

Kinetics of Reactions of C₈ Olefins on HY Zeolite

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Received February 16, 1987; revised June 22, 1987

Reactions of two C₈ olefins (*n*-octene and 2,4,4-trimethylpentene) have been studied on HY at 300°C. Skeletal isomerization is the dominant reaction of *n*-octene (initial selectivity 0.98), while cracking is the dominant reaction of 2,4,4-trimethylpentene (initial selectivity 0.80). Conversion rates of both olefins can be fitted by a kinetic expression previously applied to the cracking of *n*-paraffins on HY at 400°C. The kinetic rate constants for reaction of these olefins, independent of adsorption parameters, have been calculated, and show that the sum of the rate constants for cracking 2,4,4-trimethylpentene is ~160 times greater than that for skeletal isomerization of *n*-octene. The parameters obtained show that adsorption of olefins on HY decreases with an increased degree of branching. Methylheptenes are less strongly adsorbed than linear octenes. Trimethylpentenes are less strongly adsorbed than isobutene. This trend is also observed by comparing initial coke formation on HY from the two olefin feedstocks, which shows that *n*-octenes are adsorbed to a significantly higher extent than 2,4,4-trimethylpentene. Catalyst decay was accounted for by the time-on-stream theory of decay. The decay parameters show that aging occurs much more rapidly for 2,4,4-trimethylpentene than for *n*-octene. There appears to be no simple relationship between total coke deposited and catalyst deactivation. A correlation may exist between deactivation and the degree of dehydrogenation of the coke, but it would appear to be specific to the feed used. In both these reactions no molecular hydrogen was present in the initial products, or indeed up to 50% conversion. Methane and ethane were also absent in the initial product and do not appear in significant quantities even at 50% conversion. © 1987 Academic Press, Inc.

INTRODUCTION

There have been comparatively few systematic kinetic studies of reactions of olefins on zeolites. Most previous investigations have assumed a simple first-order process, without consideration of adsorption or decay phenomena (1). We have recently shown (2) that consideration of both these processes is required for a meaningful analysis of the reaction kinetics. Reactions of *n*-octane, *n*-dodecane, and *n*-hexadecane on HY at 400°C can be fitted to a kinetic expression which assumes Langmuir-type adsorption and uses the time-on-stream theory of catalyst decay (3) to account for aging.

Here we report a kinetic study of the reactions of two isomeric C₈ olefins: *n*-octene and 2,4,4-trimethylpentene. These were selected to provide examples of reactants which undergo skeletal isomerization and

cracking, respectively, as the dominant reaction processes.

THEORY

We have shown (2) that reactions of *n*-paraffins on HY zeolite at 400°C can be described by Eq. (1),

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

where *X* is the instantaneous 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 reaction.

Equation (1) was derived (2) on the assumption that a Langmuir-type adsorption process applies. This has been shown to be the case for adsorption of simple olefins on X and Y zeolites (4).

The instantaneous fraction converted X is related to the average conversion in a run, \bar{X} , by the equation

$$\bar{X} = \frac{1}{t_f} \int_0^{t_f} X dt, \quad (2)$$

where t_f is the duration of the run.

The constants A and B are defined by the expressions

$$A = \frac{\sum_i k_i K [C]_0}{1 + \sum_i K_i n_i [C]_0} \quad (3)$$

and

$$B = [C]_0 \frac{K - \sum K_i n_i}{1 + \sum K_i n_i [C]_0}, \quad (4)$$

where k_i are 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 2,4,4-trimethyl-2-pentene (99.44% purity) and 1-octene (99.60% purity) were obtained from Aldrich and used without further purification. The impurities present were 2,2,4-trimethylpentane (0.56%) and n -octene isomers (0.40%) in the respective feedstocks. HY zeolite was prepared from NaY (Linde Co., Lot No. 45912, SK40) by repeated exchanges with 0.5 N ammonium nitrate solution followed by calcination at 500°C. Catalysts with mesh size 80/100 were steamed for 24 h at 200°C before use.

All experiments were performed at 300°C using an integral, fixed bed, gas-phase, plug flow reactor with an independently controlled three-zone heater. The experimental apparatus and the procedures used were similar to those described in previous studies (5, 6). Blank runs were carried out at 300°C to ensure that the glass used to dilute

the catalyst was inert. The catalyst was also found to be diffusion free in a preliminary set of experiments. This we demonstrated by showing that conversions were unaffected by changing the catalyst particle size, with all other conditions, including the amount of catalyst in the reactor, held constant.

Liquid products were analyzed by a Varian gas chromatograph with a 60-m SE54 capillary column and flame ionization detector. Products up to C₈ 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 SX 1156 gas chromatograph. This enabled determination of all hydrocarbons in the range C₁–C₅, and also direct determination of molecular hydrogen if present, down to levels of 0.001% (by volume) if present, corresponding to less than 10⁻³ mol% of the feedstock. Identification of products was carried out with a Finnigan 1020 automated GC/MS.

Mass balances were performed for each reaction run to ensure that no leaks were present in the system and all products were accounted for. In each run the weight of the unconverted reactant and of each product made over the time $t = 0 \rightarrow t_f$ was determined. These results produced one data point on the plot of product yield versus cumulative conversion on each selectivity plot. Additional data points were obtained at a constant catalyst-to-reactant ratio by changing the feed rate of the reactant but keeping the weight of feed delivered constant. Experiments carried out at various catalyst-to-reactant ratios, by changing the weight of catalyst in the reactor, allowed a series of yield versus conversion loops to be drawn. These loops can be enveloped by a single curve known as the optimum performance envelope (5). We have found that these envelopes are in many cases indistinguishable from simple yield-conversion curves when studying single-component feedstocks (i.e., the loops are very flat). However, the distinction becomes very apparent when mixtures are used (5).

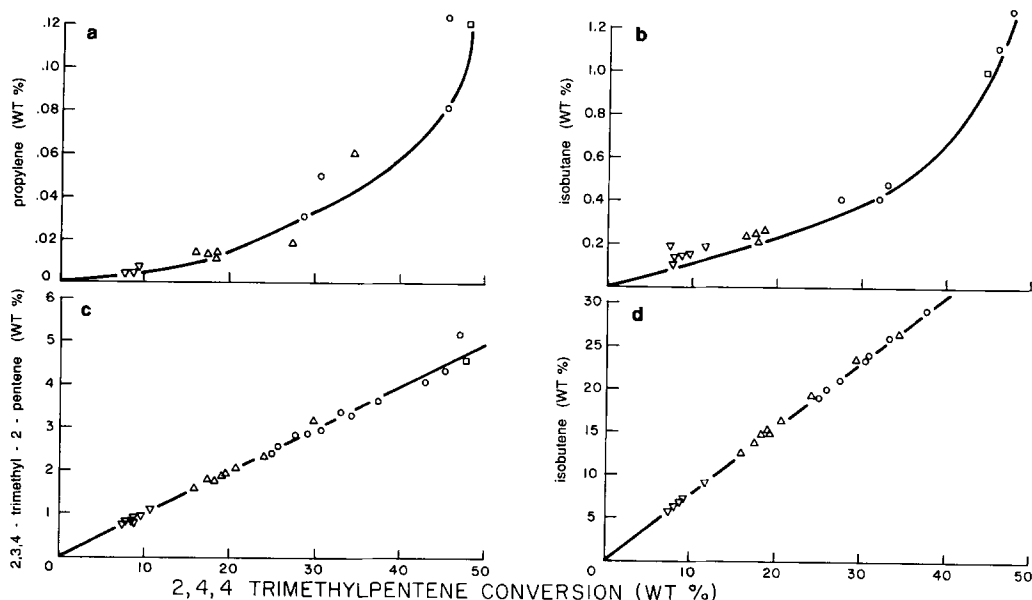


FIG. 1. Optimum performance envelopes for products of reaction of 2,4,4-TMP on HY at 300°C: (a) propylene, (b) isobutane, (c) 2,3,4-trimethyl-2-pentene, (d) isobutene. Catalyst-to-reactant ratios: (□) 0.1190, (○) 0.0366, (△) 0.0134, (▽) 0.00339.

After each run the reactor was purged with dry nitrogen at a set flow rate, at the 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 collected in a tube of drierite during regeneration allowed the hydrogen content of the coke to be calculated. The weight of carbon dioxide adsorbed 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

The reactions of 2,4,4-trimethylpentene and *n*-octene were studied on HY at 300°C. At this temperature the double-bond shift is rapid (7), so that only hydrocarbons other than 2,4,4-trimethyl-2-pentene and 2,4,4-trimethyl-1-pentene in one case and 1-octene, 2-octene, 3-octene, and 4-octene in the other were regarded as products.

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Reaction of 2,4,4-TMP

Initial product distributions were obtained by plotting optimum performance envelopes (5) for each product. Examples are shown in Fig. 1. Initial selectivities for all products are given in Table 1, which shows that cracking accounted for ~80% of the total conversion, while skeletal isomerization accounted for ~20%. With the exception of isobutane and coke, all primary products were olefins. Even at ~50% conversion, olefins accounted for over 95% of the total products.

Figure 2 shows how all the observed primary products can be accounted for by initial formation of the carbenium ions (I) and (II). Isobutene, the major initial product, is formed by β -scission of the tertiary ion (II). This is the only reaction pathway available to this ion— isomerization cannot occur through a 1,2-methyl shift as there is no methyl group adjacent to the tertiary car-

TABLE I
Initial Weight Selectivity for Reactions of 2,4,4-Trimethylpentene on HY at 300°C

Carbon number	Molecular species	Product type	Selectivity	
			Subtotal	Individual
C ₃	Propylene	(1 + 2)S	0.7987	0.0013
	Isobutene	1S		0.785
	<i>trans</i> -2-Butene	(1 + 2)S		0.0007
C ₄	<i>cis</i> -2-Butene	(1 + 2)S	0.1954	0.0010
	<i>n</i> -Butane	2S		—
	Isobutane	(1 + 2)S		0.0087
C ₅	2-Methyl-2-butene	(1 + 2)S		0.0020
C ₆	2,3-Dimethyl-2-butene	2S		—
	2,3,4-Trimethyl-2-pentene	1S		0.108
C ₈	2,3,4-Trimethyl-1-pentene	1S	0.1954	0.0685
	3,4,4-Trimethyl-2-pentene	(1 + 2)S		0.0079
	3,4,4-Trimethyl-1-pentene	1S		0.011
	2,3-Dimethyl-2-hexene	2S		—
	2,4-Dimethyl-2-hexene	2S		—
	2,2,4-Trimethylpentane	2S		—
	Aromatics	2S		—
Coke		1U		0.0027
Total:				0.997

bon atom bearing the positive charge. The alternative carbenium ion initially formed (I) is secondary, and its formation leads to

the observed skeletal isomers and minor cracking fragments (C₃ and C₅). The high initial selectivity for products formed via

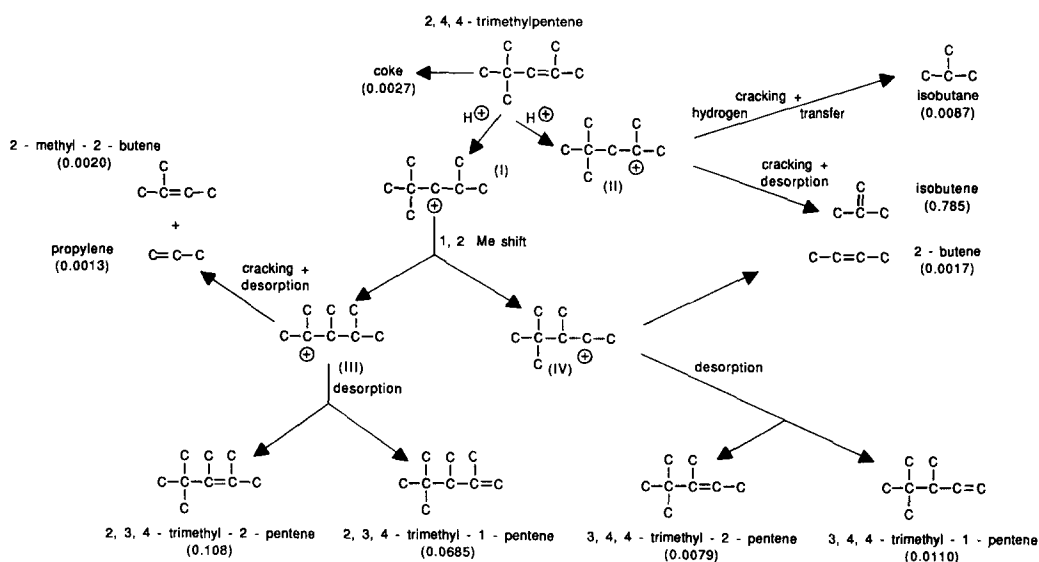


FIG. 2. Reaction network for 2,4,4-TMP on HY at 300°C.

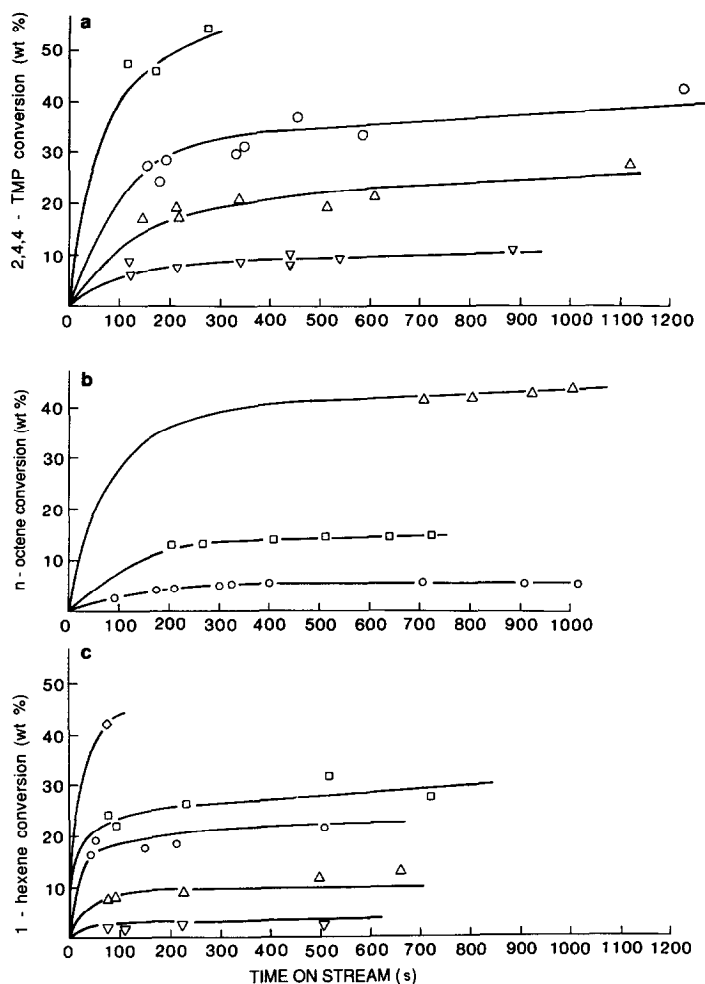


FIG. 3. Experimental values and theoretical curves for cumulative conversions on HY of (a) 2,4,4-TMP at 300°C, symbols correspond to catalyst-to-reactant ratios in Fig. 1; (b) *n*-octene at 300°C, catalyst-to-reactant ratios (Δ) 0.360, (□) 0.100, (○) 0.0333; and (c) 1-hexene at 200°C, catalyst-to-reactant ratios (◇) 0.0499, (□) 0.0204, (○) 0.048, (△) 0.00620, (▽) 0.00180.

carbenium ion (II) (0.794) compared to those from ion (I) (0.199) is a reflection of the higher stability of the tertiary ion.

The four skeletal isomers—2,3,4-trimethylpentenes and 3,4,4-trimethylpentenes—can be accounted for by formation of carbenium ions (III) and (IV), respectively, followed by desorption. The relative proportion of these two isomers (~9:1) is a reflection of the relative stabilities of the parent ions—(III) is a tertiary ion, whereas (IV) is secondary.

Dimethylhexanes were observed in small

amounts only as secondary products. Their formation is not favored as this requires the initial formation of a primary ion.

Formation of C_3 and C_5 cracking fragments is accounted for by β -scission of (III). The observed initial molar ratio for C_3/C_5 (1.08) is in keeping with the formation of these products by this monomolecular process.

Figure 3a shows experimental values of the cumulative conversions of 2,4,4-TMP as a function of time-on-stream for several catalyst-to-reactant ratios. The theoretical

TABLE 2

Kinetic Parameters for Reaction of 2,2,4-TMP and *n*-octene on HY at 300°C

Reactant	Temperature (°C)	A (mol/g · cat/min)	B	N	G (min) ⁻¹	ΣK _i (mol/g · cat/min)	k _{md} (min) ⁻¹	m
2,4,4-TMP	300	6.49 × 10 ²	-0.90	0.55	8.29 × 10 ³	6.5 × 10 ³	4.5 × 10 ³	2.82
<i>n</i> -Octene	300	1.18 × 10 ²	2.0	0.92	3.7 × 10	3.95 × 10	3.4 × 10	2.10
1-Hexene	200	3.4 × 10 ⁵	0.02	0.85	6.62 × 10 ⁴	3.3 × 10 ⁵	5.61 × 10 ⁴	2.18

curves were generated by application and time averaging of Eq. (1). Table 2 shows the optimum values of the parameters *A*, *B*, *G*, and *N*.

In cracking *n*-paraffins on HY at 400°C we found that the calculated value of the parameter *B* was -1.0 for *n*-octane, *n*-dodecane, and *n*-hexadecane. This was explained by noting that olefins were the major product of cracking at this temperature, and that the olefins are much more strongly adsorbed than the reactant paraffin (8); i.e., ΣK_in_i ≫ K. It would follow from Eq. (4) that when the value of *B* reduces to -1.0 we also have

$$\Sigma K_i n_i [C]_0 \gg 1. \quad (5)$$

If condition (5) is then applied to Eq. (3)

$$A = \Sigma k_i (K / \Sigma K_i n_i). \quad (6)$$

If we can evaluate the ratio (K/ΣK_in_i), the sum of rate constants Σk_i can be determined from the parameter *A*. In cases where *B* approaches -1.0, this ratio cannot be evaluated from Eq. (4); however, when *B* ≠ -1.0, a reasonably reliable value for this ratio can be calculated.

Since condition (5) holds in the case of the reaction of *n*-paraffins on HY at 400°C (2), it should also apply to 2,4,4-TMP at 300°C on the same catalyst. In both cases the values of [C]₀ are of similar magnitude, and the terms ΣK_in_i must be of comparable magnitude as olefins are the dominant products in both cases. If condition (5) is applied to the parameters obtained for the reaction of 2,4,4-TMP, we rewrite Eq. (4) as

$$\frac{K_{(2,4,4-TMP)} - \Sigma K_i n_i}{\Sigma K_i n_i} = -0.90, \quad (7)$$

where K_(2,4,4-TMP) is the adsorption constant for the subscripted feed. Thus K_(2,4,4-TMP)/ΣK_in_i = 0.10. Now Σk_i can be evaluated from Eq. (6) and the result is shown in Table 2.

A more detailed analysis of Eq. (7) is made possible by introducing separate terms for skeletal isomers (SI) and cracking products (CP):

$$\frac{K_{(2,4,4-TMP)} - (\Sigma K_{i(SI)} n_{i(SI)} + \Sigma K_{i(CP)} n_{i(CP)})}{(\Sigma K_{i(SI)} n_{i(SI)} + \Sigma K_{i(CP)} n_{i(CP)})} = -0.90. \quad (8)$$

We can assume that the Langmuir constants for 2,4,4-TMP and its skeletal isomers are the same. We can also assume that isobutene is the only cracking product making a significant contribution to surface coverage. Furthermore, for skeletal isomerization, one molecule of product is formed for each molecule of 2,4,4-TMP isomerized, so that

$$\begin{aligned} \Sigma n_{i(SI)} &= 1 \times (\text{selectivity for isomerization}) \\ &= 0.20. \end{aligned}$$

For cracking, two molecules of product are formed for each feed molecule cracked, so that

$$\begin{aligned} \Sigma n_{i(CP)} &= 2 \times (\text{selectivity for cracking}) \\ &= 2 \times 0.8 = 1.60. \end{aligned}$$

Substituting these values into Eq. (8) gives

$$\frac{K_{(2,4,4\text{-TMP})} - (0.20K_{(2,4,4\text{-TMP})} + 1.6K_{(\text{IB})})}{(0.20K_{(2,4,4\text{-TMP})} + 1.6K_{(\text{IB})})} = -0.90, \quad (9)$$

where $K_{(\text{IB})}$ is the Langmuir constant for isobutene.

This yields the ratio

$$K_{(\text{IB})}/K_{2,4,4\text{-TMP}} = 6.1.$$

The more highly branched olefin 2,4,4-TMP is thus found to be less strongly adsorbed than isobutene by a factor of 6.

Reaction of *n*-Octene

Table 3 shows selectivities of initial reaction processes for the reaction of *n*-octene on HY at 300°C. It is clear that the dominant reaction is skeletal isomerization forming methylheptenes and dimethylhexenes. Identification of all skeletal isomerization products is difficult because the available GC/MS computer library is incomplete above C₇.

Figure 3b shows experimental values of the cumulative conversions of *n*-octene plotted against time-on-stream for several catalyst-to-reactant ratios. The theoretical curves generated by Eq. (1) and time averaging by Eq. (2) show that the kinetic behavior is well described by assuming a Langmuir adsorption isotherm and accounting for catalyst decay using the time-on-stream theory. Table 2 shows the optimum values of the parameters thus obtained.

As the products formed are almost exclusively olefins it is again reasonable to assume that conditions (5) will apply. From Eq. (4) we write

$$\frac{K_{(\text{octene})} - \sum K_i n_i}{\sum K_i n} = 2.0$$

so that $(K/\sum K_i n_i) = 3.0$. From the value of A , $\sum k_i$ can be calculated as before. We see now from Table 2 that the rate constant for *cracking* 2,4,4-TMP is ~164 times greater than that for *skeletal isomerization* of *n*-octene on HY zeolite at 300°C. Furthermore, the individual rate constants for the various

parallel reactions of skeletal isomerization of *n*-octene, and those of *cracking* 2,4,4-TMP can be calculated by multiplying the calculated values of $\sum k_i$ by the appropriate selectivity values given in Table 1.

Because all secondary groups are expected to be approximately equally inhibiting to adsorption it is safe to assume that all the branched C₈ products formed from *n*-octene have the same Langmuir adsorption constant $K_{(\text{IP})}$. Furthermore, since $\sum n_i = 1$ in isomerization we write

$$K_{(\text{octene})}/K_{(\text{IP})} = 3.0.$$

This indicates that the adsorption constant for the linear olefin is three times greater than that for its branched isomers. As was the case with 2,4,4-TMP, branching causes a decrease in the Langmuir adsorption constant.

TABLE 3

Initial Weight Selectivity for Reactions of *n*-Octene on HY at 300°C

Carbon number	Product	Type	Initial selectivity
C ₃	Propylene	2S	0.0
	Propane	2S	0.0
C ₄	<i>n</i> -Butane	2S	0.0
	Isobutane	2S	0.0
	<i>trans</i> -2-Butene	2S	0.0
	<i>cis</i> -2-Butene	2S	0.0
C ₅	Isobutane	2S	0.0
	2-Methylbutane	2S	0.0
	<i>trans</i> -2-Pentene	2S	0.0
	<i>cis</i> -2-Pentene	2S	0.0
	3-Methyl-1-butene	2S	0.0
	2-Methyl-1-butene	2S	0.0
	2-Methyl-2-butene	2S	0.0
C ₆	1-Pentene	2S	0.0
	3-Methylpentane	2S	0.0
	2-Methylpentane	2S	0.0
	<i>n</i> -Hexane	2S	0.0
	C ₆ Olefins	2S	0.0
C ₈	Methylpentenes, dimethylhexenes	(1 + 2)U	0.980
Coke			0.020
Total			1.000

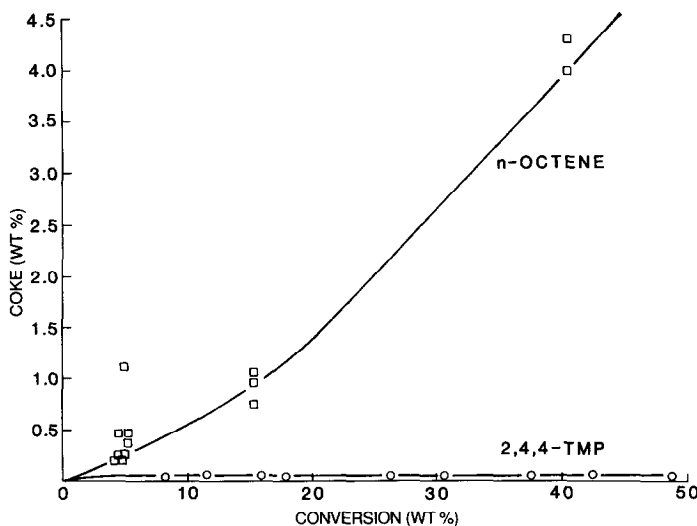


FIG. 4. Optimum performance envelopes for coke formation on HY at 300°C.

We can compare this result to the Langmuir adsorption constants for linear olefinic isomers. If branching is indeed the cause of differences in our calculated adsorption constants, we might expect little difference in the adsorption constants of all linear C_n olefin isomers. We previously reported (9) product distributions for the reaction of 1-hexene on HY zeolite at 200°C. Under these conditions only isomerization to produce 2-hexene and 3-hexene is observed. Those results can also be fitted by Eq. (1) (Fig. 3c) and the optimum value for *B* is found to be close to zero (Table 2). From Eq. (4), assuming again that condition (5) is valid, we deduce that adsorption constants for 1-hexene and 2-hexene are almost equal.

These three quite different systems show a remarkable consistency in describing the relative sizes of adsorption constants for a variety of olefins. We are of the opinion that the constants *A* and *B*, formulated from basic principles, have now been shown to be applicable to real systems. It follows that Eq. (1) is in fact an adequate model of hydrocarbon cracking and fundamentally sound.

CATALYST DECAY

According to the time-on-stream theory of catalyst decay (3), the rate of loss of active sites can be expressed as

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

where *k_{md}* is the deactivation rate constant, *θ* is the fraction of sites remaining, and *m* is the order of deactivation. The constants *k_{md}* and *m* can be calculated from optimum values of *G* and *N* (Table 2). It is apparent that the decay rate constant for the reaction of 2,4,4-TMP is ~134 times greater than that for *n*-octene. The order of the decay expression, *m*, is also larger for the branched olefin.

Figure 4 shows the percentage conversion to coke plotted against total conversion. We note that more coke is deposited by *n*-octene at any given conversion and the ratio coke/catalyst, shown in Fig. 5, is also higher in the reaction of the linear olefin. At low conversion the C/H ratio for coke formed by reaction of *n*-octene (0.5) indicates that mainly adsorbed olefins are present. At higher conversions the C/H ra-

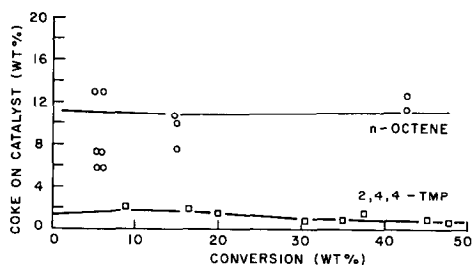


Fig. 5. Coke on catalyst shown as a function of conversion for reaction of *n*-octene and 2,2,4-TMP at 300°C on HY.

tio of this coke (~ 1.0) indicates a coke with a higher degree of dehydrogenation. In the reaction of 2,4,4-TMP a high degree of dehydrogenation ($C/H \sim 1.0$) was observed at all levels of conversion studied. This, taken together with the much greater rate of decay in 2,4,4-TMP, suggests that dehydrogenated coke is a more powerful deactivator than hydrogenated coke. Comparing the levels of coke shown in Fig. 5 with the values of aging constants in Table 2 makes it apparent that there is no quantitative relationship between aging rates and the level of coke for these two reactions on this catalyst at 300°C.

The levels of coke deposited by *n*-octene are significantly above those found for 2,4,4-TMP (Figs. 4 and 5). This too is an indication that the linear olefin is adsorbed to a greater extent than the branched iso-

mer. This fact is in agreement with trends revealed by our analysis of relative adsorption constants, i.e., increased branching of olefins results in decreased adsorption.

AROMATICS

Aromatics were formed on HY at 300°C as stable secondary products of both *n*-octene and 2,4,4-TMP (Fig. 6). More aromatics are produced from the linear feedstock. At the levels of conversion studied, aromatics formed from *n*-octene are predominantly C_8 species, with small amounts of C_9 species present at higher conversions. In contrast, the dominant aromatic species formed from the 2,4,4-TMP feedstock were C_9 ; very little C_8 was formed.

Table 4 gives a list of aromatic species identified by GC/MA in concentrated liquid samples from all the pooled liquid products of experiments on a given feed.

CONCLUSIONS

Surface coverage by olefins which adsorb on HY zeolite is governed by steric factors rather than by the stability of the resulting ion. A high degree of branching reduces the ease of adsorption and results in lower coverage despite the fact that tertiary carbons yield more stable carbenium ions.

We find that there is no relation between total coke make and catalyst deactivation but that a strong relationship exists be-

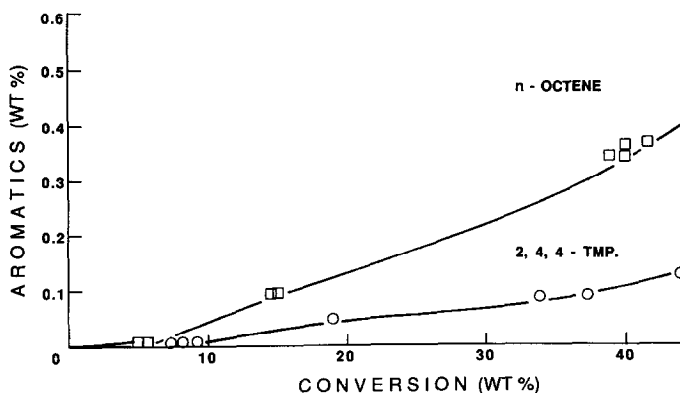


Fig. 6. Optimum performance envelopes for total aromatics formed on HY at 300°C.

TABLE 4
Hydrocarbons Found in Concentrated Liquid
by GC/MS^a

2,4,4-TMP		
C ₈	C ₉	C ₁₀
Dimethyl-Bz	Trimethyl-Bz	Tetramethyl-Bz
2,3,3-Trimethyl-1,4,-pentadiene		
3,4-Dimethyl-2,4-hexadiene		
C ₁₁	C ₁₂	
Ethylpropyl-Bz	Trimethylpropyl-Bz	
<i>n</i> -Octene		
C ₈	C ₉	C ₁₀
Dimethyl-Bz	Trimethyl-Bz	Tetramethyl-Bz
	Ethylmethyl-Bz	Dimethylethyl-Bz
		Methylpropyl-Bz
		<i>t</i> -Butyl-Bz
C ₁₁	C ₁₂	
Methyl-Np	Dimethyl-Np	

^a Bz, benzene; Np, naphthalene.

tween the level of dehydrogenation and decay. "Coke" which has a C/H ratio the same as that of the feed may simply be considered adsorbed feed. It is the fraction of total coke which has a low C/H ratio which is both less desorbable and less reactive and constitutes the real poisoning species. A correlation between the H/C ratio and catalyst deactivation may exist but would almost certainly be specific to the feed used.

The success of our kinetic formulation as a quantitative description of *n*-octene isomerization and of 2,4,4-TMP cracking, as well as its previous success in describing the kinetics of *n*-octane, *n*-dodecane, and *n*-hexadecane cracking and of 1-hexene isomerization, supports the view that the parameters *A* and *B* have fundamental meaning as outlined above and may be used to deduce

details of the reaction mechanisms which are hard, or impossible, to ascertain more directly.

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