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Carbonaceous Deposition Associated with the Catalytic Steam-Reforming of Hydrocarbons over Nickel Alumina Catalysts

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The reactions of *n*-pentane, *n*-hexane, *n*-heptane, 1-heptene, cyclohexane, benzene, toluene, ethylbenzene, and the xylenes with steam have been investigated using 75% w/w nickel/alumina catalysts at 475°C, with particular reference to the formation of surface carbonaceous deposits. Using steam/hydrocarbon ratios of between 0 and 15, up to four distinct types of surface carbonaceous deposit have been identified. Extensive carbon filament formation is observed when no steam or low steam concentrations are used. A hydrocarbonaceous polymeric species, extractable from the used catalysts with tetrachloromethane, is formed with each hydrocarbon under all reaction conditions. The chemical identity of the polymer, established by infrared spectroscopy and mass spectrometry, is apparently independent of the reactant hydrocarbon. Evidence for a reactive and a nonreactive surface carbon has also been obtained. Admission of [^{14}C]CO or [^{14}C]CO_2 with the reactant hydrocarbon leads to scrambling of the [^{14}C] label among the reaction products and the surface deposit. A mechanism for the formation of both the gaseous reaction products and the various surface residues is discussed in terms of the adsorbed intermediates. The use of carbon monoxide adsorption as a probe for exposed surface nickel shows that, although the exposure of the nickel surface is markedly reduced by the formation of surface deposits, the activity of the catalyst for the gasification of the hydrocarbons is virtually unaffected. The possibility of reaction occurring on a carbonaceous overlayer on the nickel surface is discussed.

Alumina-supported nickel catalysts have been widely used over the last 20 years for the steam-reforming of light hydrocarbon oils to give a mixture of carbon monoxide, carbon dioxide, methane, and hydrogen (*1–4*). A variety of reactions may occur during the steam-reforming process and these may be represented by the following reactions, which are represented as equilibria, although some or all may not, in fact, approach equilibrium.

$$C_nH_{2n+2} + nH_2O \rightarrow nCO + (2n + 1)H_2,$$

$$C_nH_{2n+2} + \frac{(n-1)}{2}H_2O \rightarrow \frac{(3n+1)}{4}CH_4 + \frac{(n-1)}{4}CO_2,$$

$$C_nH_{2n+2} + 2nH_2O \rightarrow nCO_2 + (3n + 1)H_2,$$

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

$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O,$$

$$2CO \rightleftharpoons CO_2 + C(ads),$$

$$CH_4 \rightleftharpoons C(ads) + 2H_2,$$

$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O,$$

$$CO + H_2 \rightleftharpoons C(ads) + H_2O.$$

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Although a variety of mechanisms have been proposed (*5–7*) a number of aspects of the steam reforming process still remain the subject of debate.

It is well established that, in the steam reforming of saturated hydrocarbons over supported nickel catalysts, the catalytic activity progressively decreases with usage. Three main causes of loss in activity have been identified, namely, (i) catalyst sintering; (ii) poisoning by sulphur-containing organic compounds present in the hydrocarbon feedstock, and (iii) the formation of surface carbonaceous residues, the so-called "catalyst carbiding." Whilst the effects of sintering (*8, 9*) and poisoning (*10, 11*) are relatively well understood and can be readily controlled, comparatively little is known as yet about the surface carbonaceous deposits, although they have been discussed in various publications (*12–17*).

The objects of the present work were to investigate the origins, type, form, and reactivity of the surface carbonaceous deposits formed during the reaction of steam with aliphatic and aromatic hydrocarbons over alumina-supported nickel catalysts, with particular reference to the mechanism of formation and the possible role of such species in the steam-reforming reaction, although no attempt has been made to simulate the precise conditions operating in an industrial reactor.

EXPERIMENTAL

Apparatus and Procedure

Figure 1 shows schematically the pulsed-flow microcatalytic reactor–radio gas chromatography system used throughout these studies. The reactor itself consisted of a pipette-shaped Pyrex glass vessel (volume ca. 20 cm^3) fitted with a coarse glass sinter upon which the catalyst (typically 0.5 g) was placed. The reactor was surrounded by an electric furnace, which maintained the temperature at the desired value ±1°C. Temperatures

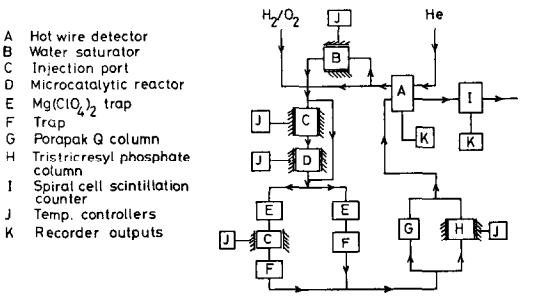

FIG. 1. Schematic diagram of pulsed-flow microcatalytic reactor system.

were measured by a glass-enclosed chromel–alumel thermocouple placed in contact with the centre of the catalyst bed. The catalyst temperature was recorded continuously before and during a reaction. Helium at a flow rate of 80 cm^3 min^{-1} was used as carrier gas throughout these studies.

The reactor was connected via glass-to-metal seals to the gas flow line, constructed from 3 mm i.d. stainless steel tubing and maintained at 200°C to prevent condensation of reactants or products.

Steam was introduced into the helium carrier gas stream by means of a water saturator. This was maintained at a temperature such that the water vapour pressure was just sufficient to give the desired concentration of steam in the gas stream. Hydrocarbons were introduced, via heated injection ports, into the gas flow using a Hamilton liquid syringe. On elution from the reactor the gas flow was passed through a trap filled with magnesium perchlorate, to remove any unreacted steam, before it entered the gas chromatographic system. During the passage of each pulse of hydrocarbon across the catalysts a small temperature excursion was observed which lasted for 2 min. Immediately the temperature returned to its initial value, the supply of steam was stopped, and the gas stream over the catalyst was switched to helium during the period required for gas analysis (~30 min). The helium–steam flow

was restored for 1 min before the injection of a subsequent pulse of hydrocarbon.

To facilitate the analysis of the reaction products, two columns, connected in parallel, were required. Separation of the light gas products (CO, CH_4, CO_2, C_2- and C_3-hydrocarbons) was achieved using a 3-m column (A) packed with Poropak Q (80–100 mesh) at ambient temperature. Full resolution of the carbon monoxide and methane peaks was found to be impossible, due to the large quantities of methane produced, although it was possible to estimate amounts of carbon monoxide when these were greater than ~5% of the methane–carbon monoxide mixture. A second 1-m column (B) packed with 15% tristricresylphosphate supported on Chromosorb P (30–60 mesh) and operated at 40°C, was used to separate the C_4- and higher hydrocarbons. Immediately before entering the chromatographic system the flow gas was passed through a cold trap, cooled in either liquid nitrogen or acetone–solid carbon dioxide, to condense out the higher boiling products. The noncondensed products were then analysed using column A. Once separation was complete, the flow was redirected through column B and the cold trap was warmed to release the condensed reaction products. When appropriate, the chromatograph eluant was passed through a spiral flow-cell scintillation detector to determine the radioactive content of the individual products.

The adsorption of carbon monoxide at 25°C was used as a probe for the exposure of nickel on both freshly reduced and used catalyst samples, using a similar method to that described elsewhere (*19, 20*). In this method, pulses of [^{14}C]carbon monoxide were passed over the catalyst, in a helium flow until saturation of the surface was achieved, the amount adsorbed being determined from the amounts of radioactivity remaining in the reactor effluent.

Samples of used catalysts were examined by electron microscopy using a JEOL 100C electron microscope. The used catalyst was removed from the reactor and lightly ground. The sample for electron microscopy was then prepared by either transferring a small quantity of the dry powder onto a carbon-coated specimen grid, or by suspending the catalyst sample in water, transferring a droplet of the resulting suspension onto the carbon-coated grid, and drying. The two methods of specimen preparation gave identical results, although the dry preparations had poorer adherence to the specimen grid.

Catalyst and Materials

The catalyst was prepared by coprecipitation from mixed aqueous solutions of nickel and aluminium nitrates with aqueous sodium carbonate solution. The precipitate was washed until the sodium ion concentration was less than 0.01% by weight. The catalyst was stored as the precipitated paste until required. Before use, each sample was dried at 120°C for 24 hr, ground, and sieved to 20–40 mesh BSS and the sieved material was calcined in air at 450°C for 2 hr. The calcined material was then reduced in a stream of hydrogen (~10 cm^3 min^{-1}) at 450°C for 16 hr. The catalyst after calcination and reduction contained 75% w/w nickel supported on γ-alumina.

All the hydrocarbons used as feedstocks were distilled before use and subsequently stored over freshly prepared Raney nickel to remove sulphur-containing compounds. [^{14}C]carbon dioxide was diluted to the required activity per unit volume with helium, rather than nonradioactive carbon dioxide, to ensure that addition of the tracer to the reaction mixture would have a minimal effect upon the equilibria in the various reactions. [^{14}C]carbon monoxide, prepared by the reduction of [^{14}C]carbon dioxide by metallic zinc (*18*) was similarly diluted with

helium. [^{14}C]benzene and [^{14}C-methyl]toluene were each diluted to the required activity with the respective nonradioactive hydrocarbon. All radioactively labelled compounds were supplied by the Radiochemical Centre, Amersham.

RESULTS

Reactions in the Absence of Steam

When up to 15 injections, each of 10 μl size, of each of a variety of hydrocarbons were passed over freshly reduced 0.5-g samples of the catalyst at 475°C in a stream of helium, the gaseous products from each injection, regardless of the starting hydrocarbon, consisted solely of methane. With each hydrocarbon only a part of each injection was detected as methane, the remainder being retained by the catalyst. The extent of this retention was different for different hydrocarbons; values for the amount of carbon detected as methane as a percentage of the amount of carbon in each injection for the species designated below were as follows:

benzene	<	ethylbenzene	<	cyclohexane	<	*n*-hexane
10.6%		22.8%		23.9%		27.1%

After being exposed to a total of 150 μl of the hydrocarbon, each catalyst was microanalysed for carbon and hydrogen content. The results, together with the total amount of carbon deposited on the catalyst, are shown in Table 1.

The used catalysts were also examined by electron microscopy. On catalysts treated with benzene, ethylbenzene, toluene, heptane, and hexane, appreciable quantities of filamental carbon, having some graphitic character, were observed, as shown in Fig. 2. However, when cyclohexane was used as feedstock, no filamental material was observed. Samples of the used catalysts were extracted by tetrachloromethane and the extracts examined by infrared spectroscopy and mass spectrometry. Similar spectra were obtained from each hydrocarbon feedstock; the peaks observed and their assignments are shown in Table 2. The mass spectra of the extract showed an upper mass limit of 350 amu and a fragmentation sequence consistent with the breakdown of a polymeric species with a $-CH_2-$backbone. Infrared analysis of the solid, used, catalysts, compressed in a KBr matrix, gave similar, although weaker, spectra to those observed with the tetrachloromethane extracts. Two types of surface carbon may therefore be recognised with all the hy-

TABLE 1

Analysis of Used Catalysts for Carbon and Hydrogen[a]

Hydrocarbon	Total hydrocarbon admitted (molecules $\times 10^{-20}$) ($\equiv$150μl)	Atoms C retained ($\times 10^{-21}$)	% C retained	C:H ratio in surface deposit
n-Hexane	6.93	2.36	56.7	1:0.5
cyclohexane	8.38	2.86	56.8	1:0.4
n-Heptane	6.18	2.98	68.8	1:0.95
Benzene	10.18	5.30	86.8	1:0.6
Toluene	8.61	2.98	49.5	1:0.8
Ethylbenzene	7.39	3.12	52.8	1:0.9

[a] Weight of catalyst, 0.50g; temp., 475°C; flow rate, 80 cm^3 min^{-1}; pressure, 1 atm; no steam present.

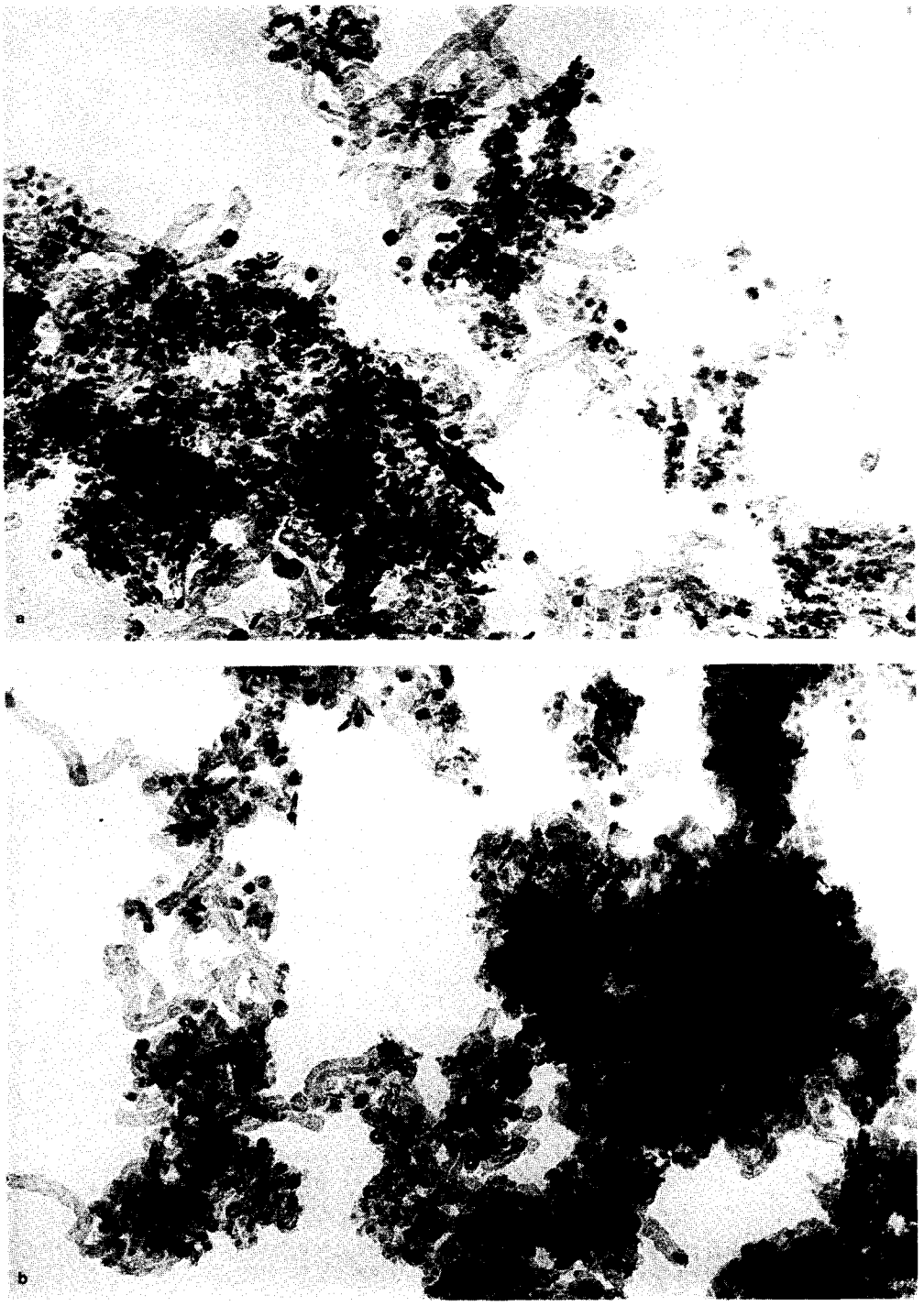

FIG. 2. Electron micrographs of catalysts used for reaction of 150 μl of (a) benzene and (b) hexane at 475°C in the absence of steam. (Magnification 160,000×.)

TABLE 2

Assignment of Infrared Spectra of Catalyst Extract

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

drocarbons examined except cyclohexane; a partially graphitised filamental carbon and an extensively hydrogenated polymeric material. Only the polymeric material was formed when cyclohexane was used.

REACTIONS USING A MOLAR RATIO OF STEAM TO HYDROCARBON OF APPROXIMATELY 2 (LOW STEAM)

The reactions of hexane, heptane, cyclohexane, hept-1-ene, benzene, toluene, ethylbenzene, and the xylenes with steam were investigated over freshly reduced 0.50-g samples of catalyst at 475°C, using a steam to hydrocarbon molar ratio of between 1.5 and 2.5 and a hydrocarbon pulse size of 10 μl. With each hydrocarbon the primary product was methane, although carbon dioxide and carbon monoxide were also observed. In each case the products from the very first injection of hydrocarbon onto the freshly reduced catalyst showed a relatively high yield of carbon dioxide, which approached the maximum possible yield based upon the amount of steam present. In subsequent injections the yield of carbon dioxide progressively decreased until, after four injections, a constant steady-state value was achieved, which was maintained for a further 11 injections. The carbon dioxide production figures are shown in Table 3.

Substantial amounts of each hydrocarbon injection were retained by the catalyst. Electron microscopic examinations of the catalysts after 150 μl of hydrocarbon had been reacted showed that, with the xylenes, ethylbenzene, toluene, benzene, hept-1-ene, hexane, and pentane, filamental carbon was present on the surface. No filaments were formed from cyclohexane or heptane. Infrared spectra of the solid, used, catalysts, in KBr discs, and of the products of the extraction of each catalyst by tetrachloromethane were similar to each other and for all the hy-

TABLE 3

Initial and Steady-State Yields of Carbon Dioxide Observed with Steam to Hydrocarbon Ratios of ~2[a]

Hydrocarbon	Steam to hydrocarbon molar ratio	Maximum possible CO_2 % production	Initial % CO_2 production	Steady-state % CO_2 production
n-Hexane	2.16	18.0	16.4	4.3
n-Heptane	2.44	17.4	9.1	3.3
Cyclohexane	1.79	14.9	8.98	6.5
Hept-1-ene	2.36	16.7	15.3	4.7
Benzene	1.5	12.5	11.8	7.0
Toluene	1.76	12.6	11.3	5.5
Ethylbenzene	2.02	12.6	9.7	5.3
Xylenes	2.0	12.5	8.9	5.6

[a] Conditions: temp., 475°C; flow rate, 80 cm^3 min^{-1}; pressure 1 atm., total amount of hydrocarbon reacted, 150 μl (10-μl pulses).

TABLE 4

Assignment of Infrared Spectra of Catalyst Extracts

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

drocarbons; the peaks observed and their assignments are shown in Table 4. Mass spectra of the extracted material were similar to those obtained from the reactions in the absence of steam, with additional fragment peaks at 55, 42, 41, and 29 amu, suggesting the presence of —CH=CH—CHO, —CH—CHO, —CH—CO (or —C—CHO), and —CHO group, respectively.

REACTIONS USING A MOLAR STEAM TO HYDROCARBON RATIO OF APPROXIMATELY 12 (HIGH STEAM)

To investigate reactions using steam–hydrocarbon reactant ratios similar to those used in the normal steam-reforming process, although not at pressures used in the industrial process, the reactions of *n*-pentane, *n*-heptane, hept-1-ene, cyclohexane, benzene, toluene, ethylbenzene, and the xylenes with steam were examined over freshly reduced catalyst samples at 475°C, using a steam to hydrocarbon molar ratio of between 9.5 and 15, dependent upon the hydrocarbon used. A pulse size of 5 μl of hydrocarbon was used throughout.

With each hydrocarbon the gaseous products were methane, carbon monoxide and carbon dioxide; in all cases part of each hydrocarbon injection was retained by the catalyst. The first injection of each hydrocarbon on to the catalyst produced a relatively low yield of carbon dioxide and a correspondingly high yield of methane. However, with successive pulses the carbon dioxide yield increased and the methane yield decreased reaching a steady-state value after four or five injections. The carbon monoxide yield remained approximately constant throughout at ~10%, based upon the carbon input to the catalyst. In the steady state, the carbon dioxide yield was almost constant for all hydrocarbons, except cyclohexane, which gave an anomalously high conversion relative to the other hydrocarbons. The steady-state combined yields of carbon monoxide and methane were approximately equal to the carbon dioxide yield and the methane/carbon monoxide ratio was ca. 3:1. Because of the analytical difficulties already noted, it was not possible to obtain precise values for the methane and carbon monoxide yields. The initial and steady-state yields of carbon dioxide, as a percentage of the carbon input to the catalyst, are shown in Table 5.

The amount of carbon deposited by each of the hydrocarbons was determined by injecting successive pulses until a total of 150 μl of the hydrocarbon had passed over the freshly reduced catalyst sample. The catalyst was then treated with oxygen at 475°C for 30 min and the amount of carbon which had been deposited was determined from the carbon dioxide yield. The results are shown in Table 6.

Electron microscopic examination of each used catalyst showed that, after 30 pulses (5 μl each), only very small amounts of filamental material were formed from benzene, toluene, ethylbenzene, xylene, and *n*-heptane. However, with hept-1-ene as feedstock, massive filament growth was observed. There was a complete absence of carbon filaments on those catalysts used with pentane, hexane and cyclohexane. Infrared spectra

TABLE 5

Initial and Steady-State Yields of Carbon Dioxide Observed with Steam to Hydrocarbon Ratios of ~12[a]

Hydrocarbon	Steam to hydrocarbon Molar ratio	Initial CO_2 production (%)	Mean steady-state CO_2 production (%)
n-Pentane	11.9	4.6	38.6
n-Hexane	13.5	3.0	35.9
n-Heptane	15.3	1.3	37.0
Hept-1-ene	14.8	2.9	36.99
Cyclohexane	11.3	13.2	45.98
Benzene	9.5	3.1	36.8
Toluene	11.0	1.9	36.4
Ethylbenzene	12.7	6.9	35.6
Xylenes	12.5	2.4	33.3

[a] Conditions: temp., 475°C; flow rate, 80 cm^3 min^{-1}; pressure, 1 atm., total amount of hydrocarbon reacted, 150 μl (5-μl pulses).

of tetrachloromethane extracts of each used catalyst were similar. The main absorption peaks and their assignments are shown in Table 7. Mass spectra of the extracted material showed the presence of species with an upper mass limit of ~400 amu and a cracking pattern consistent with a saturated aliphatic polymer. The presence of aldehyde groups in the extracted polymer was also confirmed by the presence of fragment peaks at 70, 69, 68, 57, 56, 55, 43, 42, 41, and 29 amu.

To examine the possible role of carbon dioxide and carbon monoxide as precursors to the deposition of carbon on the catalyst, [^{14}C]carbon dioxide and [^{14}C]carbon monoxide were, in turn, injected simultaneously with the hydrocarbon under normal steam-reforming conditions (high steam). The extent of retention of each labelled species was determined from the radioactivity in the reactor eluant. For catalysts, operating in their steady states, the mean values for the percentage retention of each pulse of labelled material, taken over six or seven pulses, are as shown in Table 8. It is clear that the extent of retention of both carbon monoxide and carbon dioxide is very dependent upon the hydrocarbon

TABLE 6

Carbon Retention following Reaction Using Steam to Hydrocarbon Ratios of ~12[a]

Hydrocarbon	Steam/hydrocarbon molar ratio	Amount hydrocarbon reacted (molecules × 10^{-20}) (≡ 150 μl)	Atoms C retained (× 10^{-21})
n-Pentane	11.9	7.85	1.10
n-Hexane	13.5	6.93	0.67
n-Heptane	15.3	6.18	0.45
cyclohexane	11.3	8.38	0.49
Benzene	9.5	10.18	1.53
Toluene	11.0	8.61	1.30
Ethylbenzene	12.7	7.39	1.72
o-Xylene	12.5	7.42	1.54

[a] Wt. of catalyst = 0.50g; temp., 475°C; flow rate, 80 cm^3 min^{-1}; pressure, 1 atm.

TABLE 7

Assignment of Infrared Spectra of Catalysts Used with High Steam to Hydrocarbon Ratios

Peak (cm^{-1})	Assignment
920	C—H deformation for —CHO
1380	CH_3 sym. deformation and C—CHO skeletal
1460	C—H deformations of CH_2 and CH_3
1620	C=C stretch of C=C—CHO
1670	C=C stretch of C=C—CHO
1710	C=O stretch of R—CHO
1740	C=O stretch of alkyl ester
1755	Unspecified C=O stretch
2720	C—H stretch in CHO
2860, 2930, 2960	C—H stretch in CH_3, CH_2 groups
3010	C—H stretch in C=C—H

present and that the two oxides give approximately similar retention values.

CATALYST REGENERATION AND REMOVAL OF CARBONACEOUS DEPOSITS

Various methods of catalyst regeneration and removal of surface carbonaceous material were attempted. First, a catalyst which had been subjected to 12 (5 μl) pulses of [^{14}C]benzene, under normal steam reforming conditions ($[H_2O/C_6H_6]$ = 9.5), and on which, therefore, a [^{14}C]-labelled residue was deposited, was treated with four successive pulses (each 0.2 ml, STP) of [^{12}C]carbon dioxide at 475°C. This resulted in the removal of 7.7% of the [^{14}C] from the surface, although 59.8% of the carbon dioxide input was lost to the catalyst surface.

A second method was to treat a used catalyst at 475°C with a helium–steam stream, containing 6.8% mole/mole steam, at a flow rate of 80 cm^3 min^{-1}. Initially this caused the evolution of carbon dioxide, although this ceased after a period of ~3 min. The amount of carbon removed by this procedure was 7.0% of the total deposit. Subsequent examination by electron microscopy showed that the carbon filaments still remained, whilst extraction with tetrachloromethane of the steam-treated catalyst recovered substantial amounts of the polymeric material, suggesting that neither of these forms of deposit had been reactive towards steam.

A third method which was examined, was to treat the used catalyst with an oxygen flow. When carried out at 475°C an extremely exothermic reaction resulted and the catalyst bed temperature increased to ~1000°C. Microanalysis of the treated catalyst showed that this treatment removed all the surface carbon, although the resultant catalyst after rereduction possessed no activity in steam reforming. However, when the used catalyst was subjected to this treatment starting at room temperature, an exothermic reaction was again observed, with the temperature in the catalyst bed increasing to 500°C, all the carbonaceous deposit was removed and, after a hydrogen reduction at 450°C for 16 hr, the activity was totally restored. The initial and steady state product distributions of this regenerated catalyst were identical with the respective distributions of a freshly reduced catalyst.

A final method of regeneration which was attempted, was direct reduction of a used catalyst in a hydrogen flow (10 cm^3 min^{-1}) for 16 hr at 500°C. A [^{14}C]-labelled surface, obtained by the steam reforming of 30 pulses (5 μl each) of [^{14}C]benzene

TABLE 8

Retention of [^{14}C]CO and [^{14}C]CO_2 when Reacted Simultaneously with a Hydrocarbon and Steam[a]

Hydrocarbon	% of [^{14}C]CO Retained	% of [^{14}C]CO_2 Retained
Benzene	23.4	17.7
Toluene	17.5	19.3
n-Heptane	1.2	1.6

[a] Temp., 475°C; wt. of catalyst, 0.50g; flow rate, 80 cm^3 min^{-1}.

over a freshly reduced catalyst sample, was subjected to this treatment. The reactor eluant was monitored for [^{14}C] products, but none were detected. At the end of the 16-hr period, the hydrogen was purged from the system and an oxygen flow was substituted. This resulted in the displacement of an amount of [^{14}C]carbon dioxide from the surface equal to the amount of [^{14}C] deposit initially present. Thus, hydrogen reduction did not remove any of the carbonaceous deposit, although a catalyst, so treated with hydrogen, gave a product distribution characteristic of a fresh sample, when subsequently used in the steam reforming process.

CARBON MONOXIDE ADSORPTION MEASUREMENTS

In an attempt to obtain a quantitative measure of the effects of the formation of the surface carbonaceous residues, the variation of the free metal surface area, as determined by carbon monoxide adsorption at 25°C, was examined as a function of the amount of hydrocarbon reacted over the catalyst under conditions where high steam/hydrocarbon reactant ratios were used. The amount of catalyst used for these measurements, 0.1g, was chosen such that, on the freshly reduced catalyst, the conversion of a 5-μl pulse of hydrocarbon was 98% or less, depending upon the feedstock hydrocarbon.

The amount of carbon monoxide adsorbed by freshly reduced samples of catalyst, on the same samples after one 5 μl pulse of hydrocarbon and after four 5 μl pulses, when the catalyst had attained a steady state, was determined. The amounts of carbon monoxide adsorbed by the catalyst after reaction of each of the hydrocarbons are shown in Table 9.

From these results it can be seen that, whereas, after the initial hydrocarbon pulse, the loss in surface area is similar for each hydrocarbon, over a series of pulses, the aromatic hydrocarbons cause a much greater decrease in metal area than the aliphatic hydrocarbons. When considered after a series of four hydrocarbon pulses, it is apparent that the lower the hydrogen/carbon ratio in the reactant hydrocarbon, the greater the loss in the free metal surface area.

TABLE 9

Amount of Free Nickel Surface Available for Carbon Monoxide Adsorption after Reaction of Steam with Hydrocarbon[a]

Hydrocarbon	CO uptake (molecules per 0.10g catalyst) $\times 10^{-19}$	
	After 1 reaction	After 4 reactions
n-Pentane	3.69(51.97)	3.41(48.03)
n-Hexane	3.38(47.61)	3.28(46.20)
n-Heptane	3.78(53.24)	3.33(46.90)
cyclohexane	3.85(54.23)	3.18(44.79)
Benzene	4.27(60.14)	2.31(32.53)
Toluene	3.48(48.97)	3.13(44.10)
Ethylbenzene	3.59(50.62)	2.26(31.83)
o-Xylene	3.57(50.28)	1.68(23.00)

[a] Wt. of catalyst sample = 0.10g; CO uptake on freshly reduced catalyst = 7.1×10^{19} molecules sample (0.10g); hydrocarbon pulse size = 5 μl; flow rate = 80 cm^3 min^{-1}. Figures in parenthesis give the percentage free surface relative to the freshly reduced catalyst.

The decrease in available metal surface was examined in more detail using benzene as reactant and a benzene/steam molar ratio of 9.5. A 0.10 g sample of catalyst was used in these experiments to ensure that benzene conversions of $<90\%$ were obtained with a freshly reduced catalyst sample. Using this weight of catalyst, 13% unreacted benzene appeared in the products of the first reaction over the freshly reduced sample. The results, presented in Fig. 3, show that there is a progressive decrease in metal area with increasing amount of benzene reacted to a constant value of approximately 4% of the initial value after 90–100 μl benzene had been reacted on the 0.1 g catalyst sample. It should be noted, however, that although 96% of the free metal area had

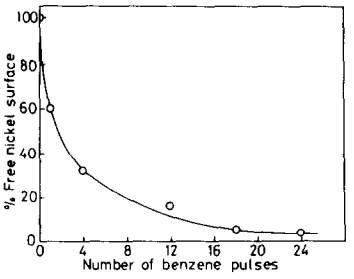

FIG. 3. Variation of available metal surface for carbon monoxide adsorption with number of 5-μl benzene pulses reacted on 0.10g catalyst at 475°C in the presence of steam. (Amount of CO adsorbed on 0.10g freshly reduced catalyst = 7.1×10^{19} molecules).

been lost, the catalyst still promoted the fast gasification of benzene; after 24 injections 80% of the benzene pulse was converted to products, suggesting that the activity may not be simply related to the metal surface area.

DISCUSSION

From the results presented above it has proved possible to identify up to four distinct types of surface carbonaceous deposit, depending upon the nature of the reactant hydrocarbon and the experimental conditions. These may be defined as follows: (a) filamental carbon; (b) hydrocarbonaceous polymer; (c) "reactive" carbon and (d) permanently retained "carbon."

The filamental carbon, detected by electron microscopy, was present on those catalysts which had been used for the reaction of hydrocarbon alone or in the presence of small quantities of steam. It was not present to any appreciable extent on catalysts used for reactions involving a high steam to hydrocarbon reactant ratio, or when hydrogen/hydrocarbon mixtures reacted over the same catalysts (*21*). The presence of carbon filaments has been observed previously by various workers studying a variety of reactions (*22–25*).

The polymeric species, obtained by tetrachloromethane extraction of the catalysts, appears to be essentially the same species, independent of the presence or otherwise of the steam. The infrared and mass spectra are consistent with a linear, extensively hydrogenated, polymer with a chain length of 25–30 carbon atoms. When steam was present as a reactant, evidence was also obtained for the formation of aldehyde groups of the type R—CHO and —CH = CH—CHO, associated with the polymer chain. Neither the hydrocarbonaceous polymer nor the filamental carbon were susceptible to reaction with carbon dioxide, steam, or hydrogen, although they could both be completely oxidised by high temperature treatment in oxygen. Bhatta and Dixon (*17*) previously identified anthracene, pyrene and naphthalene in the extracts of a steam-reforming catalyst used with *n*-butane, although these workers made no mention of a polymeric material. However, a similar polymer was obtained by tetrachloromethane extraction of an industrially used catalyst (*26*). Although the precise mechanism of formation of such a polymer is still unclear, it could be formed by a carbene insertion mechanism of the type discussed by Joyner (*27*).

Treatment of the used catalysts with either carbon dioxide or steam at 475°C resulted in the removal of ~7% of the surface carbonaceous deposit as carbon dioxide, suggesting the presence of a third type of surface carbonaceous deposit, termed the "reactive carbon". The $^{14}CO_2$ exchange suggests that the "reactive carbon" probably exists on the surface as a carbon adatom, which may be compared with the reactive adsorbed carbon atom postulated to participate in Fischer–Tropsch synthesis by Joyner (*27*) and by Ponec *et al.* (*28, 29*) and in methanation by Sexton and Somorjai (*30*) and other workers (*31, 32*).

An additional "unreactive" carbonaceous deposit was identified from microanalysis of used catalyst samples, which showed no filamental carbon, had been

steam cleaned and had been extracted with tetrachloromethane to remove the surface polymer. The microanalysis showed that this residual deposit consisted of carbon with very little associated hydrogen. Thus, it may be concluded that it was not a residue of polymer remaining after the extraction, but rather a separate identifiable surface carbon of a similar type to that found by Baker *et al.* (*22, 23*). This unreactive carbon was observed with catalysts used for the reaction of all the hydrocarbons examined, either in the absence of steam or when small amounts of steam were used. It was also formed with aromatic hydrocarbons under high-steam reaction conditions, but not with aliphatic hydrocarbons under these conditions.

With each hydrocarbon feedstock in the absence of steam only methane was formed as a product together with the retention of hydrocarbon on the catalyst surface. The reactions occurring under these conditions may be represented as:

$$\text{Hydrocarbon} \rightarrow CH_4(g) + C(a) + H(a), \quad \text{(i)}$$

$$nC(a) + xH(a) \rightarrow C_nH_x \text{ polymer (a)}, \quad \text{(ii)}$$

$$C(a) \rightarrow \text{carbon filaments}. \quad \text{(iii)}$$

The initial products from the reactions with small quantities of steam were predominantly methane and carbon dioxide, consistent with an overall process which may be represented as:

$$C_nH_{2n+2} + \frac{(n-1)}{2} H_2O \rightarrow \frac{(3n+1)}{4} CH_4 + \frac{(n-1)}{4} CO_2 \quad \text{(iv)}$$

together with a hydrocarbon retention reaction, giving rise to adsorbed carbon and hydrogen atoms, which may then undergo reactions (ii) and (iii). As the reaction proceeded, and the extent of carbon retention by the surface increased, it was observed that the yield of carbon dioxide decreased and the yield of carbon monoxide correspondingly increased, suggesting that the latter product is not a primary reaction product, but arises from reaction of the carbon dioxide with a surface carbon atom:

$$CO_2 + C(ads) \rightleftharpoons 2CO. \quad \text{(v)}$$

In the case of the hydrocarbon reactions at high steam concentrations, the [^{14}C]carbon dioxide and [^{14}C]carbon monoxide tracer results show that, under reaction conditions, the two oxides behave similarly and are in equilibrium in the system. Furthermore, the amounts of [^{14}C]carbon deposited by each carbon oxide are similar, indicating that the following reaction sequence occurs;

$$CO_2 \rightarrow CO \rightarrow C(ads).$$

The tracer results also show that the amount of carbon deposited from the carbon oxides was very much less than that formed from an aliphatic hydrocarbon feedstock. However, with aromatic hydrocarbon feedstocks the amounts of surface carbon formed from the carbon oxides and hydrocarbon were similar. Thus, it may be concluded that a similar precursor to deposition is involved with aromatic hydrocarbons and the carbon oxides, but not with the latter and aliphatic hydrocarbons, although the similarity of the polymeric deposits obtained from the aliphatic and aromatic hydrocarbon feedstocks indicates a common intermediate from both types of hydrocarbon in this process.

These results, together with the observation that, in the reactions of the hydrocarbon–[^{14}C]carbon oxide mixtures, the label was scrambled and appeared in all products, are consistent with a mechanism in which the primary routes both to the formation of products and to the retained surface carbonaceous residues may be suggested as being

$$\text{aliphatic hydrocarbon} \rightarrow CH_2(ads)$$

and

aromatic hydrocarbon → CH(ads),

although the precise stoichiometry of the adsorbed species cannot be established at this stage. Once formed, the $—CH_2$ and —CH surface species may be considered to participate in the equilibria shown in Fig. 4.

Several interesting features emerge from the carbon monoxide adsorption measurements on freshly reduced and partially used catalysts. Comparison of the results in Tables 6 and 9 shows that there is no simple correlation between the amounts of carbon deposited on the surface by the various hydrocarbon feedstocks and the amounts of nickel surface lost after each series of reactions. Thus although *n*-heptane and toluene cause similar losses of nickel area after four reactions, toluene gives rise to a much larger carbon retention than *n*-heptane. Similarly, although *n*-pentane and benzene deposit similar numbers of carbon atoms on the surface, the loss of nickel area is substantially greater with benzene. Clearly, from Table 9, the loss of nickel surface is greater with aromatic than with aliphatic feedstocks. Since, as noted above, under the reaction conditions used during these measurements—high steam—the aliphatic feedstocks, except *n*-heptane, yielded only the polymeric surface carbonaceous deposit whereas the aromatic feedstocks yielded both the polymeric species and the "surface carbon"

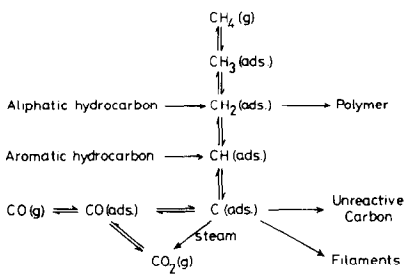

FIG. 4. Proposed reaction scheme for the formation of products and surface residues.

species, we may conclude that both species give rise to surface site-blocking and that the "surface carbon" species has a substantially greater blocking ability than the polymer. Comparison of the *n*-hexane and *n*-heptane values in Table 9 also indicates that carbon filament formation, observed only with *n*-heptane under "high-steam"-reforming conditions, has little effect upon the extent of the loss of nickel surface.

The most surprising feature to appear from the carbon monoxide studies is that, with benzene as reactant, the catalytic activity—measured by the conversion of benzene to products—and the amount of each benzene injection lost to the catalyst as carbonaceous residues only decrease marginally (~7%), whereas the exposure of the nickel surface progressively decreases to a limiting value of 4% of that initially over the same period of catalyst usage. Furthermore, both the benzene gasification and the carbon deposition reactions continued on catalysts which only exposed the 4% of nickel surface, with no further loss in nickel surface.

At first sight these observations appear to suggest that only 4% of the nickel surface available on freshly reduced catalysts is active for the conversion of benzene to products and for the formation of carbonaceous residues. However, this is unlikely since, for reasons discussed earlier, it is proposed that the formation of methane and surface polymer arise from a common surface intermediate, namely a CH_2(ads) species, and since the formation of surface polymer results in a loss of available nickel surface, as observed with aliphatic feedstocks, it might reasonably be expected that both the rates of methane formation and polymer formation would decrease in parallel with the loss of the available nickel surface. This is not the case.

Consideration of the results for the reaction of benzene under high steam conditions, shown in Table 6, shows that,

after reaction of 150 μl, the number of atoms of carbon retained by the catalyst is 1.53×10^{21} atoms. If we assume that, in the carbon monoxide adsorption experiments, the ratio of carbon monoxide adsorbed to exposed surface nickel atoms is one, although this may be gross oversimplification (*33*), the number of surface nickel atoms exposed by the same sample of catalyst may be calculated to be 3.55×10^{20}. Thus, the amount of carbon retained is considerably in excess of that required for formation of a monolayer. This is the case for all the hydrocarbons examined in Table 6.

An alternative explanation for the independence of the rates of hydrocarbon gasification and the exposure of surface nickel may be sought by considering that the reactions occur, at least in part, on the carbonaceous overlayer on the metal surface, rather than directly upon the metal. Similar conclusions have been reached previously by Somorjai and Nienwenhuys (*34*) from studies of benzene hydrogenation, cyclohexane dehydrogenation and *n*-heptane dehydrocyclisation over iridium catalysts, and by Thomson and Webb (*35*) and Hansen and Gardner (*36*) for metal-catalysed olefin hydrogenation. The precise mechanisms whereby such reactions occur are still not clear. However, in the present context, it is possible that the adsorption of hydrocarbon and its subsequent breakdown to CH(ads) or CH_2(ads) species occurs on the carbonaceous overlayer, whilst the adsorption of water as H(ads) and OH(ads) occurs on the vacant metal sites. Migration of hydrogen atoms from the metal to the carbonaceous overlayer followed by reaction with the adsorbed hydrocarbon fragments to yield methane may then occur, whilst the oxygen-containing species may react with the carbonaceous overlayer directly on the metal to yield the carbon oxides. According to such a mechanism it would be expected, in agreement with the experimental observations, that as the amount of exposed nickel surface decreased, the yields of carbon oxides would decrease relative to the yield of methane.

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REFERENCES

1. Dent, F. J., Moignard, L. A., Blackbraun, W. H., and Herbden, D., "An Investigation into the Catalytic Synthesis of Methane by Town Gas Manufacture." 49th Report of the Joint Research Committee of the Gas Research Board and the University of Leeds, 1945. (G.R.B. 20).
2. Crooks, W. M., and Rogers, M. C. F., *J. Appl. Chem.* **16,** 253 (1966).
3. Phillips, T. R., Mulhall, J., and Turner, G. E., *J. Catal.* **15,** 233 (1969).
4. Rostrup-Nielsen, J. R., *J. Catal.* **33,** 184 (1974).
5. Starch, H. H., Golumbic, N. and Anderson, R. B., "The Fischer–Tropsch and Related Syntheses." Wiley, New York, 1951.
6. Shephard, F. E., *J. Catal.* **14,** 148 (1969).
7. Ross, J. R. H., "Surface and Defect Properties of Solids," Vol. 4, Chap. 2. London Chem. Soc., 1975.
8. Williams, A., Butler, G. A., and Hammonds, J., *J. Catal.* **24,** 352 (1972).
9. Trimm, D. L., and Moayeri, M., *J. Chem. Soc. Faraday 1,* 1245 (1977).
10. Rostrup-Nielsen, J. R., *J. Catal.* **11,** 220 (1968).
11. Rostrup-Nielsen, J. R., *J. Catal.* **21,** 171 (1971).
12. Moseley, F., Stephens, R. W., Stewart, K. D., and Wood, J., *J. Catal.* **24,** 18 (1972).
13. Davies, H. S., and Lacey, J. A., 38th Autumn Research Meeting of the Institute of Gas Engineers, London, 1972. (Gas Council Report No. 975).
14. Macak, J., Licka, S., and Malecha, J., *Chem. Ind.* **105,** 517 (1972).
15. Rostrup-Nielsen, J. R., *Chem. Eng. Prog. Ammonia Safety Symp. Tech. Man.* **15,** 82 (1973).
16. Rostrup-Nielsen, J. R., *J. Catal.* **27,** 343 (1972).
17. Bhatta, K. S. M., and Dixon, G. M., *Trans. Faraday Soc.* **63,** 2217 (1967).
18. Bernstein, R. B., and Taylor, T. I., *Science* **21,** 498 (1947).
19. Bain, F. T., Jackson, S. D., Thomson, S. J., Webb, G., and Willocks, E., *J. Chem. Soc. Faraday Trans. 1,* **72,** 2516 (1976).
20. Jackson, S. D., Thomson, S. J., and Webb, G., *Radiochem. Radioanal. Lett.* **28**(5–6), 459 (1977).
21. Jackson, S. D., Thomson, S. J., and Webb, G., Unpublished results.

22. Baker, R. T. K., Harris, P. S., Thomas, R. B., and Waite, R. J., *J. Catal.* **30,** 86 (1973).
23. Baker, R. T. K., Barber, M. A., Harris, P. S., Feates, F. S., and Waite, R. J., *J. Catal.* **26,** 51 (1972).
24. Baird, T., Fryer, J. R., and Grant, B. *Nature (London)* **233,** 329 (1971).
25. Derbyshire, F. J., Priestland, A. E. B., and Trimm, D. L., *Carbon* **10,** 114 (1972).
26. Private Communication.
27. Joyner, R. W., *J. Catal.* **50,** 176 (1977).
28. Ponec, V., and Araki, M., *J. Catal.* **44,** 439 (1976).
29. Ponec, V., and Van Barneveld, W. A. A., *J. Catal.* **51,** 426 (1978).
30. Sexton, B. A., and Somorjai, G. A., *J. Catal.* **46,** 167 (1977).
31. Rabo, J. A., Risch, A. P., and Poutsma, M. L., *J. Catal.* **53,** 295 (1978).
32. Matsumoto, H., and Bennett, C. O., *J. Catal.* **53,** 331 (1978).
33. Primet, M., Dalmon, J. A., and Martin, G. A., *J. Catal.* **46,** 25 (1977).
34. Somorjai, G. A., and Nieuwenhuys, B. E., *J. Catal.* **46,** 259 (1977).
35. Thomson, S. J., and Webb, G., *J. Chem. Soc. Chem. Commun.*, 526 (1976).
36. Gardner, N. C., and Hansen, R. S., *J. Phys. Chem.* **74,** 3298 (1970).