Carbonaceous Deposits Associated With The Catalytic Steam-Reforming Of Hydrocarbons

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By

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S. David Jackson

Summary

The reactions of hydrocarbons with steam over a 75% w/w nickel supported on alumina catalyst at 475°C have been investigated using a pulsed-flow microcatalytic reactor system and radiotracers.

The product distributions have been studied for each hydrocarbon used, when no steam was present and at low and high steam to hydrocarbon ratios. Carbon-14 labelled reactants and products have been used in an attempt to elucidate the reaction mechanism. [^{14}C]Carbon monoxide and [^{14}C]carbon dioxide have been used, under various conditions, to probe the reaction pathways. Both carbon monoxide and carbon dioxide have been found to deposit carbon during a reaction and any radioactive label introduced into the reaction system has been found to be scrambled in the products. [^{14}C]Benzene and [^{14}C]methyl-toluene have also been used to examine the steam-reforming mechanism.

Four types of carbonaceous deposit laid down on the nickel catalyst can be identified:

a) carbon filaments,
b) a hydrocarbonaceous polymeric residue,
c) reactive carbon,
d) permanently retained "carbon".

The filamental deposit was observed by electron microscopy of the surface and its chemical reactivity has been investigated. The polymeric species, which was solvent extractable from the surface, has been examined directly by infra-red spectroscopy and by laser-Raman spectroscopy of the catalyst itself, as well as by infra-red spectroscopic analysis of its solution and by mass spectrometry. The polymeric species has been found to be a C_{25} - C_{30}, $-CH_2-$ backboned polymer with two aldehyde groupings; one alkyl the other conjugated. The reactive carbon was studied in situ by chemical probes, while the permanently retained "carbon" was examined by microanalysis.

Carbon monoxide adsorption has been used to determine the extent to which the nickel surface area is decreased by the presence of the surface carbonaceous residues. It has been found that, although the metal area may decrease to around 3% of that of an unused catalyst, the activity of the catalyst for hydrocarbon conversion remains approximately constant.

A reaction mechanism is proposed and discussed in terms of the carbonaceous deposits found. It is proposed that the steam-reforming reaction takes place upon both the hydrocarbonaceous polymeric deposit and the nickel surface, and that deactivation of the catalyst occurs due to the build-up of an unhydrogenated carbonaceous species.

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CHAPTER 1

INTRODUCTION

1.1. Historical Aspects of the Steam-Reforming of Hydrocarbons

Much of the research and development work concerning the metal-catalysed steam-reforming of hydrocarbons has been carried out in the United Kingdom by I.C.I. Ltd. and British Gas. After the second World War, British Gas were seeking an alternative to producing town gas (primarily CO/H_2) from coal, therefore research was instituted into producing town gas from oil (1). I.C.I. Ltd. were seeking a method of producing hydrogen for use in the methanol synthesis. As carbon monoxide is also used in the methanol synthesis, steam-reforming of hydrocarbon oils, to give a gas which was rich in carbon monoxide and hydrogen was investigated.

In 1962 Dent and co-workers (2) formulated an alumina-supported nickel catalyst, which catalysed the reaction of steam with light hydrocarbon oils to give a mixture of carbon monoxide, carbon dioxide, methane and hydrogen. This catalyst could be used for the production of a substitute for town gas at low temperatures (400-500°C) and high pressures (15-30 atm), the process later became known as the Catalytic Rich Gas (C.R.G.) process.

In the C.R.G. process the product gases are in thermodynamic equilibrium determined by the temperature, pressure and the ratio of steam to hydrocarbon in the feed-stock (3):-

$$a.\ C_xH_y + b.\ H_2O \longrightarrow \left(\begin{array}{l} CO + H_2O \rightleftharpoons H_2 + CO_2 \\ CO + 3H_2 \rightleftharpoons CH_4 + H_2O \end{array}\right.$$

By varying the conditions it is possible to produce a "lean" gas, rich in carbon monoxide and hydrogen, or to produce a "rich" gas, rich in methane (3,4). For production of a Substitute Natural Gas (S.N.G.), the normal operating conditions for the C.R.G. process are a relatively low temperature (450°C), a high pressure (25 atm) and a steam to hydrocarbon molar ratio of approximately 10:1.

1.2. Steam-Reforming Catalysts

The catalysts used for steam-reforming are usually based upon nickel supported on γ-alumina (table 1.1). The choice of metal is limited to the elements of Group VIII of the periodic table, except iron, because of the requirement that the metal must be stable in the presence of steam. Rostrup-Nielsen (6) has reported that the specific activities of the metals of Group VIII are in the order:

$$Rh, Ru > Ni, Pd, Pt > Re > (Ni_{0.7}Cu_{1.3}) > Co$$

Although not the most active, nickel is the most commonly

TABLE 1.1

COMPOSITION OF STEAM-REFORMING CATALYSTS (5)

Catalyst		Weight % of Components		
		NiO	Al_2O_3	Other oxides
I.C.I. 57-1		32	54	CaO 14%; SiO_2 0.1%
I.C.I. 46-1		21	32	K_2O 7%; MgO 13% CaO 11%; SiO_2 16%
Haldor-Topsøe	(a)	28	57	MgO 15%
	(b)	29	15	MgO 56%
C.R.G.		79	20	K_2O 1%
Nickel-Urania		16	74	K_2O 0.15%; U_3O_8 10%

used metal for steam-reforming catalysts, primarily on economic grounds. The support is usually alumina, to which small quantities of other oxides are added (table 1.1) since it exhibits the necessary stability in the presence of high pressures of steam. Of the other materials commonly used as catalyst supports, silica is volatile under steam-reforming conditions and hence unsuitable. Calcium oxide, magnesium oxide and urania are all used in small concentrations as additives to the alumina support in various catalysts. Usually they are chemically bonded to the alumina to reduce their loss due to reaction with the steam.

1.3. Reactions under Steam-Reforming Conditions

The possible reactions which may occur during steam-reforming are:-

$$C_nH_{2n+2} + nH_2O \longrightarrow nCO + (2n+1)H_2 \qquad (1)$$

$$C_nH_{2n+2} + \frac{n-1}{2}H_2O \longrightarrow \left(\frac{3n+1}{4}\right)CH_4 + \left(\frac{n-1}{4}\right)CO_2 \qquad (2)$$

$$C_nH_{2n+2} + 2nH_2O \longrightarrow nCO_2 + (3n+1)H_2 \qquad (3)$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad (4)$$

$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O \qquad (5)$$

$$2CO \rightleftharpoons CO_2 + C \qquad (6)$$

$$CH_4 \rightleftharpoons C + 2H_2 \qquad (7)$$

$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O \qquad (8)$$

$$CO + H_2 \rightleftharpoons C + H_2O \qquad (9)$$

All the equations represent equilibrium reactions although, under reaction conditions, they may not attain thermodynamic equilibrium. It can also be seen that changing one component in the system affects all other components. Consequently, any attempt to elucidate a mechanism is hampered by the difficulty of studying the individual reactions in isolation.

Mechanistically the steam-reforming of hydrocarbons is still unclear. Shephard (7) studied the hydrogenolysis of propane over a C.R.G. catalyst and found complete breakdown of the hydrocarbon skeleton to monocarbon species on the surface. If a similar system applies with water present then mechanism A may apply:-

Mechanism A (modified from (5))

$$C_nH_{2n+2}(g) \longrightarrow C_nH_m(ads)\ (\text{where } m < 2n+2) \tag{A.1.}$$

$$C_nH_m(ads) \longrightarrow nCH_x(ads) \tag{A.2.}$$

$$H_2O(g) \longrightarrow H(ads) + OH(ads) \tag{A.3.}$$

$$H(ads) + CH_x(ads) \longrightarrow CH_4(g) \tag{A.4.}$$

$$OH(ads) + CH_x(ads) \longrightarrow CH_2O(ads) \tag{A.5.}$$

$$CH_2O(ads) \longrightarrow CO(ads) + H_2(g) \tag{A.6.}$$

$$CO(ads) \longrightarrow CO(g) \tag{A.7.}$$

$$CO(ads) + OH(ads) \longrightarrow CO_2H(ads) \tag{A.8.}$$

$$CO_2H(ads) \longrightarrow CO_2(g) + H(ads) \tag{A.9.}$$

However, another possible mechanism would be one in which the reverse of the Fischer-Tropsch synthesis occurs:-

Mechanism B ((5), modified from (8))

$$RCH_2CH_3(g) \longrightarrow RCH_2\text{-}CH(diads) \qquad (B.1.)$$

$$RCH_2\text{-}CH(diads) \xrightarrow[(-H_2)]{+H_2O} RCH_2\text{-}COH(diads) \qquad (B.2.)$$

$$RCH_2\text{-}CH(diads) \xrightarrow[(-H_2)]{+H_2O} R\text{-}COH(diads) + HCOH(diads) \qquad (B.3.)$$

The diadsorbed species R-COH continues to react in a stepwise manner as per equation (B.3.). The diadsorbed species HCOH continues to react, as in mechanism A, via equations (A.6.), (A.7.), (A.8.) and (A.9.).

1.4. The Loss of Catalytic Activity

During the course of a steam-reforming reaction there is an appreciable loss of catalytic activity. Three main causes have been identified as contributing to the loss of activity, namely:-

a) sintering (the loss of catalyst surface area);
b) sulphur poisoning;
c) poisoning due to deposition of carbonaceous residues on the catalyst surface.

1.4.1. Sintering

A study of the loss of activity of a C.R.G. catalyst by sintering has been carried out by Williams, Butler and

Hammonds (9). In this study the sintering effect of steam and/or hydrogen was considered. It was found that in the initial 0-100 hours period of treatment with steam and/or hydrogen the drop in specific area was large (figures 1.1 and 1.2); the subsequent decrease was far less. It was also shown that the extent of sintering increases with increasing steam content of the treatment atmosphere (table 1.2.):-

TABLE 1.2

EFFECT OF STEAM : HYDROGEN RATIO

Conditions: 250 hours at 25 atm pressure and 500°C

steam : hydrogen	(v/v)	0:0	1:2	1:1	2:1	9:1
Specific surface area	(m^2)	95	79	76	65	52
Specific nickel area	(m^2)	27	22	22	15	13

The specific surface area was calculated from the nitrogen adsorption isotherm at -196°C and the specific nickel area was estimated from the amount of hydrogen adsorbed at 20°C. From figure 1.1 it can be seen that the nature of the atmosphere is a more important consideration than the pressure and temperature of the atmosphere. It was noted that steam plays an important part in the sintering of a C.R.G. catalyst, principally by sintering the γ-alumina base of the catalyst to α-alumina. This process is known to be accelerated under hydrothermal conditions (10,11) and that the minimum

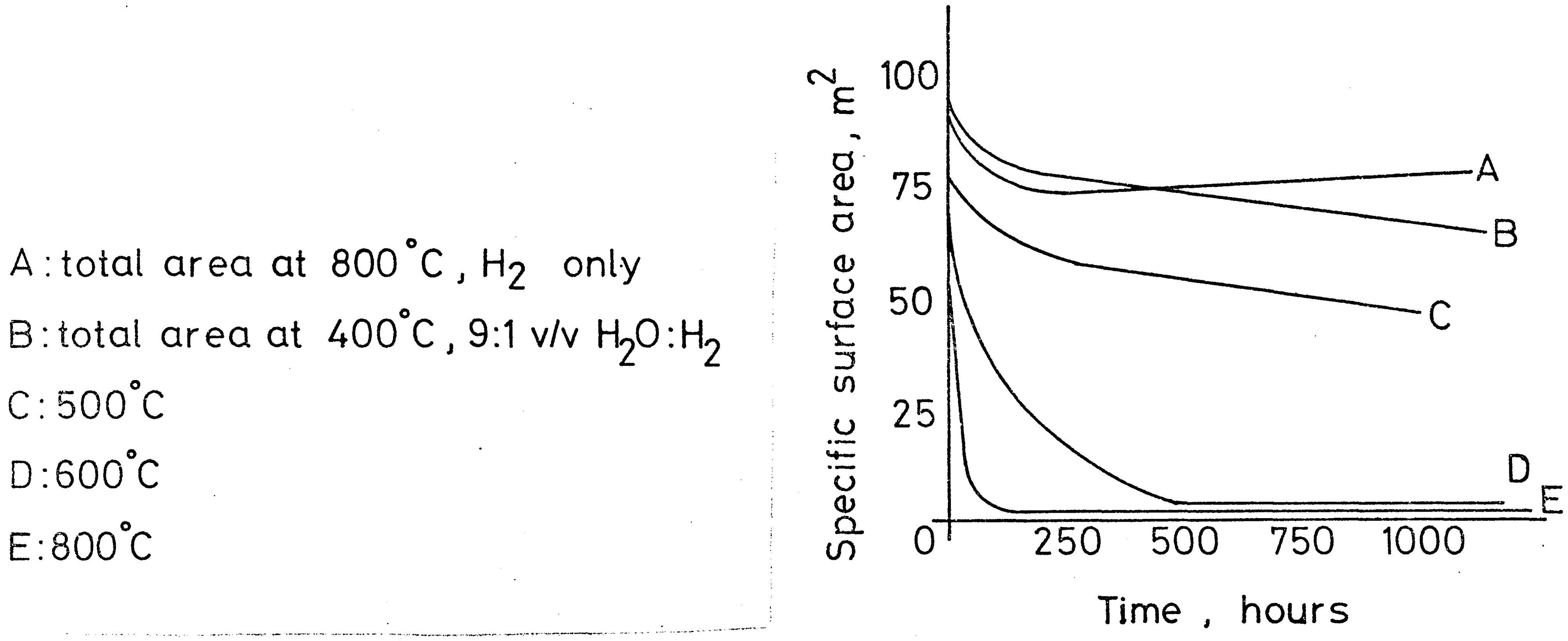

A: total area at 800°C, H_2 only
B: total area at 400°C, 9:1 v/v $H_2O:H_2$
C: 500°C
D: 600°C
E: 800°C
Specific surface area, m^2
100
75
50
25
0
250
500
750
1000
Time, hours
A
B
C
D
E

figure 1.1

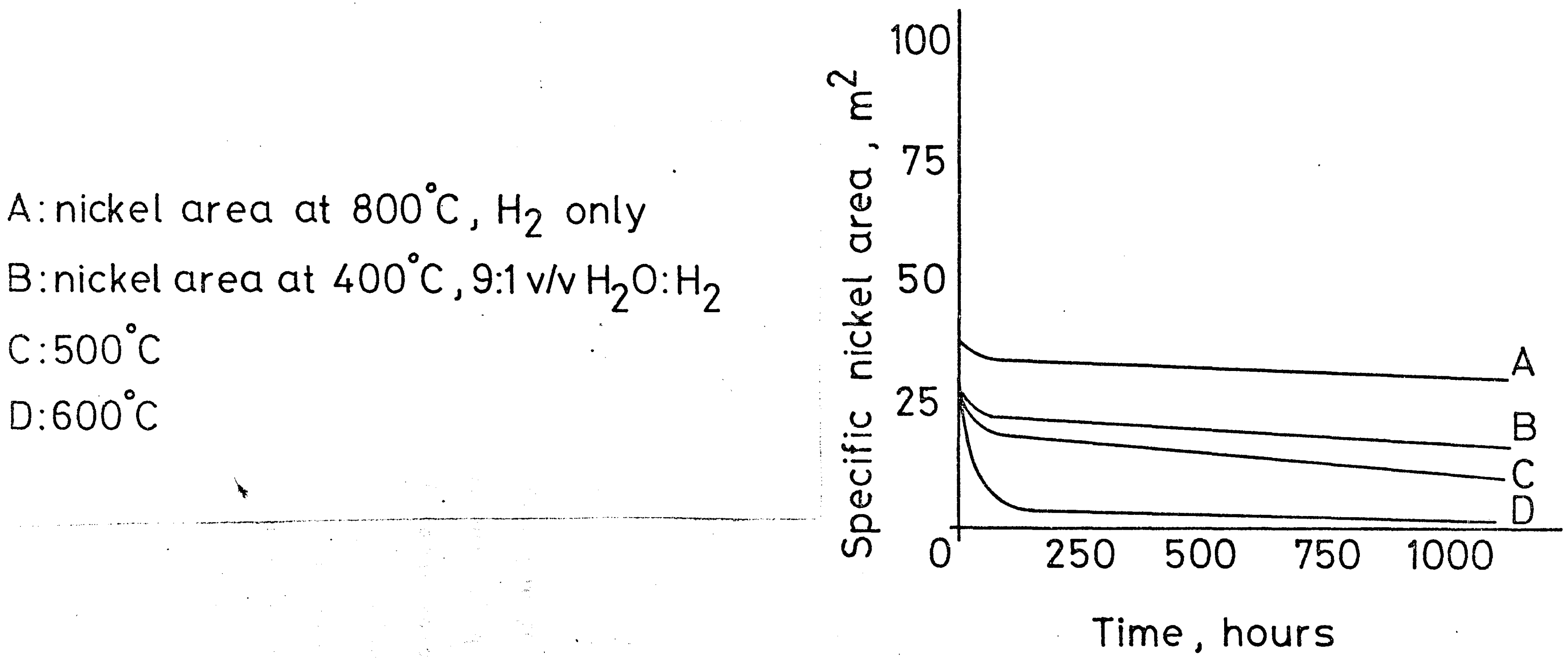

A: nickel area at 800°C, H_2 only
B: nickel area at 400°C, 9:1 v/v H_2O:H_2
C: 500°C
D: 600°C
Specific nickel area, m^2
100
75
50
25
0
250
500
750
1000
Time, hours
A
B
C
D

figure 1.2

temperature, at which α-alumina is formed is lowered from 1000°C to 400°C (12). However, in the preparation of the current C.R.G. catalyst, this initial drop in surface area is allowed for in, the sense that the residual area, after the initial sintering, is still sufficient for fast gasification. The subsequent loss of surface area, after the initial drop, is slow under normal reaction conditions (section 1.1) and hence the contribution that sintering makes to the loss of activity is small.

Moayeri and Trimm (13) have investigated the reorganisation of nickel under steam-reforming conditions. The catalyst used was a nickel film supported on silica and this was treated with steam, hydrogen or propylene. Hydrogen treatment at 572°C resulted in rapid sintering, while sintering by steam was found to be slow. This apparently is in conflict with the findings of Hammonds et al. (9), although the different behaviour may be attributable to the difference in support (silica c.f. γ-alumina). When propylene was used, carbon deposition was noted and this tended to stabilise the nickel. When no carbon deposition was observed the sintering appeared to be dependent on the quantity of hydrogen present. It is not stated whether the surface of the catalysts used with propylene were examined by electron microscopy, but as it is known that compounds containing carbon-carbon double bonds give rise to carbon filaments very rapidly on nickel (14,15), it might be expected that there would be very little sintering caused by the propylene, as the nickel may be "fixed" in small crystallites at the tips of the filaments.

1.4.2. Sulphur Poisoning

The poisoning of the catalyst by sulphur was first observed in fast flow reactions, when unpurified hydrocarbons were passed over the catalyst. Rostrup-Nielsen (16) has shown that, when hydrogen sulphide is passed over a reduced nickel catalyst in the temperature range 550-645°C, a surface layer of sulphide is formed which inhibits the steam reforming reaction. However, by varying the p_{H_2S}/p_{H_2} ratio this sulphide layer can be rendered unstable and can be slowly removed (17). In the industrial situation, sulphur-containing compounds are removed from the feedstock before it enters the main reactor by catalytic methods. Nickel molybdate and zinc oxide catalysts are used industrially at temperatures in the range of 300-400°C and these can reduce the sulphur content of the feedstock to less than 1 ppm w/w. On a smaller scale Phillips et al. (3) have removed sulphur-containing compounds from their feedstock by refluxing the hydrocarbon with freshly prepared Raney-nickel.

1.4.3. Poisoning due to Carbonaceous Deposition

The loss of activity of steam-reforming catalysts by carbonaceous deposition has been discussed in various publications (18,19,20,21,22,23) but there have been few systematic studies dealing with the type, form and reactivity of the carbonaceous deposit. Moseley, Stephens, Stewart and Wood (18) have studied the overall deactivation of a C.R.G. catalyst. This study was carried out using a high pressure (25 atm), continuous flow reactor system at 450°C, with catalyst bed lengths of 38-92cm in a 0.44cm i.d. tube, and with n-heptane as the standard feedstock. As the hydrocarbon passes through the catalyst it reacts with the steam and results in a temperature profile throughout the bed (figure 1.3.). In figure 1.3. the steam-hydrocarbon mixture enters the catalyst bed at 450°C and as the hydrocarbon decomposes, and reaction with the steam begins, the temperature decreases. The reactions may be considered as:-

$$C_7H_{16} + 7H_2O \longrightarrow 7CO + 15H_2 \qquad (1)$$

$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O \qquad (2)$$

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

Reaction (1) is endothermic and the equilibrium lies well to the left in reactions (2) and (3). As the decomposition proceeds, the concentration of steam decreases and the reaction to form methane increases. The temperature

Reaction temperature profile through 1.3 cm i.d. catalyst bed: catalyst bed 84 x 1.3 cm of 18–30 BSS particles; water feed space rate, 530 g/hr; distillate feed rate, 320 g/hr; distillate final boiling point, 170°C; pressure, 25 atm; initial inlet gas and reactor temperatures, 450°C.

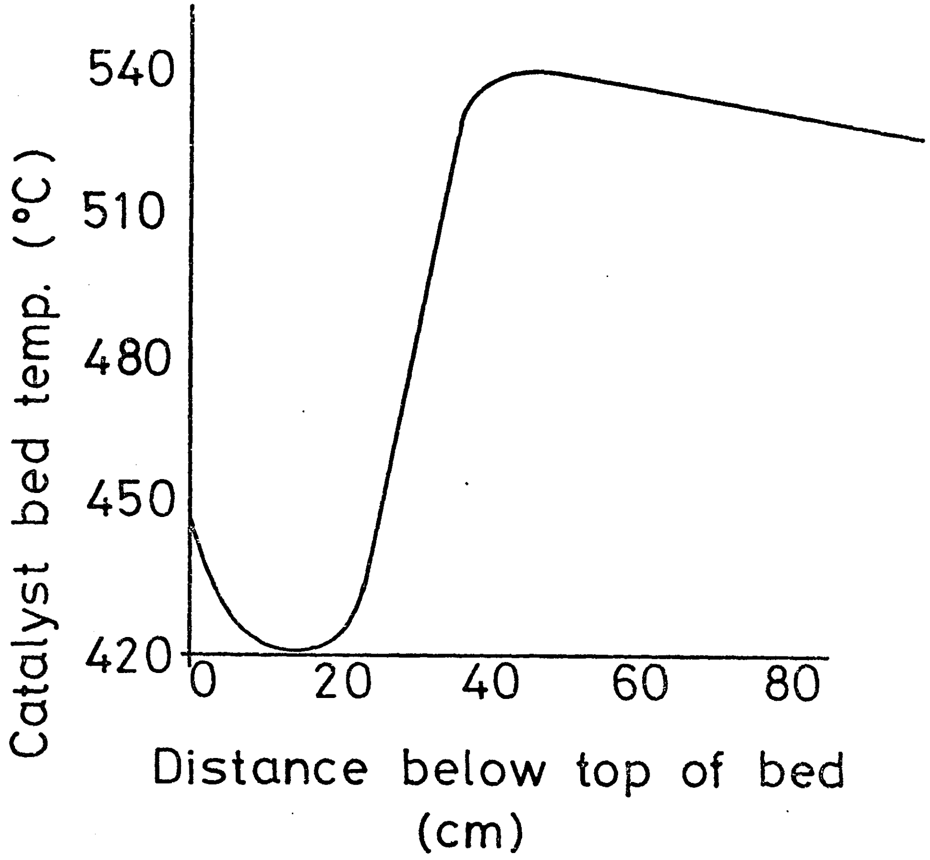


figure 1.3

therefore increases as the formation of methane from reaction (2) is highly exothermic. Finally, a temperature of 520°C, 70°C in excess of the initial temperature, is found when decomposition and equilibration of the products is complete.

Hydrocarbons of a similar molecular weight were compared to give an indication of which type of hydrocarbon caused the most deactivation of the catalyst bed; this was done by adding quantities of each to the standard n-heptane feedstock. It was found that the order of deactivation was

aromatics > cyclics > alkenes > alkanes

these latter gave the slowest deactivation of the catalyst. Increasing molecular weight also increased the rate of deactivation. The effect of temperature on deactivation was also studied and it was reported that, as the temperature of the catalyst was increased from 425°C up to 500°C, the deactivation of the catalyst decreased. However, at 500°C and above, there was massive carbon deposition. By varying the steam to hydrocarbon ratio it proved possible to show that, the higher the steam to hydrocarbon ratio, the longer the time before deactivation occurred. Consideration was also given to the effect of catalyst particle size (figure 1.4) and it can be seen that the larger the particle size the longer the catalyst remains active.

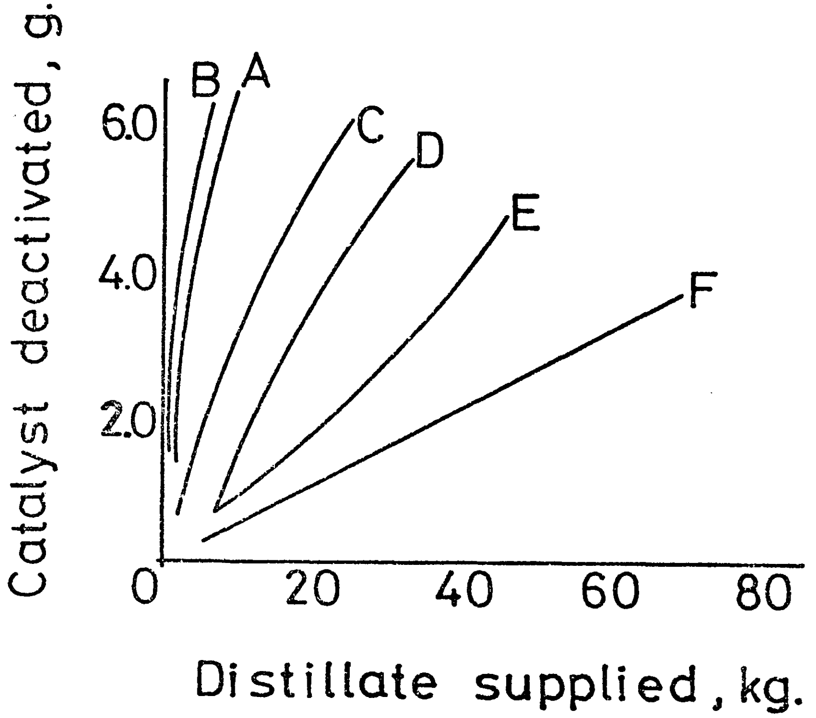


figure 1.4

Catalyst bed 38 x 0.44 cm; water feed rate, 65 g/hr; distillate feed rate, 39 g/hr; distillate final boiling point, 170°C; pressure, 25 atm; inlet gas and reactor temperature, 450°C. Effect of particle diameter on rate of poisoning: (A) 36–52 B.S.S. particle size; (B) 18–30 B.S.S.; (C) 10–14 B.S.S.; (D) 8–10 B.S.S.; (E) 6–8 B.S.S.; (F) 0.32 cm equant cylinders.

Rostrup-Nielsen (23) has studied carbon deposition on Haldor-Topsøe steam-reforming catalysts (section 1.2). The experiments were performed in a thermogravimetric system in which the catalyst was placed in a perforated gold basket and suspended from an electro-microbalance. The temperatures used in this study were $\geqslant 500°C$. As noted in the paper it is difficult to draw comparisons between this work and studies carried out at temperatures under 500°C, since there appears to be a difference in the carbonaceous deposit and the method of deposition. Below 500°C the deposit may well contain hydrogen-containing species such as anthracene, pyrene or naphthalene (24); the Boudouard reaction ($2CO \rightarrow CO_2 + C$) is not considered to contribute to the deposition (18). Above 500°C, the deposit may have a very high carbon to hydrogen ratio or it may be a species such as nickel carbide or graphitic carbon. The Boudouard reaction is considered to play an important role above 500°C, together with the cracking and pyrolysis of the hydrocarbon. Hence deposition above 500°C is more rightly ascribed to formation of coke and the reactions forming this deposit are termed coking reactions.

Rostrup-Nielsen and Trimm (25) have reported kinetics and activation energies of carbon deposition on various catalysts and have concluded that four types of carbonaceous deposit may be identified; well-ordered graphitic deposits

(26,27,28), carbon whiskers (14,22,28), non-orientated deposits (27) and various carbides (e.g. Ni_3C) (29,30). However no evidence could be found for non-orientated deposits in the reference quoted in this paper, although non-orientated deposits have been identified in other papers (14,15). Also, no mention was made of the study by Bhatta and Dixon (24), where anthracene, pyrene and naphthalene were all identified after solvent extraction of a used steam-reforming catalyst. In their study Bhatta and Dixon (24) considered the steam-reforming reaction using a 15% nickel supported on alumina catalyst, at high pressure (25-30 atm) and low temperature (450°C), in a continuous flow system, with n-butane as the feedstock. On extraction of a used catalyst, anthracene, pyrene and naphthalene were all identified by gas chromatography as surface species formed during the reaction. It was also found that the activity of the catalyst could be restored to approximately its original value by treatment with hydrogen, at 500°C, for 16 hours.

It is important to note that various studies have considered carbonaceous deposition. However, the conditions are often very different and inter-comparisons should not be drawn due to the extreme variation in deposition, which is dependent on parameters such as the steam to hydrocarbon ratio, reaction temperature and the presence of promotors in the catalyst.

CHAPTER 2

OBJECTS OF THE PRESENT WORK

2.1. Objects of the Present Work

It is well established that, in the steam-reforming of hydrocarbons over supported nickel catalysts, the catalytic activity progressively decreases with usage. As indicated in the previous chapter, such losses in activity may result from (a) catalyst sintering; (b) sulphur poisoning, or (c) the formation of surface carbonaceous residues. Whereas both the effects of sintering and catalyst poisoning are relatively well understood, comparatively little is known about the surface carbonaceous deposits.

The objects of the present work were an investigation of the type, form and reactivity of the carbonaceous deposits formed on the catalyst surface during the steam-reforming of aliphatic and aromatic hydrocarbons, with particular reference to the mechanism of their formation and their possible role in the steam-reforming reaction. By use of radiotracer techniques, whereby specifically labelled reactants, reaction intermediates or products were introduced into the reaction system, it was intended to obtain information regarding

(a) the amounts of carbonaceous deposit formed;

(b) the type(s) of species responsible for the formation of the deposit and

(c) the chemical reactivity of the deposit during the steam reforming reaction. The physical form and chemical identity of the carbonaceous surface deposit was also to be investigated using infra-red and laser Raman spectroscopy, mass spectrometry and electron microscopy.

CHAPTER 3

EXPERIMENTAL

3.1. The Microcatalytic Reactor System

A pulsed-flow microcatalytic reactor system coupled to a gas chromatograph was used throughout this study. It is shown schematically in figure 3.1.

The reactor itself (figure 3.2.) consisted of a pipette-shaped Pyrex glass vessel fitted with a coarse glass sinter (No. 1.) upon which the catalyst, typically 0.5g, was placed. The temperature of the catalyst bed was maintained at the desired value by means of an electric furnace, which surrounded the reactor vessel and whose output was controlled by a West 96 controller (0-600°C). The temperature was measured using a glass-enclosed chromel-alumel thermocouple placed in contact with the catalyst bed. The temperature was recorded continuously both before and during reaction.

The reactor was connected by glass-metal (Kovar) seals to the gas flow line, which was constructed from 3mm i.d. stainless steel tubing. To prevent condensation of the reactants or products the flow lines were maintained at approximately 200°C by use of Hotfoil flat element heating tape (type G.W.) and high temperature insulating tape (Refrasil).

A	Hot wire detector
B	Water saturator
C	Injection port
D	Microcatalytic reactor
E	$Mg(ClO_4)_2$ trap
F	Trap
G	Porapak Q column
H	Tristricresyl phosphate column
I	Spiral cell scintillation counter
J	Temp. controllers
K	Recorder outputs

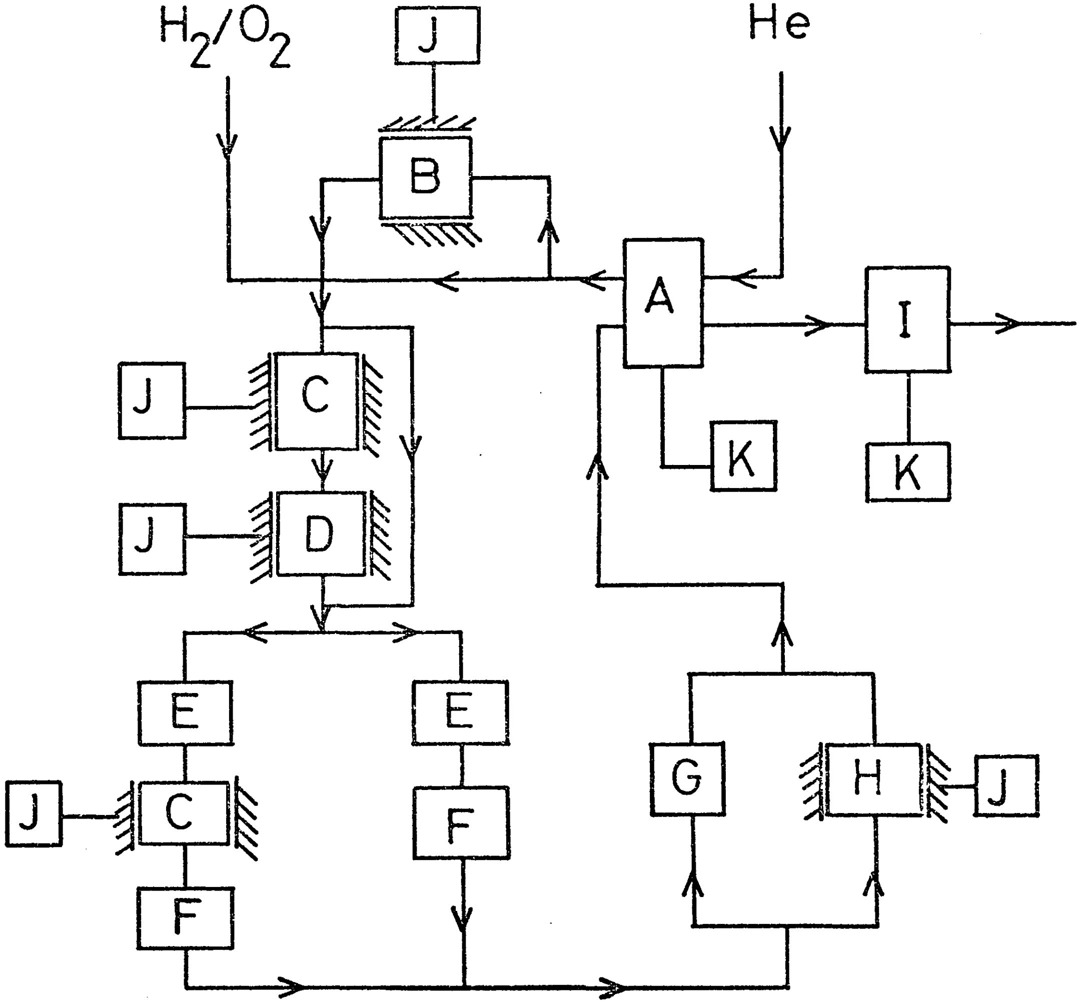


figure 3.1

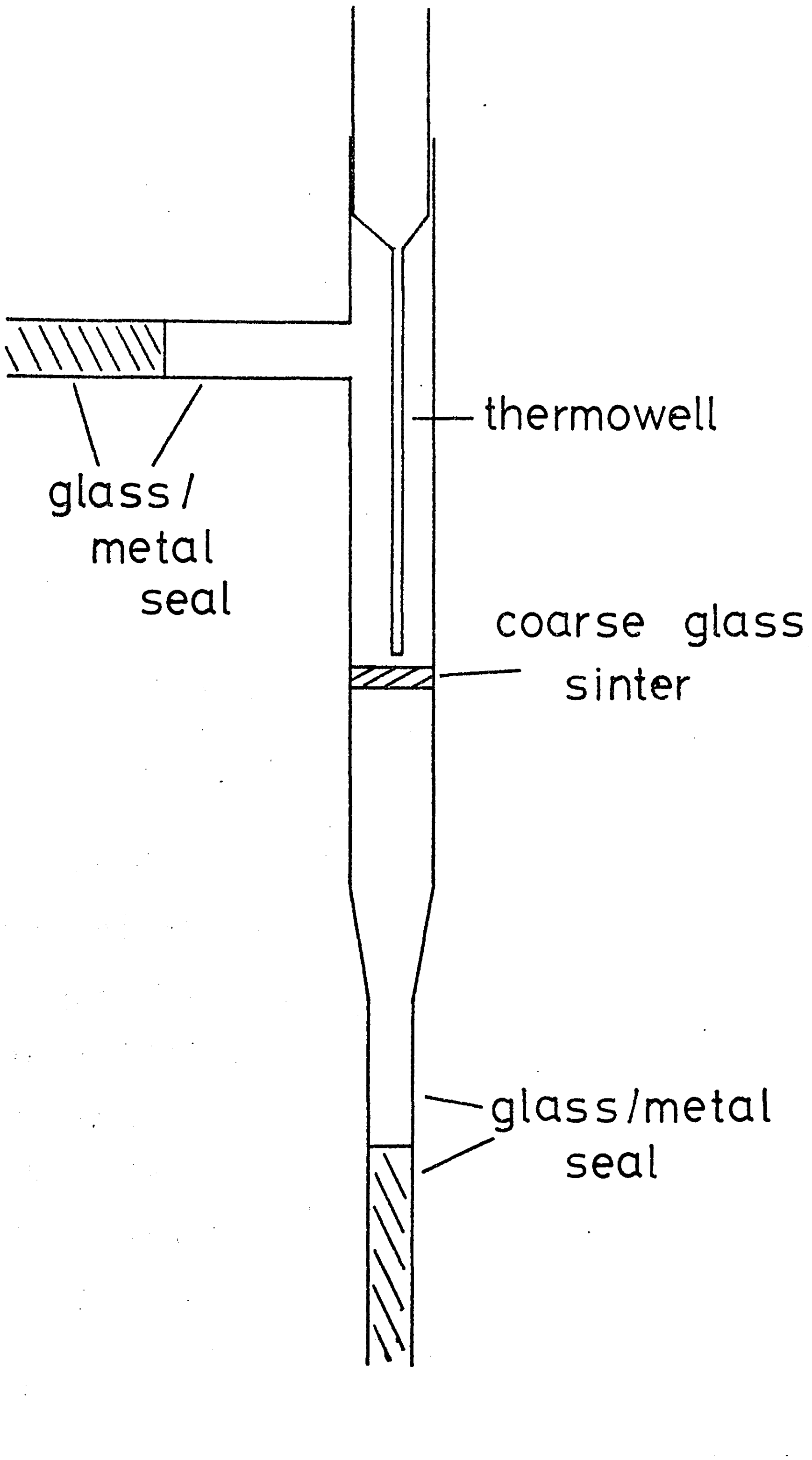
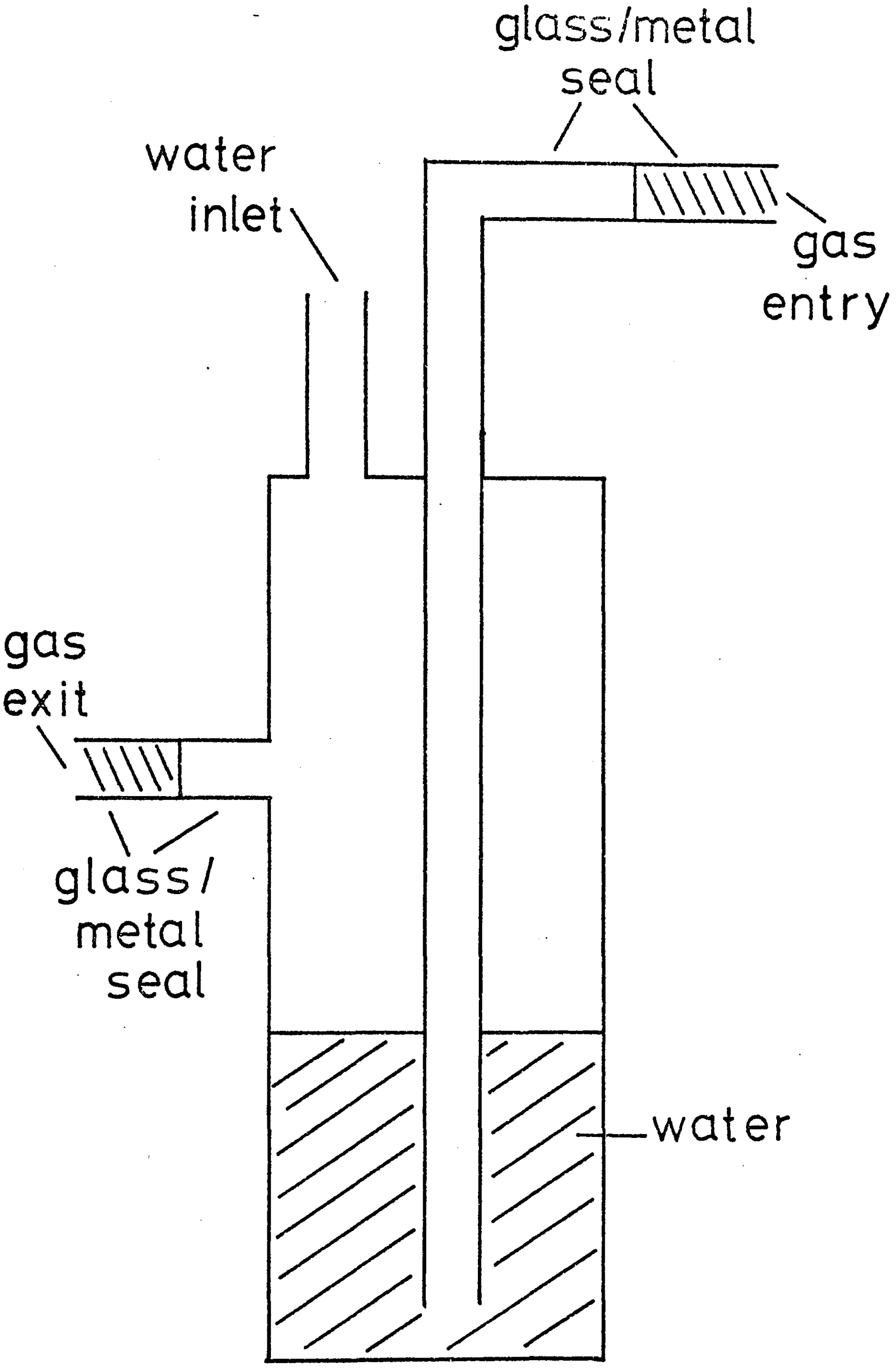


figure 3.2 The Reactor.

Gas flow rates through the system were controlled by fine metering valves (Nupro, Co. Inc.) and were measured by calibrated Rotameters (G.E.C.-Elliot, series 1100). Drallim switch valves were used to control the direction of flow of the carrier gas.

Steam was introduced into the carrier stream by means of a glass water saturator (figure 3.3), which was connected to the flow line by glass metal seals. The saturator temperature was thermostatically controlled by a water bath, to give the required vapour pressure for the various steam hydrocarbon ratios. The hydrocarbons were introduced into the gas flow by injection, using a Hamilton liquid syringe (type 701NCH), into an injection port heated to 150°C by a heating element (Solon, type 640).

The gas flow was passed through a trap containing magnesium perchlorate, to remove any unreacted steam, before entering the gas chromatographic system. A second trap, cooled by either liquid nitrogen or acetone/solid carbon dioxide, was used to condense various fractions of the reaction products; this was carried out to facilitate the switchover from one chromatographic column to the other (section 3.2).



The Water Saturator.

figure 3.3

3.2. The Chromatographic System

Analysis of the products of the reaction between steam and the various hydrocarbon feedstocks was achieved by a gas chromatograph, which was coupled directly to the micro-catalytic reactor system. Due to the range of reaction products, from hydrogen and carbon monoxide to ethyl benzene and xylenes, it was not possible to use a single column to obtain complete separation. Hence two columns (A and B) mounted in parallel, together with a cold trap system, were used. On elution from the reactor the flow gas was passed through the magnesium perchlorate trap to remove unreacted water and then through a cold-trap cooled in either liquid nitrogen or acetone-solid carbon dioxide to condense out the heavier hydrocarbons (C_4- and above).

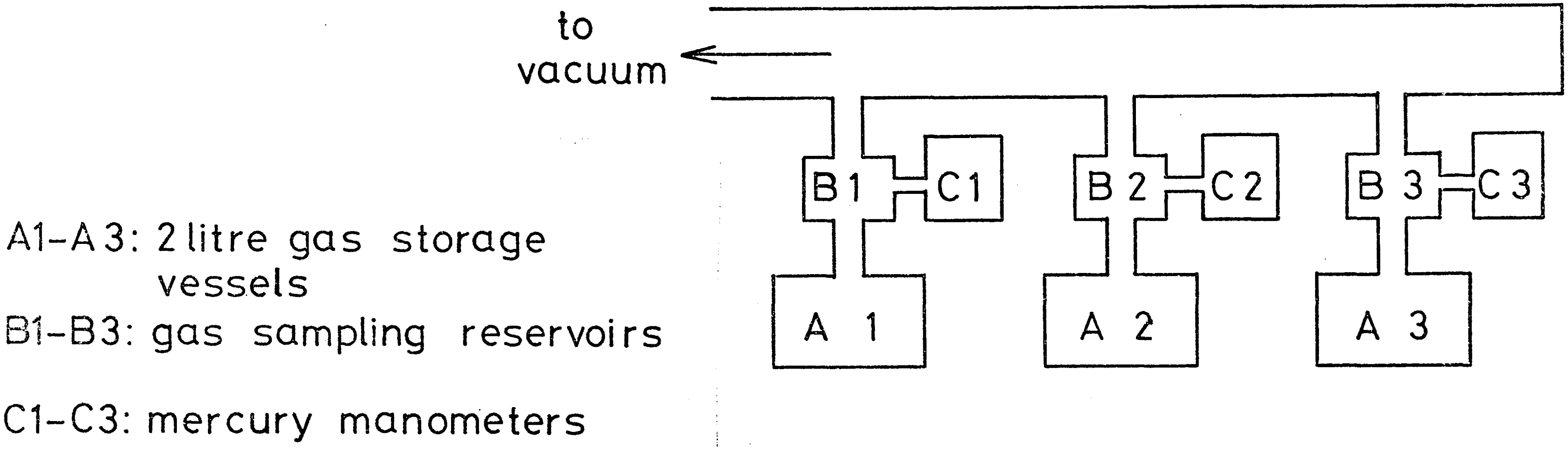
The flow gas containing the uncondensed reaction products was directed through column A. This consisted of a 3m column (i.d. 6mm) packed with Porapak Q (80-100 mesh) at ambient temperature, which separated the light gases (CO, CH_4, CO_2, C_2- and C_3- gases). Full separation of the carbon monoxide and methane components was found to be impossible however, due to the large quantity of methane produced, which tended to mask the carbon monoxide peak. Once separation was complete the flow was directed through column B and the cold-trap warmed to release the condensed hydrocarbons. Column B consisted of a 1m column (i.d. 6mm) packed with 15% tristricresyl phosphate supported on Chromosorb P (30-60 mesh), which was used at 40°C to effect the separation of C_4- and higher hydrocarbons.

A Gow-Mac Katharometer (type 10-285), in conjunction with a power unit/bridge balance circuit (Stirling Control Systems), was used as the detector, while helium was used as the carrier gas (flow rate 80cc/min).

3.3. The Vacuum Sampling System

A vacuum system was constructed to facilitate the handling of both radioactive and non-radioactive gases. The apparatus consisted of a conventional high vacuum system which could be maintained at a pressure of 10^{-4} torr or better by means of a mercury diffusion pump backed by a rotary oil pump.

The vacuum system is shown schematically in figure 3.4. Three two litre gas storage vessels (A_1-A_3), each with a small sampling reservoir (B_1-B_3) and a mercury manometer were used. Samples of gas at atmospheric pressure were removed from the sampling reservoir by a gas-tight syringe (Hamilton, type NCH1001) for injection into the microcatalytic reactor flow system. To ensure no contamination of the samples by air, the sampling reservoir was maintained above atmospheric pressure (1.2 atm). Ampoules of radioactive gas were sealed onto the vacuum system as required.



The Vacuum System.

figure 3.4

3.4. The Radiochemical Detection System

A gas proportional counter of similar design to that described by Schmidt, Bleek and Rowland (31) (figure 3.5.) was originally used. The counter was operated using helium as the carrier gas and methane was added to act as the quenching gas. Sufficient methane was added to the helium gas stream, at the exit from the chromatographic system, such that the gas entering the counter had a helium to methane ratio of 10:1. The counter was calibrated and was used for various reactions. It was discovered however that the products of the steam-reforming reaction, primarily the carbon monoxide, caused variations in the counter characteristics. On further investigation it was found that above a certain concentration of carbon monoxide (approximately 4μl per 200ml of carrier gas) the counting characteristics depended on the quantity of carbon monoxide in the counter at a given instant. The change in behaviour of the counter was such that when the carbon monoxide concentration was high, an excess of counts was detected. In consequence of this behaviour, the gas proportional counter was replaced by a spiral cell flow scintillation counter (EKCO type M5402A-1), which, although less efficient for the detection of carbon-14 beta-particles (nominally 100% for the gas proportional counter against a maximum of 70% for the scintillation counter), is not sensitive to the type or quantity of gas passing through it.

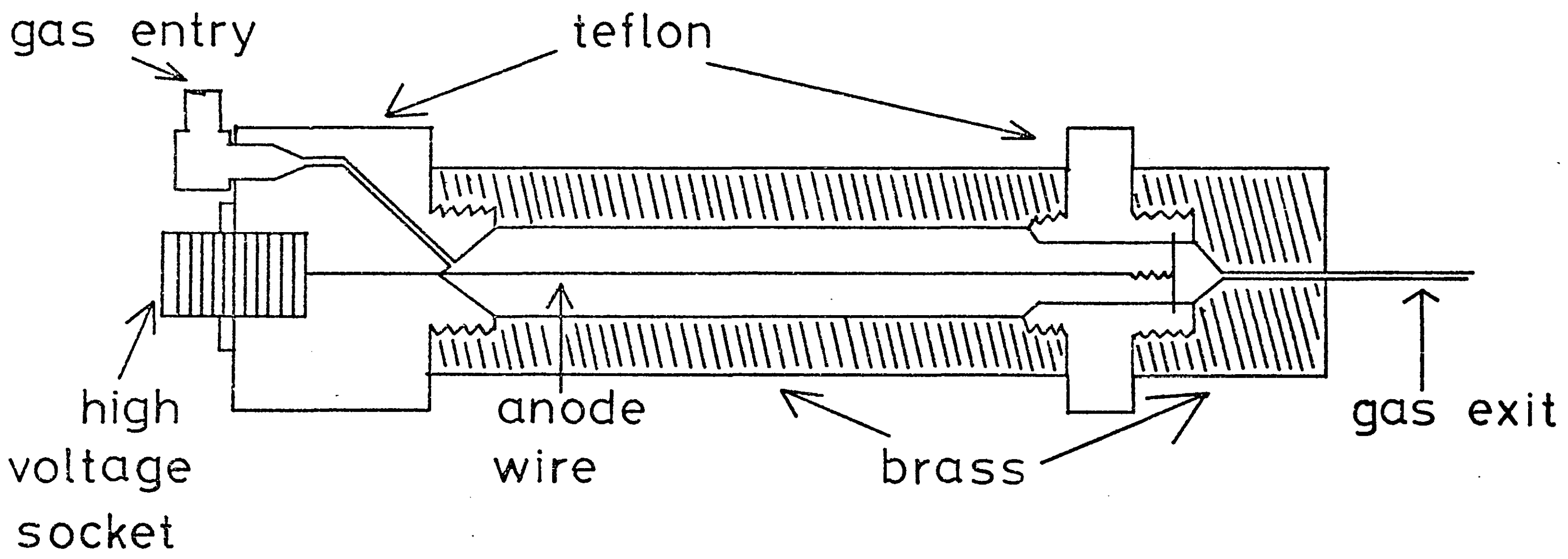


figure 3.5. The Proportional Counter.

On elution from the gas chromatographic system the eluant was passed into the spiral cell flow scintillation detector. The output from the scintillation counter was fed into a ratemeter (EKCO type M5050B) and hence into a digital scalar-ratemeter (EKCO type M5183A), which was used in the scalar mode, and a Servoscribe potentiometric chart recorder (5mV full scale deflection). The recorder trace was used to determine the time at which the counting was commenced and subsequently stopped. The operating conditions were:-

Ratemeter

Range - 1K
Time Const - 10s
Upper Disc - 956
Lower Disc - 247
Mode - Dual Disc
Scan - off
Diff. µs - 1
Int. µs - 1
Gain - 50
H.V. - 1.4 K.V.

Scalar/Ratemeter

Store - Open
Sampling Time - off
Mode - Scalar
Analogue - 10^6

3.5. Catalyst

The catalyst used contained 75% w/w nickel supported on γ-alumina. The catalyst paste was dried at 120°C for

24 hours, ground and then sieved (20-40 mesh B.S.S.). The sieved material was calcined in air at 450°C for 2 hours then reduced in a stream of hydrogen (~10cc/min) at 450°C for a minimum of 16 hours. This was carried out for all fresh samples.

3.6. Materials

Helium (B.O.C. Ltd.) was used as the carrier gas, hydrogen (Air Products Ltd.) was used to reduce the catalyst and oxygen (B.O.C. Ltd.) was used to clean the catalyst. These gases were used as supplied without further purification. Carbon monoxide (Air Products Ltd., purity 99.5%) was used for surface area measurements.

The following aromatic and aliphatic hydrocarbons were used as feedstock; n-heptane, hept-1-ene, n-pentane (all B.D.H. general purpose reagents); toluene, xylene (ortho, meta, para) (both B.D.H. "Aristar"); hexane, cyclohexane (both Hopkins and Williams "Spectrosol"); ethyl benzene (Hopkins and Williams "G.P.R.") and benzene (Hopkins and Williams "Ultrar"). All the aliphatic hydrocarbons, cyclohexane and ethyl benzene were distilled before use and subsequently stored over freshly prepared Raney Nickel to remove sulphur-containing compounds and thereby reduce the risk of sulphur poisoning of the catalyst. Benzene, toluene, and the xylenes were also stored over Raney Nickel before use.

Raney Nickel was prepared by digesting a quantity of Ni-Al alloy (Murex Ltd.) with 1M sodium hydroxide solution. The solution was heated until vigorous boiling was observed then refluxed for several hours. The suspension after being cooled was filtered and the Raney Nickel washed with water, ethanol, and finally the relevant hydrocarbon e.g. benzene, heptane. The Raney Nickel was placed in a storage vessel and a quantity of the relevant hydrocarbon was slowly poured in.

(^{14}C)Carbon dioxide 59.1 mCi/mmole, (Radiochemical Centre, Amersham) was diluted to the required activity with helium, rather than non-radioactive carbon dioxide, to ensure that, when the (^{14}C)carbon dioxide was added to the reaction mixture, there would be a negligible effect on any equilibrium reactions.

(^{14}C)Carbon monoxide was prepared by the reduction of (^{14}C)carbon dioxide with metallic zinc (32). 50gm of zinc pellets (6mm in diameter) were prepared from a moistened mixture containing 95% by weight zinc dust and 5% Aerosil silica (Degussa Ltd.). The silica was used to give greater porosity. The zinc pellets were dried at 110°C for 24 hours then placed in the converter (figure 3.6.); they were degassed by heating to 320°C in vacuo for 24 hours. Over 99.9% conversion was accomplished by circulating the

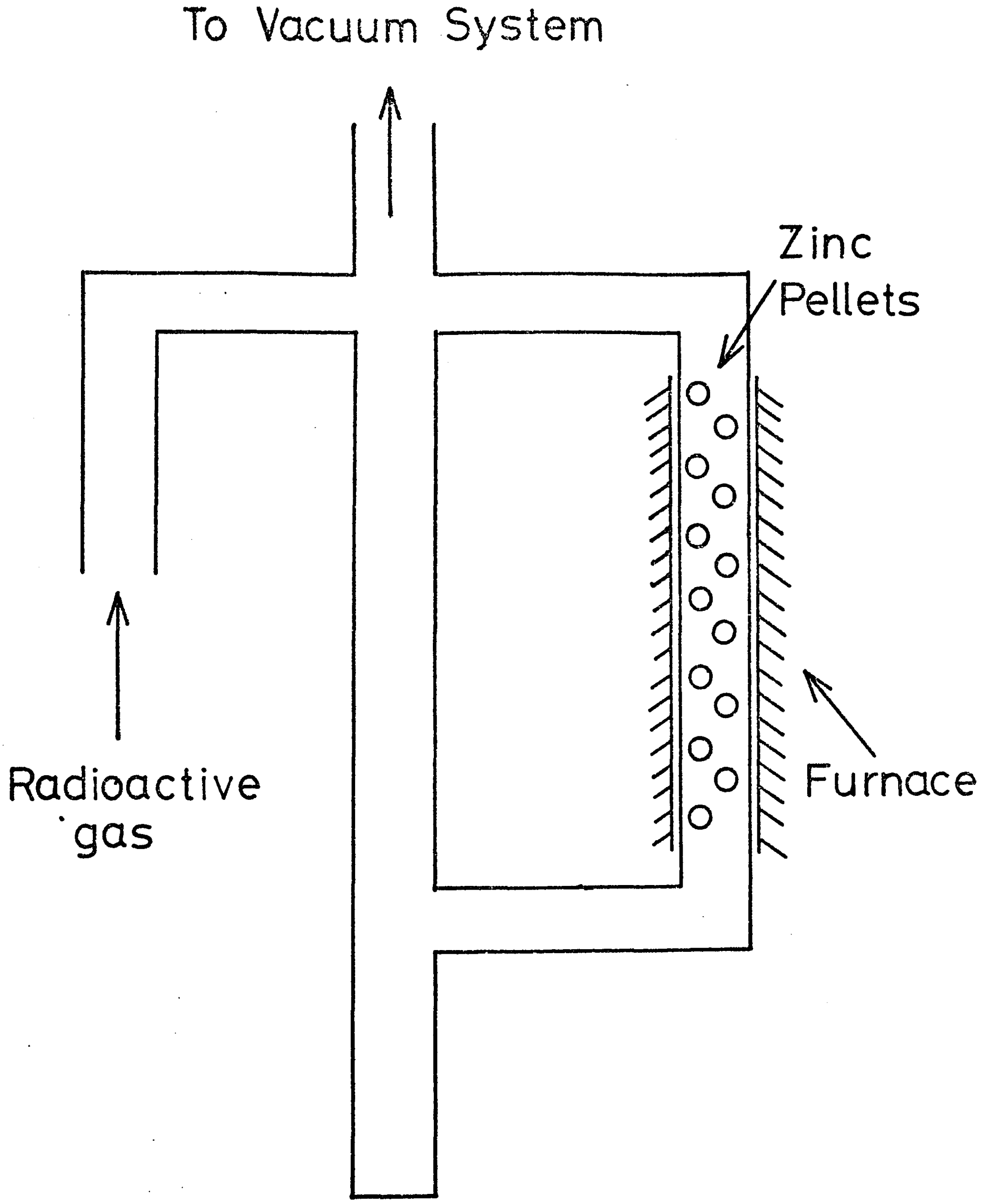


figure 3.6

(^{14}C)carbon dioxide through the converter at 400°C for 24 hours. Any unreacted carbon dioxide was removed by condensing with liquid nitrogen. The (^{14}C)carbon monoxide was then diluted to the required activity with helium.

(^{14}C)Benzene, 60 mCi/mmole, and (^{14}C)methyl-toluene, 20 mCi/mmole, (both Radiochemical Centre, Amersham) were diluted to the required activity with their respective non-radioactive hydrocarbons.

CHAPTER 4

Results and Discussion

4.1. Reactions in the Absence of Steam

4.1.1. Reactions of Hydrocarbons

When certain hydrocarbons (30 × 5μl) were passed over reduced catalysts at 475°C, in a stream of helium, the products regardless of the starting hydrocarbon, consisted solely of methane. The percentage of carbon detected as methane, in relation to the amount of carbon in the hydrocarbon feedstock, was found to be dependent upon the hydrocarbon used. Values observed were 22.8% (ethyl benzene), 10.6% (benzene), 27.1% (hexane) and 23.9% (cyclohexane).

Each used catalyst was microanalysed for carbon and hydrogen (table 4.1), (using a Carlo-Erba automatic C.H.N. analyser). From these results it was possible to deduce, for each hydrocarbon, the overall stoichiometry of the reactions occurring on the surface:

Hexane : $C_6H_{14} \longrightarrow 3CH_4(g) + 3C(a) + 2H(a)$

Heptane : $C_7H_{16} \longrightarrow 3CH_4(g) + 4C(a) + 4H(a)$

Cyclohexane : $2\ C_6H_{12} \longrightarrow 5CH_4(g) + 7C(a) + 4H(a)$

Benzene : $C_6H_6 \longrightarrow 1CH_4(g) + 5C(a) + 2H(a)$

Toluene : $C_7H_8 \longrightarrow 1CH_4(g) + 6C(a) + 4H(a)$

Ethyl Benzene : $2\ C_8H_{10} \longrightarrow 3CH_4(g) + 13C(a) + 8H(a)$

Table 4.1

Analysis of Catalysts for Carbon and Hydrogen

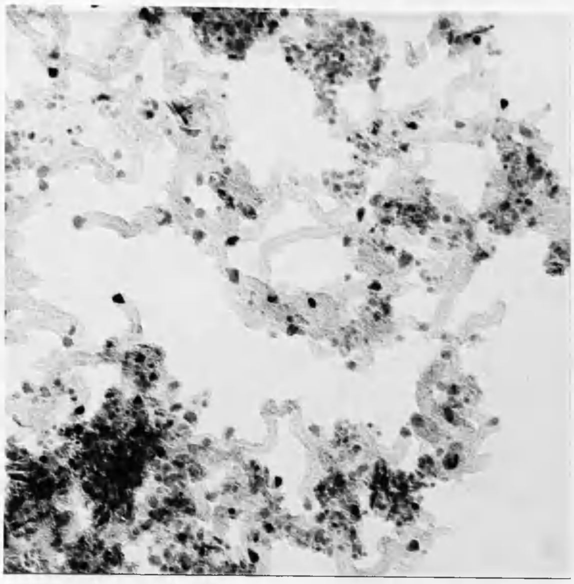
Hydrocarbon	% carbon retained	C : H ratio of surface deposit
Hexane	56.69	1 : 0.5
Cyclohexane	56.83	1 : 0.4
Heptane	68.76	1 : 0.95
Benzene	86.8	1 : 0.6
Toluene	49.5	1 : 0.8
Ethyl Benzene	52.8	1 : 0.9

(C(a) and H(a) may be associated).

The used catalysts were examined by electron microscopy using a J.E.O.L. 100C electron microscope. On the catalysts used with (30 × 5μl) ethyl benzene, toluene, benzene, heptane and hexane as feedstocks, carbon filaments were observed, as can be seen in the electron micrographs shown in figure 4.1. When (30 × 5μl) cyclohexane was used as the feedstock, no filamental material was observed on the catalyst.

Sample catalysts were extracted, by being refluxed with carbon tetrachloride for six hours. Infra-red analysis of the catalyst extracts, using a Perkin Elmer type 580 and 5cm liquid cells, gave spectra with peaks which were assigned as follows:

Peak, cm^{-1}	Assignment
925	$CH = CH_2$
1400	
1455	CH_3 asymmetric deformation and/or CH_2 symmetric deformation.
1700	$R^1R^2C = CHR^3$, C = C stretch and/or substituted aromatic stretch.
2900	CH_2 asymmetric stretch.
2970	CH_3 asymmetric stretch.
3020	$R^1R^2C = CHR^3$, C – H stretch and/or penta substituted aromatic C – H stretch.



Catalyst with filaments

scale 1000 Å

Catalyst without filaments

figure 4.1

Mass spectrometric analysis (A.E.I. M.S.12) of the extract confirmed that the residue removed from the catalyst was a hydrocarbonaceous polymeric material. The upper mass limit of this species was approximately 350 a.m.u. and the decomposition sequence suggested a $-CH_2-$ backbone. Infra-red analysis of the catalysts gave spectra, which correlated with the spectra obtained from the extract.

The temperature of the catalyst bed was recorded both before and during the passage of the hydrocarbon over the catalyst. It was found that when a hydrocarbon alone was passed over the catalyst a temperature increase, of between 4°C for aliphatics and 8°C for aromatics, was recorded indicating the occurrence of an exothermic reaction. This was observed with each of the hydrocarbons.

4.1.2. Reaction of Carbon Monoxide

When carbon monoxide was passed over a reduced catalyst at 475°C in the absence of steam the only product detected was carbon dioxide. This may be explained by the occurrence of a Boudouard reaction;

$$2CO \longrightarrow CO_2 + C$$

Confirmation that this reaction had occurred was obtained when the catalyst was subjected to an oxygen flow at 475°C and the quantity of surface carbon detected as carbon dioxide was 90% of the amount determined from the extent of carbon monoxide reaction over the catalyst. When a catalyst, which had been treated with 54ml of carbon monoxide, was examined by electron microscopy, no filaments were observed (figure 4.2). However, when a catalyst was treated with 600ml of carbon monoxide, carbon filaments were observed (figure 4.2.).

4.1.3. Reaction of Benzene with Hydrogen

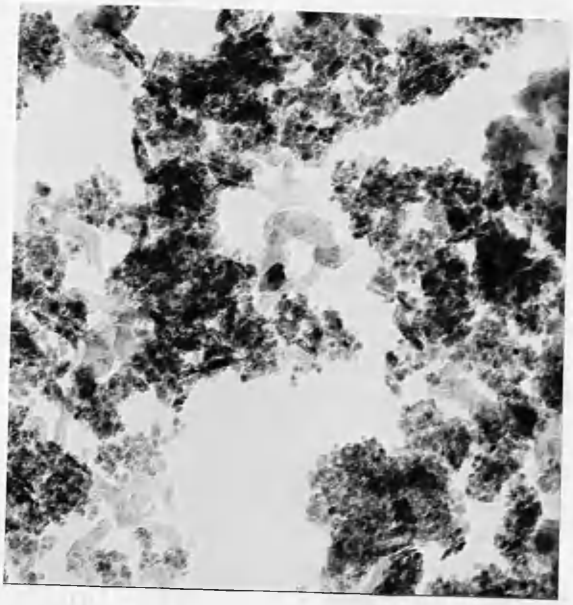
When benzene reacted over a reduced catalyst at 475°C with hydrogen in an amount sufficient to satisfy the stoichiometric equation:

$$C_6H_6 + 9H_2 \longrightarrow 6CH_4,$$

50% of the feedstock carbon was deposited and 50% was detected as methane. The ratio of carbon to hydrogen in the surface deposit, by microanalysis, was 1:0.4 and therefore the overall stoichiometry of the reaction occurring can be represented (unusually) as:

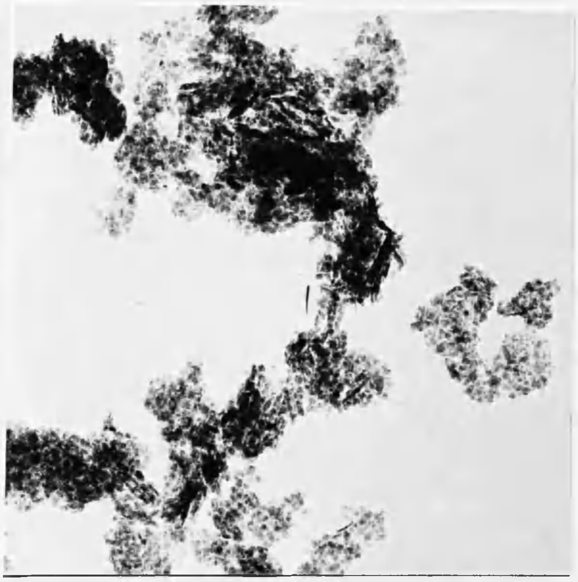
$$2C_6H_6 + 18H_2 \longrightarrow 6CH_4 + 2C_3H + 11H_2$$

A quantity of hydrogen was detected chromatographically, but this could not be estimated quantitatively, due to the non-standard response of the detector to hydrogen. Subsequent examination of the catalyst by electron microscopy showed no filamental material to be present. The used catalyst was also extracted with carbon tetrachloride and only a



Catalyst with filaments

scale 1000 Å



Catalyst without filaments

figure 4.2

negligible quantity of a hydrocarbonaceous deposit was removed. Microanalysis of this catalyst after extraction showed an appreciable loss of carbon (~61%) but no change in the amount of detectable hydrogen. The loss in carbon was not unexpected since particles of carbon were observed in the carbon tetrachloride after extraction.

Microanalysis of a catalyst, which had been used with a hydrocarbon feedstock and on which filaments were present, (note the absence of hydrogen in this preparation) showed that extraction with carbon tetrachloride resulted in a removal of ~9% of the carbon initially present. However an examination of the catalyst by electron microscopy after extraction showed that, although there was evidence for the removal of some filaments, many remained intact.

From the above results it can be deduced that the carbon deposit produced when hydrogen/hydrocarbon feedstocks were used, was such that filamental growth was completely suppressed and the deposit was sufficiently loosely held to the surface to be removed by extraction.

4.2. Reactions Involving a Low Steam to Hydrocarbon Ratio

When reactions were carried out over a reduced catalyst, at 475°C, using a low steam to hydrocarbon ratio (table 4.2.), the primary product was found to be methane, although carbon monoxide and carbon dioxide were also produced. For the

Table 4.2

Steam to Hydrocarbon Molar Ratio

	Hexane	Heptane	Cyclohexane	Hept-1-ene	Benzene
Steam Hydrocarbon Ratio	2.16	2.44	1.79	2.36	1.5

	Toluene	Ethyl Benzene	Xylenes
Steam Hydrocarbon Ratio	1.76	2.02	2.0

Table 4.3

% Carbon dioxide Production

Hydrocarbon	Initial Values	Steady State Values
Hexane	16.4	4.3
Heptane	9.1	3.3
Cyclohexane	8.98	6.5
Hept-1-ene	15.3	4.7
Benzene	11.8	7.0
Toluene	11.3	5.5
Ethyl Benzene	9.7	5.3
Xylenes	8.9	5.6

reasons discussed earlier (section 3.2.) it was not possible to obtain quantitative figures for the carbon monoxide and methane production. Quantitative figures for carbon dioxide production were obtained. These showed that, initially, the carbon dioxide production was high but that it progressively decreased to a steady state value (table 4.3.). These results can be rationalised in terms of the following reaction sequence;

Mechanism C

$$\text{Hydrocarbon} \longrightarrow CH_4 + C + H \qquad (C.1)$$

$$\text{Hydrocarbon} + H_2O \longrightarrow CO + H_2 \qquad (C.2)$$

$$2CO \longrightarrow CO_2 + C \qquad (C.3)$$

$$CO + H_2O \longrightarrow CO_2 + H_2 \qquad (C.4)$$

$$CO + 3H_2 \longrightarrow CH_4 + H_2O \qquad (C.5)$$

$$CO_2 + C \longrightarrow 2CO \qquad (C.6)$$

(As it is uncertain whether the components of these reactions are gas phase, adsorbed or both, no specification of their state has been made).

Initially the hydrocarbon reacted either as if no steam was present (reaction (C.1)) to give methane, or, with the water present (reaction (C.2)) to give carbon monoxide and hydrogen. However, although the steam to hydrocarbon ratio was greater than unity, the steam to carbon ratio was less than unity ($\leqslant 0.36$), that is, three carbon atoms to every water molecule. Thus it appeared that reaction (C.1) was the major reaction and methane the major product. It has been shown (section 4.1) that in the absence of steam, the Boudouard reaction (reaction (C.3)) was favourable and approximately 100% conversions of carbon monoxide to carbon dioxide and carbon were obtained. Hence, the carbon monoxide produced by step (C.2) reacted, via a Boudouard reaction to form carbon dioxide. If all of the water was not consumed in reaction (C.2), reaction (C.4) might have occurred. Reaction (C.5) is unlikely to be a major reaction, as there would have been insufficient free hydrogen to allow a large percentage of carbon monoxide hydrogenation. Reaction (C.6) would not be a major process in the initial stages as there would be little surface carbon present. Therefore, in the initial stages of reaction a high percentage of carbon dioxide, relative to the maximum possible, would be expected. As the amount of carbon on the catalyst surface increased, both by deposition from the parent hydrocarbon (reaction (C.1)), and by carbon deposition from reaction (C.3), reaction (C.6) would become increasingly important. Hence, the relative yield of carbon dioxide over several reactions decreased to an equilibrium value (an increased amount of carbon monoxide was observed).

A sample of each used catalyst was microanalysed for carbon and hydrogen. The results are shown in table 4.4.

Table 4.4

Carbon to Hydrogen Ratio of the Surface Deposit

	Hexane	Heptane	Cyclohexane	Benzene
C:H ratio	1:5.5	1:10.3	1:2.4	1:1.2

	Toluene	Ethyl Benzene	Xylenes
C:H ratio	1:1	1:0.8	1:0.5

The values for amount of carbon deposited depended on the position in the reactor bed from which the catalyst sample was taken: therefore an overall percentage of carbon deposition could not be obtained. Even when there was a large variation in the percentage of carbon found for a single hydrocarbon the carbon to hydrogen ratios were constant within experimental error (± 2%). The deposit from the aliphatic and alicyclic species had a lower carbon to hydrogen ratio than the deposit from the aromatic species (table 4.4).

Each of the catalysts was examined by electron microscopy. On the catalysts used with xylenes, ethyl benzene, benzene, toluene, hexane and pentane as feedstocks carbon filaments were observed. No filaments were found on the catalysts which had been used with cyclohexane and heptane as the feedstocks. Various used catalysts were extracted with carbon tetrachloride and the extracts analysed by infra-red spectroscopy. The peaks from the spectra were assigned as follows:

Peak cm^{-1}	Assignment
3000	CH_3 asymmetric stretch and/or C-H stretch of C = C - H.
2895	CH_3 symmetric stretch, CH_2 stretch
2775	C-H stretch in -CHO.
1660	$R^1CH = CHR^2$ cis stretch (C=C) and/or C=O stretch of C=C-C=O.
1400	R - CHO skeletal.
625	$R^1CH = CHR^2$ cis deformation.

The extracted materials were then analysed by mass spectrometry and a polymeric species based on a $-CH_2-$ backbone was again identified. Confirmation of a C=C-C=O species was obtained by observing mass peaks at 55 a.m.u. (CH=CH-CHO), 42 a.m.u. (CH-CHO), 41 a.m.u. (C-CHO/CH-CO) and 29 a.m.u. (CHO). The used catalysts were analysed by infra-red spectroscopy and the spectra obtained were in agreement with the spectra from the extracted material.

Temperature changes in the catalyst bed were recorded before, during and after a reaction (figure 4.3). It can be seen that each of the aromatic species gave rise only to an exothermic reaction, whereas with the aliphatic feedstocks (hexane, hept-1-ene) and cyclohexane, each gave rise to both an exothermic and an endothermic reaction. Heptane gave only an exothermic reaction.

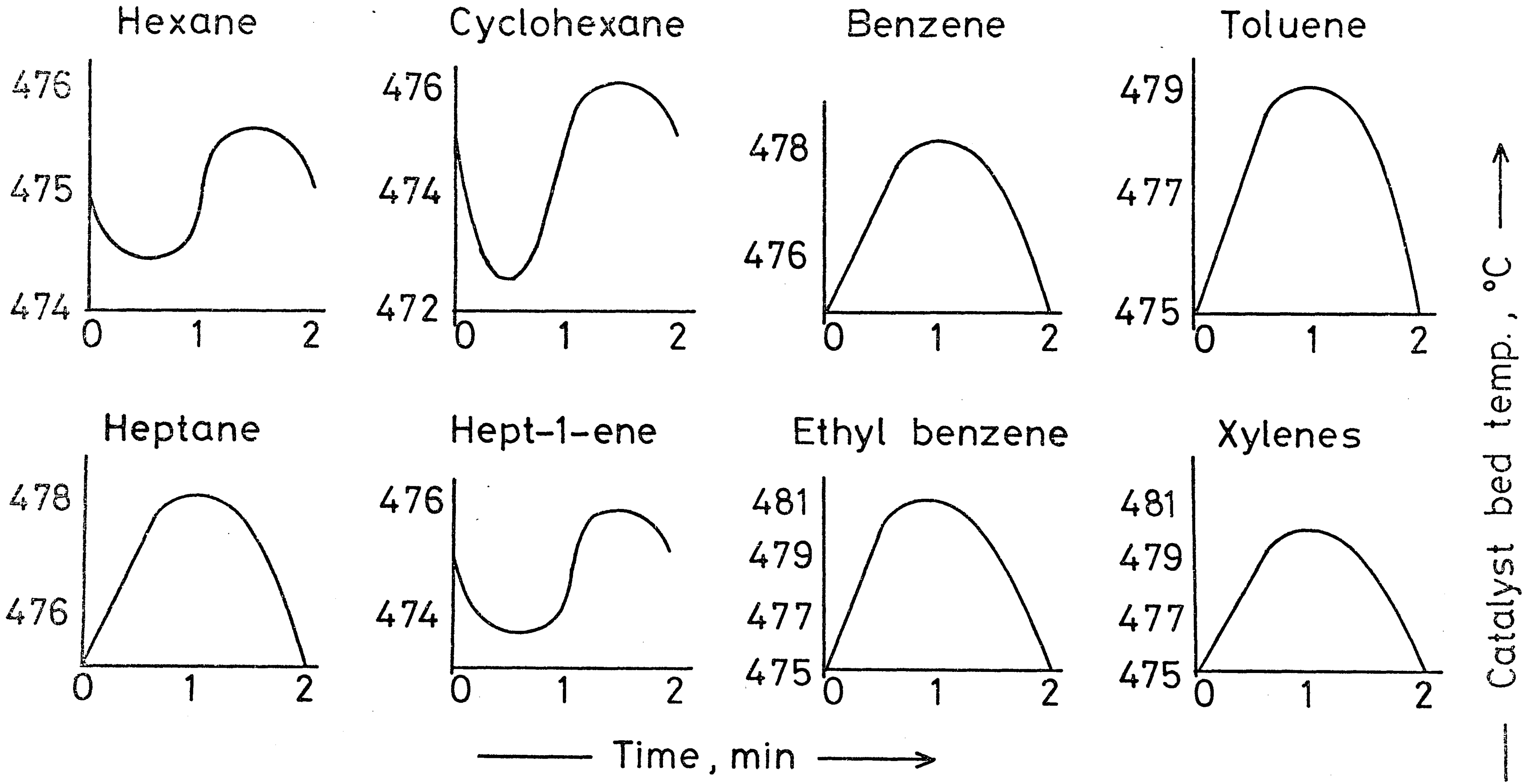

Hexane
Cyclohexane
Benzene
Toluene
Heptane
Hept-1-ene
Ethyl benzene
Xylenes
476
475
474
476
474
472
478
476
479
477
475
478
476
476
474
481
479
477
475
481
479
477
475
0
1
2
Time, min
Catalyst bed temp., °C

figure 4.3

4.3. Reactions Involving a High Steam to Hydrocarbon Ratio

Using a high steam to hydrocarbon ratio (table 4.5) the reaction of various hydrocarbons over a reduced catalyst at 475°C led to the production of methane, carbon monoxide and carbon dioxide. With all the hydrocarbons used the production of carbon dioxide was initially low but this gradually increased to a steady state value (table 4.6). The mean steady state carbon dioxide production figures were found to be constant for all the hydrocarbons studied.

A catalyst, which had been used for steam-reforming of $[^{14}C]$benzene and on which, therefore, a carbon-14 labelled surface carbonaceous residue was deposited, was subjected to injections of $[^{12}C]$carbon dioxide in the absence of steam. Carbon was exchanged in such a way that surface carbon-14 was detected as carbon dioxide. The overall loss of carbon to the surface from the carbon dioxide was 59.8%, while the amount of surface deposit removed was 7.73%. These results may be rationalised in terms of the following mechanism:

Mechanism D

$$^{12}CO_2(g) \longrightarrow {}^{12}CO(a) + O(a) \qquad (D.1)$$

$$^{14}C(a) + O(a) \rightleftharpoons {}^{14}CO(a) \qquad (D.2)$$

$$^{12}CO(a) \rightleftharpoons {}^{12}C\,(a) + O(a) \qquad (D.3)$$

$$^{12}CO(a) + {}^{12}CO(a) \longrightarrow {}^{12}C(a) + {}^{12}CO_2(g) \qquad (D.4)$$

$$^{14}CO(a) + {}^{12}CO(a) \longrightarrow {}^{12}C(a) + {}^{14}CO_2(g) \qquad (D.5)$$

Table 4.5

Steam to Hydrocarbon Molar Ratio

	Pentane	Hexane	Heptane	Benzene	Toluene
Steam Hydrocarbon Ratio	11.9	13.5	15.3	9.5	11.0

	Cyclohexane	Hept-1-ene	Ethyl Benzene	Xylenes
Steam Hydrocarbon Ratio	11.3	14.8	12.7	12.5

Table 4.6

% Carbon dioxide Production

Hydrocarbon	Initial Values	Steady State Values
Pentane	4.6	38.58
Hexane	3.0	35.86
Heptane	1.3	37.03
Hept-1-ene	2.9	36.99
Cyclohexane	13.2	45.98
Benzene	3.1	36.80
Toluene	1.9	36.35
Ethyl Benzene	6.9	35.59
Xylenes	2.4	33.30

Accordingly, the deposition may be attributed to carbon monoxide, rather than carbon dioxide, although only a negligible amount of carbon monoxide was detected in the products. However, this result is not unexpected, since a CO → CO_2 reaction did occur as results (section 4.1.) from carbon monoxide experiments showed. When carbon dioxide was passed over a reduced catalyst in the presence of an excess of water, 33% was converted to carbon monoxide/methane, 50% remained as carbon dioxide, while the remaining 17% was retained by the surface. From these results the reactions postulated as occurring in the absence of steam were still occurring, but in competition with the steam reactions. A possible reaction scheme is:

Mechanism E

$$CO_2(g) \longrightarrow CO(a) + O(a) \qquad (E.1)$$

$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O \qquad (E.2)$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad (E.3)$$

$$2CO \rightleftharpoons CO_2 + C \qquad (E.4)$$

Therefore, assuming 100% dissociation of the carbon dioxide by reaction (E.1), 34% of the carbon monoxide produced reacted via reaction (E.4), 34% reacted via reaction (E.3) and 33% was partitioned between carbon monoxide and methane in reaction (E.2).

To be able to follow carbon dioxide through its reaction sequence, under normal reaction conditions, [^{14}C]carbon dioxide was used. When [^{14}C]carbon dioxide was injected simultaneously with a hydrocarbon under normal steam-reforming conditions the retention of the [^{14}C]carbon dioxide by the surface was shown in table 4.7.

Table 4.7

Deposition of [^{14}C]Carbon Dioxide when Reacted Simultaneously with a Hydrocarbon and Steam

Hydrocarbon	% of [^{14}C]carbon dioxide retained
Benzene	17.7
Toluene	19.3
n-Heptane	1.6

Hence it can be seen that there is a large variation in the amount of [^{14}C]carbon dioxide retained and that this depends on whether the hydrocarbon is aromatic or aliphatic.

To elucidate the role of carbon monoxide in both the carbonaceous deposition and the reaction mechanism, [^{14}C]carbon monoxide was added with the hydrocarbon under normal steam-reforming conditions. Table 4.8 shows the amount of [^{14}C]carbon monoxide retained by the surface with various hydrocarbons in the feedstock.

Table 4.8

Retention of $[^{14}C]$Carbon Monoxide When Reacted Simultaneously with a Hydrocarbon and Steam

Hydrocarbon	% of $[^{14}C]$carbon monoxide retained
Benzene	23.4
Toluene	17.5
n-Heptane	1.2

It can be seen that these figures are in good agreement with the deposition figures obtained when $[^{14}C]$carbon dioxide/steam/hydrocarbon feedstocks were used. This is consistent with the carbon monoxide/carbon dioxide mechanisms (D and E) discussed above.

/

To obtain a measure of the amount of carbon deposited by each of the hydrocarbons, each was introduced in turn over a clean catalyst until a steady state was achieved. The catalyst was then treated with oxygen at 475°C for 30 min. and the amount of carbon deposited determined from the carbon dioxide yield (table 4.9).

Table 4.9

% of Carbon Retained

	Pentane	Hexane	Heptane	Cyclohexane
% carbon retained	28.1	16.0	10.5	9.7
	Benzene	Toluene	Ethyl Benzene	Ortho-Xylene
% carbon retained	24.9	21.6	29.1	25.9

All the aromatic species gave approximately the same percentage deposition, whereas there is a wide spread of values for the aliphatic hydrocarbons. Comparison of these figures with the [^{14}C]carbon monoxide and [^{14}C]carbon dioxide deposition figures (table 4.8; table 4.7), shows good agreement for benzene and toluene but not for n-heptane. The following mechanism may be postulated to satisfy these observations:

<u>Mechanism F</u>

$$\text{Hydrocarbon} \longrightarrow CH_4 + C + H \qquad (F.1)$$

$$\text{Hydrocarbon} + H_2O \longrightarrow CO + H_2 \qquad (F.2)$$

$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O \qquad (F.3)$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad (F.4)$$

$$2CO \rightleftharpoons CO_2 + C \qquad (F.5)$$

$$C + H \longrightarrow C_xH_y \qquad (F.6)$$

For aromatic hydrocarbons the carbon deposition figures are similar to those from [^{14}C]carbon monoxide and [^{14}C]carbon dioxide depositions. From these data and the product distributions, it was possible to calculate the percentage reaction for equations (F.1) to (F.5) above. For benzene 94% reacted by reaction (F.2), while the remaining 6% reacted via reaction (F.1); of the carbon monoxide produced 24% reacted via reaction (F.3), 13% by reaction (F.4) and 47% reacted by reaction (F.5), the remaining 10% came through unchanged. For toluene 89.5% reacted via reaction (F.2) while 10.5% reacted via reaction (F.1); of the carbon monoxide produced 22.3% reacted via reaction (F.3), 17.2% by reaction (F.4) and 38.6% by reaction (F.5); the remaining 11.4% came through unchanged. The carbon deposition therefore comes primarily from carbon monoxide rather than directly from the aromatic hydrocarbon.

With an aliphatic hydrocarbon however, the [^{14}C]carbon monoxide and [^{14}C]carbon dioxide deposition figures were considerably smaller than the hydrocarbon deposition figures. For n-heptane 84.75% reacted via reaction (F.1), while the remaining 15.25% reacted via reaction (F.2); therefore the major deposition came directly from the aliphatic hydrocarbon by reaction (F.1). Reaction (F.5) was not significant as a carbon-deposition reaction with aliphatic hydrocarbons, since reaction conditions were such that only a small proportion of carbon monoxide was formed and that the excess hydrogen present favoured reaction (F.3) over reaction (F.5).

Reaction (F.6) represents the formation of the polymeric species on the surface and by this reaction, which occurred for both aromatic and aliphatic hydrocarbons, hydrogen was removed from being available for reaction and was incorporated into the surface carbonaceous deposit. This is in agreement with the observation that initially the carbon dioxide production was low and the methane was large: subsequently the methane production decreased and the carbon dioxide increased. However, the production of carbon dioxide and methane was governed by reactions (F.3) and (F.4) and it was probable that the steam component also varied as the reaction proceeded. A rationalisation of the above results can be suggested as follows. The initial adsorption of the steam was on the metal and on the alumina support, with hydroxy species retained by the alumina. This would effectively remove them from availability for reaction; as the support became saturated by hydroxy groups more steam became available for reaction, rather than hydrogen. Hence the overall effect of the variation in hydrogen and steam concentrations would have been to give the change in carbon dioxide and methane productions as observed experimentally.

A sample of each steady state catalyst was microanalysed for carbon and hydrogen (table 4.10).

Table 4.10

C : H Ratios of the Surface Deposits

	Pentane	Hexane	Heptane	Hept-1-ene
C : H ratio	1:9.7	1:4.6	1:8.8	1:0.6
	Benzene	Toluene	Ethyl Benzene	Ortho-Xylene
C : H ratio	1:1.5	1:0.9	1:2.2	1:1

From table 4.10, it can be seen that the deposit from the aliphatic hydrocarbons had a lower carbon to hydrogen ratio than the deposit from the aromatic hydrocarbons.

Each steady state catalyst was examined by electron microscopy. No carbon filaments could be observed on the catalysts when pentane, hexane or cyclohexane had been used as reactants. With those catalyst samples which had been used for reactions with benzene, toluene, ethyl benzene, xylenes or n-heptane, a very small quantity of filamental material was observed. However, when hept-1-ene was used as reactant, the catalyst was covered by filaments. From table 4.10 it can be seen that hept-1-ene had the lowest hydrogen to carbon ratio for the surface deposit as would be expected with large amounts of carbon filaments.

Sample catalysts were extracted with carbon tetrachloride and the resulting solution examined by infra-red spectroscopy. The peaks observed and their assignations were as follows:-

Peaks (cm^{-1})	Assignment
3010	C–H stretching in C=C–H group.
2960, 2930, 2860	C–H stretching in $-CH_3$, $-CH_2-$ groups.
2720	C–H stretching in -CHO group.
1755	Unspecified C=0 stretch.
1740	C=0 stretch of alkyl ester.
1710	C=0 stretch of alkyl aldehyde.

Peaks (cm^{-1})	Assignment
1670	C=O stretch of C=C-CHO.
1620	C=C stretch of C=C-CHO.
1460	C-H deformations of $-CH_2-$, and $-CH_3$.
1380	$-CH_3$ symmetrical deformation and C-CHO skeletal.
920	C-H deformation for -CHO.

The extracted samples were then analysed by mass spectrometry and a polymeric species based on a $-CH_2-$ backbone was identified with an upper-limit mass of approximately 400 a.m.u. The peaks at the lower end of the spectrum were identified as follows:

Peak (a.m.u.)	Assignment
29	CHO
41 (s)	C - CHO ; CH - CO
42	CH - CHO ; CH_2- CO
43 (s)	CH_2 - CHO
44	CH_2 - CH_2O
55 (s)	CH = CH - CHO
56	CH_2- CH - CHO CH_2- CH_2- CO
57 (s)	CH_2- CH_2- CHO
68	CH - CH = CH - CHO
69 (s)	CH_2- CH = CH - CHO
70	CH - CH_2- CH_2- CHO
71 (s)	CH_2- CH_2- CH_2- CHO

The used catalysts were also examined by infra-red and laser-Raman spectroscopy, both of which gave spectra in agreement with the solution infra-red analysis of the catalyst extracts.

Temperature changes in the catalyst bed were recorded before, during and after reaction (figure 4.4). All the aromatic species gave rise only to an exothermic reaction, whereas with heptane, hept-1-ene and cyclohexane both exothermic and endothermic reactions were observed. Pentane gave only an exothermic reaction and hexane an endothermic reaction.

When a steam/helium stream was passed over a freshly reduced catalyst at 475°C an exothermic reaction took place which resulted in a temperature increase of 4-5°C in the catalyst bed and the evolution of hydrogen. When a steam/helium stream was passed over a catalyst which had been used for steam-reforming the exothermic nature of the steam-catalyst interaction decreased; a temperature rise of only 1°C was observed under similar conditions.

4.4. Catalyst Regeneration and Removal of Carbonaceous Deposits.

Four methods of regeneration and removal of carbonaceous deposits have been investigated. The first method was to subject a catalyst, which had been used for steam-reforming,

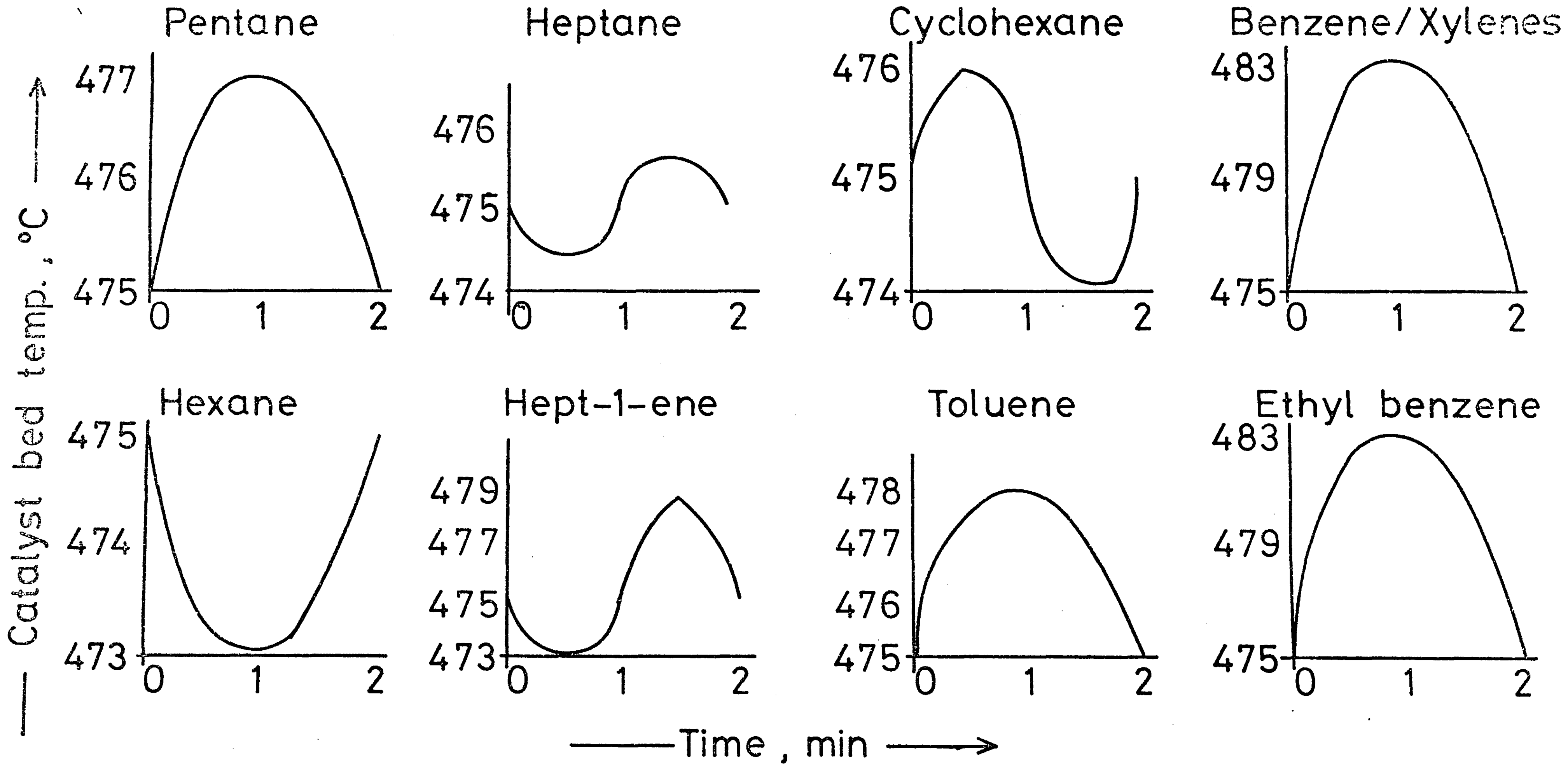

Pentane
Heptane
Cyclohexane
Benzene/Xylenes
Hexane
Hept-1-ene
Toluene
Ethyl benzene
Catalyst bed temp., °C
477
476
475
476
475
474
476
475
474
483
479
475
475
474
473
479
477
475
473
478
477
476
475
483
479
475
0
1
2
Time, min

figure 4.4

to a helium stream containing 6.82% steam: this was analogous to the industrial method of cleaning. When the steam/helium stream was passed over the catalyst, carbon dioxide was evolved. This evolution of carbon dioxide stopped after treatment with the steam/helium stream for approximately 3 min. No further reaction was observed in subsequent treatments with the steam/helium stream. The fact that this type of surface cleaning did not remove filamental material was revealed by subsequent examination of the catalysts by electron microscopy. Neither did the steam cleaning remove the polymeric material as this was still detected in extracts of these catalysts. As the amount of deposit removed by steam cleaning was 6.97%, which is in good agreement with the amount of deposit removed when a used catalyst was treated with carbon dioxide alone (7.73%) (section 4.3), it is probable that the species interacting with the steam was the same species which interacted with the carbon dioxide. Therefore, as it has been shown (section 4.3) that the carbon dioxide reacted via a reverse Boudouard reaction ($CO_2 + C \longrightarrow 2CO$, Mechanism D), a carbon adatom may be considered to be the reactive surface species, allowing a mechanism to be postulated for steam cleaning:

Mechanism G

$$H_2O \longrightarrow OH(ads) + H(ads) \tag{G.1}$$

$$C(ads) + OH(ads) \longrightarrow CO(ads) + H(ads) \tag{G.2}$$

$$CO(ads) + OH(ads) \longrightarrow CO_2(g) + H(ads) \tag{G.3}$$

$$2H(ads) \longrightarrow H_2(g) \tag{G.4}$$

$$CO(ads) \longrightarrow CO(g) \tag{G.5}$$

As no carbon monoxide is detected, reaction (G.5) will be slow compared to reaction (G.3).

The second method of regeneration and removal of carbonaceous deposits was to subject a used catalyst to an oxygen flow at 475°C. This treatment resulted in an extremely exothermic reaction. The temperature in the catalyst bed increased to ~1000°C and this resulted in a 20-25% loss of catalyst mass due to its incorporation into the walls of the catalyst chamber. Although this oxygen treatment removed all deposited carbon, (confirmed by microanalysis of the catalyst) it resulted in a total loss of catalytic activity. When the catalyst was subjected to oxygen treatment at room temperature, an exothermic reaction occurred which increased the temperature in the catalyst bed to 450-500°C. However, it was found that, although this treatment also removed all the deposited carbon (confirmed by microanalysis), the catalyst could be reactivated by a hydrogen reduction at 450°C for 16 hours. The initial and steady state product distributions of this regenerated catalyst were similar, respectively, to the product distributions of a freshly reduced catalyst (table 4.11).

Table 4.11

Comparison of Carbon Dioxide Production for a Freshly Reduced Catalyst and an Oxygen-Cleaned then Reduced Catalyst

Catalyst	Carbon dioxide production		
	1st Reaction	2nd Reaction	Steady State
Freshly Reduced	1.09%	3.6%	36.8%
O_2 cleaned then reduced	1.8%	9.07%	34.2%

Subjecting a used catalyst to a stream of hydrogen, for 16 hours at 500°C, was the third method of regeneration and removal of carbonaceous deposits which was investigated. The catalyst had been used for the steam-reforming of [^{14}C]benzene and on it, therefore, a carbon-14 labelled surface carbonaceous residue had been deposited. As it was known that benzene deposited 25% of its carbon (section 4.3; table 4.9) any removal of surface carbon by hydrogen could be detected. During the first 4 hours of the treatment, the exit gas was monitored for carbon-14 but none was detected. Therefore, at the end of the 16 hour period, the gas flow was changed to oxygen and any residual carbon was removed by an oxygen treatment at 475°C. The carbon removed from the surface by the oxygen flow was in the form of carbon dioxide and the quantity of radioactivity detected, in the carbon dioxide, within experimental error, was equal to the amount deposited by the benzene. Therefore, no carbon had been removed from the surface by the hydrogen treatment. However, a used catalyst treated with hydrogen as above gave, when steam and hydrocarbon reacted over it, the same product distributions as a freshly reduced catalyst.

The fourth method investigated was to subject a used catalyst to treatment with hydrogen peroxide. The catalyst was initially steam "cleaned" and then 200 µl of hydrogen peroxide (100 Vol.) were injected over it. It was found that this method removed carbon from the surface, the carbon being detected as carbon dioxide. Temperature changes in the catalyst bed were severe during the reaction, with the temperature rising by 75°C from 475°C to 550°C. However the catalyst was found to be active after such treatment.

4.5. Carbon Monoxide Adsorptions

Carbon monoxide was used to measure the extent of metal surface available for reaction before the catalyst was used for the reaction of steam and hydrocarbon (at high steam to hydrocarbon ratios) and again after the reaction. This was done for all the hydrocarbons used. From the results shown in table 4.12 it can be seen that the percentage of the surface free after one reaction of each hydrocarbon (compared with that of a freshly reduced catalyst) is relatively constant, although as shown earlier (section 4.3), the amount of surface

Table 4.12

% of Free Surface after Reaction of Steam and Hydrocarbon

Hydrocarbon	% of Surface Free after One Reaction	% of Surface Free after Four Reactions
Pentane	51.97	48.03
Hexane	47.61	46.2
Heptane	53.24	46.9
Cyclohexane	54.23	44.79
Benzene	60.14	32.5
Toluene	48.97	44.1
Ethyl Benzene	50.62	31.83
Ortho-Xylene	50.28	23.7

deposition from each of the hydrocarbons is different, ranging from 10% to 29% of the amount injected. The derived orders of deposition, for various quantities, can be seen in table 4.13. If these orders are compared with the H : C ratios for the hydrocarbons, it is found that for aromatic hydrocarbons:

	Ethyl Benzene	Ortho-Xylene	Toluene	Benzene
H : C ratio	1.25	1.25	1.14	1

and for the aliphatic hydrocarbons and cyclohexane

	Pentane	Hexane	Heptane	Cyclohexane
H : C ratio	2.4	2.33	2.29	2

Hence, within <u>each series</u>, the lower the H : C ratio the less the amount of deposition. It was therefore not expected that each of the catalysts should show the same percentage of free surface after reaction with various hydrocarbons.

After four reactions the free surface was again measured by a carbon monoxide adsorption. The results in table 4.12 show that all the catalysts used with aromatic hydrocarbons have less free surface than those used with aliphatic hydrocarbons and an order of: Pentane > Heptane > Hexane > Cyclohexane > Toluene > Benzene > Ethyl Benzene > Ortho-Xylene is obtained. It is interesting to note that the aromatic species gave the results expected from consideration

Table 4.13

Derived Orders of Deposition

Quantity of Hydrocarbons	Order of Diminishing Deposition
Equal Volumes:	Ethyl Benzene > Ortho-Xylene > Benzene > Toluene > Pentane > Hexane > Cyclohexane > Heptane.
Equal Molar Quantities:	Ethyl Benzene > Ortho-Xylene > Toluene > Benzene > Pentane > Hexane > Heptane > Cyclohexane.
Equal No. of C atoms:	Ethyl Benzene > Pentane > Ortho-Xylene > Benzene > Toluene > Hexane > Heptane > Cyclohexane.

of the percentage carbon deposition figures. However, the order with the aliphatic hydrocarbons was completely the reverse of that expected from the percentage carbon deposition data. Therefore, when the free surface is measured after one reaction, all of the catalysts exhibit the same amount of free surface, whereas after four reactions a distinct variation is found between the free surface available on different catalysts. When the loss in free surface for each of the catalysts, between reactions one and four, is considered the order - Hexane < Pentane < Toluene < Heptane < Cyclohexane < Ethyl Benzene < Ortho-Xylene < Benzene is obtained (table 4.12). When this series is compared with the H : C ratios of the hydrocarbons it is found that the lower the H : C ratio of the hydrocarbon, the greater the loss in free surface between reactions one and four.

The decrease of available surface was studied in greater detail for benzene (table 4.14), where it can be seen that there is an orderly progression to a "steady state" value of approximately 3% of the surface free, compared with a freshly reduced catalyst. It should be noted at this point that all of these catalysts were active, that is they still promoted fast gasification of the reactants to products, at the stage when the carbon monoxide adsorption measurements were made.

Table 4.14

Decrease in Free Surface

Benzene

	Number of Reactions				
	1	4	12	18	24
% of Surface Free	60.14	32.5	19.7	2.5	3.7

By carbon monoxide adsorption measurements it was possible to obtain a measure of the amount of deposited material removable by a steam "cleaning" treatment (section 4.4) and how much free surface was regenerated (table 4.15) by this treatment. The amount of deposit removable by the steam "cleaning" is not large (6.9%), while the amount of surface exposed by removal of the deposit is 10.7% of the original free surface or 15.9% of the surface that was covered.

Table 4.15

% of Surface Regenerated by a Steam Treatment

Benzene:

	After four reactions	After four reactions and steam treatment
% of surface free	32.5%	43.7%

CHAPTER 5

Conclusions

5.1. Conclusion

It is now possible to take an overall view of this research and to correlate the findings. The conclusions will be presented in two parts:

(a) a proposed mechanism,

and (b) an analysis of this approach to the mechanism of steam-reforming.

5.1.1. The Proposed Mechanism

A single mechanism may be postulated to rationalise the results obtained when the hydrocarbons reacted over the catalyst, in the absence of steam, at low steam to hydrocarbon ratios (table 4.2.) and at high steam to hydrocarbon ratios (table 4.5.):-

Mechanism I

$$\text{Hydrocarbon} \longrightarrow CH_4 + C + H \qquad \text{(I.1.)}$$

$$\text{Hydrocarbon} + H_2O \longrightarrow CO + H_2 \qquad \text{(I.2.)}$$

$$H_2O \longrightarrow H + OH \qquad \text{(I.3.)}$$

$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O \qquad \text{(I.4.)}$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad \text{(I.5.)}$$

$$2CO \rightleftharpoons CO_2 + C \qquad \text{(I.6.)}$$

$$C + H \longrightarrow C_xH_y \qquad \text{(I.7.)}$$

$$C + H_2O \rightleftharpoons CO + H_2 \qquad \text{(I.8.)}$$

(As this is an overall representation of the mechanism, no specification has been made as to the states of adsorption of the components). When steam was absent only reactions (I.1.) and (I.7.) occur (section 4.1.). When there was a low steam to hydrocarbon ratio (section 4.2.) or a high steam to hydrocarbon ratio (section 4.3.), all eight reactions occurred, but the extent to which each reaction occurred was dependent on the steam to hydrocarbon ratio and on the nature of hydrocarbon itself. For example different results were obtained for aliphatic and aromatic hydrocarbons.

It has proved possible during the course of this study to detect four types of carbonaceous deposit;

(a) carbon filaments,
(b) a polymeric species,
(c) a reactive surface carbon,
(d) "carbon".

The filamental material was detected by electron microscopy of catalysts which had been subjected to reaction with hydrocarbon alone and with steam/hydrocarbon at low steam to hydrocarbon ratios. When the catalysts which had been used for high steam to hydrocarbon ratio reactions and hydrogen/hydrocarbon reactions were examined, only a negligible quantity of filaments was detected. Therefore, both steam and hydrogen inhibit the growth of carbon filaments. Once formed, the only treatment which removed them from the surface was an oxygen treatment at 475°C.

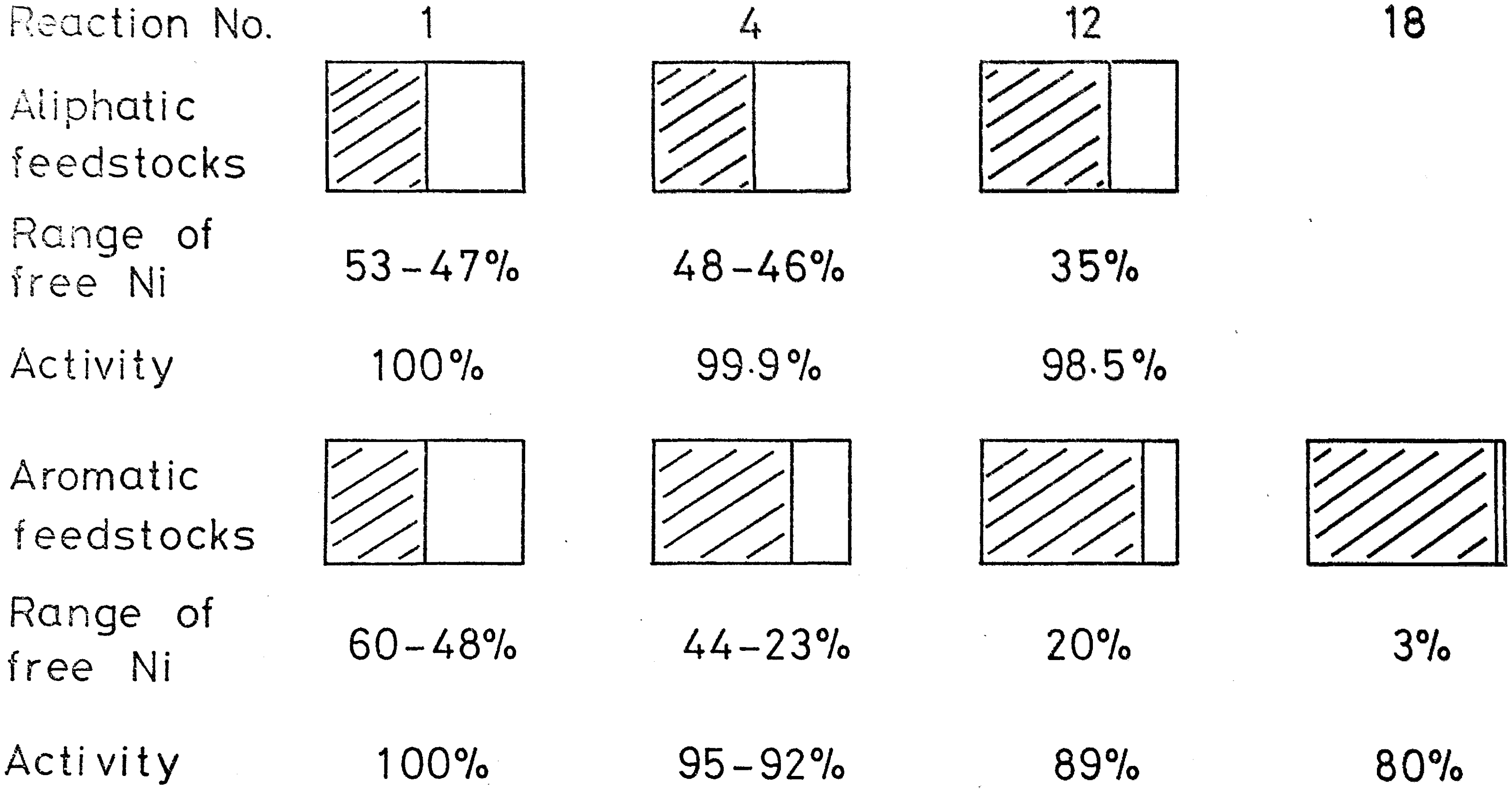
The polymeric species was detected in carbon tetrachloride extracts of used catalysts. It was studied in solution by infra-red spectroscopy, by laser-Raman spectroscopy of the catalyst surface and by mass spectrometry. The data obtained on this species indicated that it was a $-CH_2-$ backboned polymer between $C_{25} - C_{30}$ in length with probably two separate aldehyde groupings, one alkyl (R-CHO), one conjugated ($-CH = CH - CHO$).

It was thought that a reactive carbon adatom, which could be removed by treatment with steam (section 4.4.) or carbon dioxide (section 4.3.) at 475°C, was present on the surface and that it may exist primarily as a transitory species.

The remaining deposit was detected by microanalysis of catalysts which had no filamental growth, had been steam cleaned and had had the polymeric species extracted from them. It was found that catalysts used with aromatic hydrocarbons had a carbon deposit remaining on the surface, while the catalysts used with aliphatic hydrocarbons had no such deposit. Where present this deposit was analysed and found to consist of carbon with very little associated hydrogen.

From the results of the carbon monoxide adsorption measurements it was possible to obtain information on the 'free' surface of the catalyst. As the amount of free nickel surface decreases, it would be expected that the activity would also decrease proportionally: however, it was found that there was no correlation between the activity and the amount of free nickel. It has been reported (section 4.5.; table 4.12) that the loss in area between reactions one and four was very small for the catalysts used with the aliphatic hydrocarbons, yet was large for the catalysts used with aromatic hydrocarbons (figure 5.1.). This result would not be expected if reaction occurred only on the nickel surface. For example, two hydrocarbons which deposit the same number of carbon atoms would be expected to give the same loss in free nickel area. Benzene and pentane are such hydrocarbons in that they deposit approximately the same number of carbon atoms. When the catalysts were compared it was found that between reactions one and four the catalyst used with benzene lost 27.64% of its free nickel area compared with a loss of 3.94% for the catalyst used with pentane.

Turning now to later runs when the surface exposed only 3% nickel, when benzene was used as the feedstock, it appeared that either all the steam-reforming reaction



Reaction No.	1	4	12	18
Aliphatic feedstocks				
Range of free Ni	53-47%	48-46%	35%	
Activity	100%	99·9%	98·5%	
Aromatic feedstocks				
Range of free Ni	60-48%	44-23%	20%	3%
Activity	100%	95-92%	89%	80%

figure 5.1

occurred on ~3% of the nickel surface or reaction occurred on the carbonaceous deposit (table 4.14.). However, if reaction only took place on the 3% free nickel and this exposure remained constant, then carbon deposition should stop at the point when 3% of the surface remained. It was found that carbon deposition continued after only 3% of the nickel surface was left and this resulted in no change in the free nickel area. If reaction took place on the carbonaceous deposit, as well as the metal surface, there would have been no appreciable loss in activity from one reaction to another, although there may have been a large loss in free nickel surface; this was observed for all the hydrocarbons used. Similarly, when ~3% of the metal surface was free, deposition could continue without any loss of the 3% of the nickel surface still free.

However, three types of carbonaceous residues have been identified as permanent species. Under the reaction conditions used (high steam to hydrocarbon ratios) no filamental material was present on any of the catalysts, the polymeric material was present on all of the catalysts and a "carbon" species was present on the catalysts used with aromatic hydrocarbons. It was found (section 4.5.) that the larger the loss in nickel area the lower was the hydrogen to carbon ratio of the feedstock hydrocarbon and the lower was the hydrogen to carbon ratio of the surface deposit (table 4.10.). Therefore it would appear that the higher the hydrogen to carbon ratio of the parent hydrocarbon and hence the surface deposit, the more likely was reaction to take place upon the carbonaceous residue. Therefore, as the large drop in free nickel area was associated with the catalysts used with the aromatic hydrocarbons, it could be argued that the polymeric species was the catalytically active carbonaceous residue and that the catalytic activity of the polymer and the nickel, or any ratio thereof, was the same.

From the study by Moseley et al. (18) it was concluded that aromatics caused the fastest deactivation of the catalyst and alkanes the slowest, and that increasing molecular weight also increased deactivation. However, on an equivolume, or equimolar basis, the percentage carbon deposition was found to give the series (table 4.13.) pentane > hexane > heptane, with heptane giving the least deposition. Therefore, although pentane deposited more carbon than either hexane or heptane, the deposit from pentane was less harmful to the catalytic activity than the deposit from hexane or heptane. From table 4.10 it can be seen that the carbon to hydrogen ratios for the deposits from the aliphatic hydrocarbons were less than 1 : 4, with pentane having the lowest carbon to hydrogen ratio. Thus hydrogen must have been associated, in some form, with the polymeric species. With the deposit from the aromatic hydrocarbons it can be seen that to form a $-CH_2-$ backboned species, carbon must have been present on the surface with no attached hydrogen. Hence it can be postulated that the carbon deposit from an aromatic species would be much more catalytically harmful as there is less hydrogen associated with it: this is in agreement with the empirical results of Moseley et al. (18).

In the same study (18), it was shown that ortho-xylene resulted in faster deactivation of a catalyst when used as a feedstock, than toluene, than benzene. This can be rationalised, for not only do these species have a low hydrogen to carbon ratio but ortho-xylene can deposit two carbon atoms with no associated hydrogen, toluene one carbon atom, while all the carbon atoms in benzene have an associated hydrogen. Therefore, the higher the number of non-hydrogen containing carbons in the aromatic compound the more harmful the deposition to the activity. The deactivation of the catalyst would appear then to be related to the amount of unhydrogenated species on the surface.

Thus, if the hydrocarbon, on contact with the surface, breaks down to give C_1 components then a reaction scheme, in agreement with mechanism I, may be as shown in figure 5.2.

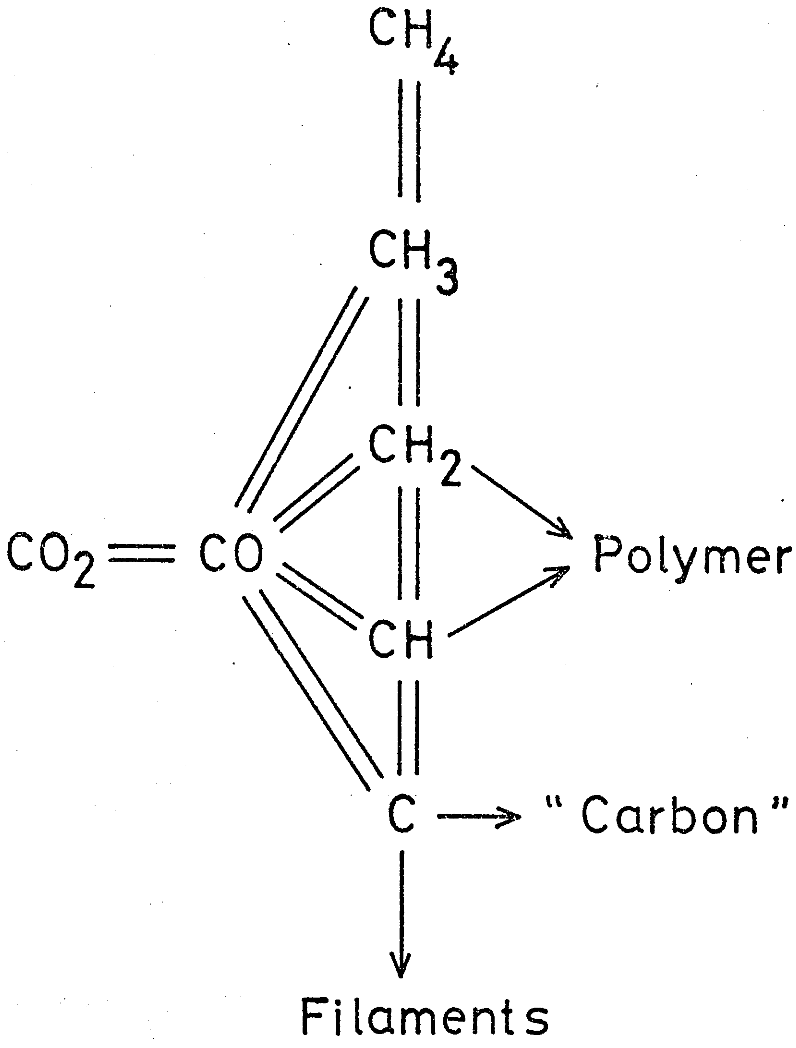


figure 5.2

5.1.2. Analysis of the Approach

The concept of one hydrocarbon molecule or fragment reacting on top of a carbonaceous layer was introduced by two groups of workers independently. Hansen and Gardner (33) suggested a concerted mechanism for the hydrogenation of olefins on metals, where an ethylene molecule may associatively adsorb on top of a trans-diadsorbed ethylene and a hydrogen transfer may take place thermally, as per the Woodward-Hoffman rules (34). The acetylenic residue is then hydrogenated to the trans-diadsorbed ethylene again by the addition of hydrogen. Thomson and Webb (35), independently, developed the concept of reaction on a carbonaceous layer to a general mechanism for olefin hydrogenation on metals. They suggested that the active site for hydrogenation was a $M - C_xH_y$ species and hydrogen transfer occurred via this species to the associatively adsorbed olefin on top of the $M - C_xH_y$ layer. Hydrogen then adds to the $M - C_xH_{y-2}$ species to regenerate the $M - C_xH_y$.

Tamaru and Ichikawa (36) studied the catalytic hydrogenation of olefins over electron donor-acceptor complexes of polynuclear aromatic hydrocarbons with alkali metals. They found that the olefin hydrogenation took place via direct hydrogen transfer from the ortho-dihydro complexes of the corresponding aromatic acceptor to the carbon-carbon double bond of the olefin. Hall et al. (37) also found evidence for hydrogen transfer from carbonaceous residues to reactants on acidic oxides.

In agreement with the theory proposed by Thomson and Webb (35), Zuhr and Hudson (38) found an initial interaction process, in their molecular beam - AES study of ethylene adsorption on Ni(110), and a secondary non-dissociated adsorbed phase. They suggested that this may well be the phase in olefin reactions on transition metals.

Somorjai and Nieuwenhuys (39) studied cyclohexane dehydrogenation and n-heptane dehydrocyclisation over Ir single crystals. In their paper the authors say: "An actual metal catalyst in hydrocarbon reactions is always covered with a carbonaceous deposit". They then compared the activity for benzene hydrogenation of an Ir(111) face and a carbided form of Ir viz. an Ir(111) C (9 x 9) face. No difference was found in the activity between the two surfaces. Similarly the dehydrocyclisation of n-heptane to toluene was compared and the same rate was obtained for both surfaces. It can be seen, therefore, that in catalysis involving hydrocarbons there is evidence for a carbonaceous layer which will allow reaction to take place upon itself.

Evidence for the formation of such species in a system similar to steam-reforming, where oxygenated species are present, can be found in a publication by Joyner (40) on the Fischer-Tröpsch synthesis. In this study Joyner suggests a CH(ads) building unit obtained from the breakdown of carbon monoxide;

$$CO \longrightarrow C + O$$

$$C + H \longrightarrow CH \ .$$

From this unit, by a carbene insertion, polymeric species are produced. Similarly, Ponec and Barneveld (41), in their study of the Fischer-Tröpsch synthesis, favour carbon monoxide dissociation: then they propose

$$C + xH \longrightarrow CH_x$$

which appears to be of prime importance in their mechanism.

Much work has been carried out on the carbon monoxide/ hydrogen methanation system and it is worthwhile to consider some of the results obtained. Sexton and Somorjai (42) investigated methanation reactions over polycrystalline rhodium. They reported that the surface, during the reaction of carbon monoxide or carbon dioxide with hydrogen, was covered by 1-2 monolayers of carbon and yet there was no change in the rate of hydrocarbon formation. The carbon deposit was shown not to be carbon present as carbon monoxide. The authors also examined the effect on the rate of methanation and product distribution of surface pretreatment with carbon monoxide or acetylene. When carbon monoxide was used to pretreat the surface, no change in rate or product distribution was observed, as would be expected. When acetylene was used to pretreat the surface however, the rate for carbon monoxide hydrogenation dropped by half and for carbon dioxide hydrogenation to a fifth of its original value; so that carbon monoxide hydrogenation equalled carbon dioxide hydrogenation. The product distributions also changed such that the amount of C_2 and C_3 compounds produced increased.

Palmer and Vroom (43) also invoke the dissociation of carbon monoxide, in their study of methanation over cobalt and nickel foils, to explain their results in that the methanation rate in the presence of hydrogen matches the rate of disproportionation of carbon monoxide. Rabo, Risch and Poutsma (44) studied carbon monoxide reactions over nickel and concluded that

$$C(a) + 2H_2 \longrightarrow CH_4$$

is faster than

$$CO(a) + 3H_2 \longrightarrow CH_4$$

and that methanation was related to carbon monoxide disproportionation. By use of spectroscopic and magnetic methods Primet, Martin and Dalmon (45) studied the reactions of carbon monoxide and carbon dioxide over a silica supported nickel catalyst. They reported that the adsorbed species that underwent breakdown was Ni_4CO, with the carbon which remained when oxygen was lost, bonded to four nickel atoms in an interstitial site. This species was distinguished from that formed from hydrocarbon cracking where a surface carbide, Ni_3C (surface) was formed.

Matsumoto and Bennet (46) using the Transient Response Method found that the active species in methanation was C(ads) and that this was a transitory species. Arakai and Ponec (47) studied the methanation of carbon monoxide over nickel and nickel/copper alloys by use of carbon-13 labelling. They concluded that (a) hydrogenation of C(ads) is faster than methanation ($CO + H_2$), (b) increasing C(ads) increased the methanation rate, (c) carbon monoxide dissociation and carbon dioxide production can proceed when hydrogen is present and (d) isotopic labelling showed a preference for the H + C(ads) reaction. It was also shown that the reaction was poisoned by sulphur and this was taken as secondary evidence in support of their mechanism as it is known (48,49) that sulphur inhibits carbon monoxide dissociation on metals.

It is now worthwhile to consider whether the results found in the methanation studies are applicable to steam-reforming. It was stated in mechanism F. that a carbon plus hydrogen reaction must occur on the surface (reaction (F.6.)) to give rise to the polymeric surface species and the results by Joyner (40) and Ponec (41) would support this. Also in the discussion of mechanism F. it was stated that aromatic species react preferentially to give carbon monoxide as the initial product and then deposit carbon via a Boudouard reaction. It is implicit in the arguments proposed in section 4.3. that hydrogen must add on to the carbon deposited by the Boudouard reaction: again this is in basic agreement with the methanation results outlined above. However, results have shown that this carbon is not removable by hydrogen addition and indeed some of the adsorbed carbon does not have associated hydrogen. The observation that steam and/or hydrogen inhibit filamental growth is in agreement with the H + C(ads) reaction if the mechanism for the formation of filaments is as proposed by Rostrup-Nielsen and Trimm (25). In their mechanism it is proposed that carbon atoms dissolve into the nickel crystallite under a pressure gradient and come out underneath the crystallite to form the filament; any hydrogen or oxygen associated with the carbon on the surface would inhibit this process.

The C(ads) species which was found to be active in methanation can most satisfactorily be compared with the reactive carbon adatom which was detected by steam and carbon dioxide treatments and was found to be only ~7% of the amount deposited. The results of Sexton and Somorjai (42) would support the postulate that a hydrocarbonaceous surface species allows a scrambling of carbon monoxide/carbon dioxide and modifies the activity of the C(ads) so that full hydrogenation to methane may be less favoured than the route to a surface polymeric species. Hence, the overall scheme shown in figure 5.2. allows agreement between the results obtained in this study and the Fischer-Tröpsch, methanation and hydrogenation results above.

5.2. Future Work

Although a good overall picture has been obtained on the processes occurring in the steam-reforming of hydrocarbons, gaps still exist and the fine details of many of the reactions are still unclear. Much information could be obtained by further work in certain specific areas. The continuation of carbon monoxide adsorption measurements in conjunction with activity measurements when the catalyst has been subjected to forty, fifty and sixty reactions would give information on the decrease of activity related to the amount of carbon deposition. The use of carbon-13 labelling for identification of the polymer species, the use of tritiated and/or deuterated water to probe the position of the hydrogen from the steam and further work on the removal of the deposits from the surface, would all be useful continuations of the present work.

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