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The Effect of Temperature on the Product Distribution and Kinetics of Reactions of *n*-Hexadecane on HY Zeolite

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Reactions of *n*-hexadecane on HY zeolite have been studied at 300 and 400°C. At both temperatures, initial cracking products, as well as initial products of skeletal isomerization and coke formation, were observed in the range C_2–C_{10}. At 300°C paraffins were the dominant initial product, whereas olefins were dominant at 400°C. This can be explained as being the result of more extensive hydrogen transfer at the lower temperature, resulting in a more unsaturated coke and more gas phase paraffins. Aromatics were formed by initial processes at both temperatures with similar selectivity. Reports that hydrogen is irreversibly lost from active sites associated with the catalyst framework, to produce saturated hydrocarbons, were not confirmed. Kinetic parameters were obtained at both 300 and 400°C and their magnitudes are found to reflect changes in product distribution at these two temperatures. The fact that, over the range of conversions studied, product olefin species are present in much greater abundance at the higher temperature gives rise to more pronounced competitive inhibition at 400°C than at 300°C. Catalyst deactivation was found to occur much more rapidly at the lower temperature. This is related to the nature of the coke deposited. It appears that coke is more deactivating when it is more dehydrogenated.

INTRODUCTION

The selectivity and kinetics of *n*-paraffin cracking have been studied on a wide variety of catalysts (*1*, *2*). In recent studies of reactions of *n*-octane and *n*-dodecane on HY at 400°C (*3*) we have shown that hydrogen transfer processes leading to coke and aromatics account for all the excess saturated species produced on cracking. Our studies do not support previous claims that hydrogen is supplied by the catalyst itself. The "anomalous" initial paraffin/olefin ratios obtained in cracking *n*-heptane on HY and ZSM-5 (*4*, *5*) can be explained (3) by including coke and aromatics in the detailed atomic mass balance of initial products without involving any hydrogen which may be present on the surface of the fresh catalyst.

Reactions of *n*-hexadecane have received particular attention in the past, because cracking C_{16} is typical of cracking in long-chain paraffins present in gas oils, and because of its ready availability. Product distributions have been reported at various conversion levels on a number of catalysts (*6*, *7*). It has long been recognized that, in formulating expressions representing the kinetics of paraffin cracking, inhibiting effects due to product species should be considered (*8*–*10*). Although inhibition due to product olefins and aromatics during reaction of *n*-hexadecane on silica alumina was considered in early studies (*8*, *9*), this important effect appears to have been neglected in more recent kinetic studies (*4*, *5*) of *n*-paraffin cracking on zeolites. We have shown that inhibition by product species must be accounted for by using a Langmuir adsorption isotherm in the reactions of *n*-paraffins, including *n*-hexadecane at 400°C on HY (*10*).

In this paper we compare the reactions of *n*-hexadecane on HY at 300 and 400°C. Detailed product distributions are reported at both temperatures, to demonstrate that hydrogen balances are maintained when all

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products including saturates, coke, and aromatics are considered. The influence of product distributions on inhibition, as well as their effect on catalyst aging as described by the time-on-stream theory, is considered (*11*).

THEORY

We have shown (*10*) that reactions of *n*-paraffins on HY at 400°C can be described by

$$\frac{dX}{d\tau} = \frac{(1 + Gt)^{-N}A(1 - X)/(1 + \varepsilon X)}{1 + B(1 - X)/(1 + \varepsilon X)}, \quad (1)$$

where X is the fractional conversion of the paraffin, τ is the feed contact time, ε is the volume expansion coefficient, G and N are aging parameters, and A and B are constants related to the rate constant for reaction, and the Langmuir adsorption constants for reactant and products.

The constants A and B are defined by the expressions

$$A = \frac{\sum_i k_i K[C]_0}{1 + \sum_i K_i n_i [C]_0} \quad (2)$$

and

$$B = [C]_0 \frac{K - \Sigma K_i n_i}{1 + \sum_i K_i n_i [C]_0}, \quad (3)$$

where k_i are the individual rate constants for the i parallel modes of reaction; K and K_i are Langmuir adsorption constants for feed C and each product P_i, respectively; n_i is a stoichiometric factor accounting for the number of product molecules of type i formed from the feed molecule; and $[C]_0$ is the initial concentration of reactant.

EXPERIMENTAL

The feedstock *n*-hexadecane (99.60%) was obtained from Aldrich and used without further purification. The impurity present (C_{16} isomers 0.40%) was taken into account in calculating initial selectivities.

HY zeolite was prepared from NaY (Linde Co., lot. No. 45912, SK40) by repeated exchange with 0.5 *N* ammonium nitrate solution. Catalysts with mesh size 50/70 were steamed for 24 h at 200°C before use. Previous investigations (*10*) have shown that this reaction is not diffusion controlled in the particle at 400°C using this particle size.

All experiments were performed at 400°C by using an integral, fixed-bed, gas-phase plug flow reactor with independently controlled three-zone heater. The experimental apparatus and procedures used were similar to those described in previous studies (*12*). Blank runs were carried out at 400°C to ensure that the glass used to dilute the catalyst was inert.

Liquid products were analyzed by a Varian 600 gas chromatograph with a 60-m SE54 capillary column and flame ionization detector. Products up to C_7 were eluted at 35°C, followed by a temperature program of 5°C/min up to 300°C. Gaseous products were analyzed by a Carle SX1156 gas chromatograph which also allowed for a direct determination of molecular hydrogen, if present. The identification of products was facilitated by use of a Finigan 1020 automated GC/MS.

After each run the reactor was purged with dry nitrogen at a set flow rate, at reaction temperature, for 15 min. Residual material in the reactor was regarded as coke. The reactor temperature was then increased to 500°C, while dry carbon-dioxide-free air was passed over the catalyst. The weight of water absorbed in a tube of drierite during regeneration allowed the hydrogen content of the coke to be calculated. The weight of carbon dioxide absorbed by a tube containing ascarite gave the carbon content of the coke. Complete combustion to carbon dioxide was ensured by passing the dried combustion product stream through a reactor at 350°C packed with copper oxide.

RESULTS AND DISCUSSION

Initial Selectivities

Reactions of *n*-hexadecane on HY zeolite at 300 and 400°C were found to produce

TABLE 1

Initial Weight Selectivities for Reaction of *n*-Hexadecane on HY at 300 and 400°C

	Type		Initial selectivity	
	300°C	400°C	300°C	400°C
C_1				
Methane	—	2S	—	—
C_2				
Ethylene	1U	1U	0.00050	0.00069
Ethane	2U	2S	—	—
C_3				
Propylene	1U	1U	0.0208	0.0620
Propane	(1 + 2)S	(1 + 2)S	0.0308	0.0103
C_4				
Isobutane	(1 + 2)S	(1 + 2)S	0.1336	0.0560
n-Butane	(1 + 2)S	(1 + 2)S	0.0280	0.0192
Isobutylene	1U	1U	0.0298	0.0938
trans-2-Butene	1U	1U	0.0198	0.0412
cis-2-Butene	1U	1U	0.0110	0.0297
C_5				
2-Methylbutane	(1 + 2)S	(1 + 2)S	0.1593	0.0745
n-Pentane	(1 + 2)S	1S	0.0091	0.0170
1-Pentene	2U	1U	—	0.00663
trans-2-Pentene	1U	1U	0.0052	0.0233
cis-2-Pentene	2U	1U	—	0.0115
2-Methyl-1-butene	1U	1U	0.0049	0.0232
2-Methyl-2-butene	1U	1U	0.0156	0.0567
3-Methyl-1-butene	—	1U	—	0.00337
C_6				
2,3-Dimethylbutane	(1 + 2)S	(1 + 2)S	0.0073	0.0092
2-Methylpentane	(1 + 2)S	(1 + 2)S	0.0486	0.0372
3-Methylpentane	(1 + 2)S	(1 + 2)S	0.0267	0.0201
n-Hexane	*(1 + 2)S*	*1U*	*0.0099*	*0.0189*
C_6 olefins	1U	1U	0.0136	0.0832
C_7				
2,4-Dimethylpentane	1S	1S	0.0040	0.00912
2,3-Dimethylpentane	1S	(1 + 2)S	0.0072	0.00927
2-Methylhexane	1S	(1 + 2)S	0.0298	0.0197
3-Methylhexane	1U	(1 + 2)S	0.0312	0.0204
n-Heptane	1U	1U	0.0050	0.0128
C_7 olefins	1U	1U	0.0036	0.0808
Toluene	2S	(1 + 2)S	—	0.0025
C_8				
2,3-Dimethylhexane	2S	(1 + 2)S	—	—
2,4-Dimethylhexane	1S	(1 + 2)S	0.0074	0.00336
2,5-Dimethylhexane	1S	(1 + 2)S	0.0062	0.00336
2-Methylheptane	1S	1S	0.0167	0.0121
3-Methylheptane	1S	1S	0.0147	0.0102
4-Methylheptane	1S	1S	0.0065	0.00413
n-Octane	1U	1U	0.0071	0.00943
C_8 olefins	2U	1U	—	0.0397
C_8 aromatics	1S	(1 + 2)S	0.00733	0.00733
C_9				
Dimethylheptanes	1S	2S	0.0106	—
2-Methyloctane	1U	1S	0.0172	0.00333
3-Methyloctane	1U	1S	0.0107	0.00823
n-Nonane	1U	1S	0.0038	0.00554
C_9 Aromatics	1S	(1 + 2)S	0.0187	0.0163
C_{10}				
C_{10} paraffins	1U	2U	0.0172	0.0060
C_{10} aromatics	2S	2S	—	—
C_{11}				
C_{11} paraffins	2S	2U	—	—
C_{11} aromatics	2S	2S	—	—
C_{16}				
C_{16} paraffins (skeletal isomers)	1U	1	0.100	0.0149
Coke	(1 + 2)S	(1 + 2)S	0.1100	0.0060
Total			1.001	1.00

over 140 individual products over the range of conversion studied. Initial selectivities and product types were obtained by plotting optimum performance envelopes (OPE) (*12*) for each product (Table 1). Some examples of such OPEs are presented in Fig. 1 for the two temperatures.

At each temperature, initial cracking products were observed only in the range C_2–C_{10}. Skeletal isomerization (C_{16} paraffins) and coke were the only other initial products. Methane was observed only as a minor secondary product at 400°C. Hydrogen was not observed as a product. Figure 2 shows the initial product distribution resulting from the cracking of 1 mole of *n*-hexadecane (i.e., in this distribution skeletal isomers and coke are not taken to contribute to either conversion or products). The fragmentation spectrum is very similar at 300 and 400°C. Similar distributions have been observed (*7*) for cracking of *n*-hexadecane on a rare earth zeolite in the range 399–482°C at different conversion levels. It was reported there that increasing the temperature caused a shift in the cracking distribution toward the lower-molecular-weight end. This shift is not apparent to any extent over the temperature range investigated here. It should also be pointed out that in the previous study (*7*) initial selectivities were not considered and distributions corresponding to increased conversion at the higher temperature were compared with those at lower conversion and temperature. It is difficult at this time to separate the influence of temperature from that of conversion on the distribution of products reported in that study.

It has elsewhere been reported that in the cracking of *n*-hexane on HY in the temperature range 350–450°C increasing amounts of olefin are found in the reaction products as the reaction temperature is increased (*13*). This was attributed to the increased ease of olefin desorption before hydrogen transfer reactions can take place. Figure 3 shows the initial molar distributions of paraffins (a) and olefins (b) that we find to be produced from *n*-hexadecane at 300 and 400°C.

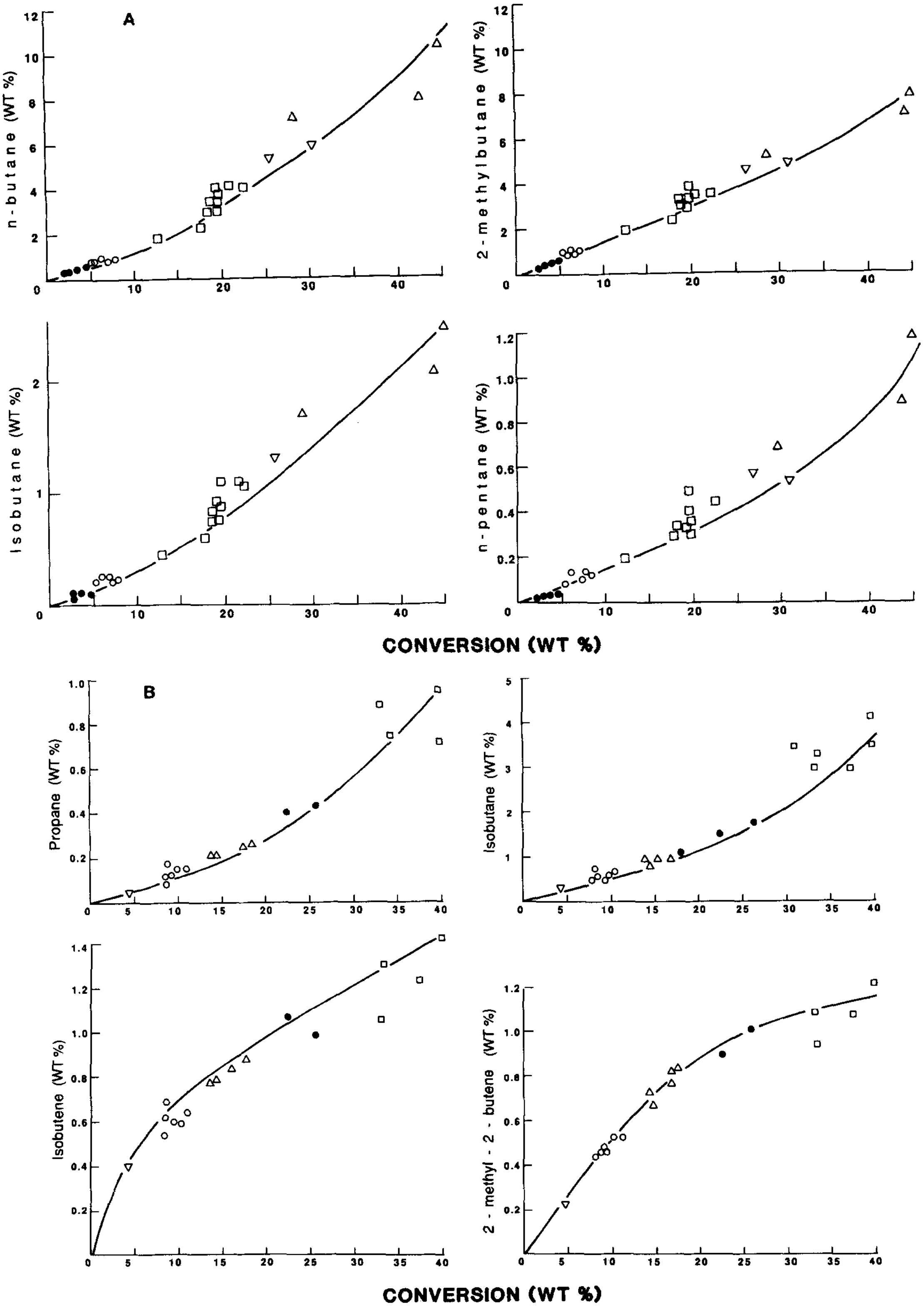

FIG. 1. Optimum performance envelopes for products of reaction of *n*-hexadecane on HY. (A) 300°C, selected catalyst-to-reactant ratios: (●) 0.0313, (○) 0.0938, (▽) 0.438, (△) 0.625. (B) (▽) 0.00156, (○) 0.00313, (△) 0.00625, (●) 0.0156, (□) 0.0625.

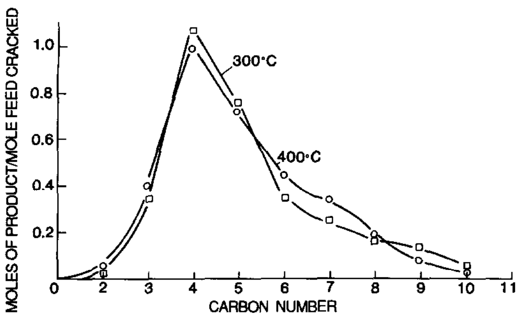

FIG. 2. Initial molar distributions of products from cracking *n*-hexadecane on HY at 300 and 400°C.

It is apparent that we too find the proportion of olefins initially formed on HY is much greater at the higher temperature.

Hydrogen Transfer Reactions

Studies on the cracking of *n*-pentane and *n*-hexane on mordenite (*14*) and the cracking of *n*-hexane on Y zeolite (*15*) at 300°C or below have shown that paraffins are the major products. It has also been reported that cracking of *n*-butane and *n*-pentane on mordenite at 400°C produced exclusively paraffins; no olefins were detected (*16*). To explain the high content of saturates resulting from the cracking of paraffins on zeolites, particularly at low temperatures, it was suggested (*13*) that hydrogen is released from hydroxyl hydrogens within the zeolite itself. Evidence for this consisted of a reported inability to restore catalytic activity after regeneration in air at 550°C (*13, 15*). It was concluded that the Brønsted hydrogen content of the catalyst itself is reduced due to olefin saturation reactions. How electroneutrality of the surface is maintained in such a model is not clear.

We have recently reported (*3*) on the cracking of *n*-octane and *n*-dodecane on HY at 400°C. It was shown, by using initial product selectivities, that all hydrogen transfer to produce excess paraffins can be accounted for by the concurrent formation of aromatics and coke. The high initial paraffin/olefin ratios reported for cracking of *n*-heptane on HY and HZSM-5 (*4, 5*) can also be explained by considering the coke and aromatics initially formed. We also find that catalytic activity can be fully restored by regeneration in dry air at 500°C, suggesting that no hydrogen associated with catalyst activity is irreversibly lost in producing the excess paraffins.

Table 2 shows the total initial molar selectivity for paraffin products from reactions of *n*-hexadecane at 300 and 400°C. If no hydrogen transfer occurred during cracking, the initial selectivity for paraffins should be one. It is clear that hydrogen transfer does occur, and to a significantly greater extent at the lower temperature. If no hydrogen is supplied by the catalyst

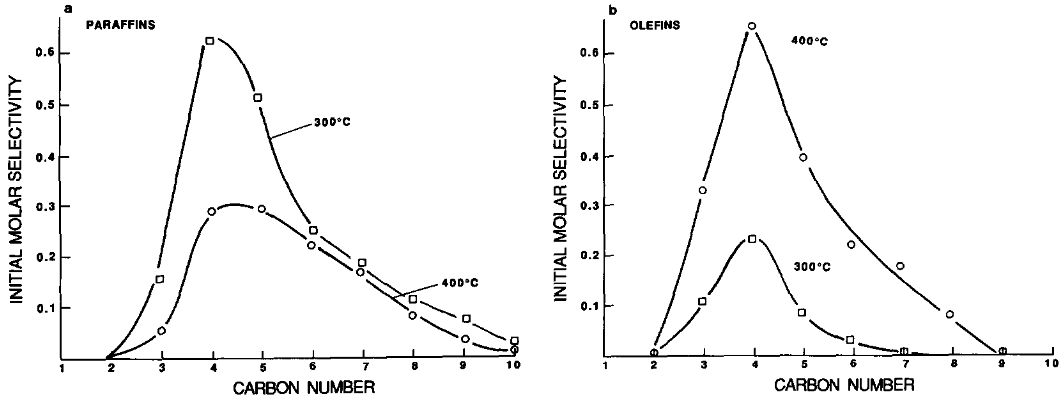

FIG. 3. Initial molar distributions for (a) paraffins and (b) olefins formed from *n*-hexadecane on HY at 300 and 400°C.

TABLE 2

Initial Hydrogen Transfer for Reaction of *n*-Hexadecane on HY Zeolite

Product	Initial molar selectivity		Hydrogen transfer (moles H_2)			
	300°C	400°C	300°C		400°C	
Paraffins	2.040	1.158	1.040		0.158	
Aromatics	0.0500[a]	0.0525[a]	0.150	0.975	0.157	0.157
Coke	0.110[b]	0.0060[c]	0.8250		—	

[a] There are 3 moles of hydrogen lost by the feed in forming 1 mole of aromatics. This requires that a factor of 3 be applied in calculating the hydrogen transferred in aromatics formation.

[b] C/H ratio was 0.85 in the initial coke. This requires that a factor of 7.5 be applied to account for the hydrogen lost by the feed molecules in forming this coke.

[c] C/H ratio was 0.5. Coke formed makes no contribution to hydrogen transfer.

itself, then the molar amounts of paraffins in excess of unity must correspond to hydrogen donated by the formation of aromatics and coke.

Figure 4 shows that, at both temperatures, aromatics in the range C_7–C_9 are produced as primary products. Higher-molecular-weight aromatic species are formed as secondary products. The initial molar selectivities for aromatics are given in Table 2. Multiplying these by a factor of 3 gives the amount of hydrogen available to form paraffins.

Figure 5 shows optimum performance envelopes for coke formation at 300 and 400°C. At both temperatures coke is seen as a stable primary plus secondary product.

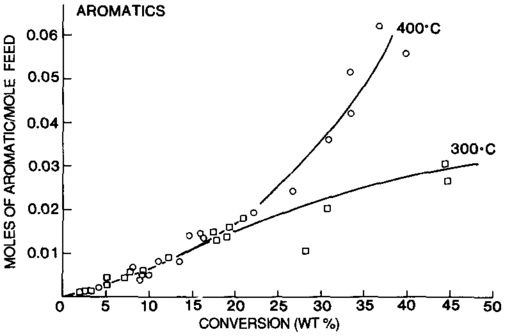

FIG. 4. Optimum performance envelopes for total aromatics formed from *n*-hexadecane on HY at 300 and 400°C.

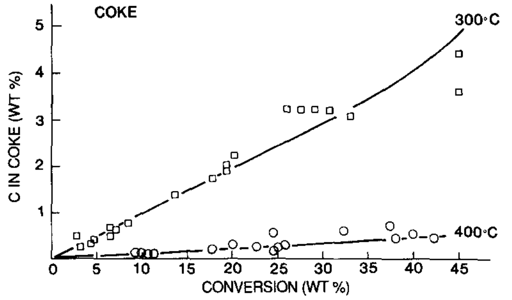

FIG. 5. Optimum performance envelope for coke formation from *n*-hexadecane on HY at 300 and 400°C.

The initial selectivity for coke formation is significantly greater at 300°C than at 400°C (Table 1). Figure 6 shows how the atomic ratio C/H varies as a function of conversion. At 400°C coke formed on HY from *n*-hexadecane (as well as from *n*-dodecane (*3*)) shows an initial ratio of C/H ~ 0.50, corresponding to adsorbed feed molecules. Only at higher conversions does this ratio increase, as an unsaturated coke is produced. At this temperature, therefore, although coke is observed to have an initial selectivity, it makes zero initial contribution to hydrogen transfer (Table 2).

In contrast to 300°C, the coke initially formed is dehydrogenated with respect to the feed. In fact, at all levels of conversion, coke produced at 300°C is more dehydrogenated than that formed at 400°C. The contribution to hydrogen transfer from coke at 300°C has been calculated from its initial selectivity and the initial C/H ratio

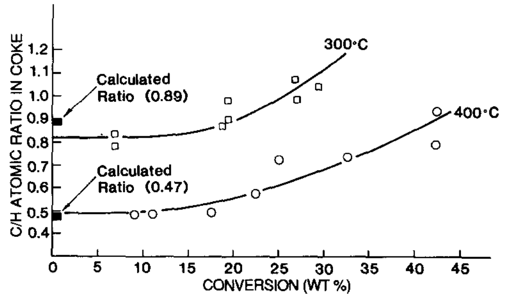

FIG. 6. Variation in C/H atomic ratios for coke from reaction of *n*-hexadecane on HY at 300 and 400°C.

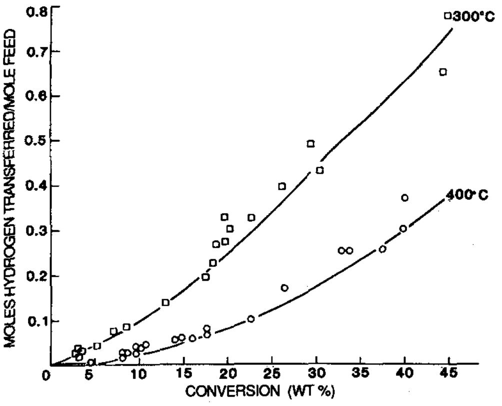

FIG. 7. Variation in total hydrogen transfer with conversion for reaction of *n*-hexadecane on HY at 300 and 400°C.

(Table 2). In this way, at both 300 and 400°C, the hydrogen transfer associated with excess paraffin formation is fully accounted for by the hydrogen donated by aromatics and coke. In all our studies of paraffin cracking on HY zeolite, as well as the studies of cycloparaffins and olefins, we have not encountered any difficulty in achieving full regeneration of catalyst activity. We have no evidence to support the proposal (*13*) that hydrogen is irreversibly donated by catalyst active sites to form paraffins. The hydrogen balances in all these studies are closed by taking into account only the organic components of the reaction.

The extent of hydrogen transfer can be followed as a function of *n*-hexadecane conversion by plotting

$$\frac{\text{moles of paraffin in product} \\ - \text{moles of paraffin in feed}}{\text{moles of paraffin in feed}}.$$

This ratio represents the moles of hydrogen transferred per feed molecule and is illustrated in Fig. 7 at both 300 and 400°C. It shows unambiguously that hydrogen transfer is significantly greater at lower temperature. This trend is present at all levels of conversion studied.

Radioactive tracer studies on coke formation during the cracking of *n*-hexadecane on silica alumina have shown that some coke is formed through incorporation of olefins in the range C_3–C_5 (*17, 18*). We show in Fig. 6 that unsaturated coke can be formed as a primary product at low temperature on HY, in the absence of any olefins in the feedstock. It appears therefore that unsaturated coke species are derived from carbenium ions on the catalyst surface. These are formed during paraffin cracking by protonation of the paraffin molecule, followed by cracking to produce a short-chain paraffin and a carbenium ion or by a hydride ion abstraction followed by cracking to yield olefins with the release of a shorter paraffin chain (*1, 2, 19*). At lower temperatures it seems that the carbenium ion has a higher probability of undergoing dehydrogenation, and perhaps cyclization, to produce coke.

As the level of conversion increases, product gas-phase olefins react with carbenium ions on the catalyst surface to product dehydrogenated species which contribute to coke formation. This process occurs at a higher conversion of C_{16} at 400°C, when short-chain olefins abound, and is in agreement with the observation that labeled short-chain olefins, added to *n*-hexadecane, contribute to the formation of coke and aromatic products during reaction on silica alumina (*17, 18*).

Product Distributions and Kinetics

We have previously (*10*) used Eq. (1) to quantify the rate of reaction of *n*-paraffins on HY at 400°C. This equation has now been applied to results at 300°C on the same catalyst, and optimum values of the parameters obtained are presented in Table 3. We see that, while the value of parameter B is -1 at 400°C, it becomes positive when the temperature is decreased. We have shown (*10*) that a value of $B = -1$ indicates that

$$K \ll \Sigma K_i n_i \tag{4}$$

and also

$$1 \ll \Sigma K_i n_i. \qquad (5)$$

Condition (4) applies when product molecules are more strongly adsorbed at the active sites than the feedstock molecules, i.e., when there is strong competitive inhibition by products. This inhibition we attribute to the olefinic and aromatic products (*8–10*). This agrees with previous work where it was shown that the addition of olefins to the feedstock inhibits the reaction of *n*-hexadecane on silica alumina (*9*). As the reaction temperature is decreased in our system, the proportion of olefin products declines. Figure 8 shows a comparison of the total molar amounts of olefins and aromatics present in our product over the ranges of conversion studied at both 300 and 400°C. Clearly, the proportion of olefins and aromatics produced is much lower at the lower temperature, reducing some of the values of n_i in (4) and (5), in particular the number of moles of olefinic products, so that conditions (4) and (5) may no longer apply. We see in Table 3 that at 300°C parameter B has a positive value, reflecting this decline in inhibition by unsaturated products.

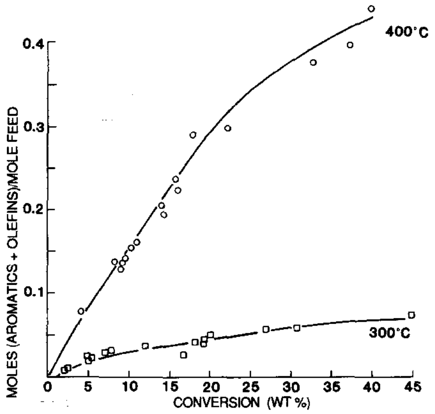

FIG. 8. Optimum performance envelopes for total aromatics and olefins formed from reaction of *n*-hexadecane on HY at 300 and 400°C.

There is also a marked change in the rate of catalyst decay over the temperature range investigated. According to the time-on-stream theory (*11*), the rate of loss of active sites is given by

$$\frac{d\theta}{dt} = k_{md}\theta^m,$$

where θ is the fraction of active sites remaining at time t, k_{md} is the deactivation rate constant, and m is the order of decay. Values of k_{md} and m have been calculated from the values of parameters G and N (*11*) and are shown in Table 3.

TABLE 3

Optimum Values for Parameters for Cracking of *n*-Hexadecane

Temperature (°C)	B	G^a (min)$^{-1}$	N^a	m^a	$k_{md}{}^a$ (min)$^{-1}$
400	−0.998	1.52	0.42	3.38	0.64^b
300	10.2	348	0.75	2.33	261

[a] Constants in the decay rate expression (*11*)

$$\theta_t = \theta_0 \left(\frac{1}{1 + Gt}\right)^N,$$

where $N = 1/(m - 1)$, $G = k_{md}(m - 1)$, and θ is the fraction of sites active at time on stream $= t$.

[b] In Ref. 10, the value of k_{md} at 400°C was reported in error to be 1.42.

We note that k_{md} is higher at the lower temperature, while the order of the decay appears little influenced by temperature. It is normally to be expected that a rate constant will increase with temperature. However, the term k_{md} also contains a factor accounting for the concentration of poisons present. The behavior of k_{md} was previously discussed with respect to catalyst decay in the cracking of cumene on HY (*20*). The increase in k_{md} at lower temperature was there ascribed to the higher concentration of poisons at 300°C. At first sight this may suggest that it is the greater yield of coke that is responsible for the larger k_{md} at low temperatures, as we have seen that the selectivity for coke formation is significantly higher at lower temperature (Fig. 5). However, in considering the yield of coke, it should be remembered that more catalyst is generally acquired to achieve a given level of conversion at the lower temperature. Figure 9 shows that when the weight of coke-on-catalyst is plotted against conversion, there is little difference in coke-on-catalyst at 300 and 400°C, most results

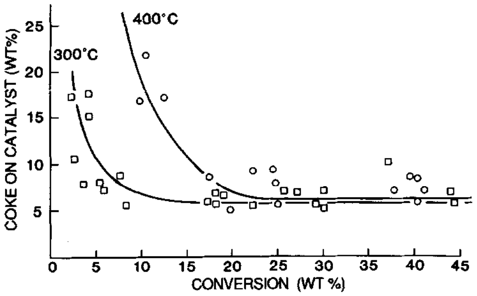

FIG. 9. Ratios of coke on catalyst plotted as a function of conversion for reaction of *n*-hexadecane on HY at 300 and 400°C.

falling between 5 and 10%. On the other hand we recall from Fig. 6 that the degree of dehydrogenation of coke is much greater at 300°C. Thus, although the weight of coke deposited per unit weight of catalyst is similar at 300 and 400°C, the nature of the coke deposited is different. We conclude that the much higher rate of decay at lower temperature is due to the higher unsaturation of the carbonaceous matter on the catalyst surface. This conclusion is in keeping with observations regarding coke on HZSM-5 (*21, 22*) where it was found that coke has the same C/H ratio as the feed, and hardens (i.e., increases in C/H ratio) very slowly with time on stream. At the same time, the rate of decay is very slow in this catalyst (*22, 23*). Our conclusion is that it is dehydrogenated coke that is the main poison, but how the level of dehydrogenation influences decay is not clear.

The fact that *m* is greater at the higher temperature and that at both temperatures it is greater than 2 indicates that pore plugging is an important contributor to catalyst decay and (*2, 4*) becomes more important at the higher temperatures.

CONCLUSIONS

In the cracking of *n*-hexadecane the molecular size distribution of initial cracking products is not affected significantly by temperature in the range 300–400°C. However, the degree of saturation of initial products is very much dependent on temperature. Paraffins are the dominant product at 300°C, whereas olefins are dominant at 400°C. The saturation of products can be accounted for by hydrogen transfer leading to the formation of unsaturated aromatics and coke and saturated paraffins.

The change in product composition with temperature has a profound effect on cracking kinetics due to the fact that olefins act as competitive inhibitors in the reaction.

Catalyst decay was found to be faster at the lower temperatures. This effect is somehow connected with the greater degree of coke dehydrogenation at low temperatures and not with the absolute coke-on-catalyst deposit, which is very similar at both temperatures.

Our results are not in agreement with previous studies which claimed that saturation of products occurs by irreversible transfer of hydrogen from active sites of the catalyst itself. In contrast to previous reports, we find catalytic activity can be fully restored by regeneration of the catalyst in air at 500°C and that the carbon and hydrogen mass balances are closed when account is taken of all the organic products of the reaction.

REFERENCES

1. Germain, J. E., "Catalytic Conversions of Hydrocarbons." Academic Press, New York, 1969.

2. Wojciechowski, B. W., and Corma, A., "Catalytic Cracking." Dekker, New York, 1986.

3. Abbot, J., and Wojciechowski, B. W., *J. Catal.* **107,** 451 (1987).

4. Corma, A., Fornes, V., Manton, J. B., and Orchilles, A. V., *Appl. Catal.* **12,** 105 (1984).

5. Corma, A., Monton, J. B., and Orchilles, A. V., *Appl. Catal.* **16,** 59 (1985).

6. Greensfelder, B. S., Voge, H. H., and Good, G. M., *Ind. Eng. Chem.* **41**(11), 2573 (1949).

7. Nace, D. M., *Ind. Eng. Chem. PRD* **8**(1), 24 (1969).

8. Voge, H. H., *in* "Catalysis" (P. H. Emmett, Ed.), Vol. VI, Chap. 5. Reinhold, New York, 1958.

9. Pansing, W. F., *J. Phys. Chem.* **69,** 392 (1965).

10. Abbot, J., and Wojciechowski, B. W., *J. Catal.* **104,** 80 (1987).

11. Wojciechowski, B. W., *Catal. Rev. Sci. Eng.* **9**(1), 79 (1974).

12. Ko, A. N., and Wojciechowski, B. W., *Prog. React. Kinet.* **12,** 201 (1983).

13. Bolton, A. P., and Bujalski, R. L., *J. Catal.* **23,** 331 (1971).

14. Miale, J. W., Chen, N. Y., and Weisz, P. B., *J. Catal.* **6,** 278 (1966).

15. Tung, S. E., and McIninch, E., *J. Catal.* **10,** 175 (1968).

16. Benesi, H. A., *J. Catal.* **8,** 368 (1967).

17. Van Hook, W. A., and Emmett, P. H., *J. Amer. Chem. Soc.* **84,** 4410 (1962).

18. Hightower, J. W., and Emmett, P. H., *J. Amer. Chem. Soc.* **87,** 939 (1965).

19. Abbot, J., and Wojciechowski, B. W., *Ind. Eng. Chem. PRD* **24,** 501 (1985).

20. Corma, A., and Wojciechowski, B. W., *Catal. Rev. Sci. Eng.* **24,** 7 (1982).

21. Abbot, J., and Wojciechowski, B. W., *Canad. J. Chem. Eng.* **63,** 278 (1985).

22. Fukase, S., and Wojciechowski, B. W., *J. Catal.* **102,** 452 (1986).

23. Dejaifve, P., Auroux, A., Gravelle, P. C., Vecdre, J. C., Gabelica, Z., and Derovane, E. G., *J. Catal.* **70,** 123 (1981).