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Coke and Deactivation

I. Stoichiometry of Coke Formation in the Catalytic Reactions of *n*-Hexene on USHY

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Mechanistic studies of the reactions of *n*-hexene on USHY zeolite at 305° and 500°C show the presence of alkyl cyclopentenes as primary products of reaction. The presence of such species, which are potential intermediates in the dehydrogenation process of the surface species, indicates that the reaction process which produces mononuclear and polynuclear aromatic species found in "coke" and in trace amounts in the desorbed phase, begins with a cyclization reaction of a saturated carbenium ion, followed by sequential dehydrogenation of the cyclic surface species. Detailed stoichiometry of the initial reaction mechanism reveals that the initial material detected as coke contains a range of molecular sizes. Small-chain species dominate the spectrum, accounting for over 80 mol% of the initial coke. This results in an average initial coke molecule of $C_{5.1}H_{9.4}$.

INTRODUCTION

We have embarked upon a series of studies with the aim of gaining a better understanding of the deactivation phenomenon and the chemistry of coke formation which is common to zeolite catalysts involved in cracking reactions. To better understand how the presence of coke on the catalyst can inhibit the cracking reaction, the chemistry of the cracking reaction will be thoroughly examined while details of the coke-forming reactions will be followed by various techniques. In the first part of this study, the coke will be examined by stoichiometry.

n-Hexene was selected as a model reactant and kinetic and mechanistic studies were carried out at 305° and 500°C on USHY zeolite. These results at different temperatures, in conjunction with those previously reported from this laboratory (*1*, *2*) at 350° and 405°C and by others (*3–5*) using *in situ* FTIR, present a broad picture of the reactions of this olefin on USHY zeolite.

The reaction mechanism, proposed by Abbot and Wojciechowski (*1*, *2*) for the reactions of *n*-hexene, involves the formation of a carbocation by protonation of the C=C by a surface Brønsted acid site of the catalyst. The resulting carbenium ion can then undergo methyl and hydride rearrangement reactions via a cyclopropyl transition state. Furthermore, the carbenium ion can oligomerize with other olefins present, including *n*-hexene. These oligomers can then undergo rearrangement and cracking reactions by the same reaction pathway.

The above mode of initiation is further supported by the *in situ* FTIR studies mentioned above. Eisenbach and Gallei (*5*) have shown that the protonation of the double bond can occur at ambient temperatures, evidence which suggests that protonation is a facile event. Their observations of tertiary C–H stretching bands and the ratio of CH_2 to CH_3 peak intensities indicate that primary carbenium ions are not formed in detectable quantities. The hydrocarbon adsorption bands at 300°C, observed by

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Blackmond and Goodwin (*3*), indicate that methyl shifts of the formerly linear surface species take place.

In situ studies also report the detection of an adsorption peak at ca. 1600 cm^{-1} which has been assigned to "coke." Systematic IR studies by Unger and Gallei (*6*) and earlier by Haldeman and Botty (*7*) on various activated carbon and soot samples have resulted in assignment of this peak to the C=C stretching vibrations of microcrystalline graphitic carbon structures which are present in polynuclear aromatic compounds. An observation common to all authors was that intermediates in the process of coke formation, such as saturated or partially dehydrogenated cyclics, were not observed and that the growth of the coke peak at 1600 cm^{-1} was the only indication of the coking process. Ghosh and Kydd (*8*) observed the same phenomena using propene as the reactant for *in situ* studies. Because this coke peak appeared without the observation of cyclic intermediates, one of the main conclusions drawn from these studies is that dehydrogenation of the feed to polynuclear aromatic coke occurs without cyclic intermediates (*3–5, 8*). Furthermore it is suggested in these studies that the coke is so highly dehydrogenated that few, if any, aromatic protons remain.

In this, the first part of a series of coke and deactivation studies, we will confirm the mechanism of reaction of *n*-hexene on USHY as described above, determine from stoichiometry and material balances the composition of the initial species which form coke, and present evidence to dispute the conclusion that dehydrogenation of the surface species to polynuclear aromatic coke occurs without partially dehydrogenated intermediates.

THEORY

A theoretical treatment of the decline in catalyst activity with time on stream, t_f, has furnished a sound methodology for the study of reactions on rapidly decaying catalysts (*9, 10*). For each reaction product, the time average yield sampled for $t = 0$ to t_f is plotted against integral conversion, $\overline{X}_R$. These plots can be enveloped by a single curve, the optimum performance envelope (OPE), which describes the selectivity behavior of a particular product in the limit as conversion approaches zero. A product is considered primary if the slope at the origin of such a plot is nonzero and secondary if this slope is zero. A primary product is thus one which is formed directly from the feed molecule without any detectable gas-phase intermediates in the reaction pathway.

EXPERIMENTAL

1-Hexene of 96.357% purity obtained from Aldrich was used without further purification. The major impurities were 2-ethyl-1-butene (1.6941%), 2- and 3-hexene (0.8860%), *n*-hexane (0.8197%), and 1-octene (0.1538%). Other trace impurities were propene, isobutene, methyl pentenes, heptenes, hexadienes, and methylcyclopentenes. These impurities constituted 0.0894% of the feed.

The catalyst, USHY, was prepared from NaY (BDH Chem., Lot. No. 45912, 13Y SK40) by repeated exchange of the catalyst with ammonium nitrate solution. Between exchanges, the catalyst was dried at 110°C for 24 h, then calcined at 500°C for 2 h. After the last exchange, the catalyst was steamed for 24 h at 200°C. The degree of exchange of the catalyst was found to be 99.7%. The bulk Si/Al ratio was determined by neutron activation analysis to be 3.3, while the framework ratio, determined by ^{29}Si MAS-NMR, was found to be 12.00. Integral reaction runs were carried out in an isothermal, plug flow reactor. Mass balances were conducted on each run and were 100 ± 2%. The specific details of the experimental apparatus and procedures have been described elsewhere (*11*).

Products, which were liquid at room temperature, were analyzed by a Varian 6000 gas chromatograph with a 60-m SE54 capillary column and flame ionization detector. Products up to C_7 eluted at 0°C, followed by a 5°C/min ramp to 300°C. Gaseous products were analyzed by a Carle SX1156 gas chromatograph, enabling the determination of the yields of all hydrocarbons in the range C_1 to C_4 and the direct determination of hydrogen, when present. The identification of products was facilitated by the use of a Finnigan 1020 automated GC/MS.

RESULTS AND DISCUSSION

Selectivity

Table 1 presents the initial molar selectivities, corrected for volume (mole number) expansion, for all products found at the two temperatures studied here and in two previous studies at 350° and 405°C (*1*, *2*). Coke selectivities are given in terms of weight. Surprisingly, between 350° and 500°C, the selectivities for the various products change very little. Only at the lowest temperature of 305°C do the selectivities show significant change, due to a dramatic increase in coke selectivity. It should be noted that at 305°C, integral conversions of less than 1% were studied. The attainment of such low conversions made identification of primary and secondary products easier, but seems to involve conditions under which the system is in a transient with respect to surface species. This transient will be dealt with later in this paper. At higher temperatures, this transient was not detected since the lowest integral conversion obtained was 8% and the system apparently reaches steady state before that point.

Interestingly enough some of the secondary products at 305°C are observed to be primary products at higher temperatures. These changes in the nature of the product are the result of the relative stability of intermediate surface species at various temperatures. Recall that the definition of a primary product (*9*) is "one which is formed from the feed with no detectable gas-phase intermediate". Thus there may exist a series of surface intermediates in the reaction pathway from feed to detectable product. At the lower temperature, these species are

TABLE 1

Molar Selectivities for Products

Product	Temperature (°C) 500	405	350	305
Hydrogen	(s)	—	—	—
Methane	(s)	—	—	—
Ethane	(s)	(s)	—	—
Ethene	(s)	(s)	—	—
Propane	0.010	0.021	0.017	(s)
Propene	0.015	0.005	0.005	0.031
2-Methylpropene	0.031	0.006	0.003	(s)
2-Methylpropane	0.018	(s)	0.003	0.036
Butane	(s)	(s)	(s)	(s)
t-2-Butene	0.008	0.001	(s)	(s)
c-2-Butene	0.006	0.002	(s)	(s)
3-Methyl-1-butene	0.001	—	—	(s)
2-Methylbutane	(s)	(s)	0.003	0.006
1-Pentene	0.001	0.001	(s)	0.004
2-Methyl-1-butene	0.003	0.002	(s)	0.003
Pentane	(s)	(s)	(s)	(s)
t-2-Pentene	0.004	0.002	0.002	(s)
c-2-Pentene	0.002	0.001	(s)	(s)
2-Methyl-2-butene	0.003	0.006	0.007	0.002
4-Methyl-1-pentene	(s)	—	—	—
3-Methyl-1-pentene	0.045	0.038	0.028	0.036
c-4-Methyl-2-pentene	0.022	0.010	0.015	0.016
t-4-Methyl-2-pentene	0.068	0.038	0.036	0.007
2-Methyl-1-pentene	0.102	0.105	0.053	0.029
2-Ethyl-1-butene	(s)	(s)	(s)	—
2-Methyl-2-pentene	0.219	0.260	0.279	0.046
c-3-Methyl-2-pentene	0.232	0.240	0.256	0.232
t-3-Methyl-2-pentene	0.116	0.200	0.200	0.093
3,3-Dimethyl1butene	(s)	—	—	—
2,3-Dimethyl1butene	0.007	0.004	0.007	0.002
2,3-DiMethyl2butene	0.010	0.008	0.009	0.003
2,3-DiMethyl butane	0.002	(s)	(s)	(s)
2-Methyl pentane	0.020	(s)	0.030	0.023
3-Methyl pentane	0.015	0.025	(s)	(s)
Hexane	(s)	(s)	(s)	0.068
Methylcyclopentene	0.007	*	*	0.009
C_7H_{14}	0.010	0.010	0.016	0.019
C_7H_{16}	0.002	*	*	0.013
C_8H_{16}	0.023	0.005	0.005	0.062
C_8H_{18}	0.002	*	*	0.006
C_9H_{18}	trace	0.001	0.006	0.005
Aromatics	(s)	(s)	trace	trace
Coke	0.010	0.007	0.020	0.240
Total	1.012	0.998	1.001	1.001

Note. (*) Denotes a product not separated from corresponding olefin. (s) denotes a secondary product. Coke selectivities are weight selectivities.

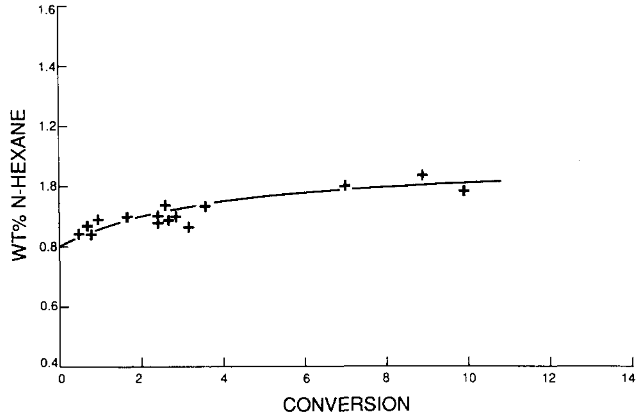


FIG. 1. Selectivity plot for *n*-hexane. Reaction conditions: 305°C; $45 < S/V < 9600$ g/g/h. Each data point represents the weight percent of *n*-hexane found in the products from a single integral conversion run. Selectivity is obtained from the slope of this yield versus integral conversion curve.

stable and accumulate on the surface or may even desorb, thus "delaying" the formation of the final product and giving it the characteristics of a secondary product. At higher temperatures, the lifetime of the intermediate is such that no significant accumulation occurs and the final product appears as primary.

There are two products which do not follow the above pattern, 2-methylbutane and *n*-hexane. Both appear as primary products at the lower temperatures, while they are observed as secondary products at higher temperatures. In addition, the hexane selectivity plot at 305°C is unusual in that its selectivity, the slope of the yield versus conversion plot in Fig. 1, continually decreases from its initial value in the first 4% of conversion. In the past (*1*, *11*), it has been reported that paraffins are primary plus secondary products of catalytic cracking. The unstable nature of *n*-hexane in addition to its unusual temperature behavior, suggests that it is partially formed via a mechanism other than the normal hydrogen transfer route, and that this mechanism is suppressed after only a few percent conversion. It is not completely clear whether this mechanism occurs at the higher temperatures, since conversions below 8% were not attainable with the experimental apparatus under those conditions.

An important initial product, which has a hydrogen-to-carbon (H/C) ratio which falls between that of the reactant, *n*-hexene, and an aromatic molecule, has been observed at both 305° and 500°C. The pressence of this product, methylcyclopentene, suggests that the reaction pathway from *n*-hexene to an aromatic species begins with a cyclization reaction. If the initial step was a dehydrogenation step, followed by a cycloaddition reaction such as the Diels–Alder reaction, then cyclo-olefins, as well as acyclic diolefins and triolefins, would be expected to appear in the desorbable products. The absence of such species and the presence of methylcyclopentene as a primary product suggests that the first step in the aromatization process is the cyclization of an acyclic, saturated, carbenium ion. The detailed mechanism of the formation of this important product, as well as minor product analyses which support this interpretation, will be outlined in a subsequent paper.

The above conclusion is in contradiction to that drawn by the *in situ* FTIR studies mentioned previously. There, no partially dehydrogenated cyclic intermediates were observed. The adsorbed olefins appeared to "collapse" into highly dehydrogenated, polynuclear aromatic species. One possible reason for the contradiction of results could be that the intermediate cyclic species in the dehydrogenation process never build up a significant surface or gas-phase concentration for their detection by FTIR. Since the detection limits of an *in situ* FTIR apparatus studying reactions occurring on a solid surface are not well established, such studies may have only been able to detect the end products of the dehydrogenation process which would be present in significant quantities. It should also be noted that the *in situ* studies did not detect mononuclear aromatics, which have been detected as trace products between 305° and 405°C, and as significant secondary products at 500°C.

Mechanism of Reaction

(*i*) *Skeletal isomerization.* The basic mechanism proposed by Abbot and Wojciechowski (*1*) for the skeletal isomerization of *n*-hexene has been modified to include the results under the new conditions. At 500°C, two new skeletal isomers are observed, 4-methyl-1-pentene and 3,3-dimethyl-1-butene. Both are secondary products and appear only at very high conversions. This is taken as an indication that the transition states required for their formation directly from the feed are difficult to achieve and are therefore likely the result of the readsorption of a primary product such as 4-methyl-2-pentene. The updated mechanism for skeletal isomerization outlined in Table 2 includes these two new products. The twelve possible skeletal isomers observed at 500°C represent all possible rearrangement products of *n*-hexene.

(*ii*) *Dimerization cracking.* The product distribution obtained in our studies can be explained by a dimerization-cracking process since, even at 500°C, C_1 and C_2 species are not observed as initial products, while C_4 and C_5 species are. The cracking reaction mechanism proposed by Abbot and Wojciechowski (*1*) for the reactions of *n*-hexene at 350° and 405°C was found to describe adequately the two new reaction conditions being reported here.

The product distribution indicates that *n*-hexene, and therefore the hexyl carbenium ion, is quite resistant to β scission. The total molar selectivity for cracking by mono- and bimolecular processes is only 15% at 500°C. This contrasts sharply with an initial cracking selectivity of over 85% for *n*-hexane under the same reaction conditions (*12*). It seems that β scission of the hexyl carbenium ion is much more difficult than the cracking of the corresponding carbonium ion by direct protolysis of the C–C bond. This is easily rationalized when we consider that upon protonation of a *n*-hexene molecule, the cationic centre can be on either the second or the third carbon of the carbocation. With the cationic centre on the third carbon, β scission cannot occur, while if it is located on the second carbon β scission involves the transfer of a hydrogen atom from a primary to a secondary position, an unlikely occurrence.

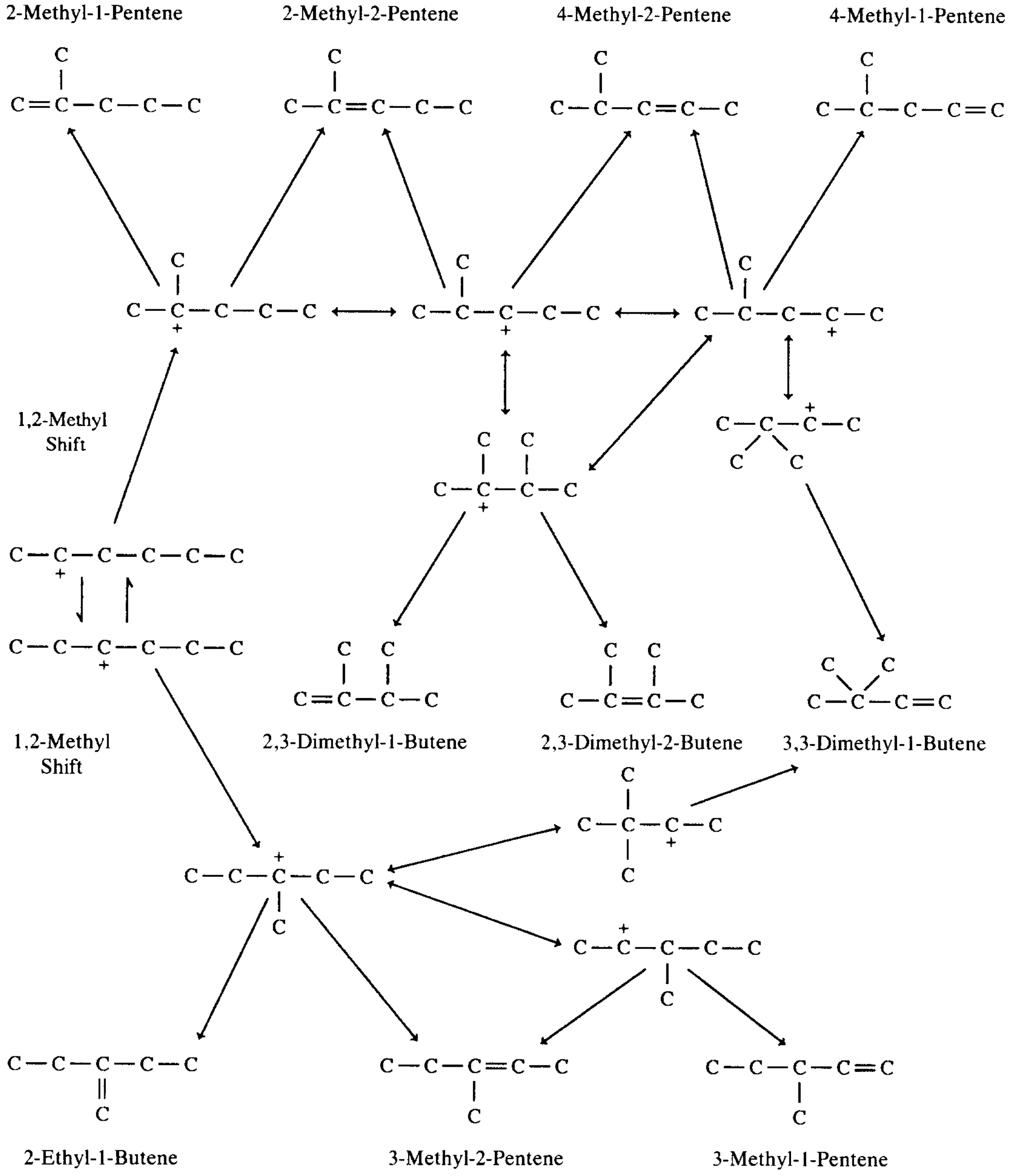
Initial Reaction Stoichiometry

(*i*) *Volatile products.* Table 3 presents the initial molar selectivity ratios for the stoichiometric olefin pairs C_7/C_5, C_8/C_4, and C_9/C_3 at the various temperatures. The C_9/C_3 ratio is less than 1 for all temperatures, indicating that the C_9 carbenium ion is unstable at all temperatures and readily undergoes β scission rather than desorption. For the C_7 and C_8 olefins, this instability occurs only at the higher temperatures. In order to relate the significance of this observation to coke formation, the possible combinations of surface and gas-phase olefinic primary products (excluding the C_9 and C_3 pair) from a dimer of *n*-hexene are listed in Table 4. Only the results at 305°C will be considered now, since it is only at this temperature that coke selectivity is great enough to allow such detailed consideration.

At 305°C, C_4 olefins are not observed initially in the gas phase. Therefore, processes

TABLE 2

Mechanism for the Skeletal Isomerization of *n*-Hexene



Reaction path	Products	Reaction path	Products
1 Methyl shift	3-Methyl-2-Pentene 2-Methyl-1-Pentene 2-Methyl-2-Pentene 2-Ethyl-1-Butene	1 Methyl shift	4-Methyl-1-Pentene
		2 Hydride shifts	2,3-Dimethyl-l-Butene-2-Butene
		1 Methyl 1 Hydride and 1 Methyl shift	3,3-Dimethyl-l-Butene
1 Methyl and 1 Hydride shift	4-Methyl-2-Pentene 3-Methyl-1-Pentene		

TABLE 3

Initial Olefin Product Selectivity Ratios

Ratio	500°	405°[a]	350°[a]	305°
C_9/C_3	0.0000	0.0504	0.2455	0.2682
C_8/C_4	0.7108	0.5408	0.8125	$+\infty$
C_7/C_5	0.7249	0.9421	1.3115	2.2376

[a] Values calculated from Ref. (*1*) with selectivities corrected for volume expansion.

1(ii), 1(iii), and 2(i) to 2(vi) inclusive (Table 4) do not occur. The preferred routes of formation for the initial products are therefore processes 1(i), 1(iv), 1(v), and 2(vii). The excess of initial C_7 olefins over C_5 olefins, as indicated by the ratio of their molar selectivities from Table 3, indicates that reaction 1(v) is more important than 1(iv) since the other active process, 1(i), produces C_7 and C_5 olefins in a 1-to-1 ratio. Thus it appears that the tendency, as conversion goes to zero at 305°C, is to leave the shorter fragment on the surface, which will then be detected as coke. This is believed to be so for reaction 1(v) and it takes place in all certainty for reactions 2(i) to 2(vi) since C_8 olefins are initial products at this temperature, while the corresponding C_4 olefins are absent. Table 4 summarizes these conclusions.

Further support for the above suggestion that the initial species which go to form coke are the shorter species comes from the various product yields. Figure 2 shows how the integral yield of stoichiometric partner olefins, C_7/C_5 and C_8/C_4, desorbed from the catalyst surface and found in the gas phase varies with integral conversion. Despite the scatter in the data, the product yield ratios are seen to decrease from the ratio of their initial selectivities to less than 1 at around 10% integral conversion. If both fragments of the disproportionation reaction had equal probability of desorption, these ratios would be expected have a value of 1. Since the larger species can also undergo further scission, the ratios are expected to be less than 1 at high conversion. The observation that these ratios are greater than 1 at low conversions suggests that under these conditions the surface retains a high concentration of adsorbed, short-chained species. As the surface reaches steady state with respect to the population of these species, it begins to release both fragments of β scission with equal probability.

TABLE 4

Desorption Combinations for Olefin Products of β Scission

		Occurs at 305°C
1. $[C_{12}H_{24}] \rightarrow$ C5(s) + C7(s)	(i) $\rightarrow$ C7(g) + C5(g)	Yes
	(ii) $\rightarrow$ C4(g) + C3(g) + C5(g)	No
	(iii) $\rightarrow$ C4(g) + C5(g) + C3(k)	No
	(iv) $\rightarrow$ C3(g) + C5(g) + C4(k)	Yes
	(v) $\rightarrow$ C7(g) + C5(k)	Yes
2. $[C_{12}H_{24}] \rightarrow$ C4(s) + C8(s)	(i) $\rightarrow$ C8(g) + C4(g)	No
	(ii) $\rightarrow$ C5(g) + C3(g) + C4(g)	No
	(iii) $\rightarrow$ 3 C4(g)	No
	(iv) $\rightarrow$ C4(g) + C5(g) + C3(k)	No
	(v) $\rightarrow$ 2 C4(g) + C4(k)	No
	(vi) $\rightarrow$ C3(g) + C4(g) + C5(k)	No
	(vii) $\rightarrow$ C8(g) + C4(k)	Yes

Note. (s) denotes a surface intermediate. (g) denotes a species which has desorbed. (k) denotes a species detected as coke.

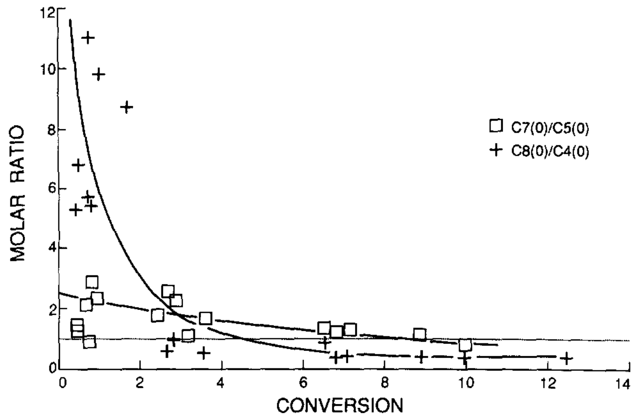


FIG. 2. Molar ratio of integral yields of stoichiometric partner species. Reaction conditions as per Fig. 1. C7(O)–C_7 olefins; C5(O)–C_5 olefins; C8(O)–C_8 olefins; C4(O)–C_4 olefins.

(*ii*) *Initial coke.* Consider the reaction of 1 mol of reactant, *n*-hexene, to products found in two "phases," coke (k) and gas (g), and having the stoichiometry

$$R \rightarrow n_k K + n_g G,$$

where n_k is moles of K (coke products) formed per mole R reacted and n_g is moles of G (gaseous products) formed per mole R reacted.

By combining carbon and hydrogen molar and mass balances with the above stoichiometry and the definition of selectivity, an equation results which we will use to calculate the average molecular weight of the species initially found in the coke phase. The mathematical development is detailed in Appendix A to this paper.

By using the initial selectivity data from the experimental results obtained at 305°C combined with the (H/C) ratios of the initial products in the gas phase and of the coke (Fig. 3), the average molecular weight of the species found in the initial coke is found to be 70.4. This, combined with an initial coke (H/C) ratio of 1.85 (Fig. 3) gives an average coke formula of $C_{5.1}H_{9.4}$ (see Appendix A for details). This analysis supports the results of the stoichiometry of the volatile products mentioned in the previous section which suggested that, at low conversions, the tendency is for the short-chain species of the dimerization-cracking reaction to remain on the surface. Here we find that the average chain length of the initial coke species is about 5, and that it is slightly dehydrogenated compared to the feed. Previously published studies have also found that the initial coke has a (H/C) ratio which is very close to that of the reactant (*3, 13, 14*). The ratio obtained here agrees with the observation that at this temperature excess paraffins appear as primary products, while only very small (and insufficient) amounts of dehydrogenated olefins (namely methylcyclopentenes) are primary and available to close the (H/C) balance. As a result, the (H/C) ratio of the initial products found in the gas phase is 2.07. The dehydrogenated initial coke thus provides

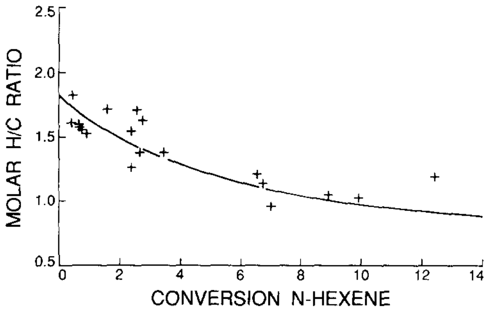


FIG. 3. Effect of conversion on (H/C) molar ratio in coke (305°C). Reaction conditions as per Fig. 1.

TABLE 5

Mechanism at 305°C

1.	C_6H_{12}	$\rightarrow 2\ C_3H_6$
	$C_6H_{12} + C_6H_{12}$	$\rightarrow C_3H_6 + [C_9H_{18}]$[a] $\rightarrow 4\ C_3H_6$
		$\rightarrow C_3H_6 + \{C_4H_8\}$[b] $+ C_5H_{10}$
2.		$\rightarrow C_3H_6 + C_9H_{18}$
3.		$\rightarrow C_4H_8 + C_8H_{16}$
4.		$\rightarrow C_5H_{10} + C_7H_{14}$
5.		$\rightarrow C_6H_{10} + C_6H_{14}$[c]
6.		$\rightarrow C_8H_{18} + \{C_4H_6\}$
7.		$\rightarrow C_7H_{16} + \{C_5H_8\}$
8.		$\rightarrow C_6H_{14} + \{C_6H_{10}\}$
9.		$\rightarrow C_5H_{12} + \{C_7H_{12}\}$
10.		$\rightarrow C_4H_{10} + \{C_8H_{14}\}$
11.		$\rightarrow C_7H_{14} + \{C_5H_{10}\}$
12.		$\rightarrow C_8H_{16} + \{C_4H_8\}$
13.		$\rightarrow$ Coke
14.	C_6H_{12}	$\rightarrow C_6H_{12}$ isomers

[a] $[C_nH_m]$ denotes an unstable species which undergoes further cracking reaction.

[b] $\{C_nH_m\}$ denotes species of unknown structures, left on the surface and detected as coke.

[c] C_6H_{10} in reaction (5) is methylcyclopentene.

the excess hydrogen used to saturate the initial gas-phase products.

The initial coke can be further investigated by considering the details of the stoichiometric balances (Table 5) necessary to explain the observed gas-phase products and the products which were anticipated by the proposed mechanism but not observed in the gas phase. Any product required to balance the presence of a stoichiometric partner species which is absent or present in insufficient quantity is assumed to be on the surface as a constituent of the coke. Stoichiometric balances 6 through 13 of Table 5 predict such "missing" primary products. Their missing selectivities are listed in Table 6. It is noted that this approach agrees with the observed tendency of the shorter fragments to be the chief initial species which lead to coke.

The weight selectivity of the missing products is somewhat less than the experimental weight selectivity for coke. The difference comes from two sources; experimental error and/or some *n*-hexene being irreversibly adsorbed and included in the coke selectivity. If we chose the latter explanation, then the (H/C) ratio of the missing products plus the irreversibly adsorbed *n*-hexene is 1.82 (see Appendix A, Part 2). This compares quite well with the experimentally determined value for the coke of 1.85.

TABLE 6

"Missing" Products Assumed to be in Coke

Species	$\mathcal{S}_i$	S_i	mole%
C_4H_6	0.0056	0.0036	2.6
C_4H_8	0.0617	0.0411	28.7
C_5H_8	0.0126	0.0102	5.9
C_5H_{10}	0.0107	0.0089	5.0
C_6H_{10}	0.0819	0.0799	38.0
C_7H_{12}	0.0061	0.0070	2.8
C_8H_{14}	0.0362	0.0474	16.9
Totals	0.2148	0.1981	

Note. $\mathcal{S}_i$ is the molar selectivity of *i*th species; S_i is the corresponding weight selectivity.

It is obvious from the above analysis that even the initial coke is composed of a wide range of species. Ultimately, the object of our coking and deactivation studies is to find a link between "coke" or some portion of coke and the catalyst's ability to carry out cracking reactions. The total weight of coke is often used as an indication of the catalyst activity; however, there is much evidence to suggest that this is an empiricism. Levinter *et al.* (*18*), in a series of coking studies, demonstrated that what was more important to catalyst activity than the amount of coke on the catalyst was the manner in which it was deposited. Abbot and Wojciechowski (*13*) showed that for *n*-hexadecane on USHY and a given set of reactions conditions, the yield of coke per gram of catalyst was similar at 300° and 400°C, and yet catalyst aging occurred much more rapidly at the lower temperature. Others have also reached a similar conclusion (*17*). It is hoped that the detailed composition and chemistry of the species found in coke, while more difficult to analyze, will allow better insights into the nature of coke and its relationship to catalyst activity.

There is some other published evidence to support these observations that small olefins are significant contributors to coke (*15*, *16*). It is obvious that these species are resistant to cracking, and will likely oligomerize rapidly. At some point, a cyclization reaction can occur. From that point on, dehydrogenation reactions can also occur, saturating would-be olefins and causing the (H/C) ratio of the surface to decrease, as seen in Fig. 3. This process causes the surface species to take on the highly aromatic nature which is often reported.

Although the detailed analysis carried out on data from 305°C can not be extended to the higher temperatures due to the very small selectivity of the coke there, the constancy of the primary reaction selectivities and hence product distributions suggests that the same processes occur throughout the temperaure range. Thus coke-forming reactions at higher temperatures are not expected to differ from those studied in detail here in anything but rate.

CONCLUSIONS

The initial coke formed directly from *n*-hexene, at 305°C, has been shown to consist of a wide variety of species which result mainly from the dimerization-cracking mechanism of *n*-hexene. By combining the detailed stoichiometric relationships of the proposed mechanism with experimentally determined selectivities and (H/C) ratios, the initial coke was found to have an average formula of about C_5H_9, suggesting that short-chained species are significant contributors to the initial coke. The constancy of the primary reactions over the 200°C range examined, suggests that coke formation at higher temperatures occurs by a similar process, differing only in rate.

The presence of methyl cyclopentenes as primary products at both 305° and 500°C, suggests that the dehydrogenation process of the surface species is initiated by a cyclization reaction of a saturated carbenium ion.

APPENDIX A

Part I

Consider 1 mol of reactant, R, going to products found in two "phases," coke phase (k) and gas phase (g), with stoichiometry

$$R \rightarrow n_k K + n_g G,$$

where n_i represents moles of species in ith phase.

Carbon and hydrogen atomic balances are

$$(C)_R = n_k(C)_k + n_g(C)_g \qquad (1)$$

$$(H)_R = n_k(H)_k + n_g(H)_g, \qquad (2)$$

where $(C)_i$ is the number of carbon atoms per average molecule in ith phase and $(H)_i$ is the number of hydrogen atoms per average molecule in ith phase.

Dividing Eq. (2) by Eq. (1) gives

$$\left(\frac{H}{C}\right)_R = \frac{n_\mathrm{k}(H)_\mathrm{k}}{n_\mathrm{k}(C)_\mathrm{k} + n_\mathrm{g}(C)_\mathrm{g}} + \frac{n_\mathrm{g}(H)_\mathrm{g}}{n_\mathrm{k}(C)_\mathrm{k} + n_\mathrm{g}(C)_\mathrm{g}}. \tag{3}$$

Define the following *carbon* selectivity parameters:

Let $\mathcal{F}_i$ be the corrected mole fraction of carbon in the ith phase. Therefore,

$$\mathcal{F}_i = \frac{n_i(C)_i}{n_\mathrm{k}(C)_\mathrm{k} + n_\mathrm{g}(C)_\mathrm{g}}$$

$$\text{and } \mathcal{F}_\mathrm{k} + \mathcal{F}_\mathrm{g} = 1. \tag{4}$$

Rearranging Eq. (4) gives

$$\frac{\mathcal{F}_i}{n_i(C)_i} = \frac{1}{n_\mathrm{k}(C)_\mathrm{k} + n_\mathrm{g}(C)_\mathrm{g}}. \tag{5}$$

Substituting into Eq. (3) yields

$$\left(\frac{H}{C}\right)_R = \mathcal{F}_\mathrm{k}\left(\frac{H}{C}\right)_\mathrm{k} + \mathcal{F}_\mathrm{g}\left(\frac{H}{C}\right)_\mathrm{g} \tag{6}$$

Corrected molar selectivities can be obtained from weight selectivity data, provided the fractional change in number of moles is available. Thus,

$$\mathcal{F}_\mathrm{k} = \begin{pmatrix}\text{wt selectivity for}\\ \text{carbon in coke}\end{pmatrix} \left(\frac{\text{wt carbon/mol } R}{\text{wt carbon/mol } k}\right) \begin{pmatrix}\text{fractional}\\ \text{mole change}\end{pmatrix} = F_\mathrm{k}^\mathrm{c}\left(\frac{72}{\overline{\mathrm{MW}}_\mathrm{k}^\mathrm{c}}\right)\varepsilon_\mathrm{k}, \tag{7}$$

where

ε_k = (moles product k per mole R reacted) − 1

F_k^i = (wt of i in k)/(wt of R converted)

$\overline{\mathrm{MW}}_\mathrm{k}^\mathrm{c}$ = wt of carbon in coke per mole of coke.

Substituting Eq. (7) into Eq. (6) and rearranging gives

$$\overline{\mathrm{MW}}_\mathrm{k}^\mathrm{c} = \frac{72(H/C)_\mathrm{k}F_\mathrm{k}^\mathrm{c}\varepsilon_\mathrm{k}}{(H/C)_\mathrm{R} - \mathcal{F}_\mathrm{g}(H/C)_\mathrm{g}}. \tag{8}$$

We would like to have Eq. (8) in terms of the coke molecular weight, $\overline{\mathrm{MW}}_\mathrm{k}$, and its total weight selectivity, F_k. The total coke weight selectivity is

$$F_\mathrm{k} = F_\mathrm{k}^\mathrm{c} + F_\mathrm{k}^\mathrm{H}, \tag{9}$$

where F_k^c and F_k^H are the weight selectivities for carbon and hydrogen in the coke respectively.

The coke (H/C) ratio is

$$\left(\frac{H}{C}\right)_\mathrm{k} = 12\,\frac{F_\mathrm{k}^\mathrm{H}}{F_\mathrm{k}^\mathrm{c}}. \tag{10}$$

Solving Eq. (10) for F_k^H, substituting into Eq. (9), and then solving for F_k^c,

$$F_\mathrm{k} = F_\mathrm{k}^\mathrm{c}\left(1 + \frac{1}{12}\left(\frac{H}{C}\right)_\mathrm{k}\right). \tag{11}$$

Similarly, the average molecular weight of the coke is related to the carbon average molecular weight, $\overline{\mathrm{MW}}_\mathrm{k}^\mathrm{c}$.

$$\overline{\mathrm{MW}}_\mathrm{k} = \overline{\mathrm{MW}}_\mathrm{k}^\mathrm{c}\left(1 + \frac{1}{12}\left(\frac{H}{C}\right)_\mathrm{k}\right). \tag{12}$$

Substituting Eqs. (11) and (12) into Eq. (8) and rearranging gives

$$\overline{\mathrm{MW}}_\mathrm{k} = \frac{72(H/C)_\mathrm{k}F_\mathrm{k}\varepsilon_\mathrm{k}}{(H/C)_\mathrm{R} - \mathcal{F}_\mathrm{g}(H/C)_\mathrm{g}}. \tag{13}$$

We now require an expression for ε_k. Let $\mathcal{F}_\mathrm{k}^*$ equal the uncorrected molar selectivity for carbon in the coke. Then,

$$\mathcal{F}_\mathrm{k}^* = F_\mathrm{k}^\mathrm{c}\left(\frac{72}{\overline{\mathrm{MW}}_\mathrm{k}^\mathrm{c}}\right)$$

and

$$\varepsilon_\mathrm{k} = \frac{\mathcal{F}_\mathrm{k}^*}{\mathcal{F}_\mathrm{k}} = \frac{72\,F_\mathrm{k}^\mathrm{c}}{\overline{\mathrm{MW}}_\mathrm{k}^\mathrm{c}\,\mathcal{F}_\mathrm{k}}. \tag{14}$$

Using Eqs. (11) and (12), we obtain

$$\varepsilon_\mathrm{k} = \frac{72\,F_\mathrm{k}}{\overline{\mathrm{MW}}_\mathrm{k}\,\mathcal{F}_\mathrm{k}}. \tag{15}$$

Recalling from Eq. (4) that $\mathcal{F}_\mathrm{k} + \mathcal{F}_\mathrm{g} = 1$, substituting Eq. (15) into Eq. (13), and rearranging we obtain

$$\overline{\mathrm{MW}}_{\mathrm{k}} = \left[\frac{5184(H/C)_{\mathrm{k}}(F_{\mathrm{k}})^2}{\{(H/C)_R - \mathcal{F}_{\mathrm{g}}(H/C)_{\mathrm{g}}\}\{1 - \mathcal{F}_{\mathrm{g}}\}}\right]^{1/2}. \quad (16)$$

Substituting the initial data obtained from the experiments conducted at 305°C,

$$(H/C)_R = 2.00 \qquad \mathcal{F}_{\mathrm{g}} = 0.7510$$

$$(H/C)_{\mathrm{g}} = 2.07 \qquad F_{\mathrm{k}} = 0.2398,$$

$$(H/C) = 1.85$$

gives

$$\overline{\mathrm{MW}}_{\mathrm{k}} = 70.4.$$

Using the initial $(H/C)_{\mathrm{k}}$, we determine $\overline{\mathrm{MW}}^{\mathrm{c}}_{\mathrm{k}}$, which gives an average initial coke molecule of

$$\mathrm{C}_{5.09}\mathrm{H}_{9.42}.$$

Part II: Detailed Breakdown of Initial Coke

Consider the detailed mechanisms of reaction in Table 5 and the corresponding selectivities of Table 1. The products of dimerization reactions listed in Table 6 are either missing or present in inadequate amounts compared with their stoichiometric partner species.

The average hydrogen-to-carbon ratio of the missing products is calculated as

$$\left(\frac{H}{C}\right) = \sum \left(\frac{H}{C}\right)_i \mathcal{S}_i = 1.79,$$

where $\mathcal{S}_i$ is the molar selectivity of ith species from Table 6.

The weight selectivity of the missing products is less than the experimentally determined coke selectivity. If we make up this difference with n-hexene, the (H/C) ratio of the missing products becomes

$$\left(\frac{H}{C}\right) = \frac{\begin{pmatrix}\text{total molar selectivity}\\ \text{missing products}\end{pmatrix}(H/C)\ \text{missing} + \begin{pmatrix}\text{molar selectivity}\\ \text{feed, } R\text{, in coke}\end{pmatrix}(H/C)_R}{(\text{total molar selectivity of coke})}$$

$$\left(\frac{H}{C}\right) = \frac{0.2148\ (1.79) + 0.0342\ (2.00)}{0.2490}$$

$$= 1.82.$$

This compares quite well with the experimentally determined (H/C) ratio of the coke (1.85).

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REFERENCES

1. Abbot, J., and Wojciechowski, B. W., *Canad. J. Chem. Eng.* **63,** 278 (1985).
2. Abbot, J., and Wojciechowski, B. W., *Canad. J. Chem. Eng.* **66,** 817 (1988).
3. Blackmond, D. G., and Goodwin, J. G., Jr., *J. Catal.* **78,** 34 (1982).
4. Blackmond, D. G., Goodwin, J. G., and Lester, J. E., *J. Catal.* **78,** 247 (1982).
5. Eisenback, D., and Gallei, E., *J. Catal.* **56,** 377 (1979).
6. Unger, K., and Gallei, E., *Erdoel Kohle Erdgas Petrochem.* **29**(9), 403 (1976).
7. Haldeman, R. G., and Botty, M. C., *J. Phys. Chem.* **63,** 489 (1959).
8. Ghosh, A. K., and Kydd, R. A., *J. Catal.* **100,** 185 (1986).
9. Ko, A. N., and Wojciechowski, B. W., *Prog. React. Kinet.* **12**(4), 201 (1983).
10. Wojciechowski, B. W., *Catal. Rev. Sci. Eng.* **9**(1), 79 (1974).
11. Abbot, J., and Wojciechowski, B. W., *J. Catal.* **107,** 451 (1987).
12. Abbot, J., and Wojciechowski, B. W., *Canad. J. Chem. Eng.* **66,** 825 (1988).
13. Abbot, J., and Wojciechowski, B. W., *J. Catal.* **109,** 274 (1988).
14. Neuber, M., *et al.*, *Stud. Surf. Sci. Catal.*, 34 (1987).
15. Campbell, D. R., and Wojciechowski, B. W., *J. Catal.* **23,** 207 (1971).
16. Mercier des Rochettes *et al.*, *Stud. Surf. Sci. Catal.*, 34 (1987).
17. Butt, J. B., and Petersen, E. E., "Activation, Deactivation and Poisoning of Catalysts." Academic Press, San Diego, 1988.
18. Levinter, M. E., Panchekov, G. M., and Tanatarov, M. A., *Ind. Chem. Eng.* **7,** 23 (1967).