JOURNAL OF CATALYSIS **104**, 80–85 (1987)

Kinetics of Catalytic Cracking of *n*-Paraffins on HY Zeolite

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Received April 18, 1986; revised September 6, 1986

It is shown that the catalytic cracking of *n*-paraffins on HY zeolite must be described by a rate expression of the form, rate $= A(1 - X)/(1 - B(1 - X))$, where A and B are numerical parameters, and X is the fractional conversion of paraffin. This form is rigorously derived from fundamental principles by assuming a Langmuir type of adsorption process. Analysis of experimentally obtained parameters A and B shows that the cracking reaction of paraffins is strongly inhibited by product olefins, and that the determination of true kinetic rate constants will in general require a detailed knowledge of adsorption constants for both reactant and products. The rate of catalyst decay in paraffin cracking increases with increased chain length and exhibits kinetics suggestive of processes involving both two-site decay, as seen in cumene cracking, and multisite decay, assumed to involve pore blocking. The longer the feed molecule the more pronounced the decay attributable to pore blocking. © 1987 Academic Press, Inc.

INTRODUCTION

Although cracking reactions of isolated *n*-paraffins have been studied since the inception of the catalytic process, the mechanism of this reaction is still under debate. It is clear that valuable mechanistic insight can be gained by examining not only the product distributions but also the kinetics of cracking using both isolated paraffins (*1*–*5*) and paraffins in combination with other hydrocarbons (*6*–*8*). However, it is important that the mathematical expressions used to formulate the required kinetic models be soundly based and fit the data adequately if meaningful mechanistic information is to be derived.

Early work on the kinetics of paraffin cracking on amorphous silica aluminas showed that simple first-order kinetic expressions can only approximate experimental results (*1*). More exact theoretical expressions were formulated by assuming the competing adsorption of reaction products on the active sites. Results from *n*-hexadecane cracking were successfully fitted by such expressions where the general Langmuir isotherm was used (*1, 6, 9*) to represent the adsorption of all components present in the reaction volume.

More recent literature has tocused on reactions of paraffins on zeolite cracking catalysts. Simple first-order kinetic expressions are usually applied (*4, 5, 7, 10*) without the refinement of a detailed consideration of the adsorption process, as was found to be necessary in the past. In this work we show that such a simplified approach is not justified. Cracking of *n*-paraffins in the range C_8–C_{16} has been studied on HY zeolite at 400°C and the results are fitted by both the first-order kinetic model and a model which assumes Langmuir-type adsorption of all species present.

It is now generally accepted that cracking catalyst deactivation occurs at such rapid rates that, in quantifying the rates of cracking, the kinetics of conversion must be treated simultaneously with deactivation kinetics. Accordingly, we have included the effects of deactivation in our models by applying the time-on-stream theory of decay (*11*) which has previously been used to describe aging phenomena in cumene cracking and gas oil cracking on a variety of catalysts.

EXPERIMENTAL

The feedstocks (*n*-octane, *n*-dodecane, and *n*-hexadecane) of >99% purity were

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obtained from Aldrich and used without further purification. The only impurities present were the corresponding monomethyl isomers in less than 1% concentration.

HY catalyst was prepared from NaY (Linde Co., Lot 45912, SK40) by repeated exchange with 0.5 *N* ammonium nitrate solution. Catalyst samples with mesh size 50/70 were steamed for 24 h at 200°C before use.

All experiments were performed by using an integral, fixed-bed, gas phase, plug–flow reactor with an 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 to ensure the glass used to dilute the catalyst was inert. Reduction of the catalyst particle size to 80/100 mesh had no influence on the cracking reaction, showing that the reaction was not diffusion controlled.

Liquid products were analyzed using a Varian gas chromatograph with a 60-m SE54 capillary column and a flame ionization detector. Gaseous products were analyzed by a Carle SX 1156 gas chromatograph. The identification of products was facilitated by use of a Finigan 1020 automated GC/MS.

THEORY

(*a*) *The Simple First-Order Kinetic Model*

Using the time-on-stream theory of catalyst decay (*11*), a first-order kinetic expression can be written as

$$\frac{dX}{d\tau} = \sum_i k_i(1 + Gt)^{-N}\left(\frac{1 - X}{1 + \varepsilon X}\right), \quad (1)$$

where X is the fractional conversion of the paraffin;

τ is the feed contact time;

ε is the volume expansion coefficient;

k_i are individual rate constants for the i parallel modes of cracking; and

G and N are aging parameters.

(*b*) *The Langmuir Adsorption Kinetic Model*

If we consider the initial adsorption of a paraffin molecule C on an active site, followed by reaction to give products P_i which absorb competitively on the same active sites as the feed, the rate of reaction will be given by

$$\frac{-d[C]}{d\tau} = \frac{K\Sigma k_i[C]}{1 + K[C] + \Sigma K_i[P_i]}, \quad (2)$$

where K and K_i are Langmuir adsorption constants for feed C and each product P_i, respectively. Equation (2) can be rewritten as

$$\frac{-d[C]}{d\tau} = \frac{K\Sigma k_i[C]}{1 + K[C] + \Sigma_i K_i n_i([C]_0 - [C])}, \quad (3)$$

where $[C]_0$ is the initial concentration of reactant, and n_i is a stoichiometric factor accounting for the number of product molecules of type i formed from the feed molecule.

Rearranging, we obtain:

$$\frac{d[X]}{d\tau} = \frac{A(1 - X)}{1 + B(1 - X)}, \quad (4)$$

where A and B are constants and X is the fractional conversion of the paraffin.

Introducing the effects of activity decay and volume expansion, Eq. (4) becomes

$$\frac{dX}{d\tau} = (1 + Gt)^{-N}\frac{A(1 - X)/(1 + \varepsilon X)}{1 + B(1 - X)/(1 + \varepsilon X)}. \quad (5)$$

In Eqs. (1) and (4), X represents the instantaneous conversion of the increment of feed which passes over the catalyst at time t. By averaging the conversion from $t = 0$ at the beginning of a run to the end of the run where $t = t_f$, values of $\bar{X}$, the cumulative average conversion, can be obtained and compared with corresponding measured values. Parameters A, B, N, and G are then optimized in order to obtain the best fit of the data.

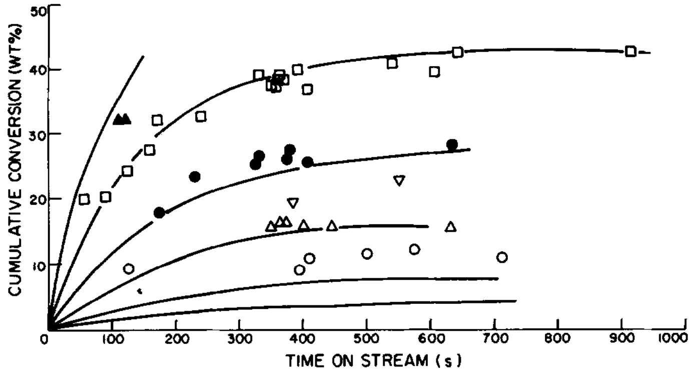

FIG. 1. Theoretical curves and experimental points for *n*-hexadecane cracking on HY at 400°C fitted by the simple-first order model. Catalyst/reactant ratios: ▲, 0.135; □, 0.0694; ●, 0.0333; ▽, 0.0165; △, 0.0066; ○, 0.0032. (Sum of squares of residuals = 0.106.)

RESULTS AND DISCUSSION

Equation (1), representing the simple first-order kinetic model, has been applied previously to results from cracking of *n*-heptane both on Y zeolite and on HZSM-5 in the temperature range 400–470°C (*4, 5, 13*). In Fig. 1 we show the fit of our results for *n*-hexadecane cracking on HY at 400°C using Eq. (1). The theoretical curves are generated by adjusting the three parameters of Eq. (1), Σk_i, G, and N, until the sum of squares of the residuals between experimental and theoretical conversions is minimized using a nonlinear optimization routine called NOTLIN.

It is apparent that this model is inadequate. The predicted conversions at low catalyst/reactant ratios are much smaller than those actually observed. We find that a reasonable fit can be obtained when the concentration term in Eq. (1) is raised to a power of 4 or 5, but this yields an expression of doubtful kinetic significance.

Figure 2 shows data for *n*-hexadecane cracking on HY fitted by Eq. (5). The value of ε, the volume expansion coefficient, was obtained by experiment and is given in Table 1. It is apparent that the correspondence between experimental conversions and theoretical curves is very good, certainly superior to that illustrated in Fig. 1. Figures 3 and 4 show that the fit for the cracking of *n*-dodecane and *n*-octane on

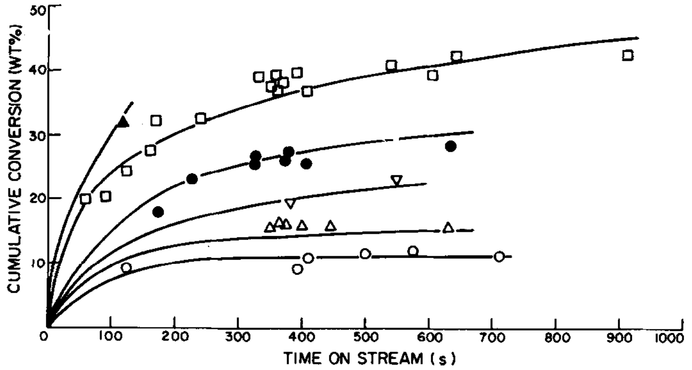

FIG. 2. Theoretical curves and experimental points for *n*-hexadecane cracking on HY at 400°C fitted by the Langmuir model (Eq. (5)). Catalyst/reactant ratios: ▲, 0.135; □, 0.0694; ●, 0.0333; ▽, 0.0165; △, 0.0066; ○, 0.0032. (Sum of squares of residuals = 0.0177.)

TABLE 1

Optimum Values for Parameters from Langmuir Model for Cracking *n*-Paraffins

Paraffin	ε	A/A(octane)	B	G (min^{-1})	N	m	k_{md} (min^{-1})
n-Octane	1.0	1	−0.994	1.11	0.80	2.25	0.89
n-Dodecane	1.3	2.9	−0.996	1.43	0.88	2.14	1.25
n-Hexadecane	2.25	7.4	−0.998	1.52	0.42	3.38	1.42

HY, all at 400°C, using Eq. (5) is also excellent. Optimum values of the four parameters, A, B, G, and N, for each paraffin are presented in Table 1. One is immediately struck by the observation that $B \approx -1$ in all cases. There must be a reason for this particular value to appear in all systems reported here.

The significance of the parameters A and B can be examined by reference to Eqs. (3) and (4). It can be shown that

$$B = [C]_0 \frac{K - \Sigma K_i n_i}{1 + \sum_i K_i n_i [C]_0}. \qquad (6)$$

A negative value of this parameter will arise only if $\Sigma K_i n_i > K$. This in turn would be expected for reactions in which the products are more numerous than and at least as strongly adsorbed as the reactant species. Since it is known from independent evidence that olefins are adsorbed much more strongly than the *n*-paraffins (*1*, *6*), it is rewarding to find that our results indicate $\Sigma K_i n_i \gg K$. The data also require that $1 \ll \Sigma n_i K_i [C]_0$ in order to satisfy the condition $B = -1$. This constitutes classical evidence of strong adsorption and high surface coverage in Langmuirian isotherms in keeping with the thesis that olefins are strongly adsorbed on the catalytically active sites.

It is clear from the calculated value of B that the rate of paraffin cracking is strongly inhibited by product olefins, which, together with smaller paraffinic species, are major initial products of cracking (*4*, *14*).

A number of studies have focused on the effects of paraffin cracking in the presence of olefins. It has been reported that the presence of traces of olefins accelerates the initial rate of paraffin cracking (*7*, *8*), although the reason for this seems uncertain. On the other hand, it has been established that the presence of olefins at higher concentrations will inhibit the cracking process (*6*). The initial rate of cracking of *n*-hexadecane on silica alumina at 399°C, for example, was found to be retarded by the addition of 1-octene (*6*). In keeping with this

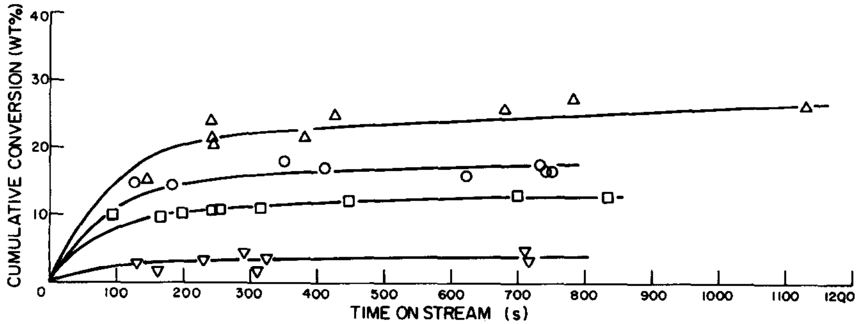

FIG. 3. Theoretical curves and experimental points for *n*-dodecane cracking on HY at 400°C fitted by the Langmuir model (Eq. (5)). Catalyst/reactant ratios: △, 0.140; ○, 0.00650; □, 0.0333; ▽, 0.0033.

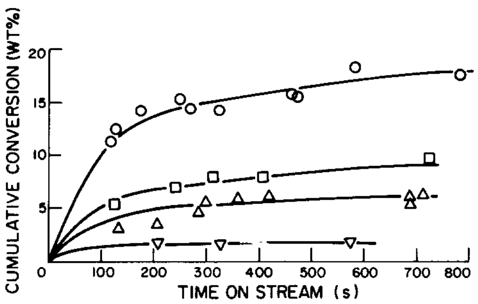

FIG. 4. Theoretical curves and experimental points for *n*-octane cracking on HY at 400°C fitted by the Langmuir model (Eq. (5)). Catalyst/reactant ratios: ○, 0.2760; □, 0.0690; △, 0.0345; ▽, 0.0035.

effect, the cracking rate of propane and butane was found to be accelerated by the continuous removal of olefinic species from the recycle stream (*15*).

The reported acceleration of the reaction by small amounts of olefins is often associated with studies of initiation processes in catalytic cracking. In these, the hypothesis pursued was that thermally produced olefins are solely responsible for cracking process initiation (*16*). Since it is now clear that olefins are not necessary to initiate the cracking reaction, the reported accelerations of rate due to the presence of olefins is unexplained.

Using the conditions relating to parameter B, it is also possible to simplify the expression for parameter A:

$$A = \frac{\sum_i k_i K[C]_0}{1 + \Sigma K_i n_i [C]_0} = K \frac{\sum_i k_i}{\Sigma K_i n_i}. \qquad (7)$$

Thus parameter A is proportional to the sum of the rate constants for all the parallel primary cracking processes. Unfortunately it also shows that a quantitative evaluation of individual cracking rate constants for the various modes of initial cracking will require prior knowledge of the adsorption constants for the reactant and all of the primary products.

An important point should be noted regarding initial rate studies in differential reactors designed to determine Σk_i in Eq. (3) under conditions where $[C] \rightarrow [C]_0$. Such studies do not justify $[C] = [C]_0$ in Eq. (3) since the products of the first cracking event already yield the same carbenium ions that compete for adsorption sites later on, at higher conversions. Thus, unless a procedure can be devised to study the products of cracking *before the catalyst surface comes to steady state*, Eq. 5 should be used to interpret even initial rate studies. The simplification of this equation for zero conversion ($X = 0$) leads to A and B as the constants being determined *even under initial conditions*. In that case, even under initial conditions, we must have $K = \Sigma K_i n_i \gg 1$ before the initial "rate constant" A actually represents Σk_i. This is clearly a very restrictive set of conditions and should not be assumed to be generally true in initial rate studies.

It has been reported that the "kinetic rate constants" for cracking *n*-paraffins on HX catalysts increase with chain length up to C_{16}, then decrease (*3*). Table 1 shows that our ratios of A/A (octane) do indeed increase with chain length. However, to proceed from this observation to a more detailed understanding of rate constant behavior, it will be necessary to understand the effect of the variation in initial product spectrum on the sum of adsorption constants in the denominator of A.

Since our results show unambiguously that the cracking of *n*-paraffins cannot in general be adequately represented by a simple first-order kinetic model and that adsorption phenomena must be taken into account, it is interesting to consider under what circumstances the simple fast-order model might be expected to describe the kinetics of hydrocarbon reactions.

In the special case when $K = \Sigma K_i n_i \gg 1$ Eq. (5) will reduce to

$$-\frac{d[C]}{dt} = \Sigma k_i [C]. \qquad (8)$$

This condition will be rare and will be satisfied most obviously when there is no change in the number of molecular species during reaction (i.e., $\Sigma n_i = 1$), and the product molecules have similar adsorption constants to the reactant. This can be expected to occur most commonly in isomerization reactions, in which the product isomers are structurally similar to the reactant. Indeed, we have found that the simple first-order kinetic model is applicable to the isomerization of 1-hexene to give 2-hexenes and 3-hexenes as the only significant products (*17*).

Catalyst Decay

According to the time-on-stream theory of catalyst decay (*11*), the rate of loss of active sites can be expressed as

$$-\frac{d\theta}{dt} = k_{md}\theta^m, \qquad (9)$$

where k_{md} is the deactivation rate constant, θ is the fraction of active sites remaining, and m is the order of deactivation.

Table 1 shows that k_{md} increases with the chain length of the paraffin. This seems to be related to increasing ease of formation of coke precursors by larger molecular species.

The values of m, the number of active sites lost per decay event, are seen to be larger than 2 in each case. Values of m in the range 2–3 have been previously reported for cracking of *n*-heptane on Y zeolite (*5*). There it was suggested that decay in such cases occurs by a second-order site-poisoning process combined with a higher-order decay by pore blocking. Our results suggest that pore blocking becomes more prevalent as a deactivation mechanism as the size of the feedstock molecule is increased. Thus our decay parameters give quantitative measure to the commonly observed fact that heavier feedstocks are more effective as catalyst poisons.

CONCLUSION

It is clear that the adsorption of product species must be considered in describing the kinetics of the catalytic cracking of paraffins. It also seems probable that the catalytic cracking of most hydrocarbons will be influenced by the competing adsorption of all other species present in the reaction. In fact, on-going work with olefins and cycloparaffins (*17*) confirms this.

At this stage it appears that pure rate constants for the various modes of cracking of pure components may not, in general, be accessible by experiment. If this is confirmed by further studies of olefins and cycloparaffins we will have to seek semiempirical expressions which can correlate the behaviors of mixed feeds. Work in this direction is in progress and semiempirical expressions of the type formulated by Kemp and Wojciechowski (*18*) for gas oil cracking may be unavoidable. In that case the hope of predicting the kinetics of hydrocarbon mixtures from an understanding of the behavior of individual components or from the study of "lumps" consisting of homologous components will fade.

REFERENCES

1. Voge, H. H., *in* "Catalysis" (P. H. Emmett, Ed.), Vol. VI, Chapter 5. Reinhold, New York, 1958.
2. Nace, D. M., *Ind. Eng. Chem.* **8,** 24 (1969).
3. Nace, D. M., *Ind. Eng. Chem.* **8,** 31 (1969).
4. Corma, A., Monton, J. B., and Orchilles, A. V., *Appl. Catal.* **16,** 59 (1985).
5. Corma, A., Fornes, V. A., Monton, J. B., and Orchilles, A. V., *Appl. Catal.* **12,** 105 (1984).
6. Pansing, W. F., *J. Phys. Chem.* **69,** 392 (1965).
7. Anufriev, D. M., Kuznetsov, P. N., and Ione, K. G., *J. Catal.* **65,** 221 (1980).
8. Weisz, P., *Chem. Tech.*, 498 (1973).
9. Pantcherkoff, G. M., *J. Chim. Phys.* **51,** 740 (1954).
10. Chen, N. Y., and Garwood, W. F., *J. Catal.* **52,** 453 (1978).
11. Wojciechowski, B. W., *Catal. Rev. Sci. Eng.* **9**(1), 79 (1974).
12. Best, D., and Wojciechowski, B. W., *J. Catal.* **47,** 11 (1977).
13. Corma, A., Monton, J. B., and Orchilles, A. V., *Ind. Eng. Chem. Prod. Res. Dev.* **23,** 404 (1984).
14. Abbot, J., and Wojciechowski, B. W., *Ind. Eng. Chem. Prod. Res. Dev.* **24,** 501 (1985).
15. Fejes, P., and Emmett, P. H., *J. Catal.* **5,** 193 (1966).
16. Scherzer, J., and Ritter, R. E., *Ind. Eng. Chem. Prod. Res. Dev.* **17,** 219 (1978).
17. Abbot, J., and Wojciechowski, B. W., in press.
18. Kemp, R. R. D., and Wojciechowski, B. W., *Ind. Eng. Chem. Fundam.* **13**(4), 332 (1974).