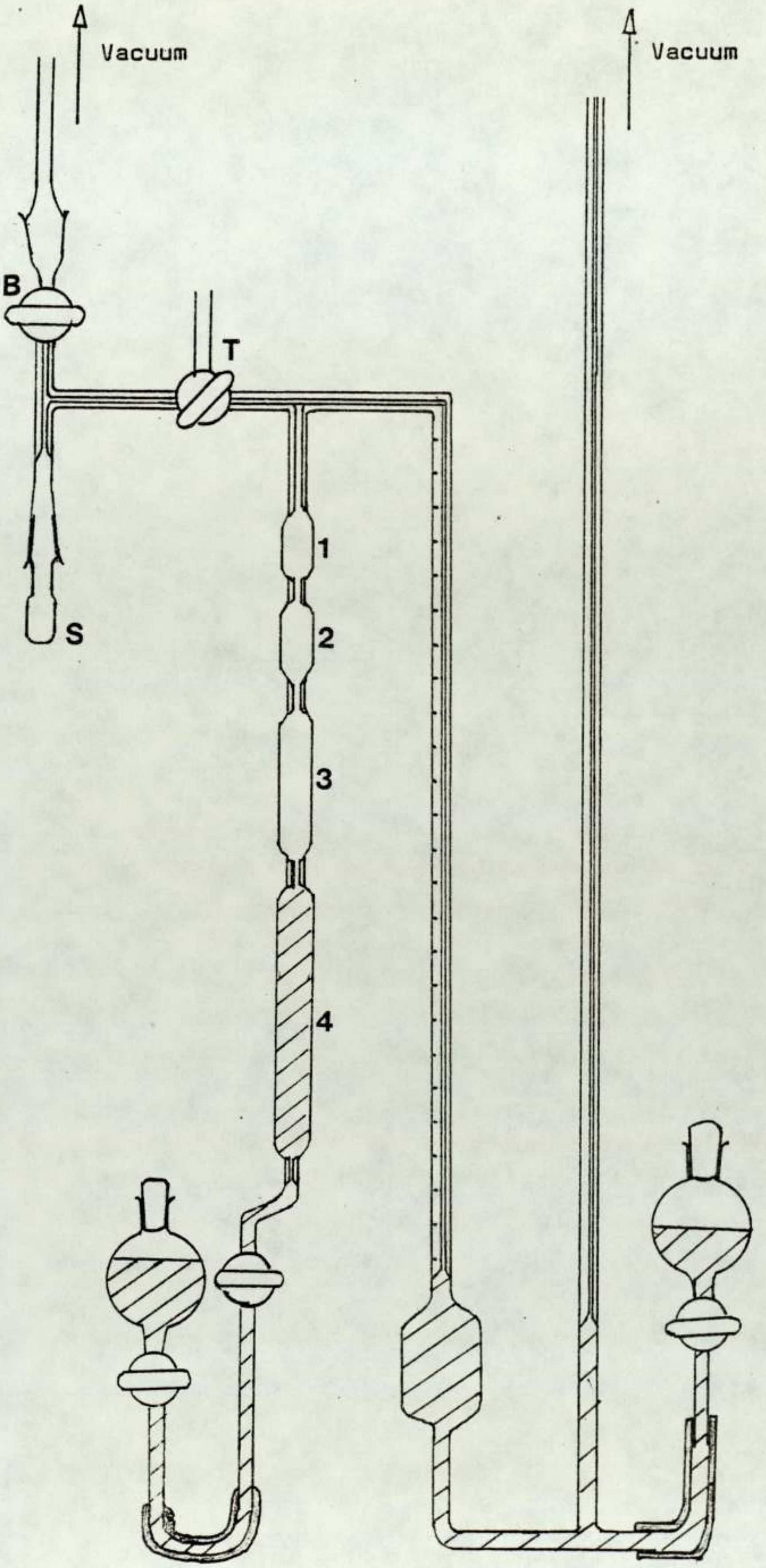
Total volume on the left hand side of tap T V_L = 6.5 cm^3

Total volume on the right hand side of tap T excluding the bulbs but including manometer V_R = 1.35 cm^3

Total volume on right hand side of tap T excluding bulbs and manometer $V_R - V_{man}$ = 0.63 cm^3

Figure 3

NITROGEN ADSORPTION APPARATUS



2.3.2 Procedure for surface area measurement

I) The sample holder, containing a pre-weighed sample, is connected to the apparatus and immersed in liquid nitrogen. V_L is measured using helium as described in section 2.3.1.

II) Tap T is closed and tap B is opened so that the sample is under vacuum. The sample is degassed by heating to 250°C until the Pirani gauge shows the pressure is 10^{-3} torr. Tap B is then closed.

III) The sample holder is allowed to cool after degassing and it is then immersed in liquid nitrogen. It is important to keep the liquid nitrogen topped up to the neck of the sample holder during the subsequent measurements.

IV) The right hand side of the apparatus is filled with nitrogen including as many of the bulbs as are required. This depends on the surface area of the sample. The level of mercury on the left hand side of the manometer is adjusted to the zero mark using the mercury reservoir. Tap T is now closed. The difference between the mercury levels on the manometer now gives atmospheric pressure. Ambient temperature should also be noted.

V) Tap T is opened to allow gas on the right hand side in to the left hand side and the sample. If any bulbs have been used the mercury level must be raised to fill them using reservoir C. The system is now left until the mercury level in the manometer is stationary. It has then reached equilibrium. The left hand manometer is adjusted to the zero mark. The difference in height between the manometer levels now gives ΔP, the equilibrium pressure.

VI) The process is now repeated from step (IV) by opening tap T to allow more nitrogen into the right hand side of the apparatus. In this way values of equilibrium pressure are obtained for increasing volumes of nitrogen adsorption by the sample.

For the first adsorption

Volume of nitrogen added $(N_1) = V_R + V_B$

Volume of nitrogen left after adsorption $= (V_R + V_L)\dfrac{\Delta P_1}{P_o}$

Volume of nitrogen adsorbed $= (V_R + V_B) - (V_R + V_L)\dfrac{\Delta P_1}{P_o}$

V_B = volume of bulbs used
ΔP = equilibrium pressure
P_o = atmospheric pressure

The volume of nitrogen adsorbed under ambient conditions was converted to STP and divided by the mass of sample used to give V_G the volume at STP adsorbed by one gramme of sample.

For the i^{th} adsorption

Volume of nitrogen added $(N_i) = N_{i-1} + (V_R + V_B) - V_R\dfrac{\Delta P_{i-1}}{P_o}$

Volume of nitrogen adsorbed $= N_i - (V_R + V_L)\dfrac{\Delta P_i}{P_o}$

2.3.3 Calculation of surface area of sample

The surface area of the sample is calculated using the BET equation.[34]

$$\frac{\Delta P}{V_G(P_o - \Delta P)} = \frac{1}{V_m C} + \frac{(C-1)}{V_m C}\frac{\Delta P}{P_o}$$

ΔP = equilibrium pressure

P_o = saturation pressure of adsorbate

V_G = volume of adsorbate adsorbed at pressure ΔP

V_m = volume of adsorbate representing a complete monolayer on the sample

$C = e^{(E_1 - E_L)/RT}$

E_1 = average heat of adsorption in the first layer

E_L = heat of liquifaction of adsorbate

For nitrogen $E_1 - E_L$ has an average value of 3,615 J mol^{-1}

A plot of $\frac{\Delta P}{V_G(P_o - \Delta P)}$ against $\frac{\Delta P}{P_o}$ gives an intercept of $\frac{1}{V_m C}$ and a slope of $\frac{C - 1}{V_m C}$.

V_m, the volume of nitrogen which forms a monolayer on one gramme of the sample can be obtained from the slope of the graph. The area occupied by one molecule of adsorbed nitrogen, as judged from the density of liquid nitrogen, is 16.2 $\mathring{A}^2$.

Thus the surface area covered by the monolayer = 4.356 V_m m^2

A typical set of results for the determination of the surface area of sample of supported PAN.P is given below.

Mass of sample = 2.23 g

Atmospheric pressure = 755 mm Hg

T K = 295

P/mm Hg	V_G/cm^{3}g^{-1}	$\frac{\Delta P}{P_o}$	$\frac{\Delta P}{V_G(P_o - \Delta P)}$
0.1	8.9	0.0001	0.2
9	17.7	0.012	6.8
82	26.5	0.108	46.0
146	29.7	0.194	80.8
206	33.5	0.270	112.0

The straight line graph obtained by plotting these results is shown in Figure 4. From the graph :-

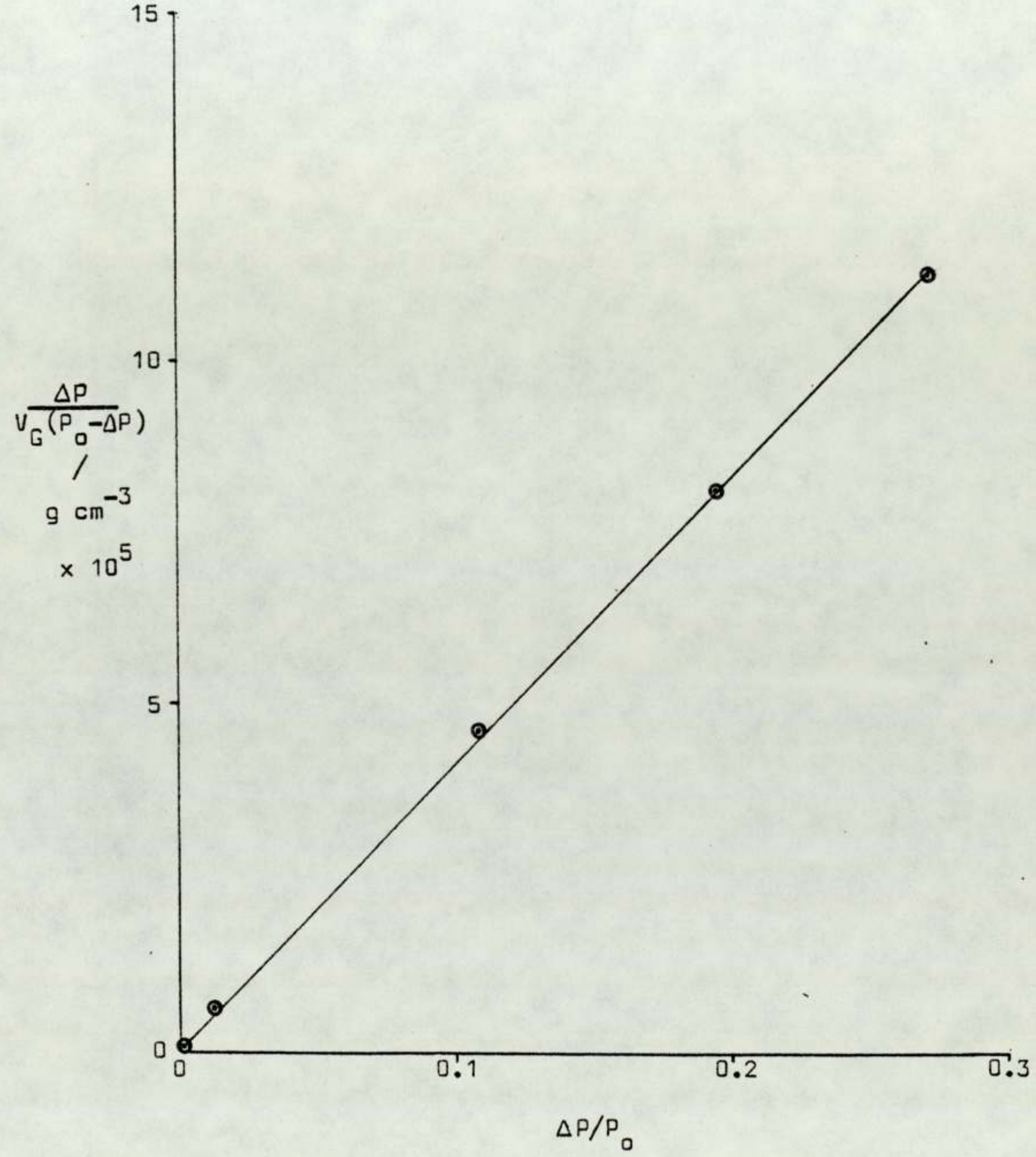
slope = 0.0409 g cm^{-3}

V_m = 24.25 cm^3 g^{-1}

Surface area = 106 m^2 g^{-1}

FIGURE 4

BET plot for nitrogen adsorption by a supported PAN.P sample



2.4 Infrared studies

2.4.1 Apparatus

2.4.1.1 Infrared spectrophotometer

Infrared spectra were obtained using a Perkin Elmer 127 Grating Spectrophotometer.

2.4.1.2 Infrared cell

An infrared cell was constructed in which the sample could be heated up to 400°C while under vacuum and a subsequent spectrum obtained without exposing the sample to the atmosphere.

A diagram of the cell is shown in Figure 5. The design is based on a cell used by Davies.[35] The cell body is made of borosilicate glass. Heating tape was wrapped around the cell body and cemented in place with sodium silicate solution. The tape was then covered with asbestos paper and asbestos string and finally with aluminium foil.

The T-piece of the cell was similar to a conventional infrared gas cell. It had a 10 cm path length and was fitted with 50 mm diameter by 6 mm wide sodium chloride windows.

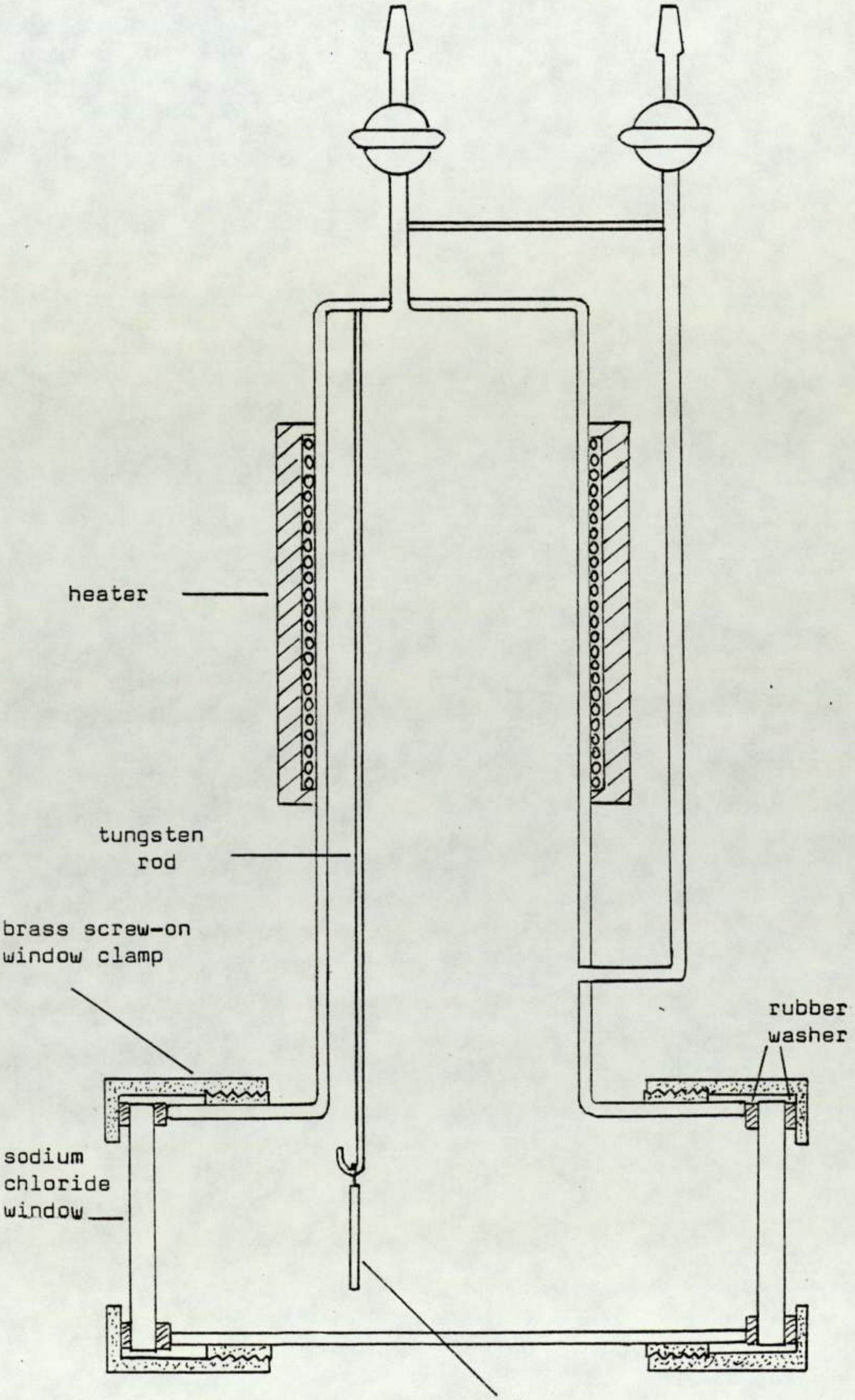
When a spectrum was being taken the cell was held vertically with the sample suspended from the hook at the end of the tungsten rod. In order to heat the sample the cell was inverted so that the sample travelled along the tungsten rod until it was inside the heater area. The cell was then held horizontally during the heating period.

The heater circuit included a variac. The temperatures obtained at different variac settings were measured by placing a chromel/alumel thermocouple inside the heater area of the cell.

The PAN.P samples whose spectra were being measured were in the form of very thin films and were very fragile. They were supported by sandwiching between two pieces of stainless steel gauze which were then stapled together. A loop of wire was attached to one end of the gauze so that it could be suspended from the tungsten rod.

Figure 5

INFRARED CELL



2.4.1.3 Multiple internal reflection spectroscopy

Multiple internal reflection (MIR) spectra were obtained using a Perkin Elmer Model 257 Grating Infrared Spectrophotometer fitted with a Model 9T single beam multiple internal reflectance attachment (Wiltec Scientific Instruments Ltd., London NW9).

The reflector plate was a KRS-5 crystal consisting of a eutectic mixture of 42 mole % of thallium bromide and 58 mole % of thallium iodide. The crystal measured 50mm by 20mm by 2mm and the exit and entrance faces were angled at 45° to the other surfaces.

The crystal surface was cleaned by washing with methanol and polishing on a felt cloth.

2.4.2 Sample preparation

Virtually all spectra of PAN and PAN.P were recorded using thin films of the polymers.

PAN films were obtained in the following way. A small quantity of a 3% solution of PAN in DMF was spread on to a glass plate. The solvent was evaporated by heating in a vacuum oven at 160°C. This left a film of PAN which could be peeled from the glass plate. Film thicknesses of 10 microns or less could be obtained in this way. Very thin films were necessary due to the very strong absorption of the PAN.P samples.

Pyrolysis of the films was carried out under vacuum in a glass tube placed in the fluidised bath or inside the infrared cell described in 2.4.1.2 . During pyrolysis and subsequent spectroscopy the films were supported between two pieces of stainless steel gauze.

2.5 Electron Spin Resonance Studies

2.5.1 Apparatus

Electron spin resonance (e.s.r.) spectra were recorded using a Japan Electron Optics Ltd.(JEOC) PE-1X type spectrometer operating in the X-band microwave region.

2.5.2 Sample preparation and spectrum measurement

When studying unsupported PAN.P, in the form of fibre or powder, 0.05g of the polymer was sealed inside a 2cm length of melting point tubing. In the few instances where supported PAN.P was studied the catalyst pellet was placed directly into the e.s.r. sample tube. The sample tube was made from 'Spectrosil' quartz tubing of 4.5mm outer diameter.

The e.s.r. instrument was operated using a modulation frequency of 100 KHz. The field was set at 3360 gauss with a scan width of ∓ 500 gauss.

2.6 Scanning Electron Microscope

The apparatus used was a Stereoscan Mark 2A produced by Cambridge Scientific Instruments Ltd.. The Stereoscan gave magnifications of 20 to 10,000 times actual size. The sample could be viewed on a cathode ray display tube and the image could be photographed.

The samples were mounted on aluminium stubs of 1cm diameter and they were then coated with a thin layer of gold and palladium to make the surface electrically conductive.

2.7 Materials

2.7.1 General chemicals

'Acrilan' polyacrylonitrile powder	Monsanto Textiles Ltd. Coleraine, N. Ireland.
'Courtelle' polyacrylonitrile fibre	Courtaulds Ltd. Coventry
Carbon fibre	Courtaulds Ltd. Coventry
Formdimethylamide	B.D.H. Chemicals Ltd. Poole

2.7.2 Gases

The following gases were supplied by British Oxygen Company. The composition of the gas mixtures was checked at the British Leyland emissions control centre in Coventry against calibrated standard gas mixtures.

Nitrogen	99.9%, oxygen free (white spot)
Nitrogen/nitrogen monoxide mixture	2000 vpm nitrogen monoxide
carbon monoxide/ carbon dioxide/ nitrogen mixture	8.5% CO / 13.5% CO_2
carbon monoxide/ nitrogen mixture	various concentrations between 80 and 2000 vpm CO
hydrocarbon/ nitrogen mixture	800 vpm propane
hydrogen/helium mixture	40% hydrogen
oxygen/nitrogen mixture	3.5% oxygen

The following gas was obtained from Air Products Ltd.

nitrogen monoxide	99%

2.7.3 Catalyst support materials

Trade name and grade	Suppliers	Chemical composition	Shape and size	Approximate surface area/m^{2}g^{-1}
Hydronyl CX0134AA03	Hydronyl Ltd. Fenton, Staffordshire.	99% alpha alumina	cylinder 3mm diameter 8mm length	10
Hydronyl CX0136AA03	" "	" "	" "	100
Procatalyse SCS79	Pechiney, Saint Gobain.	" "	sphere 4mm diameter	95
Sorbsil grade A	Joseph Crosfield Warrington, Lancashire.	silica gel	granules 3mm x 6mm	850
Celite 408	Johns Mansville GB Ltd., Richmond, Surrey.	diatomite silica	cylinder 4mm diameter 10mm length	8

CHAPTER 3

PREPARATION AND CHARACTERISATION OF THE PAN.P CATALYST

3.1 Requirements of an automobile exhaust catalyst

A successful catalyst, in addition to promoting the desired chemical reaction, must be in a physical form suited to the conditions under which it will operate. An automobile exhaust catalyst must withstand temperatures of up to 800°C together with rapid fluctuations in temperature. It will be subjected to space velocities of up to 50,000 h^{-1} and must therefore have a high attrition resistance. It must also allow the exhaust gases to flow through the catalyst bed without an excessive pressure drop. The catalyst should be long-lived. In the United States an exhaust catalyst must by law have a useful lifetime of at least 50,000 miles or 5 years.

For optimum activity a catalyst should have a high surface area to allow the maximum amount of contact between the catalyst surface and the reactant gas molecules. This also requires that the catalyst be sufficiently porous to permit rapid diffusion of the reactants to the inner surfaces.

The aim, during the preparation of the catalyst samples, was to produce a sample having a high surface area which would also withstand the high temperatures and high gas flow rates which occur in a vehicle exhaust system.

3.2 Ways of presenting the catalyst

The commercially produced polyacrylonitrile (PAN) obtained for use in this work was in powder form and as such was unsuitable for use as a catalyst which would be subjected to high gas flow rates. Other workers have compressed PAN into pellets[24,25] prior to pyrolysis but such pellets are likely to have low attrition resistance. PAN has also been deposited on to inorganic support pellets which are then heated to give a coating of the catallytically active PAN.P.[28] This technique of spreading the catalyst over a support is used in the manufacture of commercial exhaust catalysts. It uses a minimum amount of the expensive catalytic component and provides a refractory, high surface area and attrition resistant base for the catalyst. These factors, and especially the possibility of obtaining a high surface area, and thus more active, catalyst favoured the use of a supported catalyst.

3.3 Supported Catalyst

3.3.1 Choice of support

Supports are commercially available in either pellet or monolith form. The monolith is a single unit with a honeycombe structure of narrow channels. The monolith must be specially shaped to fit into the catalyst chamber to ensure that gases flow through and not around it. For this reason, together with problems of polymer deposition and surface area measurement when using monoliths, only pellets were examined. Details of the various catalyst support pellets which were examined are given in section 2.7.3.

3.3.2 Deposition of the polymer on to the support

Cooper[28] examined different methods of depositing the PAN polymer on to the inorganic support and found that the use of a solution of PAN in formdimethylamide (DMF) gave the best results. A similar technique was used in this work.

The DMF was purified by distillation before being used to prepare solutions of PAN in DMF. Oven dried support pellets were soaked in this solution overnight. The DMF solvent was then removed by rotary evaporation under reduced pressure while heating the solution and pellets at 90 – 100°C in a water bath. The resulting PAN coated pellets were pyrolysed for two hours at 260°C under vacuum and then for a further four hours at the desired pyrolysis temperature under vacuum. Samples were also prepared in which the initial pyrolysis at 260°C was carried out in air. The quantities of materials used to produce a batch of catalyst pellets were as follows :-

8g PAN
92g DMF
90g support pellets

These ratios are similar to those used by Cooper[28] in his final formulation for catalyst production. The quantities of PAN and DMF were later varied in an attempt to improve catalyst activity.

3.3.3 Visual evaluation of the supported catalyst samples

The initial PAN coating on the support pellets was transparent and invisible to the naked eye. After pyrolysis it was transformed in to black PAN.P. The support pellets were white or light brown in colour and the PAN.P coating was therefore clearly visible. Plate 2 shows the various supports in their initial states and after polymer deposition and pyrolysis. A list of the supports shown in Plate 2 and the pyrolysis conditions used is given in Table 6. All the samples, irrespective of support, which had been pyrolysed under vacuum had an even and complete exterior coating of PAN.P. However, where the initial pyrolysis at 260°C had been carried out in air, as for sample b, the polymer coating was patchy and flaky. This suggested

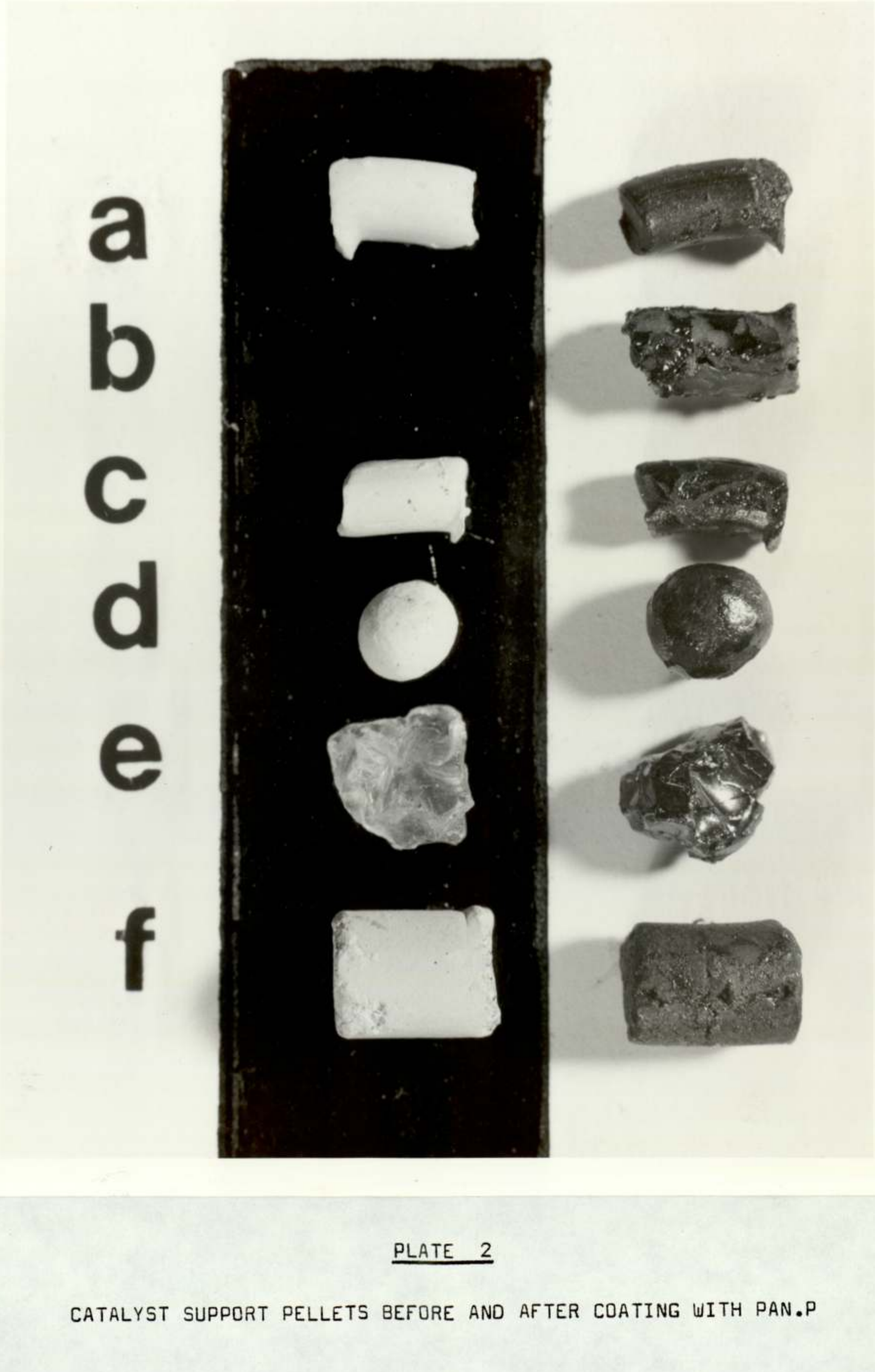


PLATE 2

CATALYST SUPPORT PELLETS BEFORE AND AFTER COATING WITH PAN.P

Table 6

The supported PAN.P catalyst samples shown in Plate 2 and the conditions of their pyrolysis

Sample	Name of support	Chemical nature of support	Approximate surface area / m^2g^{-1}	Pyrolysis conditions $^T/_{^oC}$ / Time hours / Atmos.
a	Hydronyl CX0136	Alumina	100	260 / 2 / vacuum 400 / 4 / vacuum
b	" "	" "	"	260 / 2 / air 400 / 4 / vacuum
c	Hydronyl CX0134	" "	10	260 / 2 / vacuum 400 / 4 / vacuum
d	Procatalyse	" "	80	260 / 2 / vacuum 400 / 4 / vacuum
e	Sorbsil	Silica gel	600	260 / 2 / vacuum 400 / 4 / vacuum
f	Celite	Diatomaceous silica	10	260 / 2 / vacuum 400 / 4 / vacuum

the reaction of PAN with oxygen, which occurs at temperatures above 160°C, affected the adhesion of the polymer to the support.

A complete coating of PAN.P on the exterior of the support pellet provided only a partial indication of good polymer deposition. The support pellets had a very porous structure. Most of the surface area of the support was made up of the surfaces of these pores in the interior of the pellet. This meant that to utilise the large surface area of the support the polymer had to be deposited throughout the bulk of the pellet. A visual assessment of PAN.P penetration into the pellets was made by splitting each pellet in half and examining its cross-section. Plate 3 shows cross-sections of coated support pellets prepared under various conditions. Table 7 lists the type of support shown and the details of polymer deposition.

Samples a_1, a_2 and a_3 were prepared using an 8% solution of PAN in DMF as recommended by Cooper. As can be seen only partial penetration of the polymer into the support was achieved. It was thought that the high viscosity of the 8% PAN solution might be hindering its penetration of the pellets and 5%, 3% and 2% PAN solutions were also tried. Hydronyl CX0136AA03 pellets were used for these experiments. Due to difficulties in handling the large quantities of solution involved, the total mass of PAN used was not kept constant but was decreased in proportion to the strength of the solution. Thus with an 8% solution 8g PAN was used to coat 90g support pellets and with a 5% solution 5g PAN was used to coat the same mass of pellets. This did not affect the external appearance of the pyrolysed pellets but as samples b_1 and b_2 in Plate 3 show, the pellets treated with the more dilute PAN solutions were lighter in cross-section. They were therefore less effectively coated with PAN.P than sample a_1 which was treated with an 8% solution. Sample b_3 was repeatedly soaked in a 2% PAN solution

Table 7

Samples of supported PAN.P shown in Plate 3 and their conditions of preparation

Sample	Name of support	Conditions of preparation
a_1	Hydronyl CX0136	8% solution of PAN in DMF
a_2	Hydronyl CX0134	" "
a_3	Celite 408	" "
b_1	Hydronyl CX0136	5% solution of PAN in DMF
b_2	" "	3% " " "
b_3	" "	2% solution of PAN in DMF with repeated soaking and pyrolysis
c_1	" "	8% solution of PAN in DMF which had been refluxed with sodium cyanide
c_2	Hydronyl CX0134	" " " "
c_3	Hydronyl CX0136	Sample a_1 reacted with NO at 500°C
d_1	" "	8% solution of PAN in DMF and pyrolysed in a stream of nitrogen*
d_2	Hydronyl CX0134	" " " " " " " "

Note* All the samples listed above, except d_1 and d_2, were pyrolysed for 2 hours at 260°C under vacuum and then for a further 4 hours at 400°C under vacuum. Samples d_1 and d_2 were treated similarily except that pyrolysis was carried out in a stream of nitrogen.

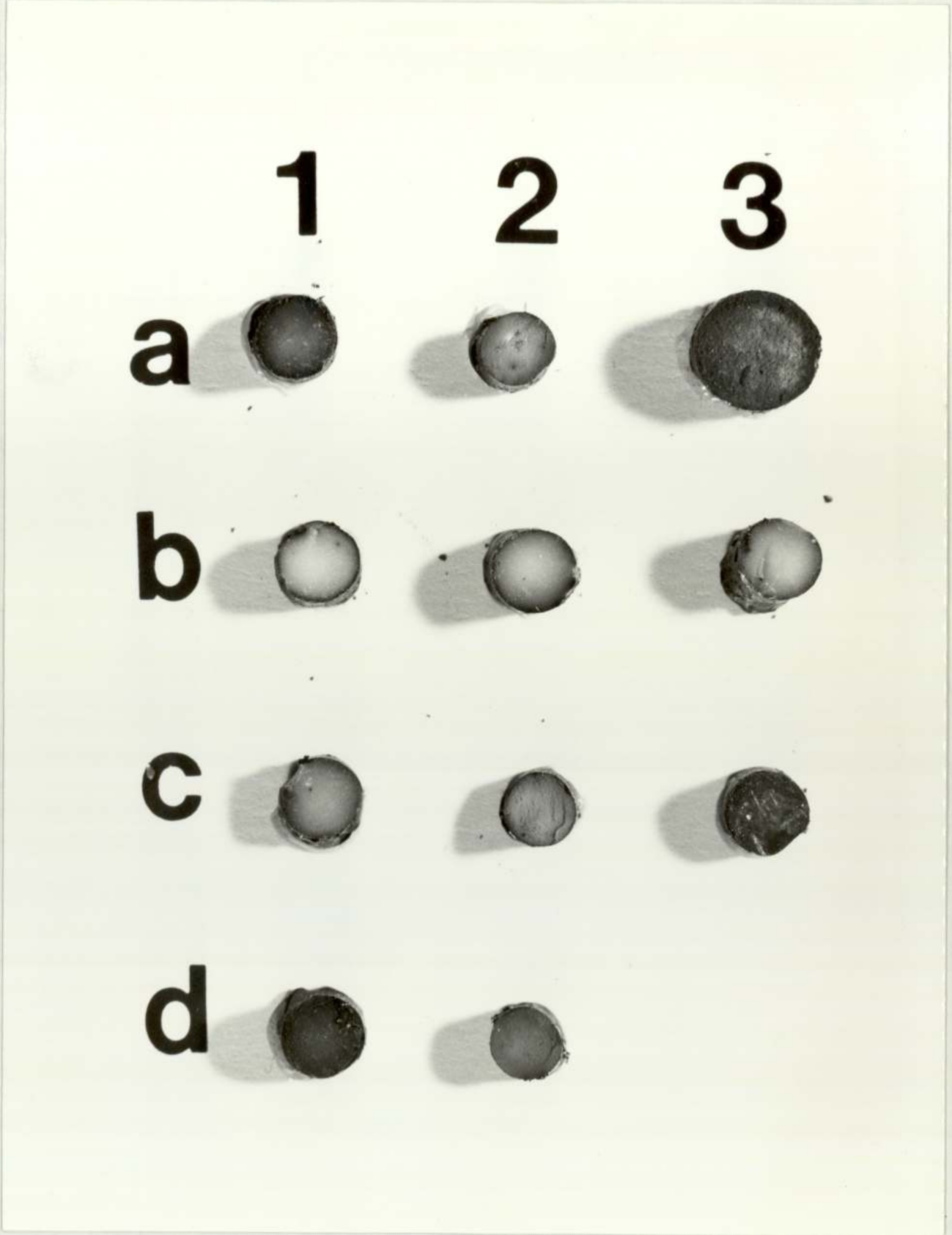


PLATE 3

CROSS-SECTIONS OF SUPPORT PELLETS AFTER COATING WITH PAN.P pyrolysed, and then soaked in more 2% solution until the full 8g of polymer had been applied to the pellets. However this did not improve the penetration of the PAN.P into the interior of the pellets.

It was also possible that the size of the polymer molecules was hindering the penetration of the polymer into the pores of the pellets. Depolymerisation of the PAN molecules would reduce the molecular size and the solution viscosity without any need to reduce the concentration of the solution. Potter[36] found that refluxing PAN solution in DMF with sodium cyanide reduced the viscosity of the solution to one third of its original value. The sodium cyanide caused oligomerisation of the nitrile groups in the PAN similar to that produced by low temperature pyrolysis of the polymer and also caused some chain scission. As this reaction did not appear to adversely affect the subsequent pyrolysis of the PAN it was used to depolymerise some of the polymer. 0.5g of sodium cyanide was added to 80g of an 8% solution of PAN in DMF and the solution was refluxed for one hour. The support pellets were soaked in this solution overnight and then processed in the usual way. After pyrolysis these pellets were visually identical with those prepared from a standard 8% PAN solution. Their cross-sections, as can be seen from samples c_1 and c_2 in Plate 3, are slightly lighter than those of samples a_1 and a_2 indicating that PAN penetration into the pellets was not improved by depolymerisation as was hoped.

Finally samples d_1 and d_2 were prepared under similar conditions to samples a_1 and a_2 except that pyrolysis was carried out under nitrogen instead of under vacuum. It can be seen that d_1 and d_2 are much darker in cross-section than the previous samples. It seems likely that this darkening of the pellets was caused by diffusion of low molecular weight PAN.P fragments into the pellets during pyrolysis. These fragments, chemically similar to PAN.P, and produced by chain scission reactions, would have been removed when pyrolysis was carried out under vacuum.

These results indicate that deposition of PAN on to the support pellets from solution only succeeds in coating the exterior surface of the pellet. Diffusion of gaseous PAN.P fragments into the pellets during pyrolysis under nitrogen appears to coat the interior of the pellets more successfully. If these fragments are catalytically active this may prove to be an effective method of producing a high surface area supported catalyst using the commercially available PAN copolymers.

3.4 Unsupported catalyst

3.4.1 PAN.P granules

It was decided to prepare some unsupported PAN.P catalyst samples from the PAN powder to compare with the supported catalyst samples. A 20% solution of PAN in DMF was extruded into water from a 3mm internal diameter glass tube. The resulting lengths of solid PAN were washed in running water for an hour to coagulate them fully before cutting into 6mm long pellets. These were then pyrolysed for 2 hours at 260°C either under vacuum or in air prior to a final pyrolysis of 4 hours under vacuum at the selected higher temperature. The resulting PAN.P granules are shown in Plate 4.

3.4.2 PAN.P fibre

Polyacrylonitrile copolymers are widely used for the commercial production of textile fibres. PAN in fibre form has a relatively large surface area compared to non-porous pellets or spheres and would be suitable for use in a heterogeneous gas reaction. It was therefore decided to prepare and test some PAN.P fibre made from commercially available PAN fibre. Some 3.3 decitex 'Courtelle' continous filament PAN fibre was obtained and attempts were made to

P ANP GRANULES

PANP FIBRE

PLATE 4

UNSUPPORTED PAN.P SAMPLES

pyrolyse this directly. However, when the fibre was heated above about 220°C it disintegrated into an amorphous mass due to the very exothermic reaction which the PAN undergoes at this temperature. This occurred even under the most gradual heating. In the commercial production of carbon fibre from 'Courtelle' the polymer is pre-heated in air to stabilise the fibre structure.[8] The 'Courtelle' fibre was therefore heated at 210°C in air for 2 hours before further pyrolysis. This treatment allowed the fibre to be heated above 220°C without it disintegrating and some samples of PAN.P fibre were obtained.

A quantity of commercially prepared oxidised 'Courtelle' fibre, which is used in the manufacture of carbon fibre, was also obtained. This had been prepared by heating 3.3 decitex continuous filament 'Courtelle' fibre in a draught oven, under tension, at 210°C for 2 hours. This oxidised 'Courtelle' fibre was converted into PAN.P simply by heating it under vacuum to the desired temperature and it was therefore used to prepare all the PAN.P fibre used in this work unless otherwise stated. A sample of PAN.P fibre is shown in Plate 4.

3.5 <u>Surface area measurements on the catalyst samples</u>

One of the aims of the catalyst preparation work, described in the previous section, was to maximise the catalyst surface area as the activity per unit mass of a heterogeneous catalyst increases with increasing surface area. It was therefore desirable to know the surface areas of the various samples. It would then be possible to compare the effectiveness of the different methods of preparation and later enable the activity of the samples to be expressed in terms of unit surface area.

The BET method, described in section 2.3, was used to measure the surface area of the samples. This technique was satisfactory for unsupported catalyst samples but was less useful for supported catalyst samples as it does not differentiate between catalyst surface and inert support surface. This can be achieved by using an adsorbate which is chemisorbed by the catalyst only. However this approach was not attempted in this work.

3.5.1 Supported catalyst samples

The deposition of a catalytic material on to a high surface area inert support is a well established technique for obtaining a high surface area of active material. Although it was not possible to differentiate between the surface areas of the PAN.P and the support using the BET method it was of interest to see if the surface area of the support changed when it was coated with PAN.P.

The BET surface areas of three different supports before and after coating with PAN.P are given in Table 8. The results for the uncoated support pellets Hydronyl CX0136AA03, Hydronyl CX0134AA03 and Sorbsil silica gel were within ±5% of the approximate surface areas given by the manufacturers. The surface area of the Sorbsil silica gel decreased after deposition of the polymer. This was probably because the PAN.P blocked some of the pores of the high surface area support. The two Hydronyl alumina supports showed a slight increase in surface area after treatment with the polymer. The surface areas increased further when the samples were pyrolysed to a higher temperature as shown in Table 8. These changes were most marked for the lower surface area Hydronyl CX0134AA03 support. Some of the untreated support pellets were heated to 600°C but this had no significant effect on their surface area indicating that the increase in surface area must have been associated with the catalyst. As noted during the visual assessment of the supported catalyst samples described in section 3.3.3, the polymer did not appear to

Table 8

BET surface areas of supported PAN.P samples

Type of support	Surface area / m^2g^{-1}			
	Uncoated support	PAN.P coated support pyrolysed at 400°C	600°C	
Hydronyl CX0136	100 (100)*	106	110	pyrolysed under vacuum
Hydronyl CX0134	9.9 (10)	10.8	12.1	
Sorbsil silica	823 (850)	706		
Hydronyl CX0136	100 (100)	109	112	under nitrogen

* Figures in brackets are approximate surface areas of supports supplied by the manufacturers.

Table 9

Estimated surface areas of PAN.P coating on samples of supported PAN.P

Type of support	Surface area of PAN.P coating/ m^2g^{-1}		
	Pyrolysis temperature		Pyrolysis
	400°C	600°C	atmosphere
Hydronyl CX0136	6	10	vacuum
" "	9	12	nitrogen
Hydronyl CX0134	0.9	2.2	vacuum

penetrate far into the bulk of the support pellet but formed a coating around its exterior. The increase in surface must have been due to this added coating of polymer with the surface area of the support remaining intact. The outer PAN.P coating must have been porous or the surface area of the support would have been greatly reduced.

If it is assumed that the difference in surface area between the uncoated and PAN.P coated pellets is due to the polymer coating then the surface area of the PAN.P alone can be calculated as shown in Table 9. The higher surface area Hydronyl CX0136AA03 support then gave the greatest PAN.P surface area and this was increased by raising the pyrolysis temperature or by pyrolysing in nitrogen rather than under vacuum. The maximum surface area obtained for the PAN.P was 12 m^2g^{-1} for the Hydronyl CX0136AA03 sample which had been pyrolysed at 600^{o}C in nitrogen. This was still a very low surface area for a catalyst.

3.5.2 Unsupported PAN.P

Results for the BET surface area measurements of various samples of unsupported PAN.P are given in Table 10.

Table 10

BET surface areas of unsupported PAN.P samples

Nature of sample	Surface area/ m^2g^{-1}	
	Before pyrolysis	After pyrolysis at 400^{o}C under vacuum
Monsanto PAN powder	7.1	Too low to measure
'Courtelle' PAN fibre	0.18(calculated)	" "
PAN granules		" "

All the unsupported PAN.P samples had very low surface areas. The volume of nitrogen adsorbed by the samples was too small to be measured on the BET apparatus. This problem was compounded by the low density of the samples which meant that only a small mass of sample could be contained in the sample tube. The BET apparatus was capable of measuring surface areas down to 1 m^2g^{-1}. The unsupported PAN.P must therefore have had a surface area of less than this. Calculation of the surface area of the 'Courtelle' fibre assuming each 3.3 decitex filament to be a non-porous cylinder gave a result of 0.18 m^2g^{-1}. The 'Monsanto' PAN powder had a measured surface area of 7.1 m^2g^{-1} but after pyrolysis at 400°C under vacuum the surface area had become too small to measure. Apparently the very small PAN particles had agglomerated during pyrolysis to form much larger PAN.P particles.

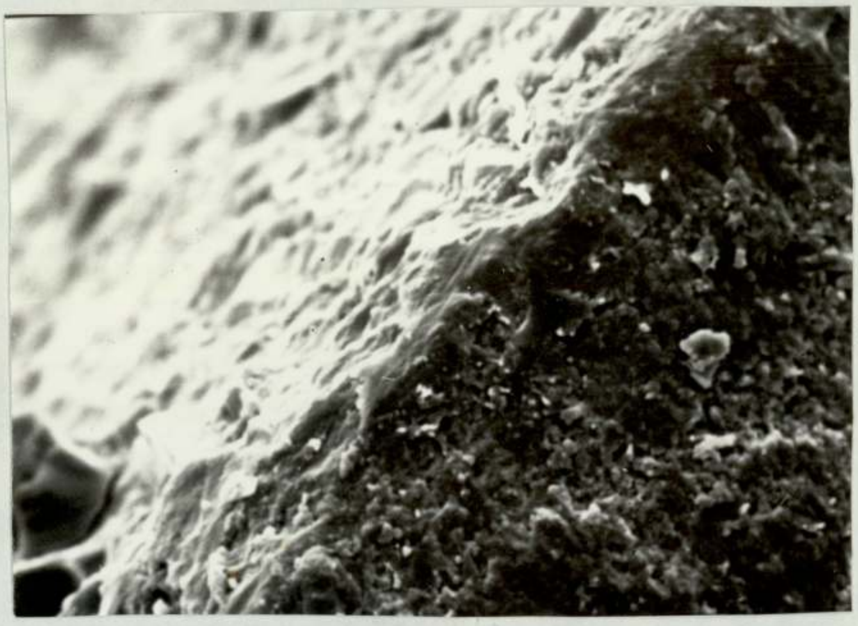
3.6 Scanning Electron Microscope studies of the PAN.P samples

The scanning electron microscope allowed a direct visual assessment of the catalyst surface. It was used mainly to study the supported catalyst samples in order to ascertain the nature and extent of PAN.P deposition on to the support. All catalyst samples were pyrolysed to 400°C unless otherwise stated.

Electronmicrographs 5.1, 5.2, and 5.3 in Plate 5 show the surfaces and cross-sections of three different PAN.P treated support pellets. The cylindrical pellets were split in half to expose their interior structures and are viewed at a point on the circumference of the exposed face. Plate 5.1 shows a 'Celite' 408 diatomaceous silica support pellet whose surface area was approximately 8 m^2g^{-1}. It is viewed from directly above the exposed cross-section. The pores of the support are clearly visible and measure between 1 and 3 microns in diameter.

5.1
Cross-section of diatomaceous silica pellet coated with PAN.P

x 1500



5.2
Cross-section of CX0134 alumina pellet coated with PAN.P

x 600

5.3
Surface of CX0136 alumina pellet coated with PAN.P

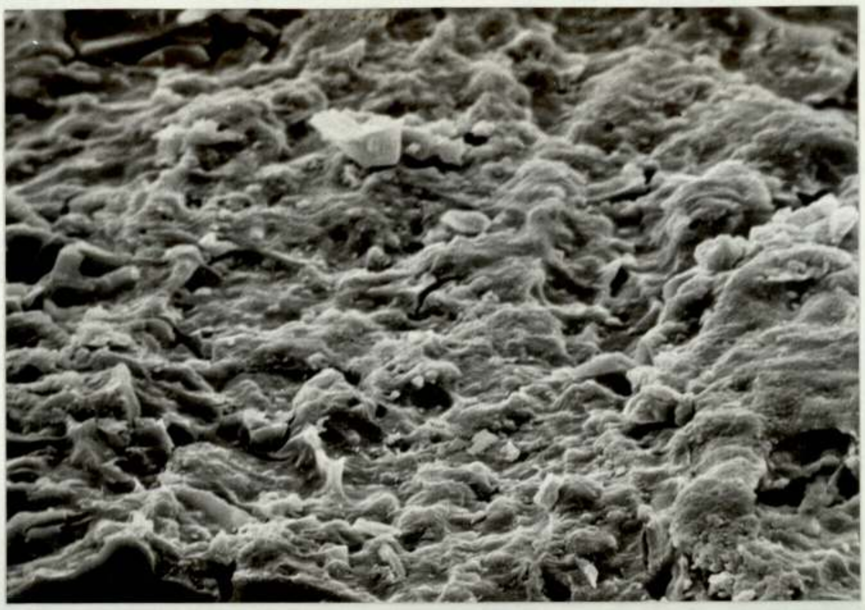
x 550

PLATE 5 ELECTRONMICROGRAPHS OF SUPPORTED PAN.P PELLETS

A layer of PAN.P about 3 microns deep can be seen on the outer surface of the support pellet. The open pores directly below this layer suggest that the PAN.P did not penetrate very far into the support. However this is difficult to assess as a thin coating of PAN.P inside the pores would be difficult to distinguish. The darkening of the pellet cross-section as described in section 3.3.3 was a more reliable guide to PAN.P penetration.

Electronmicrograph 5.2 shows a Hydronyl CX0134AA03 alumina pellet whose surface area was 9.9 m^2g^{-1}. The exterior surface of the pellet is to the left and the exposed interior surface to the right of the picture. The granular, porous nature of the interior is visible although the individual pores are too small to be seen. Again the exterior coating of PAN.P is clearly visible .

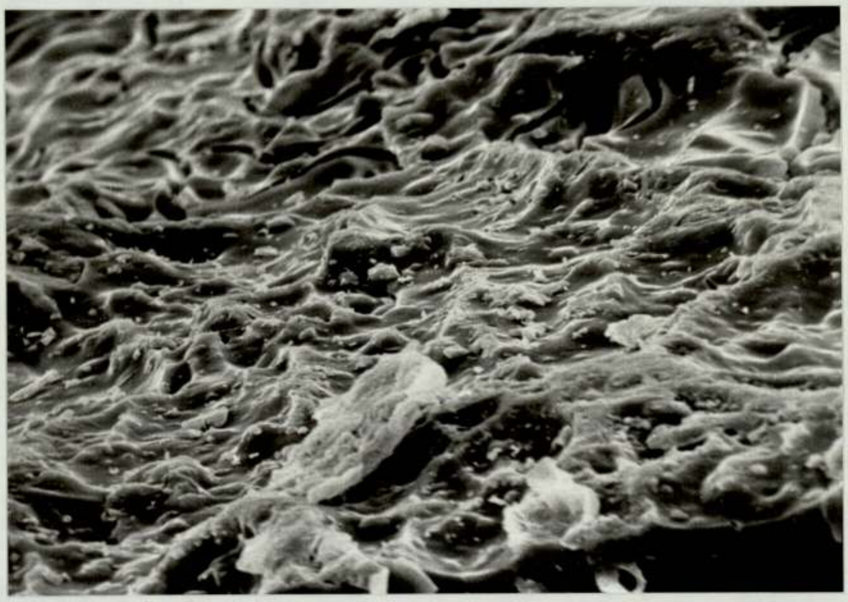
Electronmicrograph 5.3 shows a Hydronyl CX0136AA03 alumina support pellet whose BET surface area was 100 m^2g^{-1}. The exposed cross-section of the pellet is just visible at the bottom of the picture. The inner surface is much smoother than for the other two pellets due to the much smaller pore size of this high surface area support. Most of the plate is taken up with the outer PAN.P coated surface of the pellet. The cracks which are visible in the PAN.P coating are caused by shrinkage of the polymer during pyrolysis. This particular pellet had a thicker than usual coating of polymer. This occurred with pellets touching the sides of the glass container during rotary evaporation of the PAN solution as the solution was forced to the outside by the rotation. Electronmicrograph 6.2 shows a similar pellet with a more normal coating of PAN.P. It can be seen that in Electronmicrograph 5.3 the thicker PAN.P coating has obliterated much of the rugosity of the original surface. The same effect can be seen to a lesser extent by comparing the surface of the uncoated Hydronyl CX0136AA03 pellet in



6.1

Surface of CX0136 alumina support pellet

x 560



6.2

Surface of CX0136 alumina support pellet coated with PAN.P and pyrolysed to 400°C

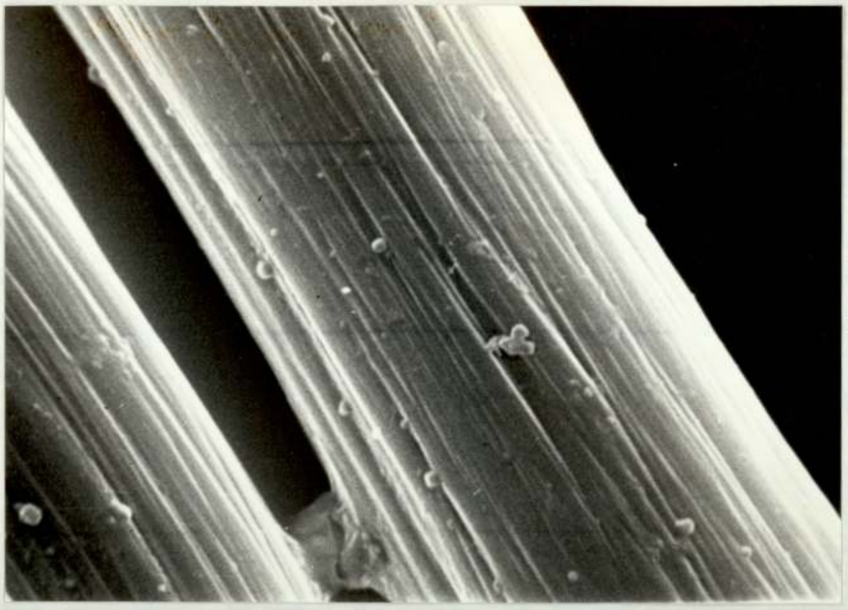
x 550

6.3

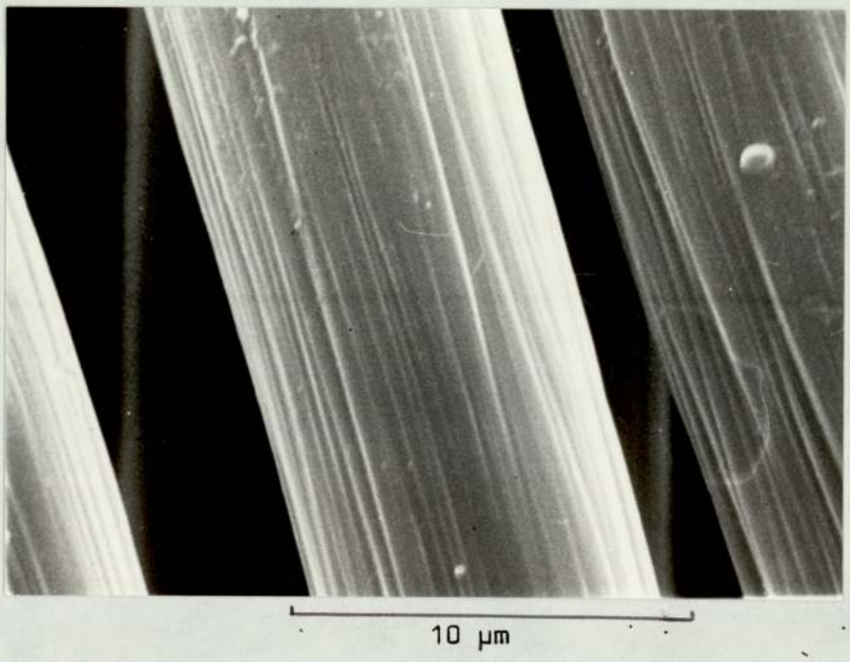
Surface of CX0136 alumina support pellet coated with PAN.P and reacted with NO at 500°C

x 600

PLATE 6 ELECTRONMICROGRAPHS OF SUPPORTED PAN.P SAMPLES



7.1
PAN.P fibre
pyrolysed to
600°C
x 5,400



7.2
PAN.P fibre, as
above, and after
reaction with NO
at 600°C
x 5,400

<u>PLATE 7</u> ELECTRONMICROGRAPHS OF PAN.P FIBRE

Electronmicrograph 6.1 with the slightly smoother surface of the PAN.P coated surface in Electronmicrograph 6.2.

Electronmicrograph 7.1 shows a filament of PAN.P fibre which had been pyrolysed to 600°C under vacuum. The fibre has a cylindrical shape and the surface striations were presumably produced when the original PAN fibre was spun by extrusion through a small hole in a metal jet.

CHAPTER 4

INVESTIGATION OF THE INTERACTION BETWEEN NO AND PAN.P USING A CONTINUOUS FLOW FIXED BED CATALYTIC REACTOR

This chapter covers a wide range of experimental work involving the interaction of NO with PAN.P in the catalytic reactor. Initially it was necessary to select the best PAN.P sample of those prepared, for use in these experiments. This was done by comparing their initial rates of NO removal in the catalytic reactor. The selected sample was then used in an investigation of the effect of reaction variables on the initial rate of NO removal. The change in NO removal rate with time at constant temperature was also studied as this gave important information about the lifetime of the PAN.P catalyst.

The work was made more complex than anticipated by the discovery that the PAN.P structure contained oxides which inhibited the reaction with NO. These oxides could be removed from the PAN.P by heating the latter in an inert atmosphere. The activity of the 'clean' PAN.P to NO was then investigated.

Finally the gaseous products of the PAN.P and NO interaction were studied as these could provide information about the mechanism of the reaction.

The reactions were carried out in a specially constructed catalytic reactor and the inlet and outlet gas streams were monitored using continuous flow gas analysers (see Chapter 2 section 2). The concentration of NO used in these experiments was similar to that found in motor vehicle exhaust gas.

4.1 Activity of the PAN.P catalyst samples to NO

The various supported and unsupported catalyst samples whose preparation is described in Chapter 3 had been assessed for surface area and appearance but their real effectiveness could only be measured by reaction with nitrogen monoxide in the catalytic reactor.

All the PAN.P samples used in this preliminary investigation had been pyrolysed at 400°C for 4 hours. They were heated to 500°C in the catalyst vessel of the catalytic reactor and a mixture of 2,000 vpm NO in nitrogen was passed through at a rate of 4 litres minute^{-1}. The initial rate of NO removal was recorded.

4.1.1 Effect of preparation conditions on the reactivity of the supported PAN.P samples to NO

The supported PAN.P samples were prepared by depositing PAN on to the support pellets from solution and then pyrolysing. Using Hydronyl CX0136AA03 support pellets, attempts were made to improve the deposition of the polymer on to the support. This was done by varying the concentration of the solution of PAN in DMF or by altering the procedure in some other way as described in Chapter 3 section 3. A visual assessment of PAN.P deposition on to the support has already been described in the above-mentioned section. These samples were now tested for their ability to remove NO. Table 11 shows the initial rate of NO removal by each of the samples. The results show that the samples prepared with an 8% solution of PAN in DMF gave the greatest initial NO removal rates and this appears to be the optimum solution concentration. Increasing the solution concentration to 10% did not give any further improvement possibly because excess PAN.P flakes off the pellets during pyrolysis. Depolymerisation of the PAN by sodium cyanide prior to its deposition on to the pellets did not improve the NO removal rate either. However, pyrolysis of the PAN

Table 11

The effect of Preparation conditions on the initial rate of NO removal by supported PAN.P samples

Reaction conditions

Support: Hydronyl CX0136AA03

Pyrolysis: 4 hours at 400°C under vacuum(unless otherwise stated)

Temperature: 500°C

Input gas mixture: 2,000 vpm NO in nitrogen

Gas flow rate: 4 litres min^{-1}

Mass of sample: 20 g

Results

Concentration of PAN solution in DMF % by mass	Other changes in preparation procedure	Initial NO removal rate / $mol\ s^{-1} \times 10^{9}$
2	Repeated soaking and pyrolysis of the pellets.	1248
5		1024
8		1658
8	PAN solution treated with sodium cyanide	1640
8	Pyrolysed in nitrogen	1731
10		1620

coated pellets in nitrogen rather than under vacuum did produce a significant improvement in NO removal rate.

These results correlate well with the degree of colouration of the pellet cross-section as shown in Plate 3. The darker the cross-section the greater the initial NO removal rate.

4.1.2 Comparison of the initial NO removal rates for the various supported and unsupported PAN.P samples

In the previous section the conditions for supported catalyst preparation which gave optimum NO removal were established using Hydronyl CX0136AA03 support pellets. These conditions, namely using an 8% solution of PAN in DMF and pyrolysing in nitrogen, were now used to prepare supported catalyst samples using a variety of inorganic supports. The activity of these samples to NO was then tested in the catalytic reactor. Some samples of unsupported PAN.P in the form of PAN.P fibre and PAN.P granules were also tested. The results for the initial rate of NO removal by these various samples are given in Table 12.

The results show that there is no correlation between the surface area per gramme of the catalyst samples as measured by nitrogen adsorption and their NO removal rate. This is because the measured surface area includes both PAN.P surface area and inert support surface area. The high surface area 'Sorbsil' silica gel gave the lowest NO removal rate probably because the polymer did not penetrate into the very small pores of this support but merely formed a film around its exterior. As the support was smooth and glass-like the PAN.P coating would have had a very low surface area.

The 'Celite' 408 diatomaceous silica supported sample gave the best NO removal rate of the supported samples although it had one of

Table 12

The Initial rate of NO removal by various supported and unsupported PAN.P samples

Reaction conditions

Pyrolysis: 4 hours at 400°C in nitrogen for supported PAN.P samples
4 hours at 400°C under vacuum for unsupported PAN.P samples

Temperature: 500°C

Input gas mixture: 2,000 vpm NO in nitrogen

Gas flow rate: 4 litres min^{-1}

Results

Type of Support	BET surface area of sample/ m^2g^{-1}	Mass of sample/g	Initial NO removal rate / mol s^{-1} x 10^9
Hydronyl CX0136	109	20	1731
Hydronyl CX0134	10.8	20	1558
Celite 408	8.4	20	2286
Sorbsil silica gel	706	20	466
Unsupported PAN.P fibre	Too small to measure	5	2320
Unsupported PAN.P granules	Too small to measure	5	910

the lowest surface areas. However, electronmicrographs of the catalyst supports showed that it had the largest pores; the average size being 1 - 3 microns in diameter. This probably allowed better penetration of the polymer into the support so that the effective catalyst surface area was greater than for the other supported samples.

The Hydronyl CX0136AA03 supported sample gave a slightly greater NO removal rate than the lower surface area Hydronyl CX0134AA03 sample. This was in line with the estimated PAN.P surface areas on these two supports as shown in Table 9 on page 55, although a greater difference in activity would be expected with such a large difference in surface area.

The mass of unsupported PAN.P sample used in these experiments was 5 g compared to 20 g for the supported samples. This was a convenient quantity of the low density unsupported PAN.P to use in relation to the size of the catalyst vessel. It represented nearly 3 times the mass of PAN.P that was contained on a 20 g sample of supported catalyst. The surface areas of the two unsupported PAN.P samples were too small to be measured by the BET method indicating that they were less than $1\ m^2g^{-1}$. The surface area of the 3.3 decitex 'Courtelle' fibre, from which the PAN.P was made, was calculated to be $0.18\ m^2g^{-1}$. It was therefore somewhat surprising to find that the PAN.P fibre gave the greatest initial NO removal rate. Thus on supported samples the PAN.P surface area may be less than $\frac{0.18 \times 5}{20} = 0.045\ m^2g^{-1}$. The PAN.P granules had less than half the initial NO removal rate of the PAN.P fibre but assuming that they were not porous their much greater bulk to surface ratio would mean that they had a smaller surface area than the fibre.

4.2 Choice of PAN.P catalyst for use in the kinetic studies of the reaction between NO and PAN.P

Following the preliminary comparison of the various PAN.P catalyst samples described in the previous section it was decided that PAN.P fibre should be used for the subsequent investigations. Its activity to NO was similar to that of the best of the supported catalyst samples; it was readily prepared using the factory-made oxidised 'Courtelle' fibre and it was considered likely to have a greater consistency from batch to batch than the other samples. Also, as the fibre consisted of PAN.P only, the possibility of support materials affecting the reaction was removed.

4.3 The effect of the reaction variables on the initial rate of removal of NO by PAN.P

In this series of experiments the effect of the main reaction variables on the initial rate of NO removal by PAN.P was monitored. The latter was calculated from the change in NO concentration in the gas stream when the gas was first passed through the catalyst chamber.

4.3.1 Mass of PAN.P

Different masses of PAN.P fibre were reacted with NO under constant reaction conditions. The results and reaction conditions used are shown in Figure 6. The straight line graph obtained shows that the initial rate of NO removal was proportional to the mass of PAN.P.

4.3.2 NO concentration

The effect of NO concentration on the initial rate of NO removal by PAN.P was thoroughly investigated by Cooper[28] using NO concentrations between 500 - 3,000 vpm in nitrogen. He found that

FIGURE 6

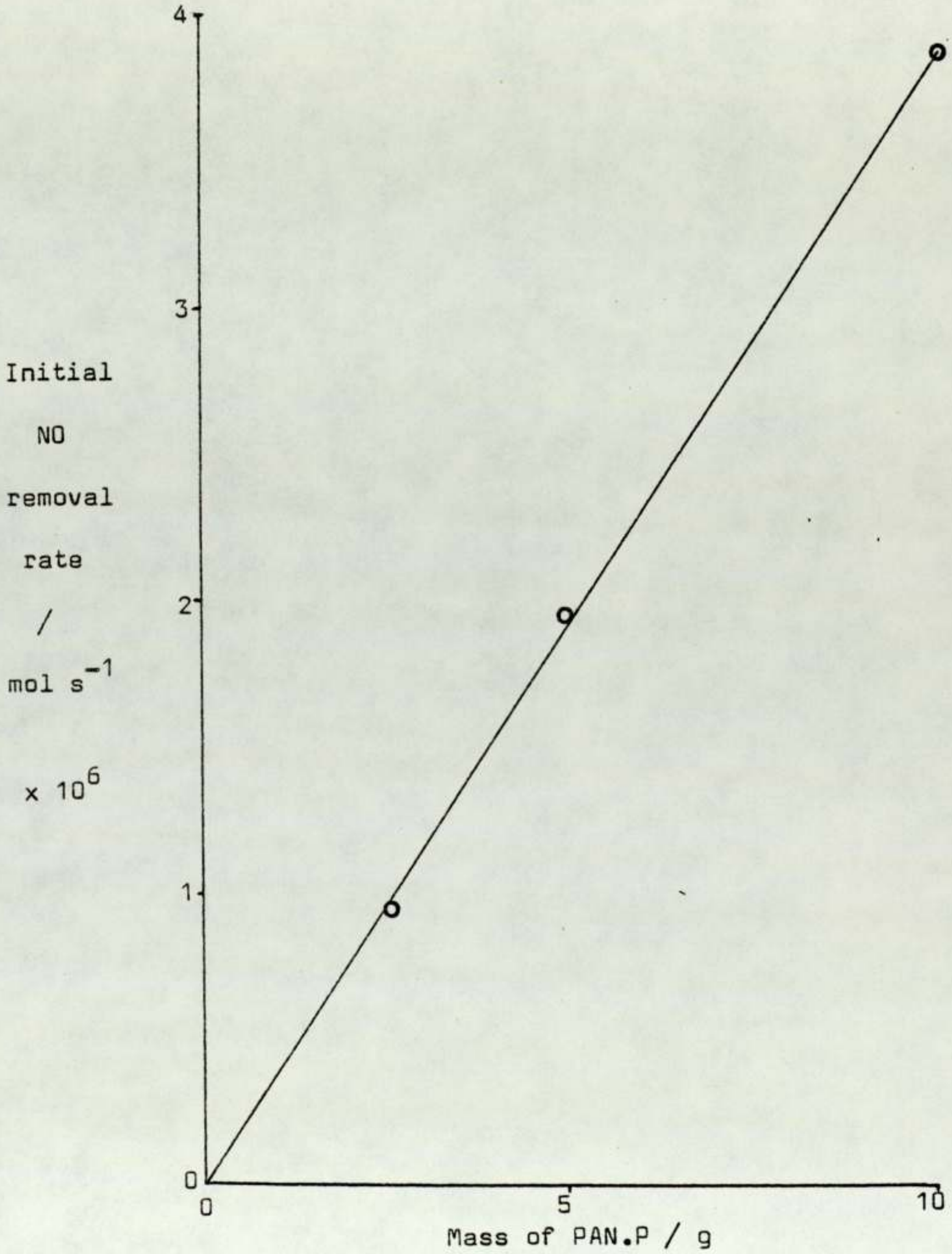
Graph of initial rate of NO removal against mass of PAN.P sample

Reaction conditions

Reaction temperature: 480°C

Inlet gas mixture: 2,010 vpm NO in nitrogen

Gas flow rate: 4 l min^{-1}



the initial NO removal rate was first order with respect to the NO concentration in the gas stream. As his work was carried out under virtually identical conditions, and as the various NO concentrations were not readily available, this work was not repeated.

4.3.3 Gas flow rate

The Beckman analyser trolley required a minimum gas flow rate of 4 litres minute^{-1} when using the NO analyser alone. This increased to 7 litres minute^{-1} when all possible gases were being monitored. It was preferable to keep the gas flow rate to a minimum as this reduced the cooling effect of the gas stream on the catalyst and made it easier to maintain a constant catalyst temperature. Thus a gas flow rate of 4 litres minute^{-1} was used whenever possible. However, the flow rate of exhaust gases from a vehicle fluctuates widely and so it was of interest to see how gas flow rate affected the rate of removal of NO by PAN.P.

Gas flow rate through a motor vehicle catalyst is usually expressed in terms of space velocity where

$$\text{space velocity/ hour}^{-1} = \frac{\text{Gas flow rate/ litres hour}^{-1}}{\text{catalyst volume/ litres}}$$

For a motor vehicle with a 1.5 litre engine and a catalyst volume of 2 litres the maximum space velocity (that obtained at 4,500 rpm) is about 50,000 hour^{-1}.

NO was passed over the PAN.P fibre at various flow rates and the initial rate of NO removal was measured in each case. The results are shown in Table 13. The bulk volume of the PAN.P fibre was taken as 0.004 litres g^{-1} when calculating the space velocities. The results show that NO removal rate increased with gas flow rate but a decreasing proportion of the total NO passing over the catalyst was removed. Thus the efficiency of the catalyst decreased with increasing flow rate.

Table 13

The Effect of gas flow rate on the initial rate of NO removal

Reaction conditions

PAN.P pyrolysis: 4 hours at 400°C under vacuum

Mass of PAN.P fibre sample: 10 g

Reaction temperature: 500°C

Inlet gas mixture: 2,100 vpm NO in nitrogen

Results

Gas flow rate / l min^{-1}	Space Velocity / h^{-1}	NO supply rate /mol s^{-1} x 10^{6}	Initial rate of NO removal /mol sec^{-1} x 10^{6}	% NO removed
4	6,000	6.2	3.7	59
6	9,000	9.4	4.1	44
8	12,000	12.5	4.6	37
10	15,000	15.6	5.2	33

The maximum space velocity through the apparatus was less than a third of the maximum for the average vehicle.

4.3.4 Effect of gas pressure

A pressure and a vacuum gauge were attached to the gas inlet line on the catalytic reactor. The pressure of the gases passing through the reactor could be varied by adjusting the flow meter on the gas line and the flow controls on the pumps drawing the gases to the analysers. Table 14 shows some results for the effect of gas pressure on the initial rate of NO removal by PAN.P.

Table 14

The Effect of gas pressure on the initial rate of NO removal by PAN.P

Reaction conditions

PAN.P pyrolysis: 4 hours at 400°C under vacuum

Mass of PAN.P fibre: 5 g

Input gas mixture: 2,090 vpm NO in nitrogen

Gas flow rate: 4 l min^{-1}

Reaction temperature: 500°C

Results

Gas Pressure/atmospheres	Initial rate of NO removal/mol $\text{sec}^{-1} \times 10^6$
1.14	2.53
1.04	2.45
1.00	2.41
0.83	2.26

The initial rate of NO removal decreased as the pressure decreased. This is consistent with the decrease in NO concentration that would occur as the pressure was reduced. Normally during an experimental run the gas pressure inside the catalytic reactor was maintained at atmospheric pressure. This minimised the possibility of leaks into or out of the apparatus.

4.3.5 Reaction temperature

PAN.P fibre was reacted with NO at various temperatures and the initial rate of NO removal was measured. The results for several PAN.P fibre samples which had been pyrolysed at different temperatures are shown in Figure 7. It can be seen that for all samples the initial rate of NO removal increased rapidly as the reaction temperature was raised above 200°C. A generalised rate equation for the above reaction would be:-

$$\text{Rate of NO removal at temperature } t = k_t[\text{NO}]^x[\text{S}]^y$$

S represents an active site on the polymer surface. For the above reactions the concentration of NO was constant at the supply concentration. Assuming that the concentration of active sites on the polymer is independent of temperature then the initial rate of NO removal should have been proportional to the rate constant k. An Arrhenius plot of initial rate of NO removal against reciprocal absolute temperature is shown in Figure 8. The results do not give a straight line but show an increase in slope at higher temperatures. This suggests that a continuous reaction did not occur throughout the temperature range investigated. The mechanism of the reaction may have changed with increasing temperature or the concentration of active sites on the polymer may have changed. Activation energies for the reaction were obtained by taking the best straight line over a given temperature range. The results are given in Table 15.

FIGURE 7

Graph of initial rate of NO removal against temperature for PAN.P samples pyrolysed at various temperatures

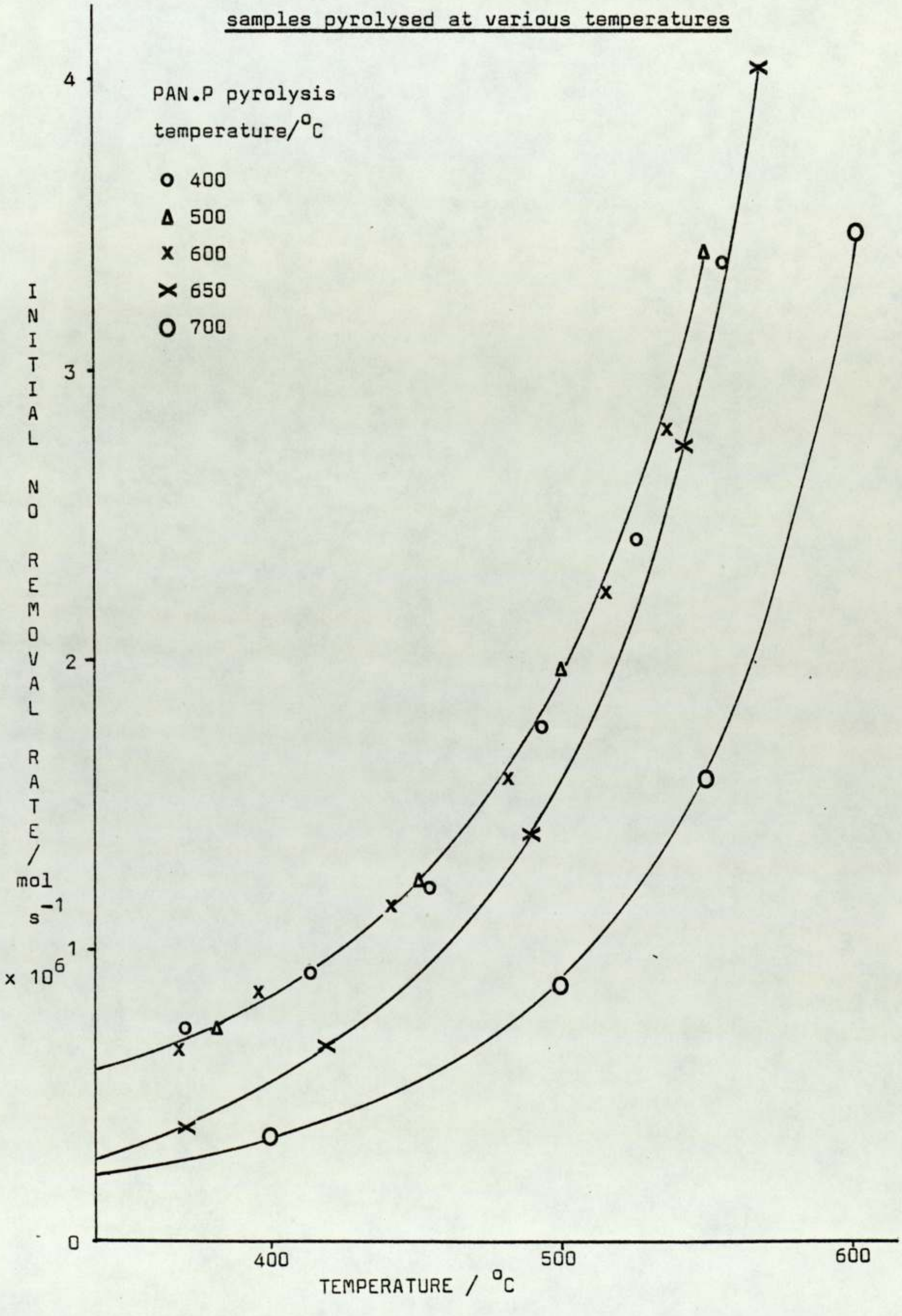


FIGURE 8

Arrhenius plot for the variation in the initial NO removal rate by PAN.P

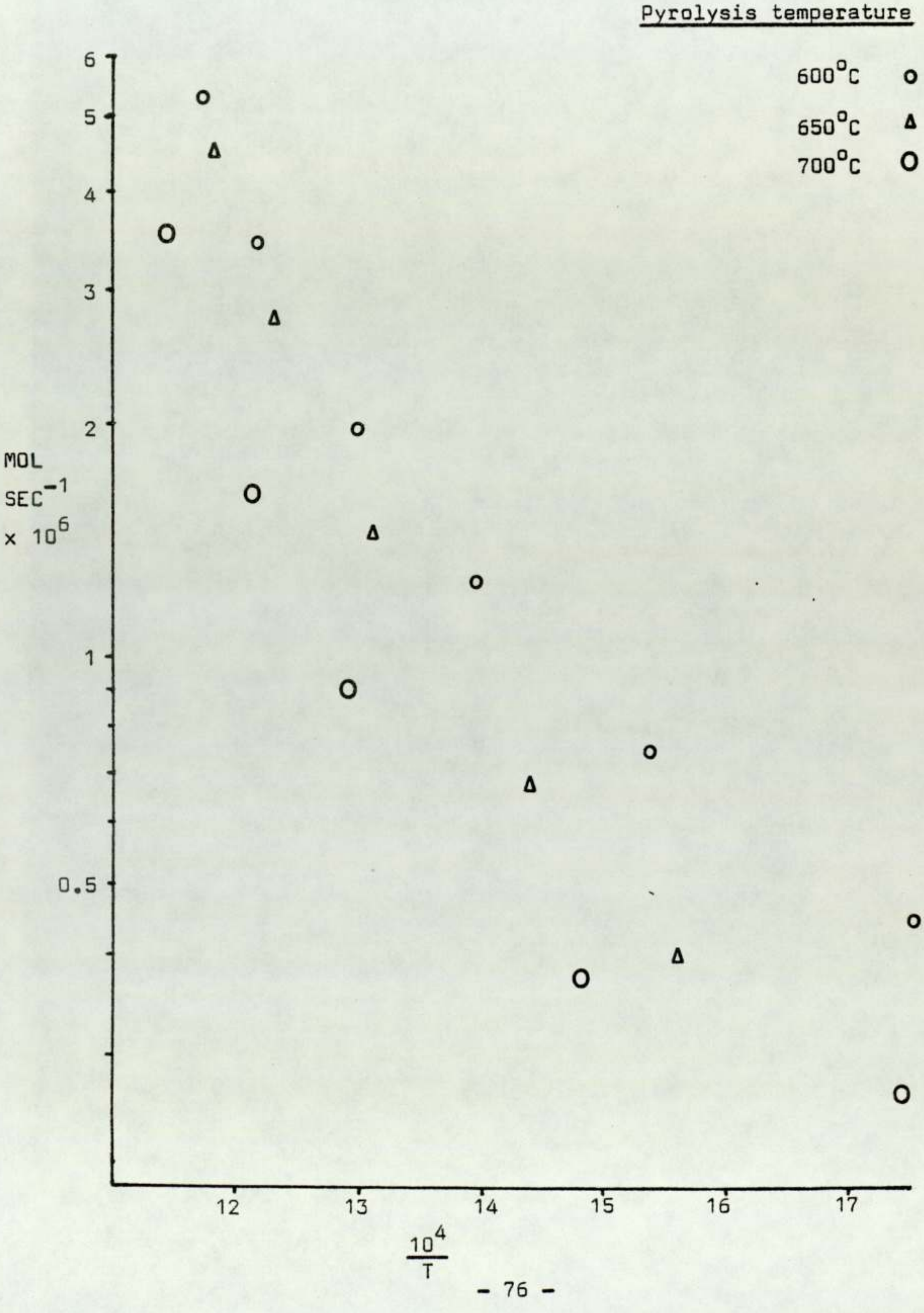


Table 15

Average Activation Energies for the Interaction of NO with PAN.P over Various temperature ranges

	Activation Energy/ kJ mol^{-1}		
Temperature Range/ ^{o}C	300 - 400	400 - 500	500 - 600
PAN.P pyrolysis temperature/ ^{o}C			
600	22.2	33.0	56.0
650	11.6	47.7	73.2
700	11.4	37.2	79.4

It must be emphasised that the activation energies listed in Table 15 are only rough average values taken over a limited temperature range to illustrate the variation in activation energy with temperature. The results show two trends. Firstly there is a dramatic increase in average activation energy as the reaction temperature increases from 300°C to 600°C which suggests that there is a change in reaction mechanism with temperature or that additional reactions occur. Secondly the activation energy varies with the pyrolysis temperature of the PAN.P. The values at the lower temperature range, between 300 - 400°C, are probably less meaningful as very little reaction occurs between NO and PAN.P at these temperatures. At the higher reaction temperatures there is a definite increase in activation energy with increasing pyrolysis temperature. Any proposed reaction mechanism must take these observations into account.

4.3.6 Pyrolysis temperature

A number of PAN.P fibre samples were prepared which had been pyrolysed at various temperatures between 300 - 700°C. All the samples were heated for 4 hours, under vacuum, at the selected pyrolysis temperature. The initial rate of NO removal by these samples over a range of temperatures is shown in Figure 7. The samples pyrolysed at 400, 500 and 600°C all gave similar results. The sample pyrolysed at 650°C showed a reduction in activity to NO compared with the lower temperature samples. A further reduction in activity occurred with the sample pyrolysed at 700°C. Samples which had been pyrolysed at temperatures below 400°C were not tested as it was found that such samples, when heated to temperatures above their pyrolysis temperature, emitted unpleasant vapours which condensed in the cooler parts of the apparatus. This indicates that the chain scission reactions which occur during the low temperature pyrolysis of PAN.P were not complete until the pyrolysis temperature approached 400°C. This is supported by thermal gravimetric analysis of PAN samples which shows that the polymer continues to experience a substantial weight loss up to about 400°C.[12]

Cooper[28] carried out similar experiments to those above using supported PAN.P catalyst samples which had been pyrolysed to temperatures between 350 - 550°C. He found that the activity of the samples to NO decreased with increasing pyrolysis temperature whereas the comparable samples above all had similar activities. One possible reason for the difference in behaviour, apart from any effect by the inorganic support, is that his samples were pyrolysed under vacuum only whereas the PAN.P fibre had undergone an initial low temperature pyrolysis in air. This 'oxidation' stabilises the polymer structure and reduces weight loss during subsequent pyrolysis.[8] It may also affect the temperature initiated structural changes which govern the activity of PAN.P to NO.

Gallard[21] measured the rate of decomposition of dinitrogen oxide by PAN.P at 250°C using PAN.P samples pyrolysed in argon at various temperatures. She found that the activity of the PAN.P reached a peak at a pyrolysis temperature of about 400°C and then decreased as the pyrolysis temperature was raised further. These results again suggest a decrease in activity of the polymer starting at a lower pyrolysis temperature than was found in this work with PAN.P fibre.

The effect of pyrolysis temperature on the activation energy for the PAN.P interaction with NO was discussed in the previous section.

4.4 Cleaning the PAN.P Surface.

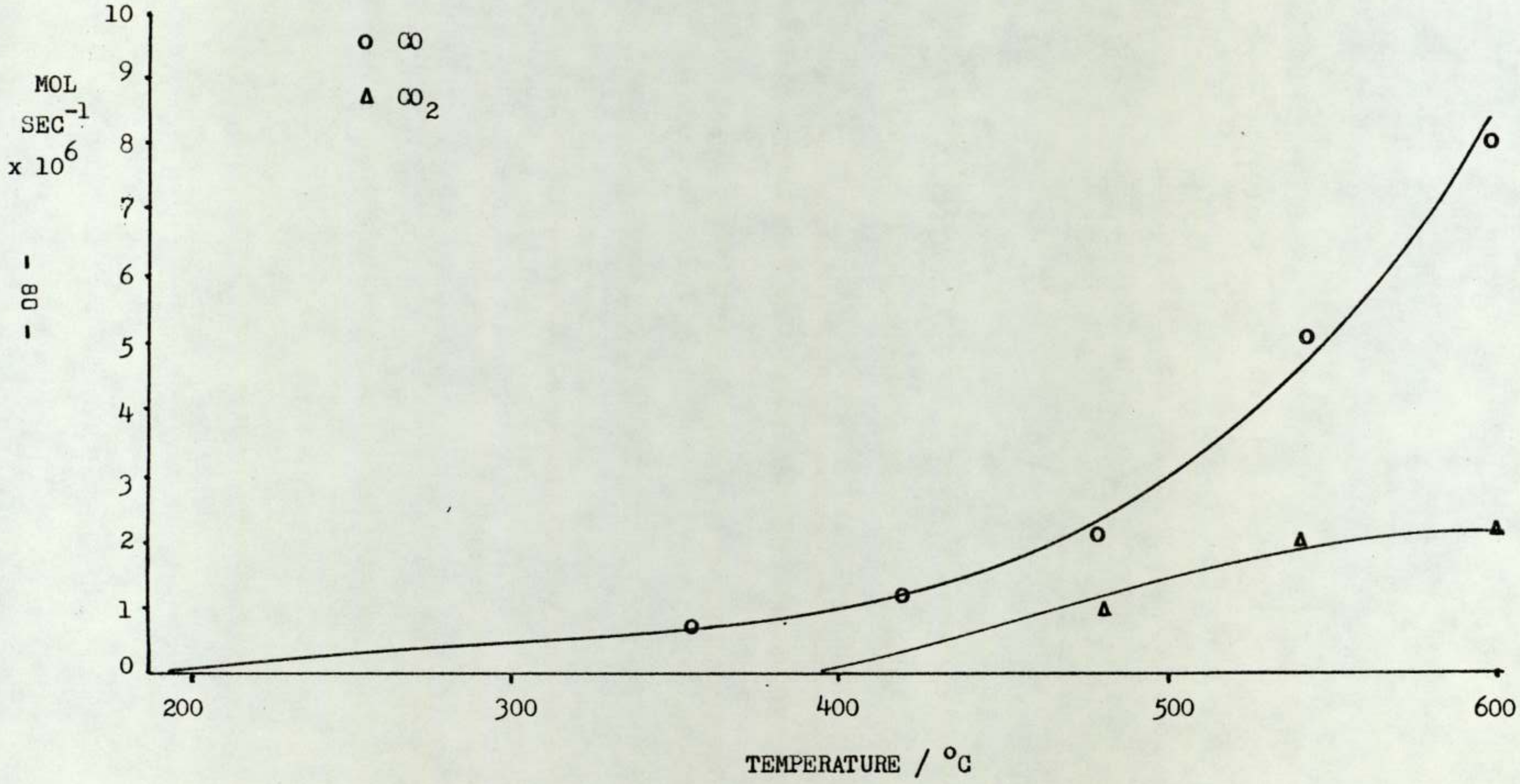
4.4.1 Effect of heating PAN.P in nitrogen

A sample of PAN.P was heated in the catalyst vessel, in a stream of nitrogen, under a programmed temperature rise of 10°C minute^{-1}. The outlet gas stream was analysed for CO, CO_2, O_2 and NO. The results of gas concentration against time are shown in Figure 9. CO was detected at about 200°C and its concentration increased as the temperature increased. CO_2 appeared at about 400°C and its concentration also increased with temperature up to about 540°C and then levelled off. No O_2 or NO were detected. The concentrations of CO and CO_2 in the outlet gas decreased rapidly if the catalyst temperature was kept constant but they immediately increased again on raising the temperature. These results suggested that the PAN.P contained oxides which decomposed at elevated temperatures. As the catalyst temperature was raised more and more of the oxides decomposed to give increasing quantities of CO and CO_2.

The origin of the oxides present in the PAN.P structure is of

FIGURE 9

Graph of the rate of CO and CO_2 evolution with temperature when PAN.P was heated alone



interest. All the fibre samples had been 'pre-oxidised' by heating in air before pyrolysis (see section 3.4.2) but any unstable oxides produced by this treatment should have been removed during pyrolysis. For comparison with the 'pre-oxidised' fibre a sample of PAN.P which had been pyrolysed under vacuum only was heated under nitrogen and also found to give increasing quantities of CO and CO_2 as its temperature was raised to 600°C. This suggested that the oxides were incorporated in the PAN.P structure after pyrolysis. It is well known that PAN.P which has been pyrolysed under inert conditions reacts readily with oxygen on exposure to the atmosphere.[12,37] Thus, it appeared that all the PAN.P samples had a surface covering of oxides which may have affected the interaction between the polymer and NO.

4.4.2 Cleaning the PAN.P Surface by repeated heating in nitrogen

In order to clean the PAN.P surface of oxides a sample of the polymer was repeatedly heated and cooled in a stream of nitrogen. Initially the PAN.P was heated to 650°C while the concentration of CO in the gas stream was monitored. The sample was then cooled under nitrogen and reheated through the same temperature rise. The CO evolution results for both periods of heating are shown in Figure 10. Much less CO was produced during the second period of heating. Further cooling followed by a third heating produced even less CO. Thus heating the PAN.P in an inert atmosphere removed the unstable oxides.

4.4.3 Reaction of NO with PAN.P after cleaning the polymer surface

Samples of PAN.P fibre which had been heated to 600°C and cooled in a stream of nitrogen in order to remove surface oxides were reacted with NO at various temperatures. The initial rate of NO

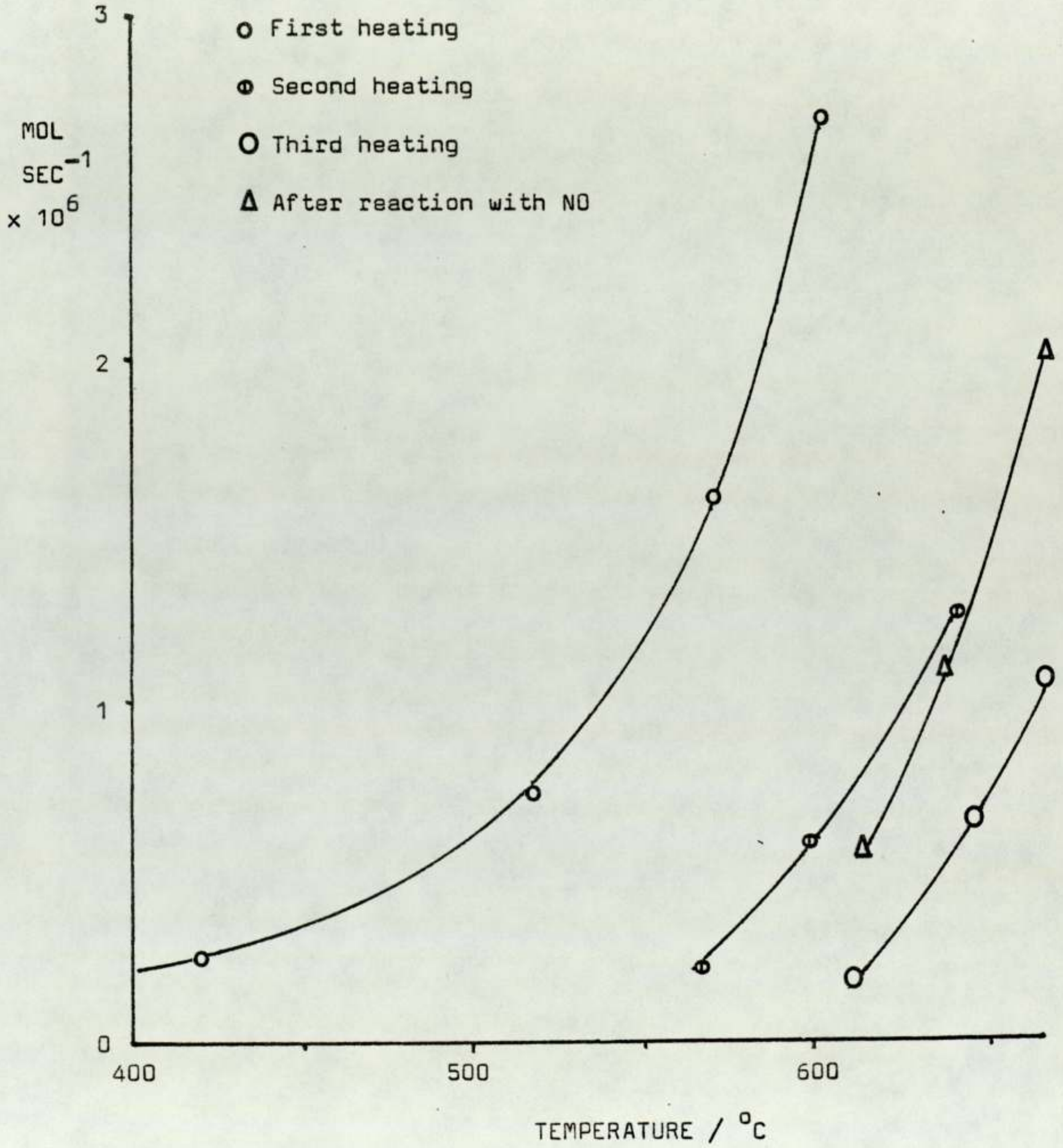
FIGURE 10

Graph of the variation in CO evolution by PAN.P when heated repeatedly in nitrogen

Reaction conditions

Mass of PAN.P: 5 g

Gas flow rate: 4 l min^{-1}



removal against reaction temperature for these samples is shown in Figure 11 along with results obtained for untreated PAN.P fibre samples. The activity of the PAN.P fibre was greatly increased by the prior heating in an inert atmosphere. This suggested that the oxides originally present in the PAN.P structure inhibited the reaction between NO and PAN.P. Heating decomposed the oxides and so removed these from the PAN.P surface.

It was also found that the higher temperature to which the PAN.P was heated (750°C was the maximum attained) the greater was the increase in activity at lower temperatures. This was consistent with surface oxide removal as Figures 9 and 10 showed that CO evolution increased with increasing temperature. Thus the higher the temperature to which the PAN.P was heated the greater the quantity of oxides removed.

In order to test further the hypothesis that surface oxides were inhibiting the reaction between NO and PAN.P, samples of PAN.P were heated to 750°C under nitrogen and then cooled to 450°C. The activity of the samples to NO was measured before and after exposure to oxygen. The results are given in Table 16.

Exposure of the 'cleaned' PAN.P to oxygen more than halved the initial rate of removal of NO. Prolonged exposure of the PAN.P to oxygen at this temperature did not completely deactivate it towards NO. At higher temperatures the extent of deactivation became progressively less which was undoubtedly related to the decreasing stability of the surface oxides at higher temperatures.

It was seen in section 4.4.6 that an Arrhenius plot for the PAN.P - NO reaction did not give a straight line graph suggesting that a continuous reaction was not occurring over the temperature range studied. It now appears that the presence of oxides on the

FIGURE 11

Initial rate of NO removal by PAN.P before and after heating in an inert atmosphere

Reaction conditions

PAN.P pyrolysis temperature:	600°C
Mass of PAN.P fibre:	5 g
Gas flow rate:	4 l min^{-1}
Inlet gas composition:	2010 vpm NO in nitrogen

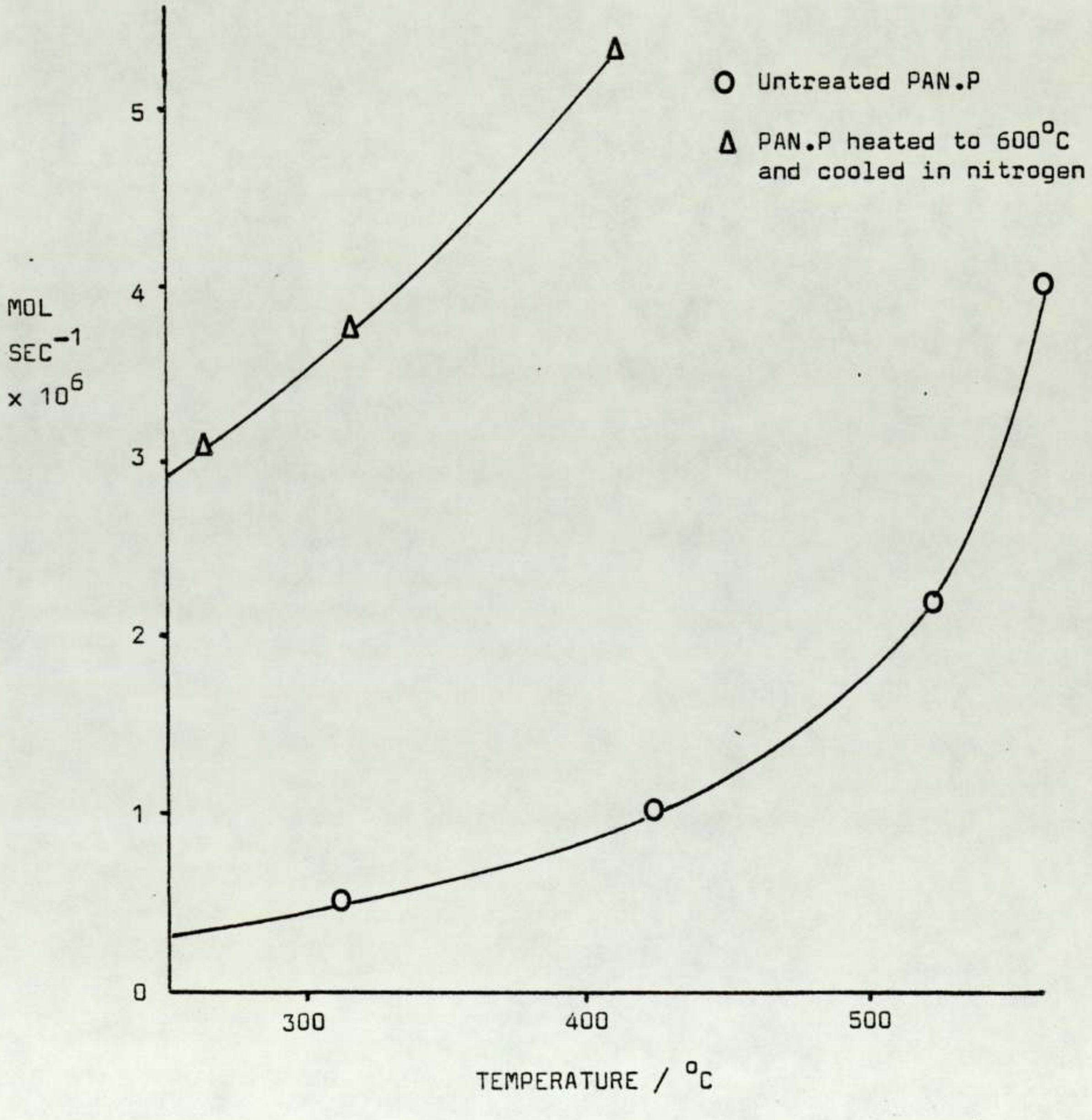


Table 16

Effect of oxygen on the Activity of PAN.P to NO

Reaction conditions

Mass of PAN.P fibre: 5 g

Reaction Temperature: 450°C

Input gas mixture: 2,090 vpm NO in nitrogen

Gas Flow rate: 4 l min^{-1}

Sample	Initial NO removal rate /(mol sec^{-1} x 10^6)
PAN.P heated to 750°C and cooled under nitrogen to 450°C	5.7
Samples as above and 3% oxygen in nitrogen passed for 2 minutes at 450°C	2.1

PAN.P surface affected the reaction. A truer activation energy was likely to be obtained if the oxides were first removed by heating. Figure 12 shows an Arrhenius plot of the results for the reaction between NO and PAN.P fibre shown in Figure 11.

Results were obtained for temperatures below 425°C only, because at higher temperatures the PAN.P removed all the NO from the gas stream. The activation energy obtained was 10.8 kJ mol^{-1}.

Activation energies obtained for 'untreated' PAN.P samples are shown in Table 15. The average activation energy over the same temperature range for a similarly pyrolysed sample to the one above was 22.2 kJ mol^{-1} although the samples pyrolysed to higher temperatures had activation energies of around 11 kJ mol^{-1}. However these latter values are of limited significance as very little reaction occurred at these temperatures with the 'untreated' PAN.P samples.

4.5 Isothermal reaction of PAN.P with NO

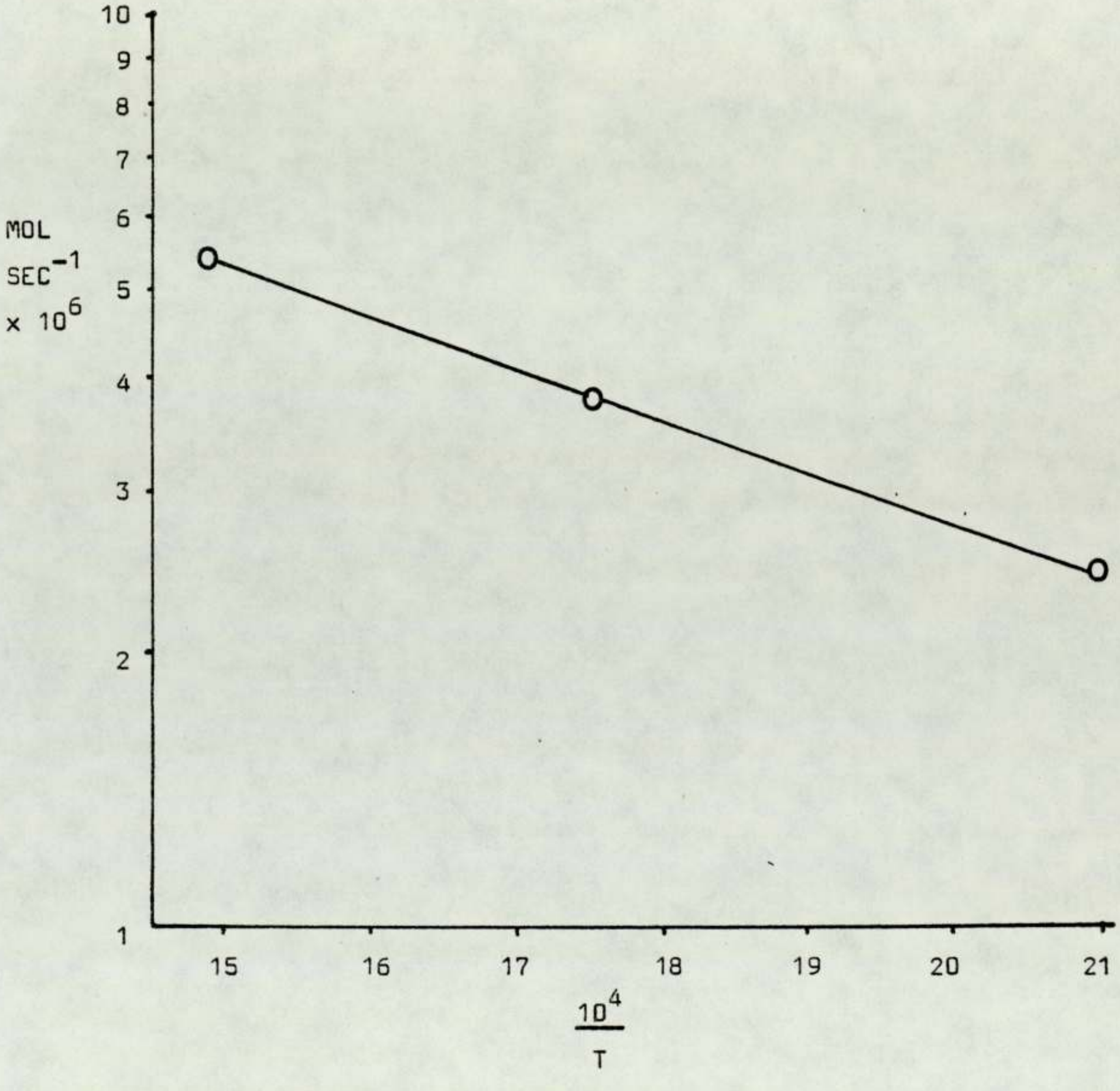
Thus far only the initial rate of NO removal by PAN.P, under various conditions, has been examined. However the variation in NO removal rate with time at constant temperature is of primary importance as this determines the useful life of the catalyst.

Figure 13 shows the change in rate of NO removal with time for samples of PAN.P fibre reacted with NO under isothermal conditions at various temperatures. All the PAN.P samples had been heated in nitrogen to 650°C to clean the polymer surface of oxides before cooling to the reaction temperature.

In each case the PAN.P initially removed all the NO from the gas stream but the NO removal rate gradually decreased with time. The rate of decrease was faster the lower the reaction temperature. At 330°C the PAN.P had lost more than 90% of its initial activity after 40

FIGURE 12

Arrhenius plot for initial rate of NO removal by a 'cleaned' PAN.P surface



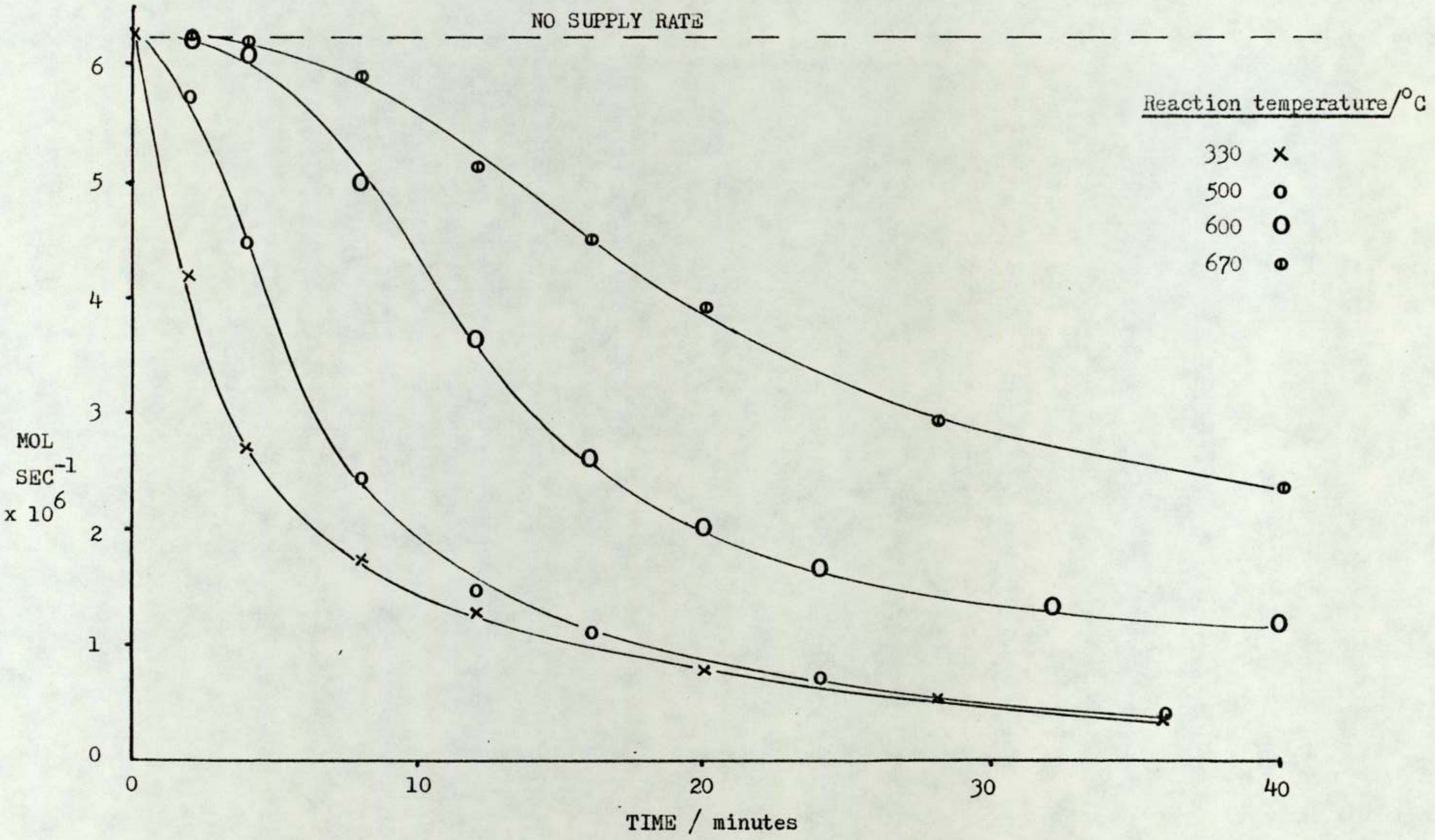


FIGURE 13 Graph of the variation in the rate of NO removal by PAN.P with time at constant temperature

minutes of reaction.

It was shown in section 4.3 that the initial rate of NO removal by PAN.P was first order with respect to both NO and PAN.P.

$$-\frac{dNO}{dt} \propto \left[NO\right] \left[S\right] \qquad S = \text{an active site on the polymer surface}$$

The NO concentration during isothermal reaction is constant at the supply concentration. If each active site S reacted with one NO molecule and was then deactivated the number of active sites at any time would be proportional to the rate of NO removal at that time.

Thus a plot of $\log \left(\frac{\text{Initial NO removal rate}}{\text{NO removal rate at time t}}\right)$ against time should give a straight line. Such a plot is shown, for reaction at 330°C, in Figure 14.

The plot is linear for the first few minutes of reaction but then curves downwards. The rate of removal of NO does not fall as rapidly as it should to give a first order plot. This suggests that an active site may react with more than one molecule of NO.

This may occur in true catalytic fashion with NO chemisorbing, and then desorbing after reaction to leave the active site free to react again. On the other hand the product of the initial reaction between the NO and the active site may be capable of reacting with further molecules of NO. A reaction was also occurring which removed the active sites. This deactivation was more rapid the lower the reaction temperature. As the rate of a reaction increases with temperature the rate of deactivation should have been faster at higher reaction temperatures. This suggests that at higher temperatures either

i) There were more active sites present

FIGURE 14

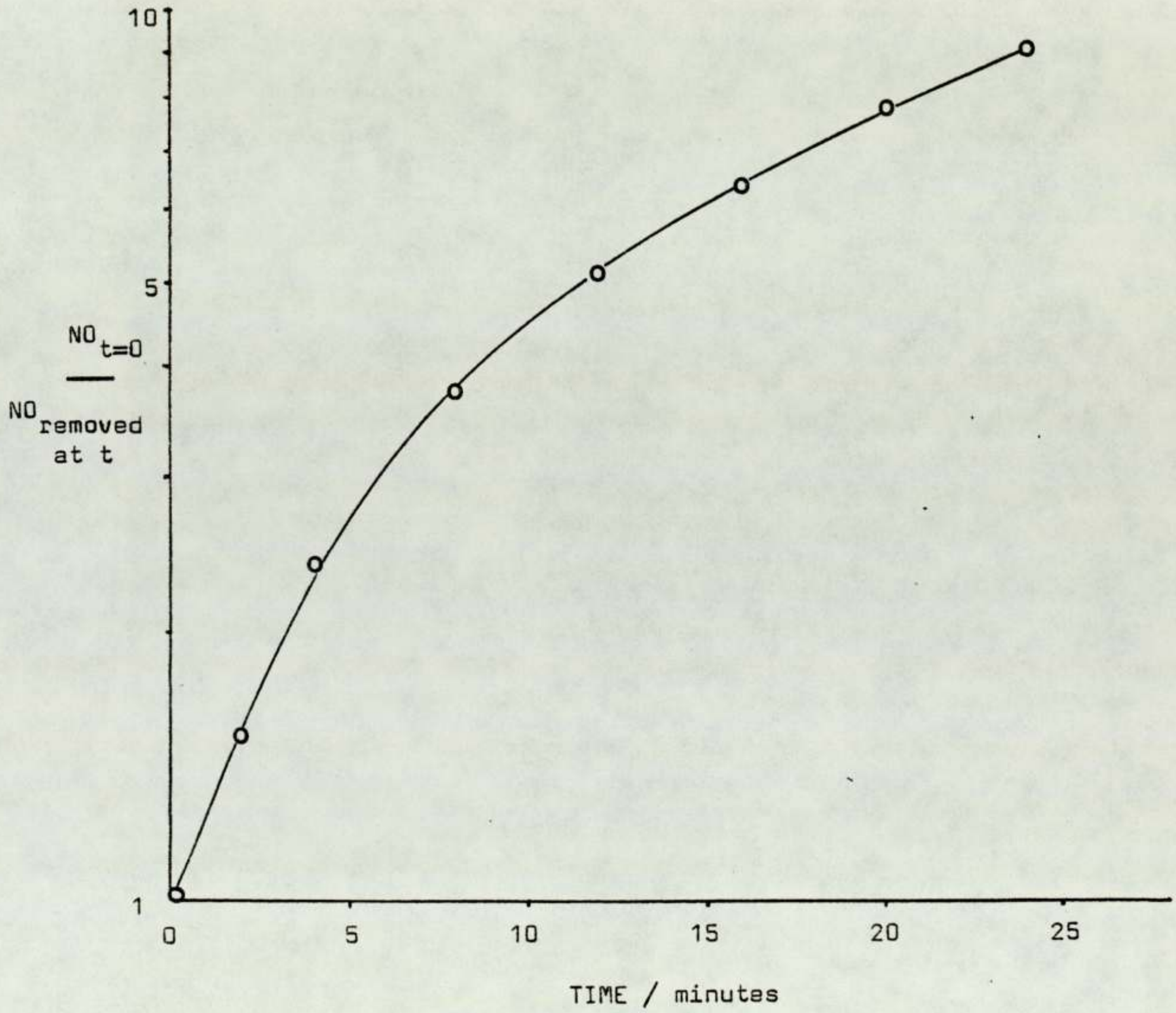
First order plot for the rate of NO removal by PAN.P

Reaction conditions

Mass of PAN.P: 5 g

Reaction temperature: 330°C

Inlet gas composition: 2,000 vpm NO in nitrogen



or ii) Each site reacted more often before it was deactivated

or iii) Regeneration of active sites after reaction, via a particular route, was more rapid.

The quantity of NO removed by the PAN.P samples during the first 40 minutes of reaction, at each temperature, is given in Table 17. The amount of NO removed increases with increasing reaction temperature.

Table 17

Quantity of NO removed by PAN.P samples in fixed time at various temperatures under isothermal conditions

PAN.P initially heated to 670°C and cooled under nitrogen.

Mass PAN.P fibre: 5 g

Reaction time: 40 minutes

Reaction Temperature /°C	NO removed /mol x 10^3	Area covered by monolayer of NO equivalent to quantity removed/m^2
330	3.00	284
500	3.66	346
600	6.96	658
678	10.01	946

The minimum areas of PAN.P surface required to accommodate these quantities of NO as chemisorbed monolayers was calculated assuming the cross-sectional area of an NO molecule to be 15.7×10^{-20} m^2. Thus at 678°C 0.01 mol NO was removed by 5 g PAN.P in 40 minutes. As a monolayer this quantity of NO would occupy a minimum area of 946 m^2.

The surface area of the PAN.P fibre was too small to be measured by the BET method which meant that it was apparently less than 1 m^2 g^{-1}.

Thus the total surface area of the PAN.P samples was less than 5 m^2. This means that each active site on the PAN.P surface must have removed several NO molecules before it was deactivated. At 678°C the PAN.P removed the equivalent of more than 200 times its surface area of NO.

4.6 Effect of heating PAN.P which has been reacted with NO

It was found that when a sample of PAN.P, which had been deactivated by reaction with NO, was heated above the reaction temperature under nitrogen it regained some of its activity to NO. There was no regain in activity if the PAN.P was heated in nitrogen at the original reaction temperature but the activity increased progressively the higher it was heated above this temperature.

Three possible reasons for this regain in activity are

i) NO which was adsorbed on the polymer surface was desorbed at higher temperatures.

ii) Species formed on the polymer surface by reaction with NO were decomposed or desorbed thus regenerating active sites.

iii) New active sites were formed at higher temperatures by changes in the polymer structure such as breakdown of surface oxides present before the reaction.

In section 4.4.3 is described an experiment to clean the surface of a sample of PAN.P of surface oxides. Figure 10 shows how the repeated heating and cooling in nitrogen reduced the amount of CO produced, indicating a progressive reduction in unstable surface oxides. After the third heating in nitrogen the PAN.P was cooled to 580°C and then 2000 vpm NO in nitrogen was passed over the sample at 5 $l\ min^{-1}$ for 45 minutes. Initially the PAN.P removed 8.34×10^{-6} mol s^{-1} NO from the gas stream but this reduced to 2.09×10^{-6} mol s^{-1} by the end of the period. The sample was then heated to 650°C under nitrogen for a fourth time and the concentrations of CO and NO in the outlet gas stream were monitored.

No NO was detected indicating that this gas was not being desorbed from the PAN.P surface. Figure 10 shows that the quantity of CO produced by this fourth heating was greater than on the third occasion although, on the basis of previous results, it should have been less. This indicated that more oxides were being formed on the polymer surface during its reaction with NO. The loss and regain in activity of the polymer can be explained if once a surface oxide is formed on an active site that site becomes deactivated. Then when the polymer is heated to a higher temperature some of the newly formed surface oxides decompose to give CO or CO_2 and generate new active sites. However, it was shown in section 4.5 that the overall reaction was more complex than each active site reacting with and being deactivated by one molecule of NO.

4.7 Gaseous products of the interaction between PAN.P and NO

In order to establish the nature and mechanism of the interaction between NO and PAN.P it was necessary to identify, if possible, the products of the reaction. It had been found that NO was removed from a gas stream passed over heated PAN.P. The NO was not reversibly adsorbed on the PAN.P surface as it was never found to be desorbed when PAN.P was heated to a higher temperature after exposure to NO.

Possible gaseous products of the interaction between PAN.P and NO included nitrogen, oxygen, dinitrogen oxide (N_2O), nitrogen dioxide (NO_2), carbon monoxide (CO) and carbon dioxide (CO_2).

All the PAN.P samples used in the following experiments were heated to 750°C and cooled under nitrogen before reaction. This treatment decomposed oxides present in the PAN.P structure as described in Section 4.4.1.

4.7.1 Infrared analysis of gases from the reaction between NO and PAN.P

Several of the gases thought to be likely products of the PAN.P and NO interaction have strong absorptions in the infrared region of the spectrum. The gases, the position of their main absorption peaks, and the threshold values for their detection[38] are given in Table 18.

Table 18

Infrared Absorption peak values and threshold detection limits for various gases

Gas Formula	Main infrared Absorption peaks /cm^{-1}	Threshold detection limit concentration/vpm
N_2O	2217, 1302, 1275	30
NO_2	1751, 1613, 1258	30
CO	2175, 2120	300
CO_2	3716, 2326*	100

* Main peaks are underlined

Nitrogen containing 2000 vpm NO was passed over 20 g PAN.P in the catalyst chamber of the reactor. Samples of the outlet gas were subjected to infrared analysis following reaction at 580°C and 730°C. The quantity of PAN.P used was sufficient to remove all NO from the gas stream at temperatures above 500°C for the first few minutes of reaction. This ensured the maximum concentration of product gases and also avoided complicating the infrared spectrum with the presence of NO.

The infrared spectrum of the gases obtained at 580°C showed a very slight absorption at 2160 cm^{-1} only. This peak could be assigned to carbon monoxide. As air was used as reference an inverse peak, due to carbon dioxide in the air, should have been present at 2320 cm^{-1}. Its absence indicated that CO_2 was present in the sample in about the same concentration as in air (ie. about 300 vpm).

The infrared spectrum of the gases collected after reaction at 730°C showed two distinct peaks at 2120 and 2175 cm^{-1} due to CO. A very slight absorption due to CO_2 was present at 2320 cm^{-1}. Thus at the higher temperature the concentration of CO in the product gases had increased while that of CO_2 had remained more or less constant.

There was no trace of N_2O or NO_2 in either sample and considering the very low concentrations at which they can be detected by infrared analysis it seems unlikely that they were significant products of the interaction between NO and PAN.P at these temperatures.

4.7.2 Continuous analysis of the outlet gases

The Beckman analysis trolley contained CO, CO_2 and O_2 analysers (as described in section 2.2.2). These instruments were used to monitor the presence of the gases in the outlet stream after passing 2000 vpm NO in nitrogen over heated PAN.P. Small quantities of CO and even less of CO_2 were detected. Oxygen was not detected. However, these instruments, designed for use with raw exhaust gas, were not sensitive enough to give accurate readings for the small quantities of each gas present. An Analytical Development Company CO analyser, giving readings in the range 0 - 2000 vpm, was used to monitor the quantity of CO produced during the NO and PAN.P reaction. CO was the major gaseous product detected thus far.

Table 19

Rate of CO production during PAN.P/NO interaction

Reaction Conditions

Gas Flow rate: 5 l min^{-1}

NO concentration: 2,150 vpm in nitrogen

Reaction Temperature/°C	Reaction Time/min	Rate of NO Removal/ mol s^{-1} x 10^6	Rate of CO Production/ mol s^{-1} x 10^6	CO production/ NO removal %
480	0	7.89	0.08	1
	4	1.30	0.04	3
	8	0.56	0.02	4
580	0	7.86	0.09	1
	8	0.56	0.06	11
705	0	7.82	0.70	9
	8	2.42	0.59	24
750	0	8.01	1.23	15
	8	5.02	1.26	25
	22	2.15	1.27	59
	> 22	2.15	1.27	59

Table 19 shows the rate of NO removal by PAN.P and the corresponding rate of CO production at various reaction times and at different reaction temperatures.

As the reaction temperature increased, the ratio of CO produced to NO removed increased. Thus CO production was greater the higher the temperature.

During the course of an isothermal reaction the rate of NO removal fell more rapidly than the rate of CO production. At 750°C the CO production rate remained constant throughout the reaction while the NO removal rate fell for the first 20 minutes and then reached a constant level.

These results suggest that there were two different mechanisms for NO removal by PAN.P. The main mechanism at lower temperatures led to rapid deactivation of the PAN.P and, apart from possibly nitrogen, did not form any gaseous products. The second mechanism occurred increasingly as the reaction temperature was raised and resulted in the production of carbon monoxide and carbon dioxide. This mechanism also led to gradual deactivation of the PAN.P until the temperature reached 750°C when a continuous reaction occurred.

4.8 Electronmicrographs of PAN.P samples after reaction with NO

Plate 6, page 60 shows electronmicrographs of the supported PAN.P sample before and after reaction with NO at 500°C. The pellet surface has a much rougher, more porous, appearance after the reaction. Electronmicrographs of PAN.P fibre before and after reaction with NO are shown in Plate 7, page 61. In this case the reaction appears to have smoothed down the striations on the fibre surface. Both effects are consistent with consumption of the polymer surface by NO.

CHAPTER 5

THE INTERACTION BETWEEN NO AND PAN.P IN THE PRESENCE OF OTHER EXHAUST GASES

5.1 The constituents of exhaust gas

The exhaust gas from a motor car is a mixture of several gases, the most important being carbon monoxide (CO), carbon dioxide (CO_2), oxygen, hydrogen, hydrocarbons (HC), water vapour and nitrogen monoxide (NO).

Some of these gases may interact in the presence of a suitable catalyst. This behaviour is utilised in the reduction of NO by CO over precious metal or metal oxide catalysts. Other reduction reactions may also occur.

$$2NO + 2H_2 \longrightarrow N_2 + 2H_2O \qquad (1)$$

$$3NO + C_3H_8 \longrightarrow \tfrac{3}{2}N_2 + 3CO + 4H_2 \qquad (2)$$

$$CO + H_2O \longrightarrow CO_2 + H_2 \qquad (3)$$

The hydrogen produced in reactions (2) and (3) may remove NO via reaction (1).

Thus the presence of other gases may help or possibly hinder the removal of NO by PAN.P.

5.2 Reactions of the individual gases with PAN.P

Initially each gas was tested to see if it reacted with PAN.P. The gas concentration was monitored before and after passage over a heated sample of PAN.P.

It was also possible that some of the gases might react with and remove the inert species formed on the PAN.P surface during its reaction with NO, and thus reactivate the PAN.P. This had occurred when air was passed over PAN.P which had become deactivated by dehydrogenation reactions.[24,25] Samples of PAN.P which had been reacted with NO until their activity was substantially reduced were treated with the individual gases at elevated temperatures and their activity to NO was retested. Care was taken to keep the temperature of the PAN.P below that of the original reaction temperature to avoid thermal decomposition of the 'inert' species.

The results for the various gases are summarised in Table 20.

5.2.1 CO and CO_2

The CO and CO_2 mixture had no apparent effect on fresh or 'used' PAN.P at 600°C.

5.2.2 Hydrocarbons

The hydrocarbons (propane) concentration was unchanged after passage over fresh PAN.P at 600°C but it was reduced very slightly, by about 1%, during the first few minutes of its passage over 'used' PAN.P. This had a negligible effect on the subsequent activity of the 'used' PAN.P to NO.

5.2.3 Hydrogen

The hydrogen concentration could not be monitored so that the effect of hydrogen could only be assessed by testing the activity of the PAN.P to NO before and after treatment. This in turn proved difficult as the stainless steel catalyst vessel catalysed the reaction between NO and hydrogen. After treating the PAN.P with hydrogen and flushing the apparatus with nitrogen, sufficient hydrogen remained adsorbed on the vessel walls to make accurate measurement of the activity of PAN.P to NO impossible.

Table 20

Reaction of the various exhaust gases with PAN.P

Gas	Reaction Temperature/ °C	Change in Gas Concentration over PAN.P	Change in Gas Concentration over 'used' PAN.P	Effect on Activity of used PAN.P to NO
8.5% CO 13.5% CO_2 in nitrogen	600	None	None	None
800 vpm propane in nitrogen	600	None	Very slight reduction initially	None
40% hydrogen in helium	400	Not measured	Not measured	None
3% oxygen in nitrogen	600	Oxygen removed	Oxygen removed	None
100% nitrogen	600	Not measured	Not measured	None

A glass vessel was constructed and used in place of the stainless steel catalyst chamber. No preheat vessel was used. The lower thermal conductivity of the glass prevented the use of temperatures above about 400°C as otherwise the hot gases softened the PTFE tubing.

The results show that at these temperatures hydrogen had no detectable effect on fresh or 'used' PAN.P. Bedjai et al[39] found that heating to above 450°C with hydrogen restored the activity of carbon which had been deactivated by reaction with NO. Thus at higher temperatures it is possible that hydrogen would restore the activity of the PAN.P.

5.2.4 Oxygen

Oxygen reacted readily with both fresh and 'used' PAN.P at temperatures above 200°C. Figure 15 shows the initial rate of oxygen removal against temperature for a 5 g sample of PAN.P fibre. The rate of formation of the product gases is also shown. These were CO and CO_2. Above 370°C NO was produced indicating that the polymer structure was being broken down.

The reaction of oxygen with PAN.P was highly exothermic. During the passage of 3% oxygen in nitrogen over PAN.P the PAN.P temperature rose from a previously constant 600°C to 750°C in two minutes.

5.3 Reaction of the oxides of carbon with NO over PAN.P

A mixture of CO and CO_2 in nitrogen was passed over PAN.P in conjunction with a mixture of NO in nitrogen. The exact concentration of the gases in the inlet and outlet streams was determined using the Beckman gas analysers.

The steel catalyst rig vessels catalysed the reaction.

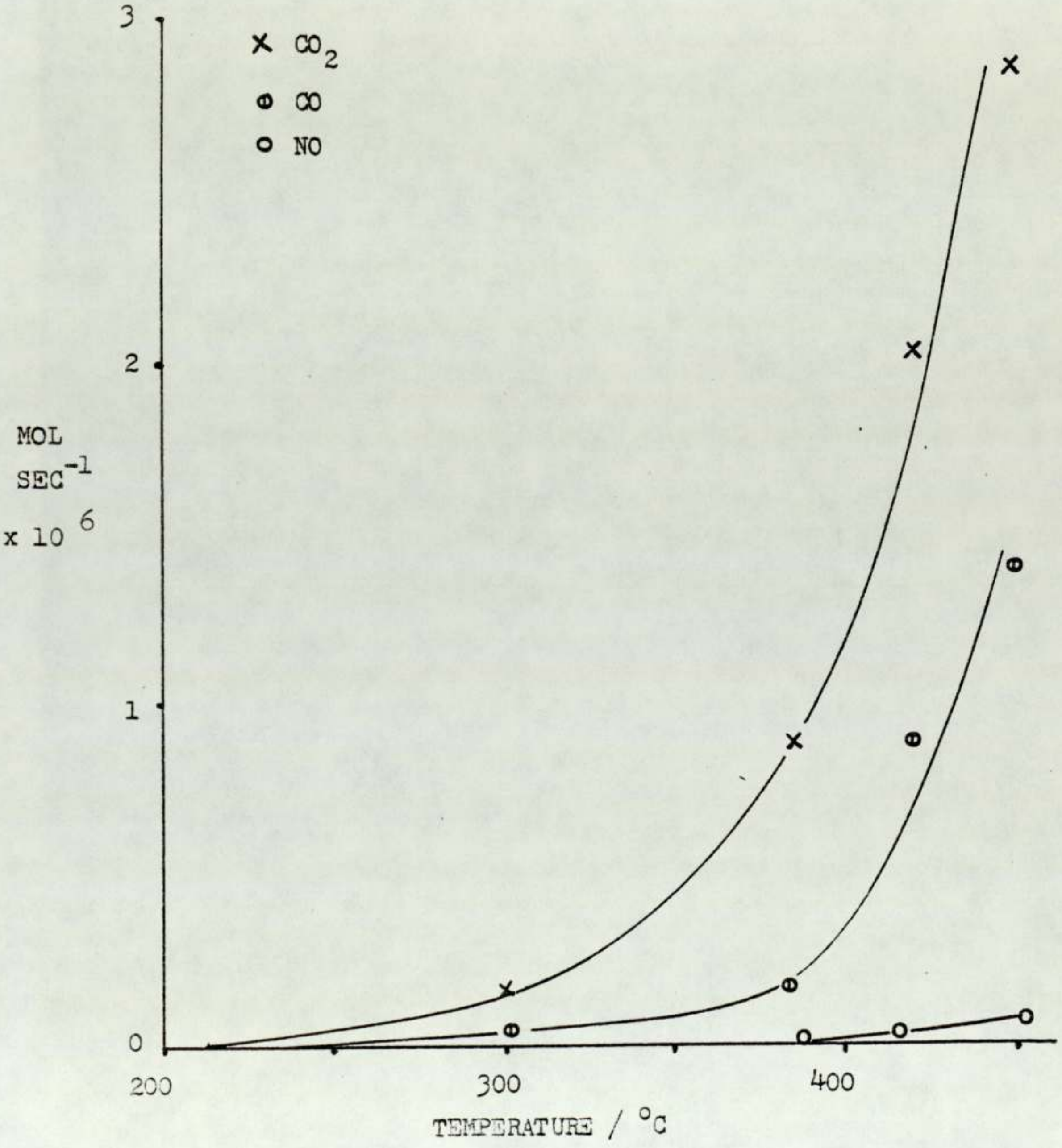
$$CO + NO \longrightarrow CO_2 + \tfrac{1}{2}N_2$$

FIGURE 15

Graph of the rate of evolution of gaseous products with temperature during the reaction of PAN.P with oxygen

Reaction conditions

Gas composition:	3% oxygen in nitrogen
Gas flow rate:	4 l min^{-1}
Mass of PAN.P:	5 g



This is the reaction utilised by conventional exhaust catalysts to remove NO as described in section 1.2.

Initially the gases were passed through the rig without any PAN.P present. The experiment was then repeated with PAN.P in the catalyst chamber. The results of these experiments are shown in Table 21.

Comparing the gas flow rates after passage over the steel vessels alone with those for steel vessels + PAN.P it can be seen that the presence of PAN.P increases the removal rate of the NO but does not affect that of CO or CO_2. Thus PAN.P does not promote the reaction between CO and NO at 500°C.

5.4 Reaction of hydrocarbon with NO over PAN.P

The hydrocarbon used was a mixture of 800 vpm propane in nitrogen.

Neither the stainless steel vessels nor PAN.P promoted any reaction between propane and NO at temperatures up to 670°C.

5.5 Reaction of hydrogen with NO over PAN.P

As mentioned in section 5.2 the stainless steel vessels catalysed the reaction between NO and hydrogen and these experiments were carried out in a glass vessel. At temperatures up to 400°C there was no apparent reaction between NO and hydrogen over PAN.P. As the concentration of hydrogen could not be monitored this conclusion was based on the quantity of NO removed from the gas stream. This was no greater than that normally removed by a similar PAN.P sample at these temperatures and the NO removal rate decreased with time as normally happened.

5.6 Reaction of oxygen with NO over PAN.P

Oxygen reacts with NO to form nitrogen dioxide (NO_2).

Table 21

Reaction of NO with PAN.P in the presence of the oxides of carbon

Reaction Conditions

Mass of PAN.P fibre:	5 g
Pyrolysis Temperature:	600°C
Reaction Temperature:	500°C
Gases:	2010 vpm NO in nitrogen 8.5% CO and 13.5% CO_2 in nitrogen
Gas Flow rate:	7 l min^{-1}

Results

	Gas Flow rates to the analysers/mol s^{-1}		
	NO	CO	CO_2
Supply gases	58.1	44.7	70.1
After passage over steel catalyst and preheat vessels	50.1	36.7	78.1
After passage over steel vessels + PAN.P	32.1	36.2	77.8

$$NO + \tfrac{1}{2}O_2 \rightleftharpoons NO_2$$

This reaction is termolecular involving two molecules of NO and one of oxygen and is slow at low concentrations of NO. Above 140°C the reaction is reversible with the equilibrium position moving to the left as the temperature is increased. The chemiluminescent analyser could be set to monitor either NO or total nitrogen oxides (NO_x). A comparison of these readings gave the concentration of NO_2. The concentration of NO_2 was always found to be negligible.

Table 22 gives some results for the rate of removal of oxygen and NO when the two gases were passed over PAN.P together. It can be seen that both oxygen and NO were removed from the gas stream at 510°C and 640°C. The initial quantity of each gas removed by the PAN.P increased at the higher temperature. The removal rate of both gases decreased with time at constant temperature.

A comparison of the NO removal rate under similar conditions but without oxygen present showed that oxygen inhibited the reaction of NO with PAN.P. At 640°C the PAN.P initially removed all the NO from the gas stream and the decrease in removal rate was less than with oxygen present.

5.7 Exhaust gases over PAN.P

Having ascertained the effects of the main constituents of car exhaust gas on PAN.P in the presence and absence of NO, the effect of exhaust gas itself was tested.

Gas was piped from the exhaust manifold of a test engine to the catalyst rig. As the gas had to be drawn through the pipe by the pumps in the analysers the pressure in the rig was only 0.83 atmospheres compared with 1 atmosphere for all previous experiments. As

Table 22

Reaction of NO with PAN.P in the presence of oxygen

A Reaction Conditions

Mass of PAN.P fibre: 5 g

Reaction Temperature: 510°C

Total Gas Flow rate: 5 l min^{-1}

	Reaction Time/min	Individual Gas Flow rate/mol $s^{-1} \times 10^6$	
		O_2	NO
Supply		74.5	4.7
After passage over PAN.P	0	59.1 (15.4)*	3.5 (1.2)
	2	65.3 (9.2)	3.8 (0.9)

B Reaction Conditions

Mass of PAN.P fibre: 2.5 g

Reaction Temperature: 640°C

Total Gas Flow rate: 5 l min^{-1}

	Reaction Time/min	Individual Gas Flow rate/mol $s^{-1} \times 10^6$	
		O_2	NO
Supply		40.9	4.2
After passage of O_2 and NO together over PAN.P	0	9.3 (31.6)	0.5 (3.7)
	2	12.8 (28.1)	1.9 (2.3)
NO alone over PAN.P	0		0 (4.2)
	2		0.2 (4.0)

*Figures in brackets show rate of gas removal mol $s^{-1} \times 10^6$

seen in section 4.3.4 this has only a slight effect on NO removal rate.

The analysis results for the exhaust gas before and after reaction are given in Table 23. The supply figures are for the gas as it arrived from the engine. The preheat figures are for the gases after passage through the stainless steel preheat vessel. Any changes produced by the preheat vessel must be doubled to allow for the identical catalyst vessel before any PAN.P effect can be assumed.

In section A of Table 23 the fuel/air ratio supplied to the engine was maintained on the rich side of stoichiometric to minimise the amount of oxygen in the exhaust gas. This also reduced the NO content of the exhaust gas and the engine was run under load to increase the NO concentration without increasing the oxygen concentration. The supply results show that the NO concentration was still relatively low at 350 vpm and very much less than the oxygen at 15,000 vpm.

Analysis results for the exhaust gas after passage through the preheat chamber show a reduction in NO and CO concentrations. As noted in section 5.3 this was due to catalysis of the reaction of NO with CO by the steel vessel. A similar effect was produced by the catalyst vessel.

Passage of the exhaust gas through the catalyst chamber resulted in a large initial reduction in the NO concentration and complete removal of the oxygen. Also, unexpectedly, there was an almost 50% reduction in the hydrocarbon concentration.

The NO removal rate decreased with time of reaction and then stabilised after 8 minutes. The initial rate of NO removal, taking into account the amount removed by reaction with CO, was 0.965×10^{-6} mol s^{-1} and this reduced to 0.31×10^{-6} mol s^{-1} after 8 minutes. In

Table 23

Reaction of PAN.P with motor vehicle exhaust gas

Reaction Conditions

Total Gas Flow rate:	7 l min^{-1}
Reaction Temperature:	$640^{o}C$
Mass of PAN.P fibre:	5 g
Pressure:	0.83 atmospheres

Results

A Rich fuel/air ratio

	Reaction Time/min	Individual gas concentrations NO/vpm	 HC/vpm	 O_2/%	 CO/%	 CO_2/%
Supply		350	635	0.15	6.60	13.2
Preheat		280	635	0.15	6.55	13.2
Catalyst	0	25	360	0.00	6.40	13.5
	2	130	370	0.00	6.40	13.5
	8	150	390	0.00	6.45	13.5
	13	150	400	0.00	6.50	13.5

B Stoichiometric fuel/air ratio

	Reaction Time/min	Individual gas concentrations NO/vpm	 HC/vpm	 O_2/%	 CO/%	 CO_2/%
Supply		900	500	0.20	3.6	13.7
Preheat		850	500	0.20	3.4	13.8
Catalyst	0	725	325	0.00	3.2	14.1
	40	725	360	0.00	3.2	14.1

experiments where 5 g PAN.P fibre had been reacted with NO in N_2 at 600^oC the initial NO removal rate had been 6.4×10^{-6} mol s^{-1} and this had reduced to 5.2×10^{-6} mol s^{-1} after 8 minutes. Thus the PAN.P sample was capable of removing all the NO in the exhaust gas for several minutes at least.

The results in section B of Table 23 are for a stoichiometric fuel to air ratio supplied to the engine which was also maintained under load. The concentrations of NO and oxygen in the exhaust stream are higher than previously.

The effect of the preheat and catalyst vessels was similar to those for section A. However the NO removal rate by the catalyst was less than previously despite a higher concentration of NO. The initial removal rate was only 0.4×10^{-6} mol s^{-1} but this was maintained at a constant level throughout the experiment.

The rate of removal of NO from exhaust gas by PAN.P was much less than the rate of removal of NO from a mixture with nitrogen under similar conditions. This suggests that some constituent of exhaust gas may inhibit the NO and PAN.P reaction.

5.8 Hydrocarbon + Oxygen over PAN.P

In the reactions of exhaust gas with PAN.P the hydrocarbon content of the gas was reduced. It was seen in 5.4 that NO did not react with hydrocarbon to any appreciable extent. Also the hydrocarbon does not react with PAN.P. The most likely explanation was reaction of the hydrocarbon with oxygen. It was of interest to see whether this was the case and whether it only occurred in the presence of PAN.P.

Initially mixtures of NO, oxygen and hydrocarbon (propane) in nitrogen were combined and passed into the catalytic reactor. The

Table 24

Reactions of NO, hydrocarbon and oxygen over PAN.P

Reaction conditions

Mass of PAN.P: 2.5 g

Gas Flow rate: 5 l min^{-1}

Reaction Temperature: 660°C

Results

A NO + hydrocarbon + oxygen

	Gas Flow rates/mol s^{-1} x 10^6		
	NO	hydrocarbon	Oxygen
Supply	3.1	1.4	11.2
After Preheat	3.1	1.4	11.2
After Catalyst	0.4	0.9	1.9

B Hydrocarbon + oxygen

Supply		2.2	14.9
After Preheat		2.2	14.9
After Catalyst		1.5	5.6

analysis results for the supply rate of the gases and the initial removal rate by the catalyst at 660°C are given in Table 24 section A. Most of the NO and oxygen were removed on passing over the PAN.P as would be expected and about a third of the hydrocarbon was removed. The preheat vessel had no effect on the concentration of the gases.

Oxygen and hydrocarbon were then passed into the reactor together and the results are given in Table 24 section B. Again both oxygen and hydrocarbon were removed on passing the gases over PAN.P at 640°C. The fact that the concentrations of these two gases did not change on passing into the preheat vessel indicates that they do not react together at 640°C in the absence of the PAN.P.

This reaction between oxygen and hydrocarbon in the presence of the PAN.P is significant as it removes oxygen which otherwise would react with and consume the polymer itself. Obviously the concentration of hydrocarbon to oxygen is too small under normal circumstances to be of any real benefit.

CHAPTER 6

SPECTROSCOPIC STUDIES OF PAN.P BEFORE AND AFTER REACTION WITH NO

6.1 Electron spin resonance studies of PAN.P

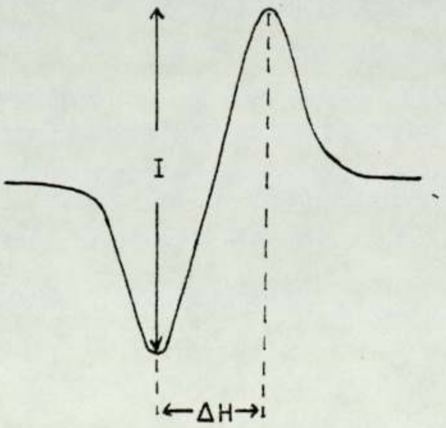
6.1.1 Electron spin resonance spectrum of PAN.P

The electron spin resonance (e.s.r.) absorption of PAN.P has been noted and measured by other workers.[21,40,41,42] Its importance in relation to catalytic properties and particularly to reactivity towards NO is discussed in section 1.6.

The e.s.r. spectrum of PAN.P consists of a single absorption peak. The e.s.r. recorder traces out the first derivative curve for this absorption as illustrated in Figure 16.

Figure 16

First derivative of the e.s.r. absorption line for PAN.P



The g value for the PAN.P absorption was found to be 2.003, which is the same as for the free electron.

6.1.2 Comparison of free spin concentrations

The area under the e.s.r. absorption curve is proportional to the number of free spins in the sample. The area can be obtained by double integration of the first derivative curve.

The absolute number of free spins is normally obtained by comparison of the sample absorption curve with that of a standard sample whose spin concentration is known. For samples of similar curve shape but differing in line width, the relative concentrations of free spins are given by

$$\frac{N_1}{N_2} = \frac{I_1 \; \Delta H_1^2}{I_2 \; \Delta H_2^2}$$

N = number of free spins

I = inter-peak height on first derivative absorption curve

ΔH = line width

It is essential when comparing spin concentrations to keep experimental conditions identical for each sample. Thus the PAN.P sample mass and the instrument settings were kept constant for each measurement. Where a series of samples was being compared all the samples were prepared in advance and the measurements were made in rapid succession. The sample preparation procedure is described in section 2.5.2. It was necessary, due to the large variation in spin concentrations, to alter the amplitude setting on the instrument when running through a series of samples. When this was done a sample was measured at both amplitude settings to check the magnitude of the change.

The number of free spins in the PAN.P samples was obtained by comparison with solid diphenyl-pyryl-hydrazyl (DPPH) which was assumed to contain one free spin per molecule giving 1.53×10^{21} spins g^{-1}.

6.1.3 Factors affecting spin concentration in PAN.P

6.1.3.1 Storage time

The PAN.P samples were pyrolysed under vacuum and once they had cooled they were exposed to the atmosphere. The samples were then stored in air filled containers. It was noted that the e.s.r. absorption of a sample reduced slightly over the first 48 hours following pyrolysis and then remained constant. Thus all samples were stored for at least two days before any comparison of free spins was made. This also applied to samples whose activities to NO were compared in the catalytic reactor.

6.1.3.2 Pyrolysis time

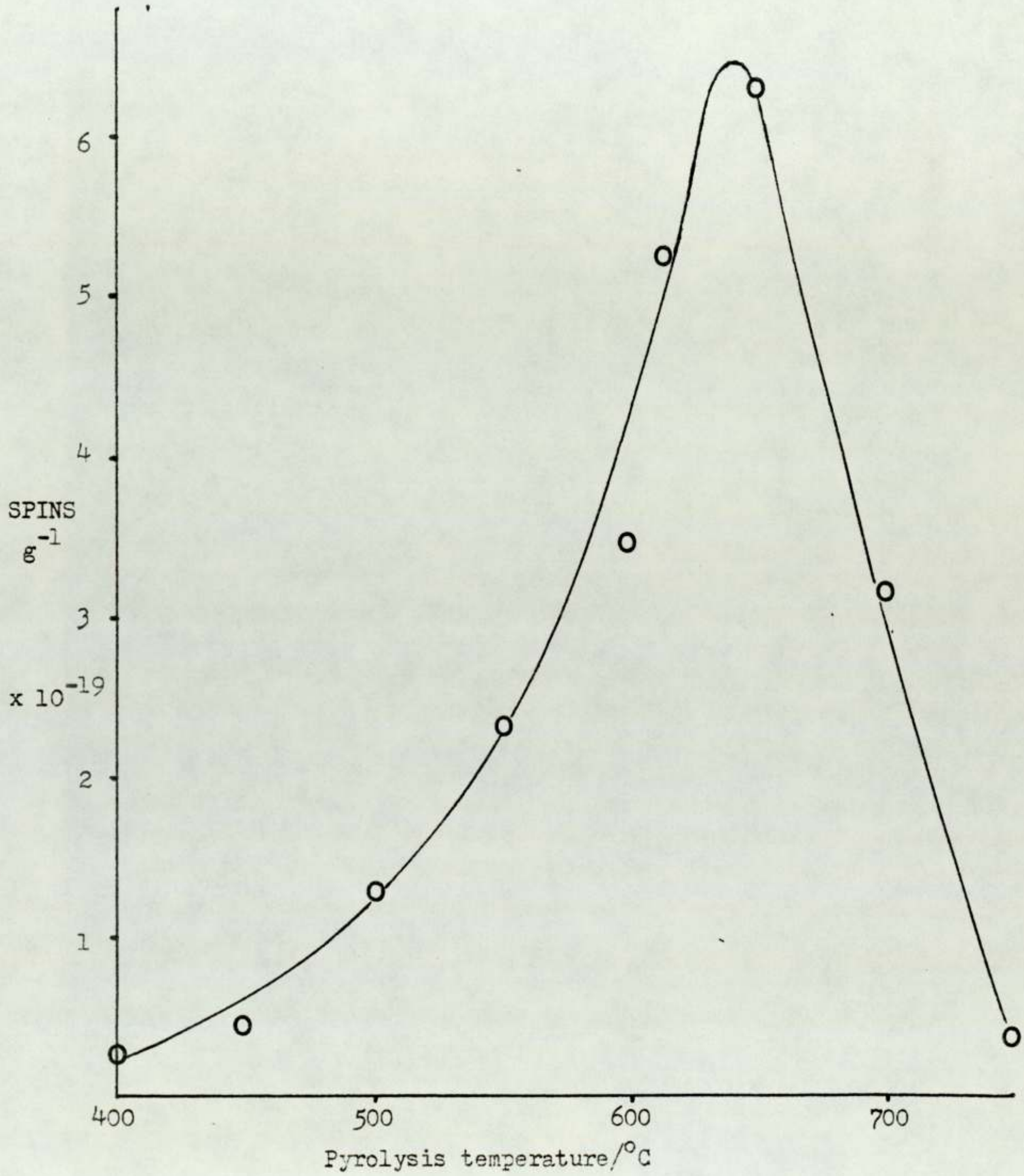
The free spin concentration for PAN.P samples increased as the pyrolysis time was increased up to 4 hours and then remained constant. Thus all PAN.P samples were pyrolysed for 4 hours.

6.1.3.3 Pyrolysis temperature

E.s.r. spectra of samples of PAN.P which had been pyrolysed under vacuum for 4 hours at various temperatures between 300 and 700°C were obtained. The intensity of e.s.r. absorption, expressed in spins g^{-1}, as a function of sample pyrolysis temperature is shown in Figure 17. The free spin concentration rose rapidly as the pyrolysis temperature was increased above 300°C until it reached a maximum at around 640°C. It then fell rapidly as the pyrolysis temperature was raised further. 700°C was the highest temperature that could be obtained using the fluidised bath. However a sample of PAN.P fibre was heated to 750°C under nitrogen in the catalytic reactor. Comparison of the e.s.r. spectrum of this sample with the others was complicated by a change in dielectric loss for this sample. This was

FIGURE 17

Graph of the variation in free spin concentration with pyrolysis temperature for PAN.P



corrected by adjusting the e.s.r. instrument and appeared to be due to an increase in the electrical conductivity of the sample. The intensity of the e.s.r. absorption for this sample had decreased still further as shown on the graph.

A sample of commercially prepared carbon fibre was also tested for e.s.r. absorption. This fibre was similar to the PAN.P fibre, they were both made from the same starting material, but had been heated to 2000°C in an inert atmosphere. Again the e.s.r. instrument had to be adjusted to allow for its high electrical conductivity. It gave no detectable e.s.r. absorption.

Measurements of e.s.r. absorption carried out on samples of PAN.P powder, prepared from Monsanto PAN powder, gave similar results to PAN.P fibre samples prepared under the same conditions.

6.1.4 Effect of NO and oxygen on the e.s.r. absorption of PAN.P

Experiments were now carried out to determine whether the free spin concentration for PAN.P was affected by its reaction with NO. The NO molecule contains an unpaired electron which may combine with an unpaired electron on PAN.P thus reducing the intensity of the latter's e.s.r. absorption. Ideally the e.s.r. absorption for PAN.P should be monitored during its reaction with NO. However this would require that the reaction be carried out in the sample cavity of the e.s.r. instrument. Initially this was not considered possible due to the high temperatures necessary for the reaction. Instead, e.s.r. measurements were made on samples of PAN.P fibre before and after reaction with NO.

As was shown in section 4 the reactivity of a PAN.P sample to NO decreased gradually as the reaction proceeded and eventually disappeared completely. This may have been due to the removal of the free spins on the PAN.P by NO or by a product of the reaction between PAN.P and NO. In either case the e.s.r. absorption of the deactivated sample would be expected to be less than for the untreated sample if the free spins were responsible for the activity to NO. However PAN.P samples which had been reacted with NO at the same temperature as their pyrolysis temperature, until deactivated, showed no reduction in their free spin concentrations. PAN.P samples which had been similarly reacted with NO at temperatures above their pyrolysis temperature showed an increase in free spin concentration after reaction. Thus heating the PAN.P to a higher temperature produced more free spins but reaction with NO had no apparent effect on the free spin concentration.

Meanwhile other work (see section 4.4) had shown that when PAN.P was heated in an inert atmosphere oxides in its structure decomposed giving CO and CO_2. The activity of the PAN.P to NO was greatly improved by this treatment and experiments were now carried out to determine its effect on the free spin concentration of PAN.P.

The sample chosen for the initial investigation was a supported PAN.P catalyst pellet prepared using a 1% solution of PAN in DMF. It had only a very thin coating of PAN.P and had no detectable e.s.r. absorption. It was heated to $600^{\circ}C$ under vacuum in a quartz e.s.r. sample tube. After cooling the tube was sealed to maintain the vacuum and transferred to the sample cavity of the e.s.r. spectrometer. The e.s.r. spectrum now showed a distinct absorption signal. The recorder pen was stopped at one of the absorption peaks and air was admitted to the sample tube. The pen moved instantly indicating a decrease in absorption peak size. A subsequent spectrum showed a large reduction in the e.s.r. absorption by the sample. The absorption continued to slowly reduce in intensity as the sample was left standing in air. After two days no absorption was detectable.

These results showed that heating the PAN.P to a high temperature under vacuum greatly increased the free spin concentration of the sample. Subsequent exposure of the sample to the atmosphere reduced the spin concentration once again.

Further PAN.P samples were heated under vacuum as above and their e.s.r. absorptions measured. The samples were then exposed to different gases to monitor the effect on their free spin concentrations. The results for NO are given in Table 25.

Table 25

E.s.r. absorption intensities of PAN.P samples before and after heating to 600^{o}C under vacuum and after subsequent exposure to NO at ambient temperature

Sample	E.s.r. inter-peak height/cm			
	Initial absorption	After heating to 600^{o}C under vacuum	After exposure to NO	After 2 days exposure to NO
A*	No absorption	18.5	1.0	No absorption
B$^{\phi}$	1.8	27.0	3.1	1.9
PAN.P fibre	5.4	22.0	6.0	5.4

*Sample A - supported PAN.P sample prepared using 1% solution PAN in DMF

$^{\phi}$Sample B - supported PAN.P sample prepared using 8% solution PAN in DMF

Oxygen gave similar results to NO and the reduction in the e.s.r. signal in both cases was instantaneous. A further slight reduction occurred with time.

Admission of nitrogen to the sample tube did not affect the e.s.r. signal. This is consistent with the fact that NO and oxygen contain unpaired electrons, which can interact with the free spins on PAN.P, whereas nitrogen does not.

Only the free spins on the PAN.P surface would be expected to react with the paramagnetic gases. The supported PAN.P sample prepared from 1% solution of PAN in DMF had a very thin coating of PAN.P and therefore a very large surface area relative to bulk for the polymer. After prolonged exposure to NO the e.s.r. absorption for this sample disappeared completely. The supported sample prepared from the 8% PAN solution had a thicker coating of PAN.P and did not completely lose its e.s.r. absorption on exposure to NO. The PAN.P fibre had a very low BET surface area (1 m^2 g^{-1}) suggesting a relatively non-porous cylindrical structure of 10 um diameter as shown in Plate 7, page . However, it lost about 75% of its free spin concentration after exposure to NO or oxygen. This suggests that most of the free spins were concentrated on the small surface area of the fibre or that the surface area was actually greater than that measured by the BET method. Marsh and Wynne-Jones[43] measured the surface areas of some carbons by the BET nitrogen absorption method at -196°C and also by carbon dioxide absorption at -78°C. They found that in some cases the latter technique gave results which were up to 200 times greater than the BET results. They suggested that for carbons with a very fine pore structure the rate of diffusion of the nitrogen into the pores at -196°C was too slow for equilibrium to be attained in a reasonable time and the surface area appeared to be much less than it really was. The concentration of free spins remaining after initial exposure to NO or oxygen decreased slightly after 2 days of continuous exposure and then remained constant. This suggests that a slow diffusion of the gases into the PAN.P occurred, indicating the presence of a fine pore structure. The free spins which remained unaffected by the paramagnetic gases were presumably contained in the bulk of the sample or in very fine pores whose entrance was blocked by the adsorption of a single gas molecule. Harker et al[44] found a similar decrease in the free spin concentration of carbon samples which were exposed to NO. Outgassing of their samples at room temperature did not restore the e.s.r. absorption but it was partially restored by heating to 100°C under vacuum. This indicated that the NO was not just physically absorbed onto the surface. The PAN.P samples were not outgassed at room temperature following exposure to NO and prior to e.s.r. measurement but it was shown in section 4.4 that PAN.P samples had to be heated to elevated temperatures to restore their activity after exposure to NO or oxygen. The regain in activity coincided with an increase in e.s.r. absorption and the evolution of carbon oxides. This suggests that chemisorption of NO or oxygen at the free spin sites was followed by reaction to form a surface oxide. Subsequent heating decomposed the oxide to give CO or CO_2 and regenerate a free spin.

The reason why there was no apparent decrease in the free spin concentration of the PAN.P sample after reaction with NO also becomes clear. The PAN.P was exposed to the atmosphere after pyrolysis under vacuum and oxygen was then chemisorbed at all the accessible free spin sites. Subsequent e.s.r. absorption measurements detected only the inaccessible free spins whose concentration remained constant before and after reaction with NO.

6.2 Infrared studies of the PAN and PAN.P samples

The chemical changes which occur during the pyrolysis of PAN are complex and still not proven after extensive study. The reaction was even more complex in this work as commercially produced PAN copolymers were used to prepare the PAN.P samples.

Infrared spectroscopy provided a simple and reliable means of following the changes in chemical structure which occurred during pyrolysis and of comparing samples produced under different conditions. It also enabled comparison to be made between the PAN.P samples used in this work and those used by other workers.

6.2.1 PAN copolymers

Two polyacrylonitrile copolymers were used in this work and their respective infrared transmission spectra are shown in Figure 18. The 'Courtelle' was prepared from a mixture of 91% acrylonitrile, 8% methyl acrylate and a small fraction of itaconic acid. The only noticeable difference between the infrared spectrum for 'Courtelle' and that for pure PAN[45] was that 'Courtelle' had an additional strong absorption peak at 1,720 cm^{-1}. This was undoubtedly due to the carbonyl group introduced into the structure by the methyl acrylate comonomer.

The second copolymer, produced by Monsanto Ltd, was of unknown chemical composition. It also had a strong carbon absorption centred on 1,730 cm^{-1}. There were two further peaks at 1,230 cm^{-1} and 1,035 cm^{-1} not present for PAN homopolymer.

6.2.2 Pyrolysed PAN

6.2.2.1 Samples pyrolysed under vacuum

Films of PAN, 10 µm or less in thickness were heated under vacuum to various temperatures. The infrared transmission

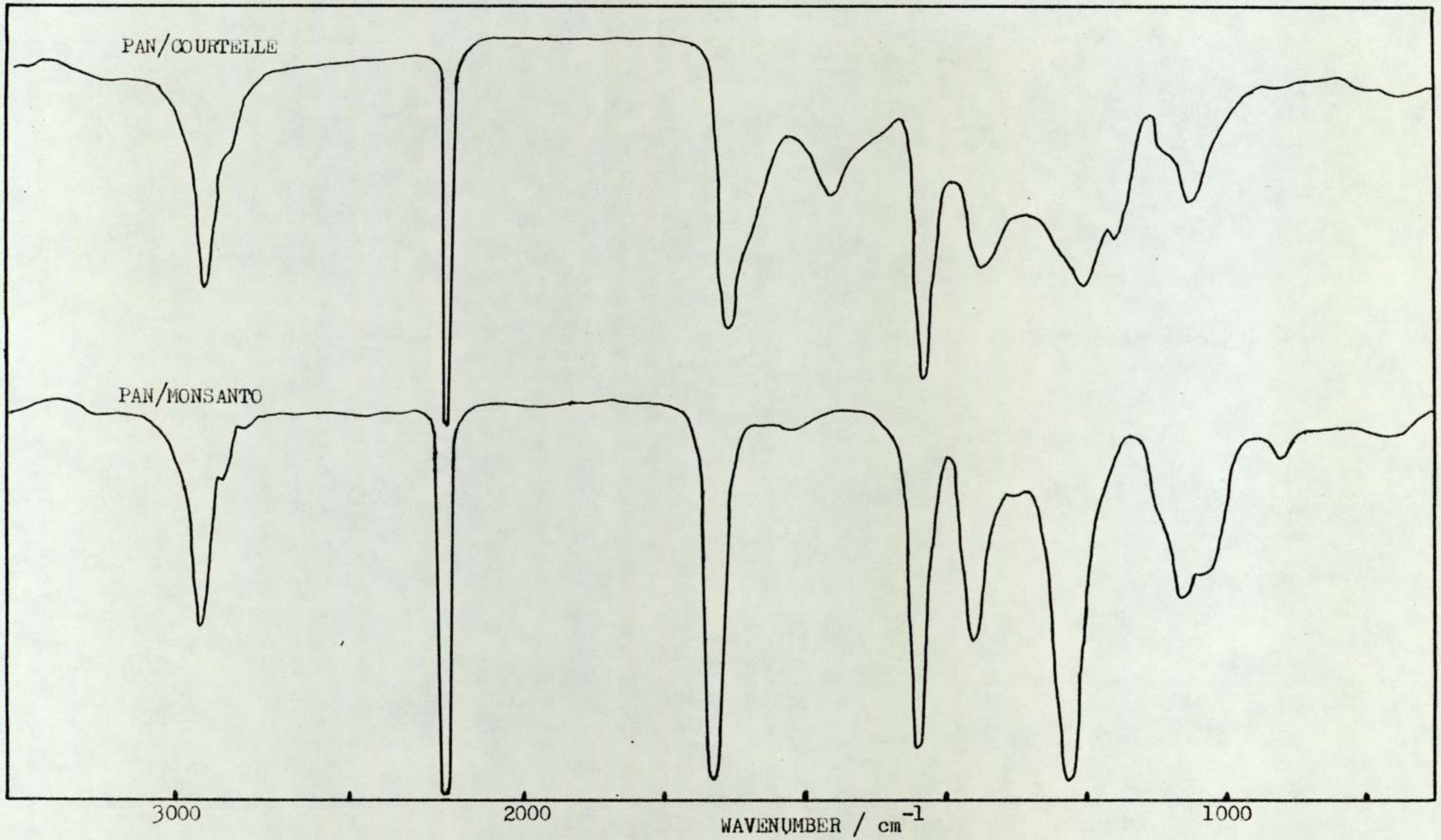


Figure 18 Infrared spectra of acrylonitrile copolymers from Courtaulds Ltd.(PAN/COURTELLE) and Monsanto Ltd

spectra of these films were then obtained and the results for a sample of 'Courtelle' are shown in Figure 19. The 400°C spectrum is in agreement with published spectra of PAN.P at around this temperature.[8] As the temperature was raised above 500°C the spectrum became featureless apart from the broad intense absorption between 1,700 - 1,000 cm^{-1}.

6.2.2.2 Samples pyrolysed in air

When PAN is heated in air the polymer reacts with the atmospheric oxygen at temperatures above 150°C. This process has been described in detail in section 1.5. Figure 20 shows infrared transmission spectra of samples of PAN.P prepared by heating PAN to 350°C under vacuum and to 350°C in air. The latter spectrum shows less detail, especially above 2,500 cm^{-1}, but the main difference is the appearance of shoulders at 1,720 cm^{-1} and 1,660 cm^{-1}. A differential spectrum was obtained by placing the vacuum PAN.P sample in the reference beam and the air sample in the sample beam. The broad absorption between 1,800 cm^{-1} and 1,600 cm^{-1} suggests the presence of carbonyl groups formed by oxidation of the PAN.P.

6.2.3 Studies using an infrared cell

Although in the previous section the PAN samples were pyrolysed under vacuum it was necessary to expose them to the atmosphere before an infrared spectrum could be obtained. It is known that freshly pyrolysed PAN.P reacts readily with atmospheric oxygen[12,37] and it was thought that this may have a significant effect on the PAN.P infrared spectrum. A less detailed PAN.P spectrum, especially in the 1,700 - 1000 cm^{-1} region, would be desirable when looking for changes in the PAN.P spectrum after reaction with NO. With this in mind an infrared cell was constructed which would enable spectra of PAN.P to be obtained without exposing the pyrolysed polymer to the atmosphere. The

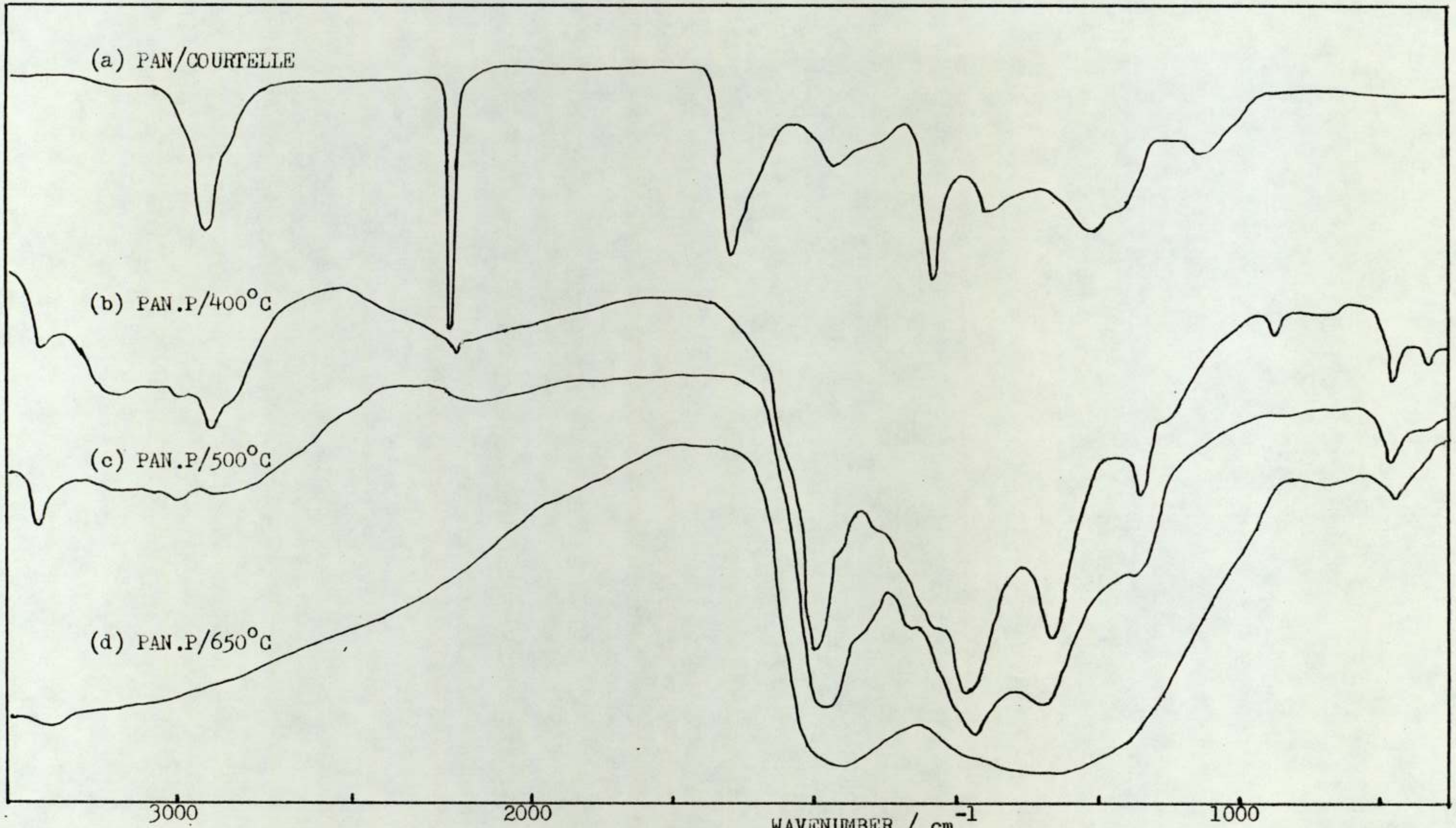


Figure 19 Infrared spectra of acrylonitrile copolymer and PAN.P pyrolysed to various temperatures

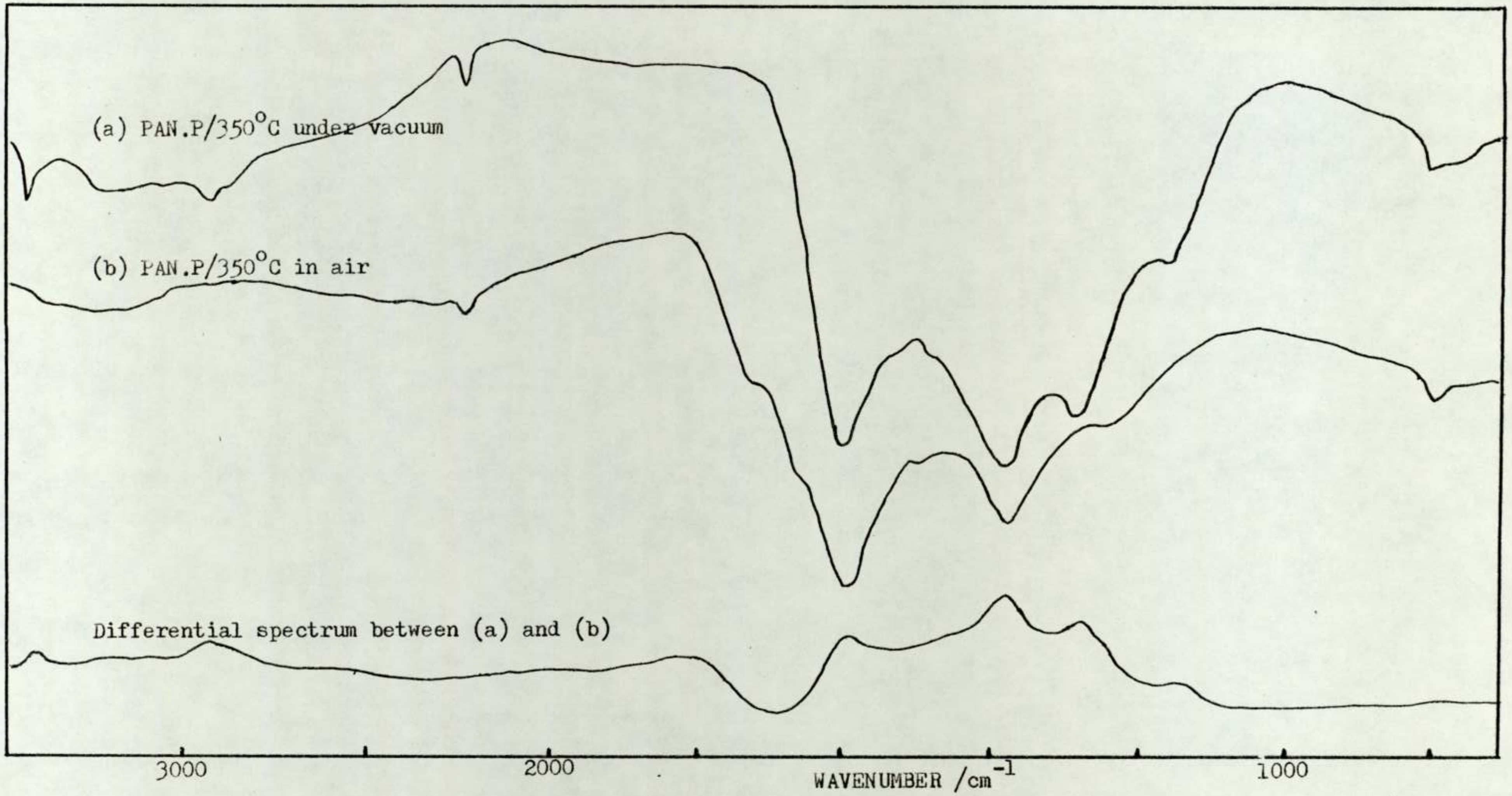


Figure 20 Infrared spectra of PAN.P samples pyrolysed in air and under vacuum

cell is described in detail in section 2.4.1.2. Figure 21 shows infrared spectra of PAN pyrolysed to various temperatures up to 400°C while inside the cell. The spectra are typical of those described in the literature for the pyrolysis of PAN at these temperatures. A comparison of spectrum (b) in Figure 19 and spectrum (c) in Figure 21 shows that they are virtually identical. Both samples were pyrolysed to the same temperature under vacuum but the former was exposed to the atmosphere before its infrared spectrum was obtained. This is also confirmed by comparing spectra (c) and (d) in Figure 21 which are of the same sample before and after exposure to the atmosphere. Again there is no change. This shows that any reaction which occurred between the fresh PAN.P and atmospheric oxygen did not affect the infrared spectrum of PAN.P. It is also interesting to note that 'Courtelle' copolymer was used to obtain the spectra shown in Figure 19 and Monsanto copolymer for those in Figure 21. Although the infrared spectra for the individual copolymers are slightly different the spectra after pyrolysis to 400°C are virtually identical.

6.2.4 PAN.P samples after reaction with NO

The aim of these experiments was to see if there was any change in the infrared spectrum of PAN.P following exposure to NO. The presence of new absorption peaks due to a PAN.P-NO complex or reaction product would help to establish how the two interact.

Initially samples of PAN.P prepared by heating PAN to 400°C under vacuum were reacted with NO at 400°C. The reactions were carried out using 100% NO under static conditions and also by passing 2,000 vpm NO in nitrogen over the PAN.P for several minutes. No change was detected in the PAN.P spectrum.

Further reactions were carried out in the infrared cell. This

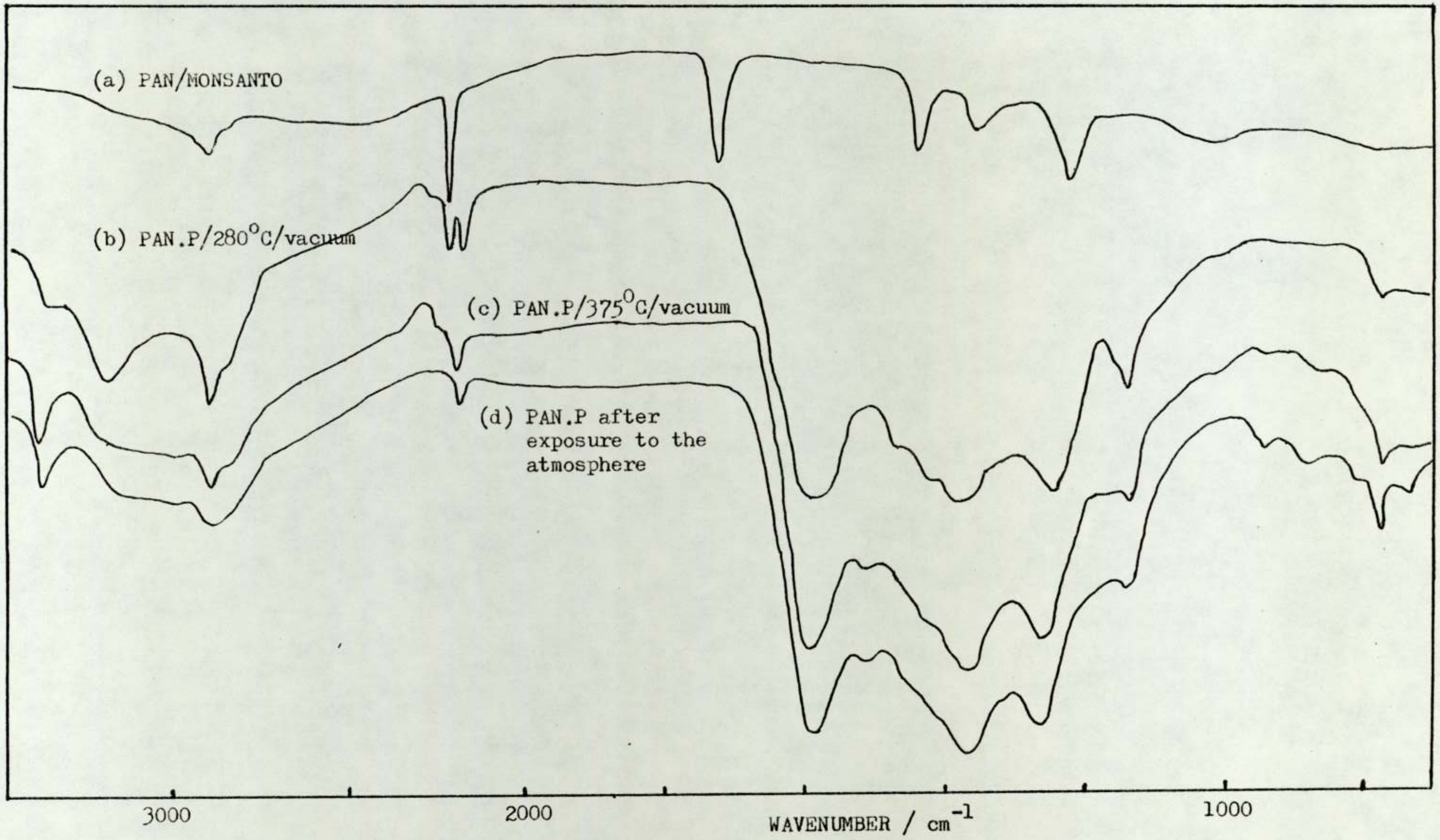


Figure 21 Infrared spectra of acrylonitrile copolymer before and after pyrolysis under vacuum in an infrared cell

had the advantage that the PAN could be pyrolysed under vacuum, exposed to NO, the cell re-evacuated, and a spectrum obtained of the PAN.P film without the sample being exposed to the atmosphere.

The PAN.P was pyrolysed to 400°C inside the cell, this being the highest temperature attainable. 100% NO was admitted to the cell to a pressure of 50 cm of mercury. PAN.P samples were exposed to NO at 400°C, and also at ambient temperatures, having been allowed to cool after pyrolysis. It was possible that a PAN.P-NO complex would be more stable at lower temperatures. However exposure to NO at these temperatures did not noticeably alter the infrared spectra of the PAN.P samples.

Following the e.s.r. studies (section 6.1) it appeared that PAN.P which had been pyrolysed to 650°C would have the largest concentration of sites capable of interacting with NO and would therefore be the sample most likely to show some change in its infrared spectrum due to the interaction. The heater in the infrared cell was not capable of such temperatures and pyrolysis was carried out in a glass tube placed in the fluidised bed. Initially the films were pyrolysed under vacuum and then cooled to ambient temperature while remaining under vacuum. NO was admitted to the tube and allowed to interact with the PAN.P film for a few minutes. The tube was then re-evacuated before finally allowing air to enter, and removing the film to obtain its infrared spectrum. The reaction was carried out at ambient temperature as it was thought that any PAN.P-NO complex which was formed would be more stable at a lower temperature. E.s.r. studies had shown that NO greatly reduced the number of free spins present in PAN.P when the two were mixed at room temperature. However, no difference could be detected between films of PAN.P which had been treated with NO under the above conditions and those which had not.

The PAN.P films were then reacted with NO at 650^{o}C. The films were pyrolysed as previously and allowed to cool under vacuum. NO was admitted to the glass tube which was then reheated to 650^{o}C in the fluidised bed for 30 minutes. Following this the tube was cooled and evacuated before admitting air. The PAN.P film was then removed and its infrared spectrum obtained. Infrared spectra of a PAN.P film pyrolysed to 650^{o}C under vacuum and of a similar PAN.P film reacted with NO as described above are shown in Figure 22. The only difference between the two spectra is a very small peak at 2,210 cm^{-1} on that of the NO treated sample. Several samples were heated in NO to 600^{o}C or higher and all showed this peak. The peak was not detected on any sample which had not been heated in NO to these temperatures.

6.2.5 Multiple internal reflection spectroscopy

It is likely that the reaction between the PAN.P film and NO is limited to the surface of the film. This means that with transmission infrared spectroscopy the number of infrared absorbing species due to a PAN.P-NO surface complex would be very small compared to the total number of absorbing species throughout the bulk of the film. Thus any absorption due to a PAN.P-NO species may remain undetected because it is swamped by the PAN.P absorption or because there is an insufficient concentration of the species in the infrared beam.

Multiple internal reflection (MIR) spectroscopy can overcome this problem because the infrared beam only penetrates the sample surface for a few microns and does this several times along the length of the specimen. The proportion of surface species in the path of the beam is therefore very much greater than with transmission spectroscopy.

MIR spectroscopy was used to examine similar PAN and PAN.P films to those described in the transmission spectroscopy work. Spectra for

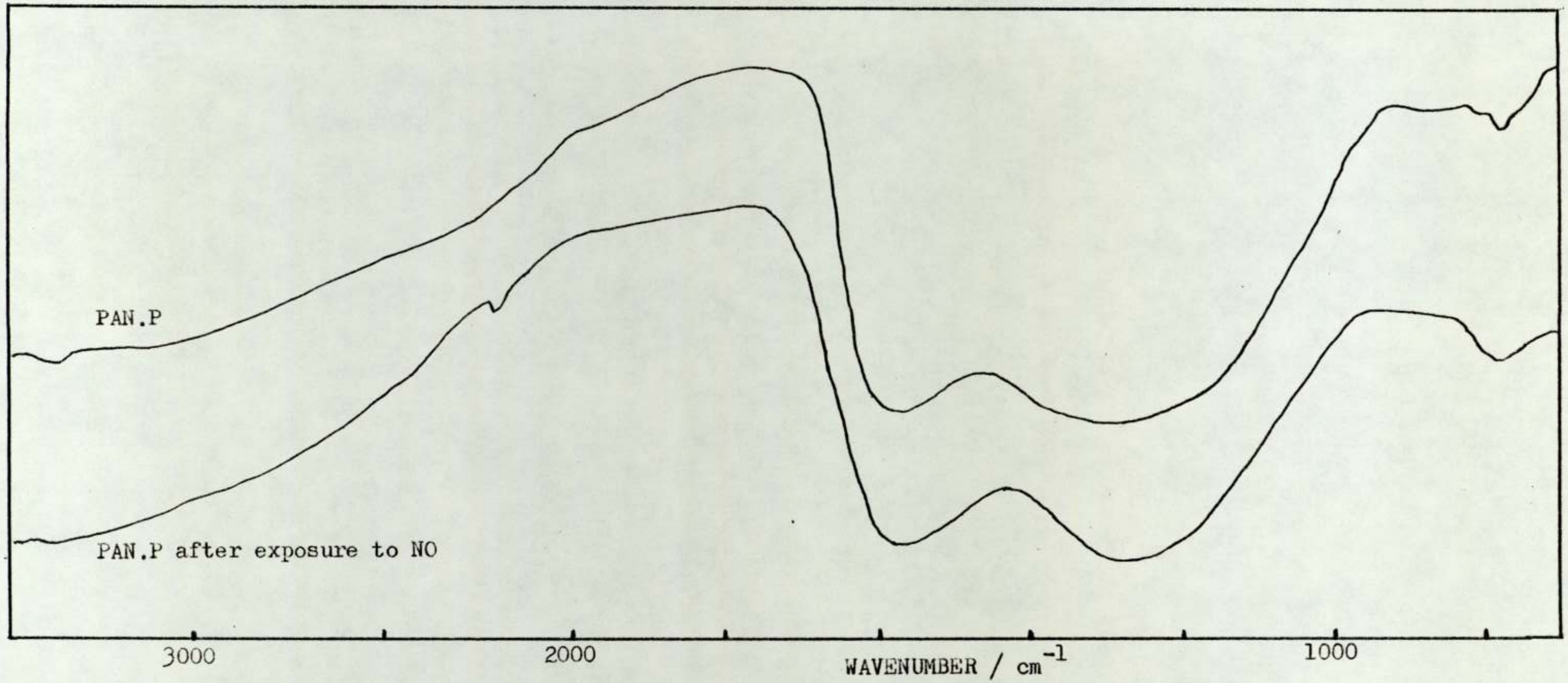


Figure 22 Infrared spectra of PAN.P before and after exposure to NO at 650°C

PAN and for PAN.P samples prepared at temperatures up to 400°C under vacuum were similar to those obtained by transmission spectroscopy. However as the pyrolysis temperature of the film increased above 400°C the spectra became less detailed and the absorption was so intense at wavenumbers below 1,700 cm^{-1} that no individual peaks were discernible. Spectra could not be obtained for films pyrolysed to temperatures above 500°C.

To obtain good MIR spectra it is essential to have good contact between the crystal and the sample surface. This helps prevent scattering, and thus loss, of the infrared radiation as it crosses the boundary between crystal and sample. Also the sample must not absorb too much of the radiation. The PAN.P films became harder and more brittle as they were pyrolysed to higher temperatures making good surface contact increasingly difficult. They also absorbed much more intensely. A combination of these factors was probably responsible for the poor quality spectra obtained with the high temperature films.

Unfortunately the samples which should give the greatest interaction with NO are those pyrolysed to 650°C and as mentioned it was impossible to obtain MIR spectra of these. Films pyrolysed to 400°C showed no change after treatment with NO at temperatures up to 400°C. However relatively little reaction occurs between NO and PAN.P pyrolysed to these temperatures. As soon as the pyrolysis temperature was raised much above 400°C the resulting spectra deteriorated in quality.

MIR spectra were also obtained of the 'Courtelle' fibre, oxidised 'Courtelle' fibre, and PAN.P fibre none of which could be obtained by transmission spectroscopy. These are illustrated in Figure 23. The MIR spectrum of the 'Courtelle' fibre is similar to that obtained by transmission spectroscopy of 'Courtelle' film except that the

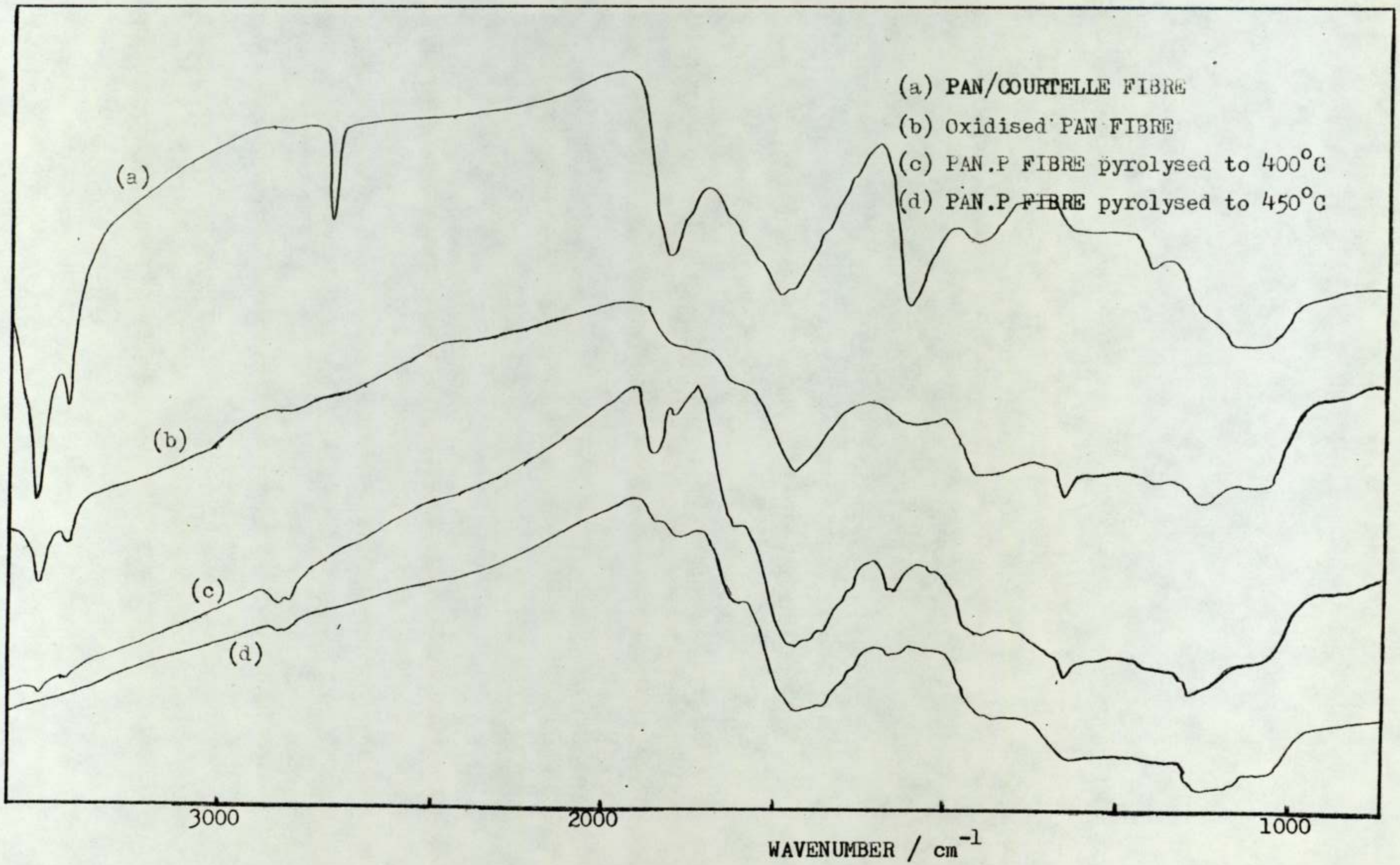


FIGURE 23 Multiple internal reflection spectra of acrylonitrile copolymer fibre and samples of PAN.P fibre

absorption peak centred on 1,590 cm^{-1} is more intense in the former. The oxidised 'Courtelle' sample is 'Courtelle' fibre which had been heated for 2 hours at $210^{o}C$ in air. It is the starting material for the preparation of PAN.P fibre. This again gave a similar spectrum to that obtained for oxidised 'Courtelle' film by transmission spectroscopy.

The third spectrum is that of PAN.P fibre which had been pyrolysed to $400^{o}C$ under vacuum for 3 hours. It has a peak at 1,745 cm^{-1} not seen on transmission or MIR spectra of PAN.P film. This peak is also absent from the MIR spectrum of the oxidised 'Courtelle' fibre. It is assumed that the peak is due to carbonyl groups produced by rearrangement of oxides on the surface of the PAN.P fibre. It is interesting to note that when PAN.P fibre was heated in nitrogen (Figure 9, page 80) CO_2 started to be evolved in detectable quantities at about $400^{o}C$. The 1,745 cm^{-1} peak has reduced to a shoulder on the spectrum for PAN.P fibre which had been heated to $450^{o}C$. Absorption peaks at 2,315 and 2,325 cm^{-1} suggest that CO_2 was physically adsorbed on the PAN.P surface. These peaks were characteristic of the MIR spectra of PAN.P samples pyrolysed to temperatures above $400^{o}C$.

6.2.6 Summary of infrared spectroscopy results

PAN.P samples prepared from 'Courtelle' and 'Monsanto' copolymers had identical infrared spectra which were also similar to spectra published for PAN.P prepared from PAN homopolymer.[46,47] It was not the intention of this work to interpret the spectra in terms of the structure of PAN.P. This has been attempted by other workers.[12,46,47,48]

Heating the polymer in air produced increased absorption in the carbonyl region, 1,600 - 1,800 cm^{-1}, due to oxidation of the polymer. Similar changes have been noted and interpreted by other workers.[8,46,47]

Generally, treatment of the PAN.P samples with NO produced no discernible change in the infrared spectrum of the polymer. However, samples which had been reacted at 650°C with NO and then cooled in an atmosphere of NO showed a small peak at 2,210 cm^{-1}. This peak is at a much higher frequency than the recorded absorption frequencies[49] for the organic nitroso (-C-N=O) or nitrosamine (C-N-N=O) groups which might be formed by the bonding of NO or N_2O to the polymer surface. Shelef[3a] has reviewed the recorded NO absorption frequencies for the various types of bonding which occur when NO is chemisorbed on inorganic materials. All occur at lower frequencies than the above peak except the ionically bonded NO^+ ion which absorbs in the 2,100 - 2,400 cm^{-1} range. However, the interaction of NO with the free spins on the PAN.P surface suggests that it is more likely to form a covalent bond. The peak at 2,210 cm^{-1} coincides with a strong absorption peak for the N_2O molecule and it is possibly due to N_2O which was formed during the reaction between PAN.P and NO and then physically adsorbed on the polymer surface. N_2O is itself decomposed by PAN.P at elevated temperatures[18] and it was not detected following reaction between PAN.P and NO at temperatures above 580°C (section 4.7.1). However, in the above case the PAN.P was allowed to cool to ambient temperature in the presence of excess NO and decomposition of the N_2O possibly ceased at the lower temperatures. N_2O has been detected by other workers following the reaction of NO with PAN.P[28] and with carbon.[39,44]

CHAPTER 7

FINAL DISCUSSION AND CONCLUSIONS

The results obtained in this work have been discussed in detail in the chapters in which they are presented. This chapter brings together these results, which cover various aspects of the PAN.P and NO interaction, to provide an overall picture of the reaction and the factors which affect it. A reaction mechanism is proposed and a critical survey is made of the use of PAN.P to remove NO from gas streams.

7.1 The effect of preparation conditions on the activity of PAN.P to NO

7.1.1 Supported and unsupported samples: a general comparison

Supported PAN.P samples were prepared in order to maximise the PAN.P surface area by coating the polymer onto a high surface area support. Unfortunately it was impossible to determine the actual PAN.P surface area on a supported sample as the BET method did not differentiate between polymer and inorganic support surface. Examination of the catalyst pellets suggested that only the exterior of the pellet was coated in PAN.P and that the inner pores, which constituted the major part of the surface area, were not penetrated. Various techniques were tried to improve polymer penetration into the pellets (section 3) but these had limited success. Pyrolysis of the PAN coated pellets in nitrogen rather than under vacuum gave pellets with a considerably darker cross-section suggesting improved polymer penetration. This was assumed to be due to the diffusion of polymer chain fragments into the pellet during pyrolysis in nitrogen. These fragments were removed during pyrolysis under vacuum. However the activity of the nitrogen pyrolysed samples to NO was not significantly greater than that of the other samples. It is claimed[27] that very high surface area supported PAN.P samples can be prepared by the vapour phase polymerisation of acrylonitrile 'in situ' in the support pellets using radioactive radiation to initiate the reaction. As the present work was concerned with the use of commercially available PAN this approach was not attempted.

Unsupported PAN.P in the form of PAN.P fibre was used for the majority of this work as it had an activity to NO which was comparable to the best of the supported samples. It was commercially available in a 'pre-oxidised' form which only required heating to the required pyrolysis temperature and was likely to be more stable to thermal decomposition and oxidative degradation.[8,28] The surface area of the PAN.P fibre was too small to be measured using the BET apparatus described in section 2. Calculation based on the assumption that the fibre was a non-porous cylinder gave a surface area value of 0.18 $m^2\ g^{-1}$. Rand and Robinson[50] measured the surface areas of carbon fibres, prepared from a similar starting material to that used for PAN.P fibre, using a very sensitive BET nitrogen adsorption apparatus and obtained values of around 0.5 $m^2\ g^{-1}$.

The uncertainty in surface area for both supported and unsupported samples made it difficult to obtain a true comparison of their activities to NO. It does seem that there is still scope for increasing the surface area and thus activity of the supported PAN.P samples if a more effective method of polymer deposition onto the support could be found.

7.1.2 The effect of pyrolysis temperature on PAN.P structure and reactivity

The PAN.P samples prepared and tested in this work showed activity towards NO when pyrolysed to temperatures between 400 - 700°C. Samples pyrolysed to temperatures below 400°C could not be tested in the catalytic reactor as they emitted unpleasant fumes when heated above their pyrolysis temperature. This indicated that the oligomerisation and chain scission reactions characteristic of the low temperature pyrolysis of PAN (see section 1.5) were incomplete. Between 400 - 700°C weight loss by the polymer is greatly reduced and hydrogen is the principal product.[12,41] This is thought to correspond to the conversion of the conjugated polyimine structure (Structure 1, page 10) to the condensed aromatic structure (Structure 3, page 11) which would appear to be responsible for the catalytic activity of PAN.P. Nitrogen is evolved when the polymer is heated above 800°C indicating a conversion from PAN.P to pure carbon.[12]

Various significant physical changes also occur in the polymer over this temperature range. Most notable is the change in e.s.r. absorption by the polymer. In this work (see section 6.1) the e.s.r. absorption reached a peak at a pyrolysis temperature of about 650°C and then decreased rapidly. Other workers have also measured the variation in free spin concentration of PAN.P with pyrolysis temperature. Wynne-Jones[40] found that it reached a peak at about 750°C, Fiedler[41] found the peak concentration occurred at 650°C, while Gallard[21] obtained the maximum e.s.r. absorption at 450°C. This appearance of free spins in PAN.P has been associated with the formation of conjugated double bonds in the polymer structure.[52] The decrease in free spins in PAN.P has been explained by the appearance of graphitic zones in the polymer in which recombination of electrons in doublets with opposite spins can occur.[23]

The phenomenon of e.s.r. absorption has, of course, been observed in other polymers. Harker, for example, has studied the free spins in cellulose carbons.[44] They show a similar variation in concentration with pyrolysis temperature to PAN.P. The unpaired electrons are considered to be π-type rather than σ-type as they are not detected unless aromatic layers are present to stabilise them. One free spin is believed to be associated with each aromatic layer plane and the electron is delocalised over all the carbon atoms in the layer. Paramagnetic susceptibility measurements indicated that the spins became progressively delocalised at higher pyrolysis temperatures which is consistent with growth in the size of the layer planes with increasing temperature. In support of this theory Jackson and Wynne-Jones have also found that the total number of layers present in a sample corresponds with the maximum attainable free spin concentration.[40] The same workers also note that nitrogen containing polymers, such as PAN.P, do not attain as high a free spin concentration as some other pyrolysed polymers. They also lose their e.s.r. absorption at temperatures below that at which nitrogen is lost so that true graphitisation has not occurred.

Jackson and Wynne-Jones also measured the electrical conductivity of a number of pyrolysed polymers[40] although not PAN.P. However these polymers had large e.s.r. absorptions which varied with pyrolysis temperature in a similar way to that of PAN.P. Their electrical resistivities, which changed in a similar manner for each polymer, decreased as the pyrolysis temperature was increased between 500 - 700°C. It then reached a minimum value and remained constant as the pyrolysis temperature was increased further. As the resistivity of the polymer decreased its e.s.r. absorption was increasing. The polymers which reached their minimum resistivity first (i.e. at the lowest pyrolysis temperature) likewise reached their maximum e.s.r. absorption first. The two did not occur at the same temperature however.

Brophy[51] measured current noise in samples of PAN.P pyrolysed to different temperatures. He found an increase in current noise for samples pyrolysed above 700°C which departed from the general trend for samples pyrolysed below this temperature. He said that this was consistent with a change in the structure of PAN.P at above 700°C. Thus a number of physical properties of PAN.P change in a regular manner with pyrolysis temperature and indicate a gradual change in the polymer structure. However the activity of PAN.P to NO did not appear to show any obvious trend with pyrolysis temperature. Samples pyrolysed between 400 - 600°C had similar activities but as the temperature was increased above 600°C the activity decreased with increasing temperature. Before going on to discuss other possible reasons for this decrease in activity it is necessary to point out that it was not possible to follow any change in PAN.P fibre surface area which may have occurred with increasing pyrolysis temperature. The surface area of supported PAN.P samples was found to increase slightly with increasing pyrolysis temperature up to 600°C (section 3.5.1). Such a change in the fibre samples may have masked an actual slight decrease in activity to NO as the pyrolysis temperature increased from 400 - 600°C. This would be in agreement with Cooper's[53] results as he found the activity of supported PAN.P samples decreased as their pyrolysis temperature was raised between 350 - 500°C. However, his samples were pyrolysed in vacuum only whereas the PAN.P fibre was preheated in oxygen prior to vacuum pyrolysis and this may have affected changes in structure and reactivity which occurred with increasing pyrolysis temperature.

Marsh and Wynne-Jones[43] measured the surface areas of pyrolysed polymers including PAN.P by CO_2 adsorption at -78°C. This technique gave much larger surface area values than the more usual nitrogen adsorption method and it indicated a large decrease in PAN.P surface area as the pyrolysis temperature was increased above 600°C. This was considered to be due to pore closure and would obviously have a significant effect on polymer activity. This surface area technique does not appear to be widely used by other workers and it has also been found that the adsorption of polar gases such as carbon dioxide on carbons is greatly increased by the presence of surface oxides on the carbon.[54] Such oxides were found to be present on the surface of PAN.P samples. However it is interesting that the decrease in activity of the PAN.P to NO should coincide with a decrease in CO_2 adsorption. The decrease may be due to a reduction in the concentration of oxides on the polymer surface. If an oxide is formed at a free spin site by reaction with oxygen then this would agree with the observed reduction in the free spin concentration of PAN.P above 650°C.

7.2 Effect of free spin concentration on activity of PAN.P to NO

Gallard[21] found a close correlation between the activity of PAN.P samples for the decomposition of N_2O and their free spin concentrations. However she did note that different polymers with similar free spin concentrations did not have similar activities for N_2O decomposition[21,22] and therefore free spin concentration was not the only factor which determined catalytic activity. Harker[44] compared the free spin concentration of cellulose carbons with their activity to NO at 0°C and 250°C. The free spin concentrations of the carbons varied in a similar way to that for PAN.P samples, reaching a peak at about 600°C. At 0°C he found a correlation between free spin concentration and the amount of NO adsorbed on the carbon surface. At 250°C there was no obvious relationship.

In this work there was, initially, no apparent connection between activity of the PAN.P samples to NO and their free spin concentration except that loss in activity coincided roughly with a decrease in free spin concentration. Samples pyrolysed to temperatures between 400 - 600°C showed a marked increase in free spin concentration with increasing temperature (Figure 17, page 115) but all had similar activities to NO (Figure 7, page 75). However it became apparent that when freshly pyrolysed PAN.P was exposed to the atmosphere all the accessible free spins were removed by reaction with oxygen. Thus e.s.r. measurements of the sample detected only the inaccessible free spins which were not involved in the reaction with NO. It is, however, assumed that the number of inaccessible free spins varied in proportion with the total number and thus gave a true indication of the variation of free spin concentration with pyrolysis temperature.

Exposure of freshly pyrolysed PAN.P to NO was also found to reduce the polymer's e.s.r. absorption indicating that reaction between NO and PAN.P also involved the free spins. However, before an air-exposed PAN.P sample would react with NO it was necessary to heat it to elevated temperatures to decompose the surface oxides and generate new free spins. This meant that the rate of oxide decomposition controlled the rate of NO removal and any variation in the thermal stability of the surface oxides with PAN.P pyrolysis temperature would affect the relative activities of the PAN.P samples to NO. The true relationship between free spin concentration of PAN.P and its activity to NO could only be determined by measuring the e.s.r. absorption and NO removal rate for samples which had not been exposed to the atmosphere. Practical difficulties and lack of time precluded such an investigation.

It was mentioned in the previous section that Harker[44] considered the free spins in carbon to be associated with aromatic layer planes which increased in size with increasing pyrolysis temperature. He suggested that the increasing delocalisation of the free spins at higher pyrolysis temperatures should reduce the strength of any bond formed between a free spin and a free radical. This suggests that the surface oxides on PAN.P should be removed more easily on the samples pyrolysed to higher temperatures. The average activation energies for NO removal by air-exposed PAN.P samples shown in Table 15, page 77, give an indication of the relative difficulty in removing surface oxides from samples pyrolysed to different temperatures. The activation energy for reaction between NO and a 'clean' PAN.P surface was found to be 10.8 kJ mol^{-1}. The much higher values obtained for the oxide covered PAN.P was due to the initial need to decompose the surface oxides and generate new free spins before reaction with NO could occur. The values in Table 15 suggest that decomposition of the surface oxides became more difficult, and not easier as suggested by Harker, as the PAN.P pyrolysis temperature increased.

7.3 Nature of the reaction between NO and PAN.P

Before proposing a mechanism for the PAN.P and NO reaction it is convenient to summarise the information which has been obtained about the reaction and is given in detail in section 4 and section 6.

(i) The initial rate of NO removal by PAN.P is first order with respect to NO concentration and surface area of PAN.P. (See section 4).

(ii) The NO appears to interact with the free spin sites on the polymer surface and the activation energy for this reaction is 10.8 kJ mol^{-1}. (See section 4.4.3).

(iii) Under isothermal conditions, at temperatures below about 700°C, the rate of reaction of NO with PAN.P decreases with time until the PAN.P is deactivated. This loss in activity occurs more slowly as the reaction temperature is increased and at temperatures above 700°C the loss is only partial and a continuous reaction occurs between PAN.P and NO. (See section 4.7.2).

(iv) Oxides are formed on the PAN.P surface during the reaction and small quantities of CO and CO_2 are also produced. Nitrogen is also assumed to be a product as no NO_2 or N_2O were detected in the outlet gas stream and NO was not reversibly adsorbed.

(v) Infrared studies suggest that N_2O may be formed on the PAN.P surface and Cooper[53] detected significant quantities of N_2O during static experiments between NO and PAN.P at 500°C.

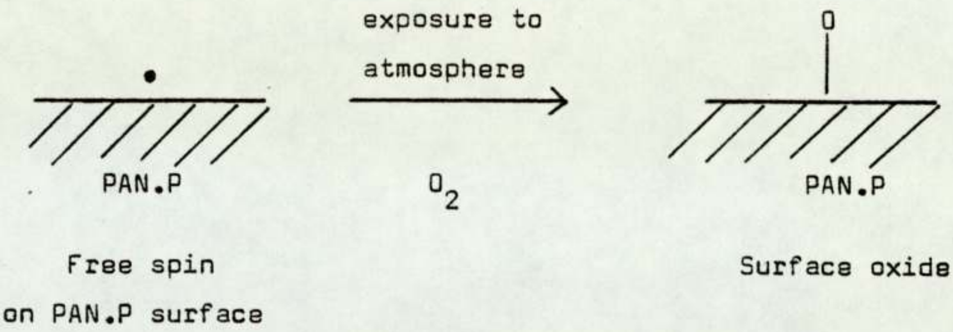
(vi) More than one molecule NO is removed per active site on polymer surface. (See section 4.5).

(vii) PAN.P which has been deactivated by reaction with NO can be reactivated if heated to temperatures above the reaction temperature. CO and CO_2 are evolved during this process and both the amount of these gases produced and the regain in activity increase as the temperature is increased.

This suggests that oxides which are formed at the active sites on the polymer surface are decomposed to give CO or CO_2 and regenerate active sites.

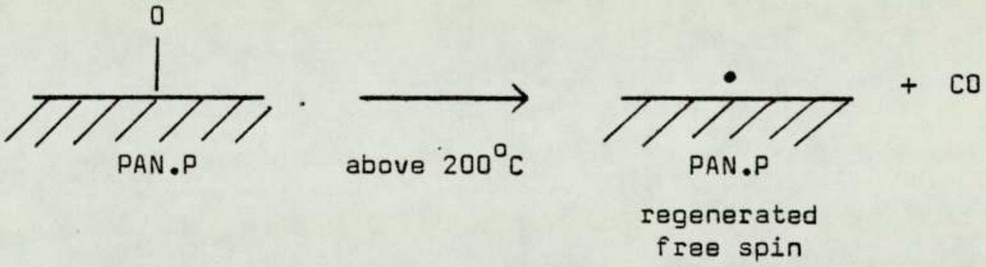
The following reaction mechanism is proposed on the basis of the above information. Starting with a freshly pyrolysed sample of PAN.P, which has been cooled under vacuum after pyrolysis, the proposed sequence for reaction with NO would be:

(1)



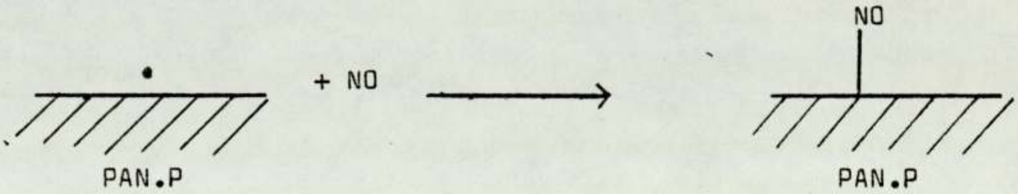
Once all the accessible free spins have reacted with oxygen to form surface oxides the polymer will not react with further oxygen or NO at ambient temperature.

(2)



Above 200°C the surface oxides start to decompose to form oxides of carbon and regenerate free spins on the polymer surface. The surface oxides vary in thermal stability with increasing numbers decomposing as the temperature is raised to 700°C.

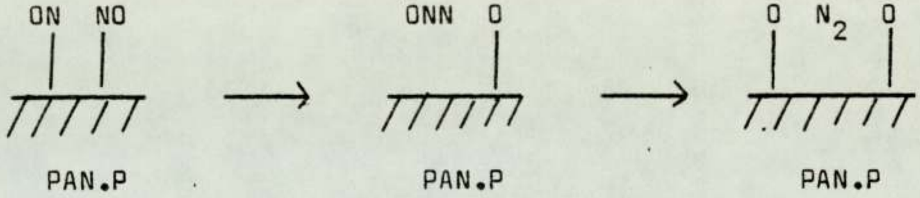
(3)



NO (or oxygen if present) is chemisorbed at a free spin site on the polymer surface. A reaction involving free spins is consistent with the low activation energy for the reaction of 10.8 kJ mol^{-1}. It is likely that the NO is attached by the nitrogen end as Dousmanis has shown that the unpaired electron is 65% located on the nitrogen atom.[4]

The PAN.P-NO complex formed in (3) may be very short lived as Shah[57] found that charcoal reduced NO to nitrogen at -78°C. The main products of the reaction between NO and PAN.P are surface oxide and nitrogen. N_2O has also been detected at temperatures below 500°C and is possibly an intermediate in the reaction.[53] This suggests a reaction on the polymer surface involving two molecules of NO.

(4)



The second NO molecule may come directly from the gas phase. The reaction involving surface oxide formation deactivates the polymer surface to NO. However, under isothermal conditions, the rate of decrease in NO removal rate by PAN.P (see Figure 14, page 90) suggests that some active sites on the polymer surface react with more than one molecule of NO. As small quantities of CO and CO_2 are also produced during the reaction it appears that some of the oxides decompose spontaneously to regenerate an active site which can react with further NO. Eventually the PAN.P surface becomes covered with oxides which are thermally stable at the reaction temperature and reaction with NO ceases. Heating the deactivated PAN.P above the reaction temperature restores some of the activity to NO and produces CO and CO_2 indicating that some of the surface oxides have been decomposed and new active sites produced.

At 750°C the PAN.P lost about 75% of its initial activity to NO and then the NO removal rate remained constant. CO and CO_2 were produced by the reaction indicating that continuous oxidation of the PAN.P by NO was taking place.

$$2NO + 2(C) \longrightarrow N_2 + 2CO$$

$$2NO + (C) \longrightarrow N_2 + CO_2$$

The reaction between PAN.P and NO is very similar to that which has been found to occur between carbon and NO.[44,55,56] There is also a close similarity in the variation of e.s.r. absorption and electrical conductivity with pyrolysis temperature for carbon and PAN.P and various other pyrolysed polymers.[40,44,51] Carbon samples also possess surface oxides which behave in a similar manner to those found on PAN.P.[54] Out of interest a sample of cellulose (cotton wool) was pyrolysed to 600°C under vacuum and tested in the catalytic reactor. The initial rate of NO removal by the carbon between 200 - 600°C increased in a similar way to PAN.P Its activity to NO per unit mass was superior to that of PAN.P fibre. However, further work is necessary to confirm this result. A sample of carbon fibre which is basically graphitised PAN.P was also tested and this had negligible activity to NO at temperatures up to 700°C.

The reaction sequence proposed for NO and PAN.P based on the experimental data suggests that PAN.P is not in fact a true heterogeneous catalyst for NO decomposition. The NO reacts initially with the PAN.P surface to form a surface oxide and nitrogen. Reaction ceases when all the active sites have been converted to oxides unless the oxides decompose to form oxides of carbon and regenerate the active sites. Continuous reaction therefore involves the removal of carbon atoms from the PAN.P surface.

7.4 Reaction in presence of other gases

PAN.P did not react with any of the gases present in motor vehicle exhaust gas other than oxygen and NO. The reaction of PAN.P with oxygen was rapid at elevated temperatures and also highly exothermic. The polymer structure was broken down to produce CO, CO_2 and NO.

The PAN.P continued to react with NO in the presence of oxygen but the rate of NO removal was reduced. As up to 3% by volume of oxygen can be present in the exhaust gas it poses a serious drawback to the use of PAN.P as an NO removal catalyst. It was found that PAN.P catalysed the reaction between O_2 and hydrocarbon so that running the engine on a rich fuel/air mixture which will simultaneously reduce the oxygen content and increase the hydrocarbon content of the exhaust gas, may help. It was difficult to assess the effect of hydrogen on the deactivated polymer or on the reaction of PAN.P with NO because of the low reaction temperature which had to be used but at higher temperatures hydrogen has been found to be effective in removing the surface oxides from carbon.[39]

The rate of NO removal by the PAN.P when actual exhaust gas was passed over it was much less than when NO alone was passed. It appeared that some constituent of the exhaust gas was inhibiting the reaction between NO and PAN.P. This may have been the oxygen which was present in much greater quantity than the NO.

7.5 The use of PAN.P for the removal of NO from exhaust gas: a critical survey

PAN.P removes NO from gas streams at elevated temperatures. At $500^{o}C$ and 4 l min^{-1} flow rate PAN.P fibre initially removed over 2.4×10^{-5} mol min^{-1} g^{-1}. Shelef[2] found the decomposition rate for NO over conventional inorganic catalysts was within the range 1.5×10^{-9} to 1.5×10^{-8} mol m^{-2} min^{-1}. BET measurements indicated that the surface area of the PAN.P fibre was less than 1 m^2 g^{-1} so that the rate of NO removal by PAN.P was more than 3,000 times greater than for the best of the inorganic catalysts.

At 4,000 rpm a 1,500 c.c. car engine has an exhaust gas flow rate of about 5,000 l min^{-1}. Assuming an NO concentration in the exhaust gas of 1,500 vpm this would give an NO output of 0.14 mol min^{-1}. At 500°C, assuming an NO removal rate of 2.4×10^{-5} mol min^{-1} g^{-1}, 6,000 g PAN.P would be needed to remove all the NO from the exhaust stream. PAN.P fibre has a bulk volume of about 0.004 l g^{-1} so that the above mass of PAN.P fibre would occupy 24 litres. A slightly larger volume of supported PAN.P would be needed to give the same removal rate. At higher temperatures the NO removal rate by PAN.P is greater but at lower temperatures it is much reduced. This would be a problem on short journeys when the PAN.P would never get warmed up sufficiently to be effective. A further problem is the rapid loss in activity of the PAN.P to NO caused by the build-up of oxides on its surface. At temperatures above 700°C a continuous reaction occurs between NO and PAN.P but this entails consumption of the PAN.P to form oxides of carbon. It is hoped that the presence of a reducing gas such as hydrogen would remove the surface oxides and reactivate the PAN.P surface without affecting the polymer structure. This reaction did not appear to occur at temperatures below 400°C but may well do so at higher temperatures. Finally, the oxidation of the PAN.P by oxygen present in the exhaust gas has been discussed in the previous section.

Thus if PAN.P is to be used to remove NO from a gas stream the following conditions are required:

(1) Temperatures above 400°C - preferably 600°C.

(2) No oxygen present.

(3) Sufficient hydrogen (or other reducing gas) to remove surface oxides from the PAN.P surface.

These conditions obviously severely limit the usefulness of PAN.P for the removal of NO from motor vehicle exhaust gas. However, PAN.P may prove useful for the removal of small quantities of NO from gas streams under more controlled conditions.

SUGGESTIONS FOR FURTHER WORK

The special electronic properties of highly conjugated organic polymers means that their study is of interest irrespective of their potential application as heterogeneous catalysts. Thus there are several aspects of the interaction between PAN.P and NO which merit additional study as they may help to further elucidate the reaction mechanism.

(1) Infrared analysis of the gaseous products of the reaction between NO and PAN.P at low temperatures (below 500°C) may detect N_2O and therefore confirm its formation as a minor product and possible reaction intermediate. Infrared analysis of gases desorbed from the PAN.P surface after low temperature reaction with NO would also be useful for the same reason.

(2) It would be of interest to follow the rate of NO removal by an oxide free PAN.P surface, under isothermal conditions, at a temperature at which the resulting surface oxides were thermally stable. If one NO molecule deactivates each active site (free spin) on the polymer surface then the decrease in NO removal rate with time should be first order (see section 4.5 and Figure 14).

(3) It would be of interest to measure the e.s.r. absorption of PAN.P samples which had not been exposed to the atmosphere. This would provide a true picture of the variation of free spin concentration with pyrolysis temperature. The freshly pyrolysed samples would have to be transferred to a nitrogen filled cabinet for weighing and sealing in e.s.r. sample tubes.

(4) Measurement of the activity to NO of PAN.P samples which had not been exposed to the atmosphere would enable the true effect of

pyrolysis temperature on polymer activity to be established. In order to avoid exposure of the PAN.P samples to the atmosphere pyrolysis could be carried out in a stream of nitrogen in the catalyst chamber of the catalytic reactor. It would also be possible, using the results from (3) above, to see if there is any correlation between free spin concentration and activity to NO.

(5) It would be of interest to measure the surface area of the PAN.P fibre samples using the technique involving CO_2 absorption at $-78^{o}C$ to see how the results vary with PAN.P pyrolysis temperature.

(6) The total amount of surface oxide on a PAN.P sample could be measured by heating the sample in the catalytic reactor in a stream of nitrogen and measuring the CO and CO_2 content of the outlet gas, with time, until all the oxide had decomposed. The variation in surface oxide content with pyrolysis temperature and e.s.r. absorption of the sample could then be obtained. If all the samples were heated under an identical rate of temperature rise, a comparison of the thermal stability of the oxides would also be obtained.

(7) It would be useful to know if hydrogen can reduce the surface oxides and reactivate PAN.P when passed over the polymer at elevated temperatures. It is also possible that PAN.P may catalyse the reaction between NO and hydrogen at elevated temperatures as it does the reaction between oxygen and propane. The study of these reactions would require the construction of a suitable quartz reaction vessel which could be fitted into the heater unit of the catalytic reactor in place of the steel vessel.

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