JOURNAL OF CATALYSIS 33, 184–201 (1974)

Coking on Nickel Catalysts for Steam Reforming of Hydrocarbons

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Received June 1, 1973

Formation of coke from hydrocarbons at conditions for steam reforming was studied in a thermogravimetric system. A number of catalysts were investigated at 500°C to elucidate which properties of the catalyst may be important for eliminating coking. The study was supplemented by decoking experiments and examination of samples of catalysts exposed to coking under industrial conditions. The formation of coke at 500°C was not accompanied by poisoning of the nickel surface as reported for lower temperatures. At temperatures below 650°C, coking was observed neither on the support nor on a catalyst exposed to total poisoning by sulfur. Coking on some support materials was studied at 750°C.

Formation of coke may be depressed by enhanced steam adsorption on the catalyst. This may be achieved by the presence of alkali or by the use of magnesia-based catalysts, the preparation method being important for the function of the latter catalyst type. The activity for the reforming reaction may influence the coking rate. The results are evaluated on the basis of a simple sequence proposed earlier, and some implications for the operation of tubular reformers are discussed.

INTRODUCTION

In a previous study (*1*) some factors were discussed that influence the activity of nickel catalysts for the conversion of higher hydrocarbons to gaseous products by steam reforming:

$$C_nH_m + nH_2O = nCO + \left(n + \frac{m}{2}\right)H_2 \quad (1)$$

$$CO + H_2O = CO_2 + H_2 \quad (2)$$

$$CO + 3H_2 = CH_4 + H_2O. \quad (3)$$

Another study (*2*) described parameters that may affect the formation of carbon on the nickel surface from the products carbon monoxide or methane, as may occur when the equilibrium composition shows a positive affinity towards decomposition of these components. Carbonaceous deposits may also be formed by breakdown of the hydrocarbon:

$$\text{“}C_nH_m = \text{polymers} = \text{coke”} \quad (4)$$

and these deposits may be stable in a steady state even if the equilibrium predicts no formation of carbon. The present study deals with some properties of the catalyst that may influence the competition between Reactions (1) and (4).

It is generally assumed (*3–6*) that (4) may take place either by reaction on the nickel surface or by cracking on the support material and in the gas phase, the cracking reactions being more pronounced at elevated temperatures.

The well-known effect of alkali on the selectivity of Reaction (1) was discussed by Andrew (*3*). The function of alkali was ascribed to neutralization of acidic sites on the support active for cracking, and to a promoting effect on the reaction between coke and steam. Nicklin *et al.* (*6*) claimed that urania may also improve the selectivity, and a small amount of alkali was added to neutralize acidic sites. Macak *et al.* (*5*), who studied coking and decoking reactions in a thermogravimetric system, observed no effect of urania on the gasification of carbonaceous deposits, but the amount of coke formation during reforming of *n*-heptane at 550–650°C was less when the catalyst contained urania.

With no steam present the differences were less. The better selectivity of the urania-containing catalyst was related to a larger adsorption of steam reflected by the kinetic expression, as also proposed by Bhatta and Dixon (*7*). Other experiments at 750°C by Macak *et al.*, where the residence time was changed showed a maximum in coke accumulated over a given period of time. Another maximum was found when varying the temperature.

Saito *et al.* (*8*) studied the coke formation in reforming experiments at 770°C with *n*-hexane, and found the coke yield to depend on preparation methods and the composition of the support. Coking on a magnesia-supported catalyst was much less than that on catalysts supported on alumina or silica. Alkali caused a marked decrease of coke formation on the two latter catalysts. Since no correlation was indicated between the activities for the coking and reforming reactions, the two reactions were assumed to take place on different parts of the catalyst surface. Other experiments (*9*) showed the rate of coke formation to be nearly first order with respect to *n*-hexane. The coking rate showed a maximum at around 550°C. Since most of the experiments by Saito *et al.* were performed at temperatures above 700°C, they were most likely strongly influenced by thermal pyrolysis and cracking on the support.

In reforming studies in the temperature range 400–500°C, Moseley *et al.* (*10*) and Bhatta and Dixon (*11*) observed a deactivation of the catalyst that was explained by formation of a film of polymers blocking the nickel surface. Bhatta and Dixon identified high molecular hydrocarbons in an extract of the deactivated catalyst. This deactivation was found to decrease with increasing steam carbon ratio and temperature (*10*) and to be independent of the partial pressure of the hydrocarbon (*11*). The accumulated amounts of carbon during the deactivation appeared to be negligible.

Balandin *et al.* (*12, 13*) investigated reforming reactions at 360–400°C. During initial periods of the experiments of a few minutes, self-poisoning was indicated by coking followed by an exponential decrease of methane in the product gas, whereas the amounts of carbon oxides were only slightly affected. The deposition of coke ceased when the methane content stabilized.

It is apparent that the nature of coking accompanying the reforming reactions varies with the temperature range in question. At low temperatures, a significant deactivation of the gasification Reaction (1) is observed, while the accumulated amounts of carbonaceous deposits remain small. The deactivation rate decreases with temperature, whereas at the same time the coking increases, showing a maximum at higher temperatures. At high temperatures, thermal pyrolysis and cracking on the support material may contribute to the formation of coke.

Since the main interest of the present study is coking problems in tubular reformers, the investigations have concentrated on the temperature level of the inlet layer of a reformer tube, i.e., around 500°C. At the same time, as indicated by the previous activity studies (*1*), the influence from cracking reactions may be neglected at this temperature.

METHODS

Coking Studies

The experiments were performed in the thermogravimetric system described previously (*2*). The feed system was modified for addition of liquid hydrocarbons and steam. Preliminary experiments revealed that systems including pumps and evaporators of various types gave unreliable results, because the coking rate was very sensitive to short time fluctuations of the steam-to-carbon ratio. Therefore, steam was generated by passing the equivalent amount of H_2 and some N_2 over wires of copper oxide at 280°C. The hydrocarbon was added by passing a flow of N_2 or Ar through the gently boiling hydrocarbon. This stream was passed through a large volume thermostat maintained at a temperature approximately 10° below the boiling point of the hydrocarbon. In this way, stable feed rates could be established after a period of 1 hr. The flows of hydrocarbon and steam were measured by weighing the amounts adsorbed over a given interval on molecular sieves (Union Carbide 13X). Preheated N_2 was added to the stream before adsorption to avoid condensation in the tubes.

The gases were purified as described previously (*2*). The liquid hydrocarbons were desulphurized over NiMo-catalyst and ZnO before use. The upper and lower 10% of the constant boiling range were removed by a final distillation to avoid any fractioning in the feed system.

Catalysts. The notations of the catalysts are equivalent to what was used previously (*1, 2*):

A-types:	Catalysts based on magnesia containing 6 wt% Al.
B-types:	Catalysts based on magnesium aluminium spinel.
C-types:	Catalysts based on alumina.
D-types:	Catalysts on various supports.
E-types:	Catalysts containing noble metals.

The properties of the individual samples have been listed earlier (*1*). In addition, the investigation included some samples of catalyst (P-types) exposed to coking in a pilot plant with a single industrial size reforming tube.

The pore volume distribution of a few samples was measured by Hg-penetration in an Aminco Porosimeter.

Procedure. The catalyst was heated up in H_2 (0.18 g mol/hr) until temperature and sample weight stabilized. Steam and hydrocarbon were added to the reactor, when the feed rates were constant, and the change in catalyst weight was followed on the recorder. Unless otherwise specified, the experiments were performed at the following standard conditions:

Pressure:	Atmospheric
Temperature:	500°C
Catalyst:	0.7 g (0.79 ml) as 2–3 mm particles
Hydrocarbon:	0.6 g *n*-heptane/hr
H_2O/C:	2.0 moles/atom
$N_2(+Ar)$ in feed:	0.125 g mol/hr
H_2:	0.018 g mol/hr
N_2 seal gas:	0.670 g mol/hr

Decoking Studies

Some experiments on decoking of catalyst by means of steam were performed following the techniques described by Weisz and Goodwin (*14*). A sample (approximately 2 g) of coked catalysts from the pilot plant was placed in a tubular reactor surrounded by an electrically heated furnace. At the bottom of the reactor was placed some low temperature shift catalyst (approximately 20 g) to convert CO into CO_2.

The coked catalyst was exposed to a large excess of steam (H_2O: 10 mol/hr, N_2: 1 mol/hr). The CO_2 evolved was absorbed by a solution of 0.15 *N* $Ba(OH)_2$ in a conductivity cell (Radiometer CDC 104). The conductivity was measured and recorded automatically, thus showing the progress of the gasification. Each run was completed by a period at 800°C in pure air to ensure total combustion. The total amount of CO_2 absorbed was determined by titration of the solution after the run.

RESULTS

Empirical Plots

Some preliminary results were reported earlier (*15*).

Typical plots of weight of coke versus process time, obtained in the coking studies, are shown in Fig. 1. It appears that after a certain period of time with insignificant weight increase, coking accelerates and the coking rate arrives at a constant value reflected by a straight line. No sign of a decrease of the rate with time was found even when the coke content of the catalyst was close to 15%. At high coke contents, the void between the particles was gradually filled up with coke, but apparently these restrictions did not affect the coking rate.

On this basis, the amount of coke on the catalyst, C, may be expressed by the induction period, t_o, as defined in Fig. 1, and the slope of the straight line k_c:

$$C = k_c(t - t_o) \qquad (5)$$

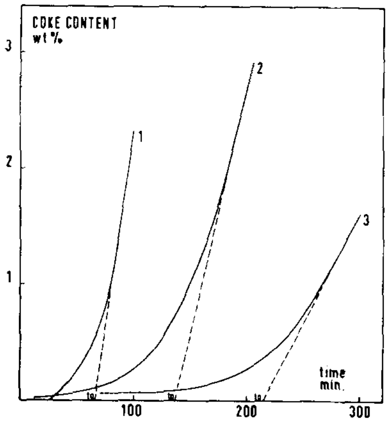

FIG. 1. Mean coke content of catalyst bed and process time. Catalyst: 0.7 g A1. Standard conditions, n-heptane, 500°C. 1. exp. 239($H_2O/C = 1.3$), 2. exp. 236($H_2O/C = 1.5$), 3. exp. 231($H_2O/C = 2.0$).

and the coking rate by:

$$r_o = \frac{dC}{d(t - t_o)} = \frac{dC}{dt} = k_c. \qquad (6)$$

Experiments based on samples from the same catalyst batch showed standard deviations for k_c and t_o of 25% and 12%, respectively, and for this reason most of the experiments were repeated or, when possible, parameters were changed during a single run. The uncertainty may reflect that the conversion, and with that the mean concentration, of n-heptane in the hydrocarbon may vary from experiment to experiment. First, the activity varies from sample to sample as shown previously (*1*); second, even a small displacement of the basket from the axis of the reactor may change significantly the channeling around the basket. It is conceivable that this may affect k_c more than t_o. In general, it appears doubtful to extrapolate quantitatively the results obtained in the thermogravimetric system to normal flow reactors. However, the results may still be used to identify catalyst properties important for the elimination of coking.

TABLE 1

COKING AT VARIOUS FEED RATES, 500°C*

Exp. no.	Cat. wt. (g)	Particle size (mm)	Total feed (g mol/hr × 22.4)	Space velocity $\left(\frac{\text{g mol } C_7H_{16}}{\text{g} \cdot \text{cat} \cdot \text{hr}} \times 22.4\right)$	H_2O/C $\left(\frac{\text{mol}}{\text{atom}}\right)$	$p_{C_7H_{16}}$ (atm)	p_{H_2O} (atm)	k_c $\left(\frac{\mu g}{\text{min}}\right)$	t_o (min)
				A:	(partial pressures)				
518	0.70	2-3	27.0	2.0	1.3	0.05	0.46	466	140
519	0.70	2-3	19.4	2.0	1.3	0.07	0.66	453	126
520	0.70	2-3	27.3	2.0	1.5	0.05	0.53	236	195
521	0.70	2-3	19.0	2.0	1.5	0.07	0.76	358	206
				B:	(space velocity)				
510	0.69	2-3	20.5	2.0	1.7	0.07	0.78	220	157
515	0.56	2-3	17.0	2.5	1.3	0.08	0.73	596	85
514	1.13	2-3	17.2	1.2	1.3	0.08	0.73	545	74
				C:	(particle size)				
517	1.11	1-2	16.9	1.2	1.3	0.08	0.73	388	92
516	1.11	4-5	17.0	1.2	1.3	0.08	0.73	411	96
513[a]	0.61	9 × 9	16.4	2.3	1.3	0.08	0.75	545	74
512[a]	0.20	6 × 6	16.7	6.7	1.3	0.08	0.73	324	125
511[a]	0.21	6 × 6	18.7	6.4	1.5	0.07	0.75	110	223

* N_2 used as balance; catalyst: A17; feed: n-heptane.

[a] A single cylinder (no basket).

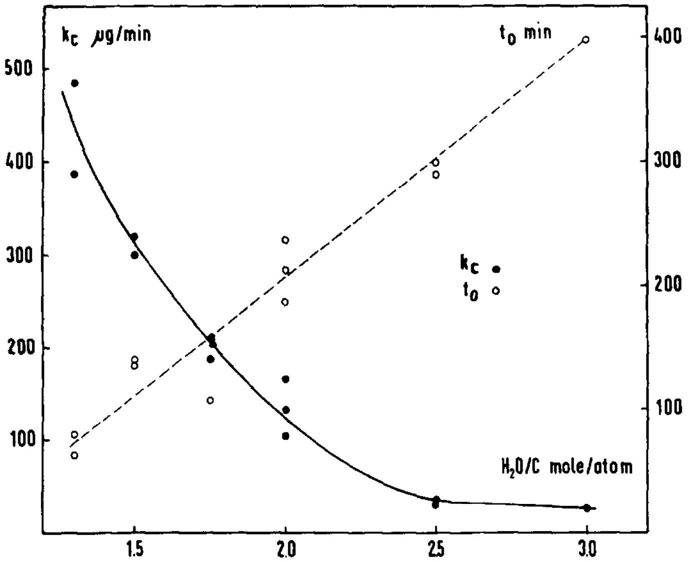

FIG. 2. Coking rates and steam/carbon ratio. Feed: *n*-heptane; catalyst: 0.70 g A1. Standard conditions at 500°C.

Process Parameters

The results shown in Table 1 demonstrate that the steam-to-carbon ratio is more important for k_c and t_o than is the partial pressure of the hydrocarbon. Moreover, the amount of catalyst placed in the basket, and thereby the space velocity, appeared to have no influence on the results, and use of other particle sizes or of a single catalyst pellet instead of the basket caused no drastic changes.

A series of experiments at 500°C was performed with catalyst A1 to study in more detail the relation between k_c and t_o, and the steam-to-carbon ratio. As shown in Fig. 2, k_c increases strongly when decreasing the steam/carbon ratio, whereas t_o decreases linearly. In another series of experi-

TABLE 2

INFLUENCE ON COKING RATES OF H_2 AND CO_2*

Exp. no.		H_2O/C (mole/atom)	Addition to feed			Coking rates	
			Gas	Amount (g mol/hr × 22.4)	Partial pressure (atm)	k_c (µg/min)	t_o (min)
411	a	2.0	N_2	2.8	0.12	199	159
	b			11.8	0.36	193	
412	a	2.0	H_2	0.4	0.016	138	113
	b			9.4	0.24	205	
413	a	2.0	H_2	0.4	0.016	181	147
	b			9.4	0.24	243	
544	a	1.3	CO_2	0	0	600	53
	b			9.0	0.33	700	
548[a]	a	1.3	CO_2	0	0	960	55
	b			9.0	0.33	1060	

* Standard conditions, 500°C; feed: *n*-heptane; catalyst: 0.7 g A1.

[a] 1.5 – 2 mm particles.

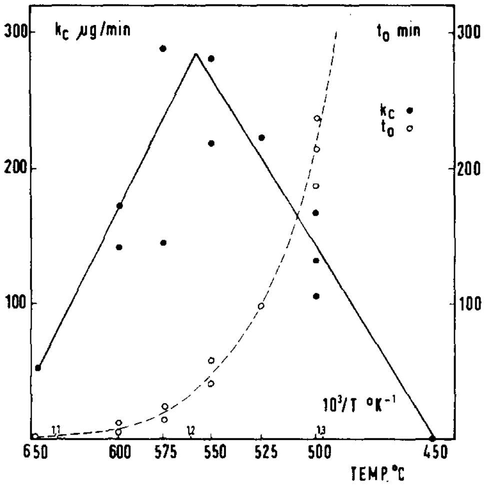

FIG. 3. Temperature dependence of coking rate. Feed: *n*-heptane; catalyst: 0.70 g A1. Standard conditions at $H_2O/C = 2.0$ mol/atom (at 450°C: $t_o > 720$ min.).

ments, the influence of some gases was studied by changing the partial pressure during the run. The results from Table 2 show that dilution of the feed gas with nitrogen did not affect k_c, which is in accordance with the results from Table 1. The addition of carbon dioxide resulted in a slight increase of the coking rate, whereas a more pronounced effect was observed when increasing the hydrogen partial pressure in the feed.

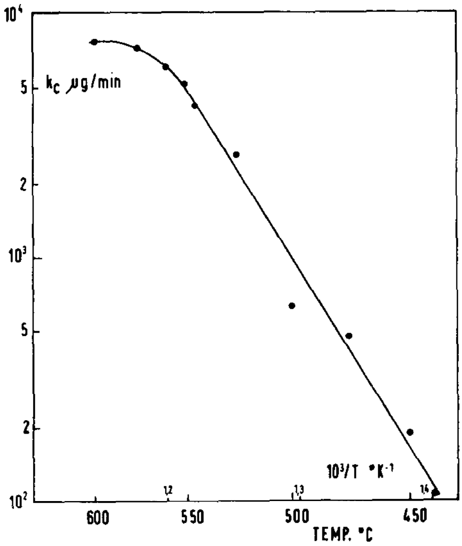

FIG. 4. Temperature dependence of coking rate. Feed: *n*-heptane; catalyst: 0.69 g A17. Standard conditions at $H_2O/C = 1.3$ mol/atom.

The temperature dependence of the coking parameters is demonstrated in Fig. 3. Although the uncertainty of k_c is substantial, the results indicate the existence of a maximum at around 550°–575°C. Results from an experiment where the temperature was changed during the run are shown in Fig. 4. Again, a maximum of k_c is indicated. The higher accuracy of k_c allows calculation of an apparent activation energy of 40.0 kcal/mole for temperatures below 550°C.

TABLE 3

COKING RATES OF VARIOUS HYDROCARBONS*

Exp. no.	Hydrocarbon	Reactivity k_a (gatom/g/hr)	Coking rate k_c (μg/min)	Coking rate t_o (min)
319	Ethylene	—	17500	<1
318	*n*-butane	—	2	—
306	*n*-hexane	—	95	107
308	Cyclohexane	7.2	64	219
307	Benzene	0.53	532	44
231/232/245	*n*-heptane	1.9	135	213
310	tri-methyl-butane	3.6	5	(56)
323	*n*-decane	1.9	—	(90)
324	*n*-dodecane	—	(12)	(6)

* Catalyst: 0.7 g A1; standard conditions: $H_2O/C = 2.0$ mol/atom, 500°C (k_a from reforming experiments at 30 atm, 500°C(*1*)).

Experiments with different types of hydrocarbons indicated the coking rate to depend strongly on the unsaturated character of the hydrocarbon. As shown in Table 3, the highest rate was obtained with ethylene. Apparently, a maximum in tendency to coking exists among *n*-paraffins. Thus, *n*-butane and *n*-decane result in less coke than do *n*-hexane and *n*-heptane. It should be noticed that the behavior of trimethyl butane is close to that of *n*-butane, resulting in a coking rate inferior to that obtained with *n*-heptane. Cyclohexane differs little from *n*-hexane. The experiments were performed under standard conditions, i.e., at a fixed steam to carbon ratio. Therefore, the partial pressures of the hydrocarbons were nearly inversely proportional to their molecular weights.

In some experiments the conversion into gaseous products was followed during the coking of the catalyst. Although the conversion is not reflecting the true activity of the catalyst because of channeling around the basket, it may indicate whether the catalyst is exposed to deactivation. As shown in Fig. 5, no significant changes in the conversion were apparent at low temperatures where no coking occurred, but at 500°C a small decrease was observed with increasing coke content. This is not considered to be related to a poisoning of the nickel surface by carbonaceous deposits, a phenomenon that is prevailing at lower temperatures (*10*). It should probably be ascribed to flow restrictions into the basket due to gradual blockage of the void between the particles, which may enhance channeling around the basket.

Examination of Coked Catalysts

To elucidate these effects the study was supplemented by an investigation of some catalyst samples exposed to coking in an industrial size monotube pilot plant. The intrinsic activities of samples P1 and P4 containing 11 and 4.5 wt% carbon were estimated from ethane-reforming experiments under standard conditions (*1*) using the catalyst as 0.1–0.3 mm particles. When the results shown in Table 4 are compared with the activities of the corresponding unused catalysts shown in Table 5, it is apparent that the high coke contents have caused no significant changes of the intrinsic activities of the catalysts. The differences are within the range observed between batches (*1*).

Examination in an electron microscope revealed that the coke formed during the coking studies was of whisker-like structure, normally with a nickel crystallite placed at the free end, similar to the situation reported earlier (*2*) for carbon originating

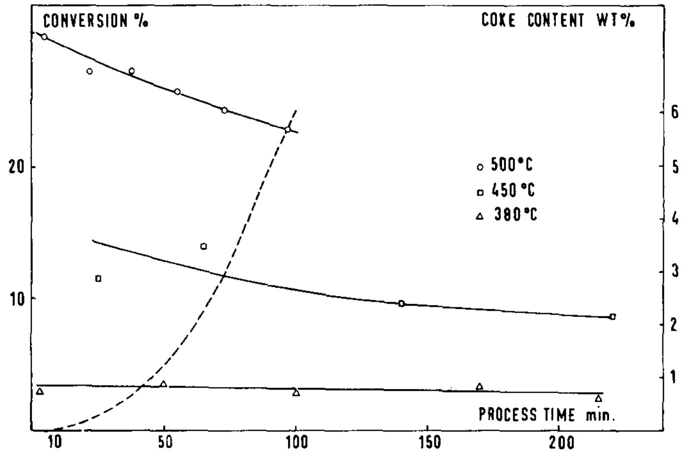

FIG. 5. Hydrocarbon conversion and process time. Feed: *n*-heptane; catalyst: 0.7 g A1. Standard conditions at $H_2O/C = 1.3$ mol/atom. Dashed curve shows increase of coke content at 500°C. No coking was detected at 450 and 380°C.

TABLE 4

EXAMINATION OF CATALYSTS EXPOSED TO COKING BY MALOPERATION IN A MONOTUBE PILOT PLANT CATALYST A. ALL SAMPLES PLACED IN THE TEMPERATURE RANGE 450°–550°C

		Carbon content			Activity of 0.1–0.3 mm particles (C_2H_6-reforming)		
Sample[a] (no.)	Approx. age of coke (hr)	Bulk (wt%)	External layer (wt%)	Coke structure (electron microscope)	r_i (mol/g/h) × 10	r_s[b] (mol/m² Ni/h) × 10³	Comments
P1(A43)	150	11	19	Flake	2.5	208	Maloperation during start-up. No deactivation
P2(A43)	150	6	12	Flake	1.6 (2.5)[c]	100 (130)[c]	Maloperation during start-up. No deactivation
P3(A43)	<5	1		Whiskerlike			Maloperation during start-up.
P4(A42)	500	4.5	7	Flake	1.8 (1.4)[c]	118 (50)[c]	Slowly coking deactivation apparent.
P5(A42)	350	1.4	6.0	Flake	1.1	105	Slowly coking deactivation apparent.

[a] Corresponding unused catalyst listed in brackets.

[b] Ni-surface corrected for sulphur content.

[c] Data for regenerated catalyst in brackets. (Regeneration: coke burn-off in air and steam at 750°C, reduction in H_2 at 850°C).

from decomposition of carbon monoxide and methane. A fibrous structure was also found on P3 sampled shortly after a mishap, whereas catalyst sampled a few hundred hours after a mishap or after a similar period with slow build-up of coke showed a flake-like structure, which was difficult to identify. Most likely, this structure is formed by sintering of the fibrous structure. The difference between the two structures is revealed by their reactivities when exposed to steam. The fibrous structure was easily removable, whereas only part of the aged coke is reactive. When adding a few percent of air to the steam, a complete decoking was achieved on all samples at temperatures above 450°C.

Analyses of the radial distribution of coke in the catalyst particle showed a strong accumulation of coke close to the external surface as demonstrated by the results in Table 4.

It is remarkable that the coke deposits did not influence considerably the pore volume distribution and the total pore volume of catalysts P1 and P4, as indicated for P1 in Fig. 6. Apparently, the presence of coke in P1 is reflected only by formation of a small amount of pores with radii less than 100 Å. On this basis, no change of the diffusivity of the catalyst during coking should be expected. However, it should be noticed that during operation in the pilot plant with the catalyst fillings of whole catalyst pellets (rings: OD/ID – H = 13/6 – 7 mm/mm/mm), from which P4 and P5 originate, a deactivation was apparent from changes in the axial temperature profile and from the exit gas analyses showing increasing amounts of ethane and ethylene. On the other hand, operation with P1-2 was stable. Samples P4 and P5 and the corresponding unused catalyst were characterized by having practically no pores with radii higher than 300 Å. It is natural, then, to assume that deactivation of P4 and P5 can

TABLE 5
Coking Rates on Various Catalysts. Type A

		Activity for ethane reforming at 500°C			Coking rates at 500°C			
					n-heptane[a] ($H_2O/C = 2.0$)		Ethylene[b] ($H_2O/C = 6.0$)	n-heptane[b] (No steam)
Catalyst		r_i (mol/g/hr) × 10	r_s (mol/m² Ni/hr) × 10³	α_{H_2O}	k_c (μg/min)	t_o (min)	k_c (μg/min)	k_c (μg/min)
A-types:								
Group 1: Fixed composition (25 wt% Ni), Na: 0.04–0.16 wt%. Preparation route 1								
A1		2.4	120	−0.33	135	142	1600	15600
A15		4.4	145		1420	40		
A43		1.4	71		462	40		
A3	red. in dry H_2	8.2	118		131	127	1100	17500
A4	(A3 red. in $H_2O/H_2 = 3$)	2.0	53		635	40	2750	20200
A17		1.4	52					
A18		4.2	122	−0.52	575	108		22000
A41		2.8	61		596	19		
Group 2: Fixed composition (25 wt% Ni), Na < 0.01 wt%								
A19	A1 washed in H_2O	4.0	198	0.00	800	73		
A20	Prep. route 2	8.2	222		2010	33		
A21	A20 sintered	2.0	183	−0.26	1200	27	7500	
A22	Prep. route 1	11.9	287	−0.48	140	91	1890	
A23	A22 sintered	2.9	282	−0.17	1710	27	6170	14000
A25	Prep. route 3	10.5	165		178	152	2820	
Group 4: Other metals (total content of metals 25 wt%), Na < 0.01 wt%. Prep. route 1								
A13	Ni/Cu = 0.7/1.3	0.020	1.6		0			
A14	Ni replaced by Co	0.016	0.29		0			
Group 5: Promoted with alkali								
A34	A1, 0.14% K	0.79	27	−0.42	33[b]	—		
A35	A1, 0.53% K	0.097	3.7	−1.81	0[b]	—		11800
A42	A41, 0.44% Na	1.0	22		59	66		

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[a] Mean of at least two experiments (if nothing else noticed).

[b] Single experiment.

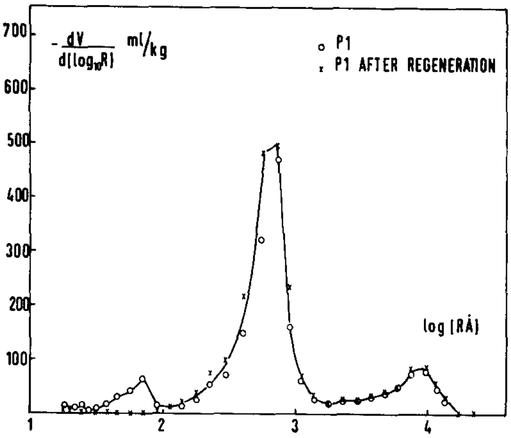

FIG. 6. Pore volume distribution of catalyst P1 before and after burn-off of coke. Before regeneration: surface area, 13.8 m^2/g; porosity, 218 ml/kg. After regeneration: surface area, 9.8 m^2/g; porosity, 263 ml/kg.

be explained by a blockage of the pore mouths by coke formed mainly close to the external surface, whereas a blockage of the larger pores of P1 and the unused catalyst appears more unlikely. A direct measurement of the diffusivity may not reveal this effect, as even a small destruction of the external film during sampling may disturb the results.

In situations where coking results in break-down of the catalyst and accumulation of coke in the void between catalyst particles, channeling through non-coked tubes of an industrial reformer may contribute to an overall decrease in the catalyst performance. Channeling around coked passages may also explain the decreasing conversion observed during the coking experiments.

Various Catalysts and Supports

Experiments with different catalyst preparations revealed great differences in coking data as indicated in Tables 5 and 6. While the activity studies (*1*) showed the specific activity to be within the same range for a great number of catalysts, the coking results demonstrate that k_c and t_0 are influenced substantially by preparation methods (A20 and A22), calcination temperature (A20 and A21, A22, and A23), and activation procedure (A3 and A4). However, it is evident that values of t_0 obtained for most of the A-type catalysts are higher than those for catalysts based on alumina (C-type) or silica alumina (D9). The addition or the presence of potassium and, to a smaller degree sodium, results in markedly reduced coking, reflected by increased t_0, whereas addition of calcium and magnesium to an alumina based catalyst (C9, C11) appears to be without any effect on t_0.

Catalysts containing nickel–copper alloy (A13) or cobalt (A14) as metal phases showed no coking, and similar results were obtained on alumina catalysts containing platinum (E1), ruthenium (E8), and rhodium (E12). Even when the steam/carbon ratio was decreased to 0.6–0.3, no coking was detected on the precious metals. It should be noted that catalysts A13, A14, and E1 all showed poor activity for ethane reforming.

A sample of A1 saturated with sulphur in the equipment for determination of sulphur capacity before the coking experiments showed no coking, and the same result was obtained on the nearly inactive catalyst (D14) based on carbon.

Experiments using ethylene as feed showed very short induction periods, but the values of k_c correlate with those obtained with n-heptane.

A few experiments with n-heptane were performed with no steam present, steam being replaced by nitrogen. Very high coking rates, were observed, but no correlation with the results with steam present, activity data or nickel surface areas is apparent.

Some series of experiments were performed on support materials containing no metals. At standard conditions at 500°C, no coking was observed over magnesia (S1) even with ethylene as feed. When heating η-alumina (S4) in steam and n-heptane at a rate of 2°C/min coking was indicated at 715°C. The experiment was repeated with S1 with nitrogen replacing steam, and coking was observed at 690°C at a heating rate of 4°C/min. Experiments at 750°C with S4 where the partial pressure and the

TABLE 6
COKING RATES OF VARIOUS CATALYSTS. B–E TYPES

Catalyst		Activity for ethane reforming at 500°C			Coking rates at 500°C		
					n-heptane[a] ($H_2O/C = 2.0$)		Ethylene[b] ($H_2O/C = 6.0$)
		r_i (mol/g/hr) × 10	r_s (mol/m^2 Ni/hr × 10^3)	α_{H_2O}	k_c (μg/min)	t_o (min)	k_c (μg/min)
B-Types: Based on $MgAl_2O_4$							
B1		1.6	366	0.0	880	84	2550
B6	0.52% K	0.54	61	(−0.3)			620
B4	1.53% K	0.074	8.3	−1.08	0	—	17
C-Types: Based on Al_2O_3							
C1	ηAl_2O_3	5.5	80	0.13	2470	12	
C6	C1, 1.7% K	1.8	29		56	63	
C8	C1, 1.3% Na	3.2	47		5	—	
C9	C1, 1.1% Ca	2.2	30		130	12	
C11	C1, 1.2% Mg				518	2	
C2	γAl_2O_3	9.2	163		175	15	1750
C3	γAl_2O_3	8.2	227		2180	12	6670
C10	C3, 2.1% K	1.9	46		1.8	—	
D-Types: Based on various materials							
D4	ZrO_2	0.067	2.6		43	60	
D9	SiO_2/Al_2O_3	1.1	25		26	9	
D14	Carbon	0.04	5		0	—	
E-Types: Noble metals based on Al_2O_3							
E1	0.5% Pt	0.53	221		—	>270	
E8	0.5% Ru	5.4	2059		—	>240	
E12	— Rh	4.1	2502		—	>180	

[a] Mean of two experiments.
[b] Single experiment.

steam carbon ratio were varied, showed both parameters to affect significantly the coking rate as demonstrated in Fig. 7. This result is contrary to what was indicated in Table 1 for nickel catalysts at 500°C.

Results from a series of experiments performed at 750°C on various support materials shown in Table 7 demonstrate that coking from cracking depends on the composition of the support, the acidic materials resulting in the highest coking rates. It is apparent that the calcination temperature of magnesia may influence the coking rate. Moreover, the addition of alkali to η-alumina has a pronounced effect.

The retarding effect of alkali on coking reactions is accompanied by its ability to improve the reaction between coke and steam as illustrated by some experiments performed with the coked catalyst sample P1 with and without addition of alkali. The results indicated that the reactivity of the carbonaceous deposits increased when alkali is present.

DISCUSSION

Coking Parameters

Equation (5) implying a constant coking rate after a certain induction period, differs from the Voorhies expression (*16–18*)

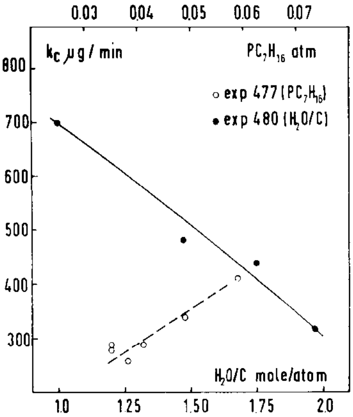

FIG. 7. Coking rates on support S4 (0.4 g) at 750°C. Feed: *n*-heptane (6.2 g/h). Exp. 477: Variation of $p_{C_7H_{16}}$ (H_2O/C = 2.0, N_2 as balance). Exp. 480: Variation of H_2O/C ($p_{C_7H_{16}}$ = 0.06 atm, N_2 as balance, total feed: 1.07 g mol/hr).

normally fulfilled in coking studies on cracking catalysts:

$$C = k_v t^n, \tag{7}$$

n being less than 1. Thus, Ozawa and Bischoff (*18*), who used an apparatus similar to that of the present work, found an initial rapid coke formation in their investigation at 350–500°C of ethylene cracking over a silica-alumina catalyst. Contrary to this, Lobo and Trimm (*19, 20*), who studied coking from olefins on metal films in a static thermogravimetric system, observed a trend of the coking process in accordance with the present work. This might indicate a fundamental difference between coking on cracking and metal catalysts. It could be related to the observation that coking is accompanied by deactivation of the surface of a cracking catalyst (*18*), whereas coking on the nickel surface apparently results in no decrease of the intrinsic activity.

Moreover, the temperature dependence around 500°C of the coking rates derived from the data of Voorhies (*16*) and Ozawa and Bischoff (*18*) is much less than reflected by the high apparent activation energy of 40 kcal/mole calculated from Fig. 4. For coking from olefins on nickel at temperatures around 500°C and with no steam present, Lobo and Trimm (*19, 20*) found activation energies in the ranges of 29–34 kcal/mole. This value cannot be compared directly with that obtained from Fig. 4, which also includes the temperature dependence of the gasification Reaction (1).

Lobo and Trimm observed a maximum in coking rate as tentatively indicated for the reforming reactions in Fig. 3 and as found by Macak *et al.* (*5*) and by Saito *et al.* (*9*). This may indicate that the maximum found in coking from reforming reactions should not be related to the gasification step. When increasing temperature, Lobo and Trimm observed a minimum in coking rate at 600°–650°C above which the coking rates increased with an activation energy in the range 43–50 kcal/mole being close to that of thermal pyrolysis. Lobo and Trimm explain the existence of the maximum as an effect of decreasing adsorption with temperature. For temperatures around 500°C they assume diffusion of carbon through nickel to be the rate-determining step, and that zero order kinetics mean that the nickel surface remains accessible for the hydrocarbon. This explanation is in accordance with the present results and to the whisker growth mechanism discussed earlier (*2*), although surface diffusion may be involved as well.

The evaluation given by Macak *et al.* (*5*) is in contrast to these results, as it is suggested that the carbonaceous deposits are blocking the nickel surface, and that the reactants have to diffuse through the coke layer to react on the nickel surface. At low temperatures, the coke layer exposes permeability for reactants and products, but above 570–600°C graphitization causes increased diffusion restrictions and a reduced reaction rate. This explanation is also in conflict with the observations made for low temperature gasification (*10, 11*) showing formation of a polymer film blocking the surface.

Selectivity in Terms of a Simple Sequence

As discussed earlier (*1*), coking on the nickel surface may be related to a gradual conversion of the hydrocarbon radicals by dehydrogenation and polymerization into strongly adsorbed species, which may form carbon. A similar reaction pattern was discussed by Whalley *et al.* (*21*) on the basis of FEM studies of the adsorption of ethylene on nickel. Since the strongly adsorbed residues may be expected to be bound to the surface at more than one carbon atom, the initial step of the coking reaction competing with the gasification reaction most likely involves a dimerization of the hydrocarbon radicals. When using the terminology introduced previously (*1*) in the discussion of the kinetics of ethane reforming, this means that the steps:

$$2(\mathrm{C}_n\mathrm{H}_u) - (S_1)_n = (\mathrm{C}_n\mathrm{H}_v)_2 - (S_1)_{2n} + (u - v)\mathrm{H}_2 = \text{polymers} = \text{coke} \quad (8)$$

are competing with the gasification step,

$$\mathrm{CH}_x - S_1 + \mathrm{O} - S_1 = \mathrm{CO} + \frac{x}{2}\,\mathrm{H}_2 + 2S_1. \quad (9)$$

It is difficult to evaluate whether CH_x or the initially formed radicals, participate in (8). Moreover, the dimerization products may have some reactivity for (9) before they are converted into non-reactive residues. However, there may be some evidence for the initially formed radicals being important for (8) as different coking rates were obtained with various hydrocarbons (Table 3).

The sequence for ethane reforming may be extended by following steps to a general n-paraffin, C_nH_m, ($n > 2$), assuming a stepwise irreversible degradation of the carbon chain and no desorption of intermediates:

$$\mathrm{C}_n\mathrm{H}_m + 2S_1 + yS_3 = (S_1)_2 - \mathrm{C}_n\mathrm{H}_z + y(S_3) - \mathrm{H} + \frac{m - y - z}{2}\,\mathrm{H}_2 \quad (10)$$

$$(S_1)_2 - \mathrm{C}_n\mathrm{H}_z + S_1 + \mathrm{H}_2 = (S_1)_2 - \mathrm{C}_{n-1}\mathrm{H}_{z'} + S_1 - \mathrm{CH}_x \quad (11)$$

$$(S_1)_2 - \mathrm{C}_2\mathrm{H}_{z''} + \mathrm{H}_2 = 2S_1 - \mathrm{CH}_x. \quad (12)$$

This implies that $p_{C_2H_6}$ should be replaced by $p_{C_nH_m}$ in the expression for the rate of step (9) derived earlier (*1*):

where k_r and k'_A are rate constants for the surface reaction (*9*) and for the hydrocarbon adsorption, respectively, whereas K_w is the equilibrium constant for steam adsorption, which is influenced by the metal and the carrier material as well.

The formation of non-reactive residues may be slow compared with the reactions with the gas phase, as demonstrated by Frennet and Lienard (*22*). Therefore, in a simple sequence, a certain residence time of the hydrocarbon radicals on the nickel surface is required to form the strongly adsorbed species that may react further to a polymer film blocking the surface or aggregate to carbon. The residence time of C_nH_z radicals may be expressed by:

$$\tau_{\mathrm{C}_n\mathrm{H}_z} = \frac{x_{\mathrm{C}_n\mathrm{H}_z}}{r_9} \quad (14)$$

$x_{C_nH_z}$ being the surface concentration of C_nH_z (mol/m²Ni).

From the simple sequence is obtained:

$$x_{\mathrm{C}_n\mathrm{H}_z} = \frac{k'_A}{k_\mathrm{H}} \cdot p_{\mathrm{C}_n\mathrm{H}_m} \cdot p_{\mathrm{H}_2}{}^{y/2-1} \cdot \frac{1}{D}\,(\mathrm{mol/m^2\,Ni}), \quad (15)$$

where k_H is the rate constant for (11) reflecting the reactivity of the adsorbed radical for hydrocracking.
Then:

$$\tau_{\mathrm{C}_n\mathrm{H}_z} = \frac{1}{k_\mathrm{H} \cdot p_{\mathrm{H}_2}} \cdot D = \frac{1}{k_\mathrm{H} \cdot p_{\mathrm{H}_2}} \left(1 + \frac{nk'_A}{k_r \cdot K_w} \cdot \frac{p_{\mathrm{C}_n\mathrm{H}_m}}{p_{\mathrm{H_2O}}} \cdot p_{\mathrm{H}_2}{}^{1-y/2} + K_w\,\frac{p_{\mathrm{H_2O}}}{p_{\mathrm{H}_2}}\right) \quad (16)$$

For simplicity the nucleation rate for the growth of carbon may be expressed by:

$$r_N = N \cdot (\tau - \tau_c), \quad (17)$$

where τ_c is some critical residence time on the surface of the hydrocarbon radicals required to form precursors for coke. When

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$$r_9 = \frac{k'_A \cdot p_{\mathrm{C}_n\mathrm{H}_m}/p_{\mathrm{H}_2}{}^{y/2}}{\left(1 + \frac{nk'_A}{k_r \cdot K_w} \cdot \frac{p_{\mathrm{C}_n\mathrm{H}_m}}{p_{\mathrm{H_2O}}} \cdot p_{\mathrm{H}_2}{}^{1-y/2} + K_w\,\frac{p_{\mathrm{H_2O}}}{p_{\mathrm{H}_2}}\right)^2} = \frac{k'_A \cdot p_{\mathrm{C}_n\mathrm{H}_m}/p_{\mathrm{H}_2}{}^{y/2}}{D^2}\;(\mathrm{mol\ C}_n\mathrm{H}_m/m^2\ \mathrm{Ni/h}), \quad (13)$$

τ is less than τ_c, no coking may occur, resulting in a stable performance of the catalyst. This treatment of the coking reactions remains speculative. In principle τ_c depends on the reactivity for gasification of the polymerized coke precursors, which has not been considered in the simple sequence. Moreover, the details of carbon nucleation at the actual conditions have not been reported. But there is some evidence that the nucleation rate depends on the mobility of the carbonaceous species (*23*) and the presence of surface steps and grain boundaries (*21, 23, 24*).

When no steam is present, the residence time is large and coking may take place at very low temperatures. Thus, it was demonstrated earlier (*2*) that coke is formed rapidly at 230°C when heating catalyst A1 in pure methane.

When steam is present, the residence time is small, and the surface mobility of the carbonaceous species for nucleation may become the limiting step. Apparently, the mobility is too small at temperatures below 450–500°C under the conditions used by Moseley *et al.* (*10*), and polymers are accumulating on the surface, which is gradually blocked, and the reaction ceases. A slow dehydrogenation of the film may continue, without further accumulation of carbonaceous deposits. After some period of time the polymers have aged and may not be removed as initially by treatment in hydrogen (*11, 25*).

It is known that the solubility of carbon in nickel increases significantly at temperatures around 500°C. Thus, several studies have shown segregation of carbon to occur by cooling nickel to the temperature range below 500°C, or disappearance of coke by heating above approximately 500°C (*26–28*). The increased solubility may result in improved surface mobility or formation of an "intermediate carbide" as proposed by Renshaw *et al.* (*29*), and these factors may enhance the nucleation and growth of carbon whiskers. As emphasized above, additional studies are required to elucidate this evaluation.

Although the simple sequence should be considered only as an example it may be useful for a preliminary classification of parameters influencing the selectivity for gasification. Thus, the expression (16) may qualitatively illustrate the influence from the steam-to-carbon ratio. The role of steam adsorption in (16) may appear complex, because $K_w \cdot p_{H_2O}$ and the reciprocal term as well are included in D. As discussed earlier (*1*), the various kinetic expressions indicate that both terms may be significant and, in principle, D becomes a hyperbola function of p_{H_2O} showing a minimum. However, the experimental data and practical experience clearly indicate coking to decrease, when only p_{H_2O} is increased. Therefore, it might be assumed that practical values of D are placed on the declining branch of the hyperbola.

Catalyst Parameters

The simple sequence demonstrates the importance of the equilibrium constant for steam adsorption, K_w. This is in accordance with the experimental results in Tables 5 and 6 which show larger induction times for coking, t_o, for catalysts having negative kinetic orders with respect to steam, i.e., catalysts containing alkali or being based on magnesia. The small alkali content in the catalyst studied by Nicklin *et al.* (*6*) and Bhatta and Dixon (*7*) may have influenced the results, which showed a negative reaction order with respect to steam.

It might be argued that alkali may change the rate of Reaction (*8*) since it may affect the hydrogen content of the adsorbed radicals (*30*) or the heterogeneity of the nickel surface (*1*). However, this appears unlikely, because the results obtained in the experiments with no steam present showed no significant effect of alkali on the coking rate. The decoking experiments indicated that alkali may improve the reactivity of the carbonaceous deposits, which in terms of the discussion above means a larger value of the critical residence time, τ_c. It is an open question whether this effect can be related simply to the improved steam adsorption causing an increased "virtual" steam pressure for the reaction.

TABLE 7
COKING ON VARIOUS SUPPORT MATERIALS*

Exp. no.	Support no.	Remarks	Correspond. catalyst	Coking rates k_c (μg/min)	t_o (min)
482	S1	$MgO(Al_2O_3)$, Mg/Al = 7/1	A22	60	7
487	S2	S1 sintered	A23	330	37
492	S3	$MgAl_2O_4$	B1	90	44
477	S4	ηAl_2O_3	C1	410	2
484	S5	S4 + 2.8 wt% K	(C6)	30	—
490	S6	αAl_2O_3	C5	184	40
491	S7	ZrO_2	D4	170	16
481	S8	SiO_2/Al_2O_3	D9	340	—

* Standard conditions: $H_2O/C = 2.0$, 750°C; hydrocarbon feed: *n*-heptane.

The experiments with metal-free supports (Table 7) showed no coking at a temperature level around that of the inlet layer of a tubular reformer. This may dispose of the principle of neutralizing the acidic sites of the catalyst (*6*) at these temperatures. At higher temperatures, the acidity strongly influences the cracking reactions and the coking rate.

It is apparent from (16) that coking should be retarded by high values of k_r, the rate constant for the gasification step. This is influenced by the heterogeneity of the surface and is diminished by the presence of alkali or the use of some carrier materials (*1*) as shown by the specific activities r_s listed in Tables 5 and 6. However, this effect is difficult to evaluate, as it is overlapped by other phenomena. First, it is difficult to vary only k_r in a series of catalyst samples. Secondly, it is not possible to calculate the selectivity for coking, because the coking experiments cannot be considered as being differential, and this will result in smaller coking rates for the most active catalysts as outlined earlier. Thirdly, the reaction in the basket is most probably affected by gas film diffusion resulting in a temperature drop across the gas film due to the endothermic reaction. The adiabatic temperature decrease by reaction to equilibrium at standard conditions was calculated to be 54°C, and it is evident that this may have influenced the results, as the temperature of the catalyst is determined by its activity:

$$T_s - T_o = \frac{r_w(-\Delta H)}{h \cdot a}, \qquad (18)$$

where:

T_s, T_o:	temperature of catalyst surface and bulk gas phase, respectively;
r_w:	reaction rate for reaction (1) per unit weight;
ΔH:	enthalpy of reaction;
h:	heat transfer coefficient;
a:	surface to weight ratio of catalyst bed.

The reaction rates of the various catalysts cannot be determined from the coking experiments, but the relative levels may be estimated from the ethane reforming experiments by r_i listed in Tables 5 and 6. The heat transfer effect may explain the substantial difference between coking rates for catalysts A3 and A4, differing only in nickel surface area and activity. These differences were provoked only by the use of two different activation procedures of samples from the same unreduced catalyst. Being the more active catalyst, A3 may have a lower catalyst surface temperature and thus a lower coking rate. A similar effect might have contributed to results reported in literature (*5, 6*).

The phenomenon may also play a role in

industrial reformers. For a normal tubular reformer for production of synthesis gas for the manufacture of ammonia (pressure 30 kg/cm^2, $H_2O/C = 3.8$ mole/atom, mass velocity 1.0 g/cm^2 sec) the temperature drop at a gas temperature of 500°C and a naphtha conversion level of 5% may be estimated to be approximately 10°C and less than 0.1°C for catalysts A22 and B4, respectively. For this calculation were used reaction rates estimated from the naphtha reforming experiments reported earlier (*1*), and the enthalpy of reaction was calculated by assuming 5% of the naphtha to be converted into the equilibrium mixture according to (2) and (3), considering inactive the remaining part of the naphtha. This assumption is justified by the results of Phillips *et al.* (*31*).

The presence of substantial amounts of carbon dioxide or hydrogen in the feed may cause a decrease of the enthalpy of reaction calculated as indicated, and may thereby result in a higher catalyst temperature. This may explain the marginal effects of carbon dioxide and hydrogen on the coking rate reported in Table 2.

A number of catalysts with poor specific activity showed very little or no coking. This may be ascribed to low values of the rate constant for adsorption k'_A, which may be influenced by surface heterogeneities (*1*) and the properties of the metal.

Thus, the result on the nickel–copper catalyst A13 is in accordance with previous observations (*2*) that showed only negligible formation of carbon when it was exposed to nearly pure methane at 500°C. The result was explained by methane, contrary to carbon monoxide, not being adsorbed on the alloy. The failing carbon formation on the sulphur poisoned A1 catalyst, which was in accordance with previous results in pure methane and carbon monoxide (*2*), may also be explained by restricted adsorption caused by the blockage of the nickel surface. Probably, the surface of the cobalt catalyst A14 was blocked by superficial oxidation as indicated earlier (*1*). In atmospheres containing no steam, coke from carbon monoxide and methane (*2*) and from olefins (*19*) was formed on cobalt as on nickel. The evaluation of the different behavior of the nearly inactive nickel catalysts D4 and D14 and of the very active catalysts C2 and C3, requires further investigation.

The alumina-based catalysts containing noble metals showed no coking, which is in accordance with the observations of Lobo and Trimm (*19*) in olefin atmosphere with no steam present. Due to this and the high activity of E8 and E12 the result cannot be related to low values of k'_A or high values of K_w. The different behavior of the noble metals might be related to reduced mobilities and solubility of carbon in the metal phase thus retarding the nucleation process, or to low values of the rate of reaction (8) caused by another composition of the surface radicals. Further studies are required to elucidate these effects.

Various Hydrocarbons

The results obtained with various hydrocarbons as feed shown in Table 3 may indicate that the initially formed hydrocarbon radicals rather than the CH_x-radicals are involved in the initial coking step (8). The coking rate from trimethyl butane being close to that of *n*-butane might reflect that trimethyl butane is decomposed to radicals resembling those originating from *n*-butane, whereas radicals containing more carbon atoms and being more strongly bound are formed during the terminal fission of the carbon–carbon bonds of the *n*-heptane molecule. The high coking rates from ethylene and benzene may indicate high values of k'_A and the existence of surface radicals favoring dimerization reactions. The low reactivity of benzene corresponds to a low value of k_H. The low coking rates of *n*-decane and *n*-dodecane may be explained by a higher value of k_H and probably by a lower adsorption rate caused by the smaller partial pressure of these heavier hydrocarbons at standard conditions.

The presence of a small amount of hydrocarbon radicals containing more than one carbon atom is not in conflict with the observations made previously (*1*) indicating paraffins to yield no higher hydrocarbons as products. As discussed previously (*1*), the existence of these radicals may vary from hydrocarbon to hydrocarbon, benzene showing less conversion into CH_x-radicals. Moreover, it was indicated that the amount of radicals with more than one carbon atom decreases with temperature, due to increased conversion into CH_x-radicals. This might explain the maximum in coking rate when increasing temperature as roughly indicated in Figs. 3 and 4.

CONCLUSIONS

The coking reactions during steam reforming of naphtha appear very complex, and this makes general conclusions doubtful when based on experiments with only a limited number of catalysts. The coking rate on the nickel surface at temperatures close to 500°C depends on steam-to-carbon ratio, temperature, the type of hydrocarbon, and the catalyst. The ability of the catalyst for steam adsorption appears important for depressing the formation of coke. This property may be improved by the presence of alkali or by use of magnesia as support. The preparation method for magnesia-based catalysts may influence significantly the ability for preventing formation of coke. Alkali appears to have no detectable effect on coking rates when steam is not present.

The gasification activity of the catalyst may change coking rates in various ways, the temperature decrease across the gas film surrounding the catalyst being an important parameter. No coking is observed over catalysts with poor activity or catalysts exposed to total sulphur poisoning.

The coking reaction at 500°C is not accompanied by poisoning of the nickel surface as reported for lower temperatures, where the surface is blocked by a film of carbonaceous residues. However, the pore mouths may be blocked and cause increased diffusion restrictions.

Coking on the support material is not detected at temperatures below 650°C. Above 700°C, cracking rates depend on the composition of the support. The acidic properties of the support appear critical, and the presence of alkali or the use of magnesia results in less coke. Again, the preparation method of magnesia appears important.

Tubular reformers operate with an axial temperature profile, where the temperature may increase 200°–400°C through the catalyst bed, and this introduces further implications. At the temperature range of the inlet layer, 450°–550°C, coking may occur only on the nickel surface. Whether carbon is deposited is determined by the process conditions and the properties of the catalyst as discussed above. However, depending on the activity of the catalyst, the reactivity of the feed, and the space velocity, a certain amount of the hydrocarbons may pass unconverted to the hotter part of the tube, where coking on the nickel surface is more critical. At temperatures close to 700°C, coking may result also from cracking on the support material, depending on its composition, or from thermal pyrolysis of the unconverted hydrocarbons. Even methane may form coke in this way as experienced in some reformers operating at extremely high throughputs (*4, 32*), or at conditions where the equilibrium gas is very close to having a positive affinity to formation of carbon by the decomposition of methane (*2, 33*). Sulphur poisoning may also cause coking in the hot part of the tube, the hydrocarbons passing through the deactivated inlet layer.

An effective catalyst for tubular reforming of naphtha should be able to depress coking from both routes. The use of alkali may improve steam adsorption and eliminate effectively the presence of acidic sites. However, the alkali results in a very small activity, implying that naphtha is passed to hotter parts of the tube, where coking becomes more critical. A catalyst based on active magnesia may show a high gasification activity, a smaller but still enhanced steam adsorption, and a low cracking activity of the support. Due to the high activity for gasification, the hydrocarbons are converted mainly in the colder part of the tube. Both principles have resulted in catalysts with proven industrial operability (*4, 34, 35*).

ACKNOWLEDGMENTS

The author thanks Dr. Haldor Topsøe for permission to publish this work. Thanks are given to Mrs. U. Ebert Petersen for her skillful and patient assistance in performing the experiments.

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