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Catalytic Reactions of Branched Paraffins on HY Zeolite

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Catalytic reactions on HY zeolite have been studied for 2,2,4-trimethylpentane at 300 and 400°C and for 2-methylpentane at 500°C. Initial selectivity values were obtained for all reaction products. Molecular hydrogen was formed as an initial product from reaction of 2-methylpentane, although this was not previously observed for reaction of *n*-hexane on HY. This shows that hydrogen can be formed as a primary product when the structure of feed molecule contains a hydrogen atom bonded to a tertiary carbon. In this respect reactions of paraffins on solid acid catalysts are analogous to those in liquid superacid media. In general, there are three distinct processes which can lead to evolution of molecular hydrogen during cracking processes: (a) thermal reactions, (b) hydrogen production in association with the formation of coke and aromatics, and (c) dehydrogenation resulting from interaction of a Brønsted proton with a "tertiary" hydrogen atom in a branched molecule. The tendency to liberate hydrogen increases with temperature for each process. Formation of unsaturated coke deposits from reaction of 2,2,4-trimethylpentane was found to be significantly greater at 300°C than at 400°C. Coke formation was, however, not accompanied by the production of volatile aromatic species, showing that coke and aromatics may be produced by independent pathways. © 1988 Academic Press, Inc.

INTRODUCTION

There has been much recent interest in the mechanism and kinetics of cracking reactions of paraffins on acid catalysts, particularly zeolites (*1–9*). We have previously described a kinetic model, where a Langmuir adsorption isotherm and the time-on-stream theory of catalyst decay (*10*) have been successfully applied to describe reactions of linear paraffins on HY zeolite (*5*). A detailed examination of initial selectivity values for all reaction products in these studies has also revealed that apparently anomalous olefin/paraffin ratios can be explained by taking into account hydrogen transfer processes leading to the formation of coke and aromatic species as primary products (*6*). Here we extend our studies to include the reactions of the branched paraffins 2,2,4-trimethylpentane and 2-methylpentane to demonstrate the general applicability of our methodology and the proposed kinetic model. In particular, we have carefully examined the formation of molecular hydrogen to determine the conditions for its production during the cracking of paraffin molecules.

THEORY

It has been shown (*3, 5, 7*) that reactions of *n*-paraffins on HY zeolite in the temperature range 300–500°C can be described by assuming a Langmuir isotherm to account for adsorption, and the time on stream theory (*10*) to account for catalyst decay. Experimental results were fitted by

$$\frac{dx}{d\tau} = \left[\frac{A(1 - x/1 + \varepsilon x)}{1 + B(1 - x/1 + \varepsilon x)}\right] (1 + Gt)^{-N}, \quad (1)$$

where x is the fractional conversion of reactant, τ is the feed contact time, G and N are aging parameters, A and B are parameters related to reaction rate constants as defined below, ε is the volume expansion coefficient, and t is the time on stream.

The parameters A and B are defined by

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

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

where k_i are rate constants corresponding to i modes of reaction, K and K_i are Langmuir adsorption constants for the reactant and ith product species, respectively, n_i is a stoichiometric factor representing the number of moles of product i formed from reaction of one mole of reactant, and $[C]_0$ represents the initial concentration of reactant.

EXPERIMENTAL

The feedstocks, 2-methylpentane (99.40%) and 2,2,4-trimethylpentane (100.00%), were obtained from Aldrich and used without further purification. Impurities present in 2-methylpentane (2,3-dimethylbutane, 0.21%, and 3-methylpentane, 0.39%) were taken into account in calculating initial selectivities.

HY zeolite was prepared from NaY (Linde Co., Lot No. 45912 SK40) by repeated exchange with ammonium nitrate solution, followed by calcination at 500°C. The exchange level of the catalyst used was determined to be 97.3% by atomic absorption. Catalysts with mesh size 80/100 were steamed for 24 h at 200°C and 1 atm pressure before use.

All experiments were performed at 300, 400, or 500°C at 1 atm pressure by using an integral, fixed bed, gas-phase plug flow reactor with an independently controlled three-zone heater. The experimental apparatus and procedures were similar to those described in previous studies (*11*). Blank runs were carried out at the appropriate reaction temperature to determine the extent of thermal cracking.

Liquid products were analyzed by a Varian 600 gas chromatograph with a 60-m SE54 capillary column and a 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 carried out using 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 on the catalyst 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.

The catalyst crystallinity was checked before and after reaction. Good crystallinity was observed but no comparison to standard 100% samples was made. There was no observable change in crystallinity after many reaction cycles.

RESULTS AND DISCUSSION

Initial selectivities of products formed on HY from reactions of 2-methylpentane at 500°C and of 2,2,4-trimethylpentane at 300 and 400°C were determined by plotting optimum performance envelopes for each product (*11*). Blank runs, in the absence of catalyst, enabled the extent of thermal conversion to be determined. This was found to be negligible for 2,2,4-trimethylpentane in the range 300–400°C. At 500°C, thermal conversion of 2-methylpentane occurred to a smaller extent than that previously observed for *n*-hexane (*3*). Catalytic conversions for 2-methylpentane were determined by subtraction of the thermal conversion at the corresponding time on stream for each experimental run. As for reaction of *n*-hexane (*3*) at 500°C, initial formation of methane could be accounted for by thermal processes alone.

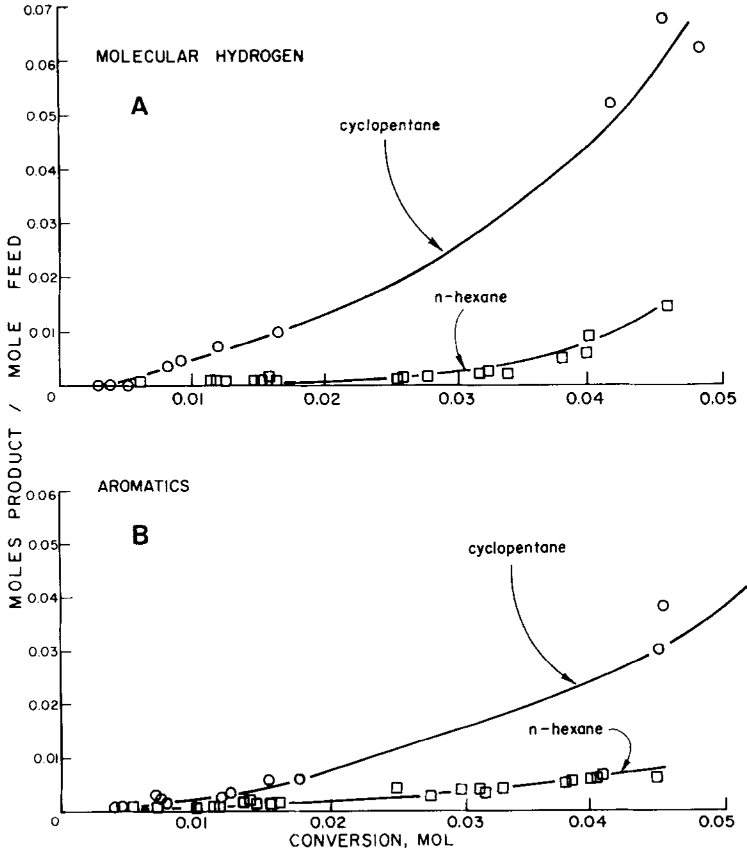


FIG. 1. Optimum performance envelopes for the formation of molecular hydrogen and aromatics from reaction of cyclopentane and *n*-hexane on HY at 500°C.

Hydrogen Formation

There has been lively recent interest in the source and significance of molecular hydrogen formation during the catalytic cracking of paraffins (*1–4*). In our studies of reactions of linear paraffins in the range C_8–C_{16} on HY at temperatures up to 400°C (*5–7*) hydrogen has not been observed at any level of conversion investigated. This finding is in agreement with studies on cracking of *n*-heptane on Y zeolite in the range 400–470°C (*4*). We have also not detected molecular hydrogen during reaction of feedstocks containing mixtures of linear and branched paraffins on either HY or HZSM-5 at 400°C (*12, 13*).

More recently we reported on reactions of *n*-hexane and cyclopentane at 500°C on HY (*3, 14*). In both cases, although molecular hydrogen was observed as a secondary product, it was not formed initially. This was explained by proposing that hydrogen is formed in association with the production of coke and aromatics, both mainly observed as secondary products. Hydrogen yield was found to be greater for cyclopentane than for *n*-hexane at a particular conversion level, corresponding to higher yields of unsaturated products (Fig. 1). We have also reported that significant levels of aromatics and unsaturated coke deposits can be produced at lower temperatures without any evolution of molecular hydrogen (for example, reaction of *n*-hexadecane on HY at 300°C (*7*)). It therefore seems that this dehydrogenation process is favored by

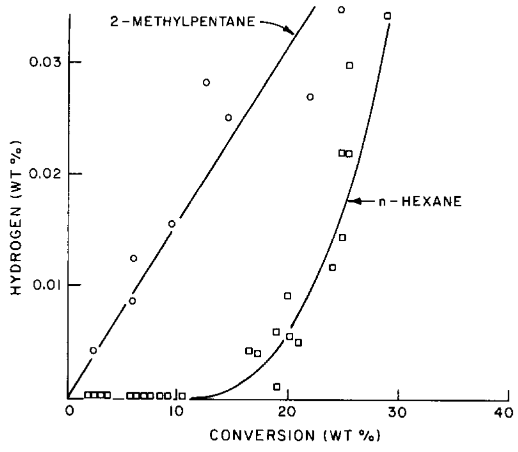


FIG. 2. Optimum performance envelopes for hydrogen formation from reaction of *n*-hexane and 2-methylpentane on HY at 500°C.

high temperatures. Hydrogen evolution in association with coke formation has previously been proposed (*15*), and a free radical mechanism has been suggested. This is probably the process responsible for some or all the secondary hydrogen produced here.

Figure 2 shows optimum performance envelopes for hydrogen formation during reaction of *n*-hexane and 2-methylpentane on HY at 500°C. It is apparent that hydrogen is a primary product from the branched paraffin, whereas it is observed only as a secondary product from the linear feed (*3*). This is the first instance in which we have reported molecular hydrogen as an initial product.

This difference between the reaction of linear and branched hexane isomers is analogous to those observed in superacid media at low temperatures (*16*). It has been established that for linear paraffins, protonation of the molecule in superacids leads to formation of a shorter paraffin and a carbenium ion via protolysis, with very little tendency to form molecular hydrogen (*16*). However, when the hydrocarbon molecule is branched and has a hydrogen atom attached to a tertiary carbon, hydride extraction becomes facile, leading to molecular hydrogen and a carbenium ion (*16*). We have also studied reactions of mixed paraffin feeds containing monomethyl isomers on HY at 400°C (*13*), when molecular hydrogen was not observed. It appears, therefore, that this mode of hydrogen formation also becomes more favorable at high temperatures.

Molecular hydrogen was not, however, observed during reaction of 2,2,4-trimethylpentane on HY in the range 300–400°C, even though this feed contains a "tertiary" hydrogen in the structure. Studies of reactions of paraffins in liquid superacid media (*16*) have shown that when the tertiary hydrogen atom is shielded due to plentiful branching in the molecule, the tendency to form hydrogen can be severely reduced. Thus, although isoalkanes containing a tertiary C–H bond show preferential reactivity for the C–H bond, increased branching can cause a shift in reactivity in favor of C–C bond protolysis as a result of steric hindrance (*16*). This is illustrated by reference to reactions of substituted pentanes in FSO_3H–SbF_5 (*16*). For 2-methylpentane, the dominant reaction observed is C–H bond cleavage, to produced molecular hydrogen, whereas for the more highly branched molecule 2,4-dimethylpentane, this is a minor reaction, and protolysis of the C–C bond to produce C_3 + C_4 cracking fragments is mainly observed. This is consistent with our observation that molecular hydrogen is not observed for reaction of the trimethylpentane on HY.

A third possible source of molecular hydrogen is the thermal decomposition of the feed. At 500°C we have not detected hydrogen as a thermal product from linear paraffins, nor was it observed as a product from 2-methylpentane or 2,2,4-trimethylpentane at the reaction temperatures used in this study. We have, however, detected traces of thermally produced hydrogen from 2,3-dimethylbutane at 500°C, and it seems certain that molecular hydrogen would be a product of thermal decom-

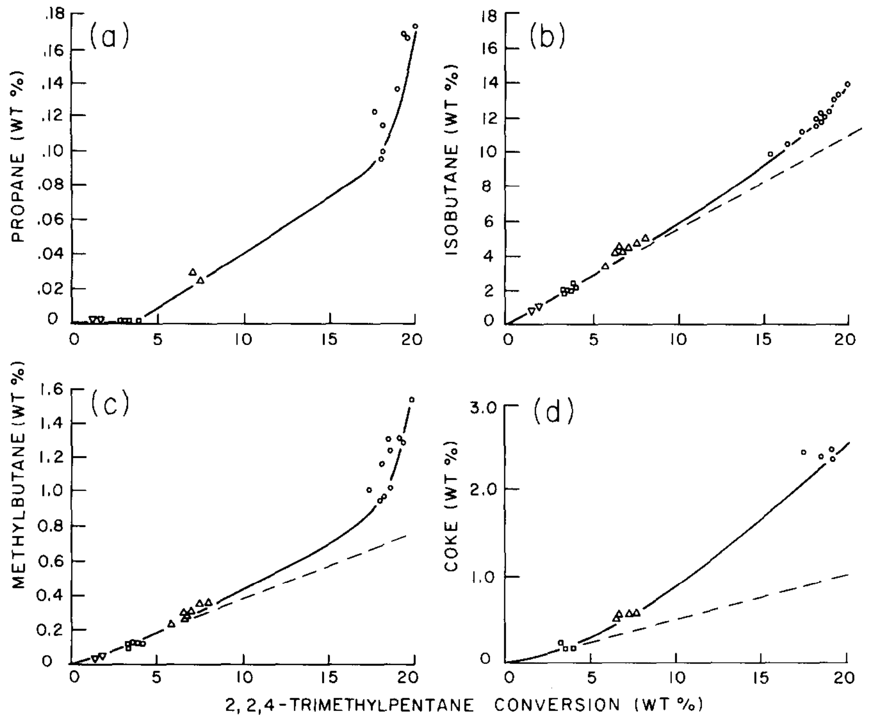


FIG. 3. Optimum performance envelopes for products of reaction from 2,2,4-trimethylpentane on HY at 300°C: (a) propane, (b) isobutane, (c) methylbutane, (d) coke. Catalyst-to-reactant ratios: ○, 0.388; △, 0.11; □, 0.037; ▽, 0.0148. (Dashed lines show initial selectivities.)

TABLE 1

Initial Weight Selectivities for Reaction of 2,4,4-Trimethylpentane on HY Zeolite at 300 and 400°C

		Type[a]		Initial weight selectivity[b]			
		300°C	400°C	300°C		400°C	
C_3	Propylene	1S	1S	0.0091		0.0178	
	Propane	2S	2S	—		—	
C_4	Isobutane	(1 + 2)S	(1 + 2)S	0.540	0.927	0.495	0.954
	Isobutene	1U	1U	0.350		0.410	
	n-Butane	2S	2S	—		—	
	trans-2-Butene	1U	1S	0.022		0.028	
	cis-2-Butene	1U	1U	0.015		0.021	
C_5	Isopentane	(1 + 2)S	(1 + 2)S	0.0167		0.020	
	n-Pentane	2S	1S	—		—	
	Olefins	2S	1S	—		0.0094	
	Coke	(1 + 2)S	(1 + 2)S	0.0500		0.00386	
			Total	1.003		1.005	

[a] 1, primary; 2, secondary; S, stable; U, unstable.

[b] Initial selectivities were obtained by measuring the slope at the origin for the corresponding optimum performance envelope (see Fig. 3).

position for the other feedstocks if the temperature were raised sufficiently.

Catalytic Cracking of 2,2,4-Trimethylpentane

Figure 3 shows examples of optimum performance envelopes (*11*) for reaction of 2,2,4-trimethylpentane on HY at 300°C. Initial selectivity values at both 300 and 400°C are given in Table 1. It is apparent that in the temperature range 300–400°C the dominant reaction process is cracking to produce two C_4 fragments, principally isobutane and isobutene. Cracking into two C_4 fragments accounts for 93 and 95% of the initial cracking selectivity at 300 and 400°C, respectively. The only other cracking mode observed in this temperature range corresponds to a monomolecular cleavage to produce $C_3 + C_5$, as the initial molar ratios for C_3/C_5 are close to unity at both temperatures (Table 2).

The remaining primary product from reaction of 2,2,4-trimethylpentane was coke, observed as a stable primary plus secondary product at both temperatures (Fig. 4A). The initial selectivity for coke formation was significantly higher at 300°C than at 400°C, as we have seen previously when comparing coke formation from *n*-hexadecane on HY at these two temperatures (*7*). The degree of unsaturation of the coke produced from reaction of 2,2,4-trimethylpentane on HY was also significantly higher for any given conversion level at the lower temperature, a trend we have also previously seen for reaction of *n*-hexadecane (*7*). Initial C/H atomic ratios for coke produced by reaction of 2,2,4-trimethylpentane were 1.10 at 300°C and 0.65 at 400°C, these ratios increasing with the extent of conversion at both temperatures. Figure 4B shows that, although coke formation is significantly higher at 300°C, levels of coke-on-catalyst are similar at 300 and 400°C, most results falling in the range 4–5% by weight. We have also previously observed (*7*) that levels of coke-on-catalyst from reaction of *n*-hexadecane on HY at 300 and 400°C do not vary significantly with temperature or conversion level.

TABLE 2

Initial Molar Selectivity for Products Formed from Reaction of 2,2,4-Trimethylpentane on HY

		Initial molar selectivity[a]		Initial hydrogen transfer
		300°C		
Paraffins	C_3	—	1.086	1.086
	C_4	1.06		
	C_5	0.0264		
Olefins	C_3	0.0247	0.812	1.088[b]
	C_4	0.788		
	C_5	—		
Coke		0.0500	0.0500	
		400°C		
Paraffins	C_3	—	1.005	1.005
	C_4	0.973		
	C_5	0.0317		
Olefins	C_3	0.0483	0.998	1.001[c]
	C_4	0.934		
	C_5	0.0153		
Coke		0.00386	0.00386	

[a] Initial molar selectivities were calculated from the corresponding initial weight selectivities in Table 1, using the relationship: initial molar selectivity = initial weight selectivity × MW of feed/MW of product.

[b] Initial hydrogen transfer selectivity calculated for coke on the basis of C/H ratio = 1.10.

[c] Initial hydrogen transfer selectivity calculated for coke on the basis of C/H ratio = 0.65.

Aromatics were not observed as either primary or secondary products from reaction of 2,2,4-trimethylpentane on HY in the range 300–400°C. This is in contrast to reaction of *n*-octane at 400°C (*6*), where aromatics are produced as both primary and secondary products. Aromatic species from 2,2,4-trimethylpentane could only be identified in trace amounts by GC/MS in concentrated liquid samples from all experiments. Mononuclear aromatics from C_8–C_{12}, as well as methyl- and dimethylnaphthalenes, were identified.

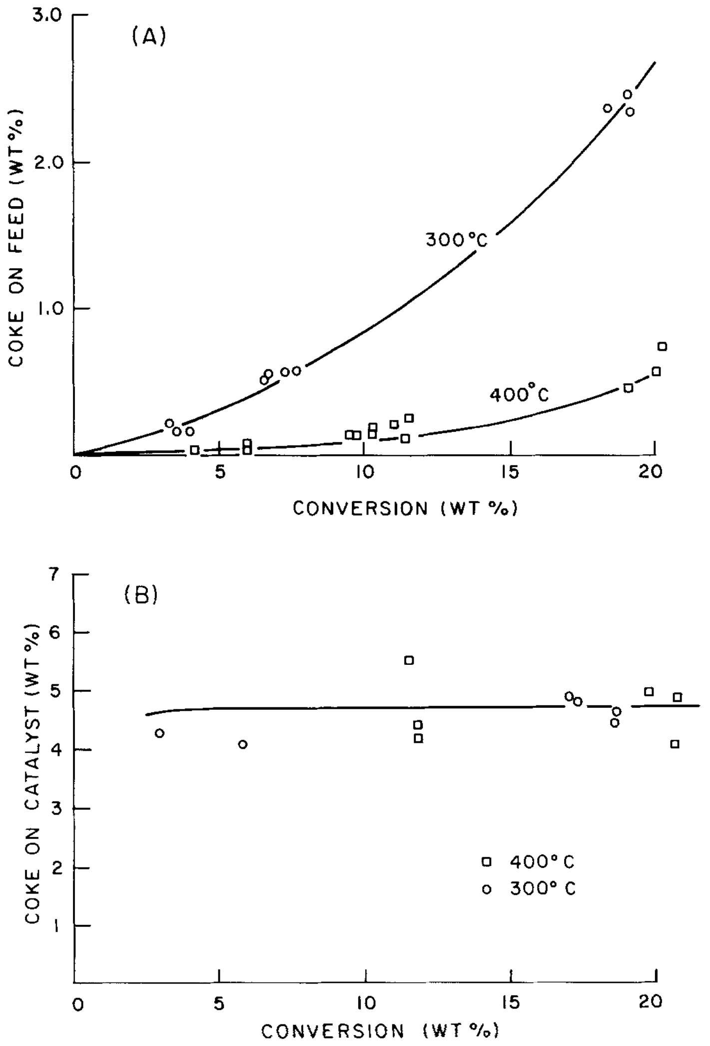


FIG. 4. (A) Optimum performance envelopes for coke from reaction of 2,2,4-trimethylpentane on HY at 300 and 400°C. (B) Coke on catalyst for reaction of 2,2,4-trimethylpentane on HY at 300 and 400°C.

This lack of aromatics, compared to a reaction of the corresponding linear C_8 paraffin, is presumably related to the much greater difficulty in forming a chain of sufficient length to cyclize into the C_6 aromatic nucleus. This can occur directly from the linear C_8 molecule, but the longest chain in 2,2,4-trimethylpentane has only five carbon atoms. It has been established using radioactive tracer studies (*17*, *18*) that aromatics (and coke) are produced as secondary products during cracking of *n*-hexadecane on silica–alumina by condensation of small olefins. However, condensation of two isobutene product molecules would lead to 2,4,4-trimethylpentene, which would again be limited in its ability to cyclize into aromatic structures by the five-carbon chain. We have previously seen that during reaction on HY, this C_8 olefin produces fewer aromatics than the corresponding linear isomer (*19*). No trace of any C_8 olefins could be detected for reaction of 2,2,4-trimethylpentane at any conversion level at either 300 or 400°C.

We have generally found that aromatic species and unsaturated coke deposits are produced concurrently during reaction of paraffins, olefins, and cycloparaffins on HY zeolite (*6, 7, 14*). Although it seems clear that polynuclear aromatics and olefins are important coke precursors (*20, 21*), mononuclear aromatic species appear to play only a minor role as coke intermediates (*20, 22*). Reaction of 2,2,4-trimethylpentane provides an example where highly unsaturated coke deposits are formed on the catalyst, in the absence of mononuclear aromatic products. It appears that the coke produced here is mainly built up directly from product olefinic molecules, principally isobutene. It would appear that mononuclear aromatics and coke can be produced by different pathways, one of which is absent here due to limitations in forming the required cyclic structures from the small, branched, olefinic product species.

There have been a number of recent studies on paraffin cracking (*4, 8, 9*) in which it has been shown that the initial molar ratio for paraffins/olefins formed is not unity. In our studies of cracking linear paraffins on HY in the temperature range 300–500°C we have also found that this ratio differs from unity (*6*). However, in contrast to other workers, we have found that, in each case, the excess of paraffins produced can always be accounted for by a corresponding amount of hydrogen transfer from the formation of coke and aromatics (*6*). The value of this ratio depends on the mode of fragmentation of the particular paraffin. For linear molecules in the range C_6–C_8, when the dominant cracking reaction produces one paraffin and one olefin species, the initial paraffin/olefin ratio reflects the propensity toward hydrogen transfer reactions on the particular catalyst at the reaction temperature. Attempts to evaluate the relative importance of various cracking mechanisms for the paraffin molecule on different acid sites from the value of this ratio (*4*) appear questionable.

From Table 2 it is apparent that the initial molar ratios for paraffin/olefin are higher than unity for reaction of 2,2,4-trimethylpentane on HY. The calculated ratios are 1.34 and 1.007 at 300 and 400°C, respectively. However, as we have previously reported for linear paraffins, Table 2 shows that a complete hydrogen balance is maintained at both temperatures when all initial products, including coke, are considered.

Cracking of 2-Methylpentane

Examples of optimum performance envelopes for products formed from reaction of 2-methylpentane on HY at 400°C are presented in Fig. 5. Table 3 shows the initial catalytic selectivities for each product. Apart from molecular hydrogen, all initial products were either olefins or paraffins in the range C_2–C_6.

The formation of C_2, C_3, and C_4 species can be accounted for by the simple mononuclear processes

$$C_6 \rightarrow C_3 + C_3 \qquad (4)$$

$$C_6 \rightarrow C_2 + C_4 \qquad (5)$$

previously observed during reaction of *n*-hexane on HY at this temperature (*3*).

A simple monomolecular process cannot, however, explain the initial formation of C_5 species. Although methane was observed as an initial product, its formation can be accounted for by thermal processes alone. The initial molar ratio for C_2/C_4 from Table 4 (0.267) also indicates that formation of C_2 and C_4 species cannot be explained by Eq. (5) alone. These observations can be explained by assuming parallel bimolecular modes of cracking for 2-methylpentane, as we have previously reported for reaction of *n*-hexane (*3*). Disproportionation reactions have also been suggested to explain product distributions for cracking of other short-chain paraffins, including butane on solid

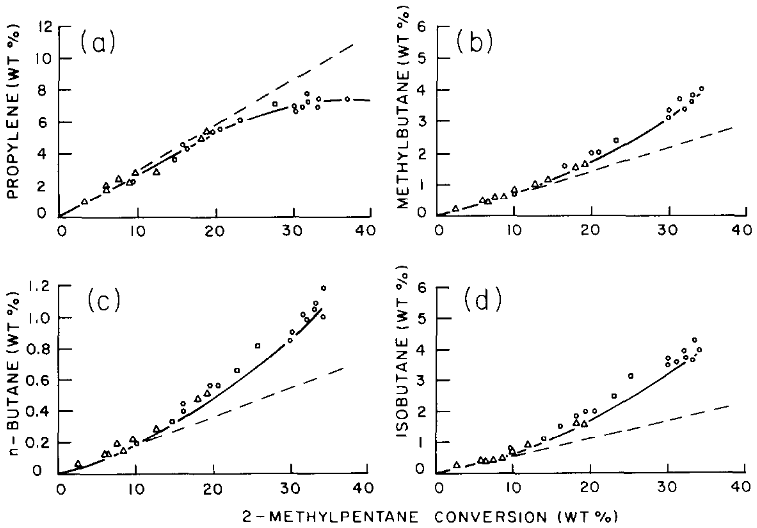


FIG. 5. Optimum performance envelopes for products of reaction from 2-methylpentane on HY at 500°C: (a) propylene, (b) methylbutane, (c) *n*-butane, (d) isobutane. Catalyst-to-reactant ratios: ○, 0.370, □, 0.0147; △, 0.00741. (Dashed lines show initial selectivities.)

TABLE 3

Initial Weight Selectivities[a] for Reaction of 2-Methylpentane on HY at 500°C

	Product	Type[a]	Initial selectivity[b]	
	Hydrogen	1S	0.0020	
C_2	Ethylene	(1 + 2)S	0.018	0.018
	Ethane	2S	—	
C_3	Propylene	1U	0.300	0.539
	Propane	1S	0.239	
C_4	Isobutane	(1 + 2)S	0.0772	0.1378
	n-Butane	(1 + 2)S	0.0205	
	Isobutene	1S	0.025	
	trans-2-Butene	1S	0.0096	
	cis-2-Butene	(1 + 2)S	0.0055	
C_5	Isopentane	(1 + 2)S	0.092	0.0978
	n-Pentane	(1 + 2)S	0.0034	
	C_5 olefins	1S	0.0024	
C_6	2, 3-Dimethylbutane	1U	0.0390	0.1983
	3-Methylpentane	1U	0.121	
	n-Hexane	(1 + 2)S	0.0190	
	C_6 olefins	1S	0.0193	
	C_7 olefins	2S	—	
	Toluene	2S	—	
	C_8 aromatics	2S	—	
	C_9 aromatics	2S	—	
	Coke	(1 + 2)S	0.0070	
		Total	0.9999	

[a] 1, primary; 2, secondary; S, stable; U, unstable.

[b] Initial weight selectivities were obtained by measuring the slope at the origin for the corresponding optimum performance envelope.

TABLE 4

Initial Molar Selectivity for Products Formed from Reaction of 2-Methylpentane on HY at 500°C

Product		Initial molar selectivity[a]		Initial hydrogen transfer
Hydrogen		0.0860		
Paraffins	C_3	0.467	0.905	0.99
	C_4	0.1449		
	C_5	0.1140		
	C_6	0.179		
Coke[b]		0.007		
Olefins	C_2	0.0553	0.754	
	C_3	0.6143		
	C_4	0.0616		
	C_5	0.00295		
	C_6	0.01976		

[a] Initial molar selectivities were calculated from the corresponding initial weight selectivities in Table 3, using the relationship: initial molar selectivity = initial weight selectivity × MW of feed/MW of product.

[b] Initial C/H ratio = 0.5 indicates mainly adsorbed feed.

superacid catalysts (*23*) and *n*-heptane on a Y zeolite (*9*).

The appearance of C_5 as an initial product can be attributed to a bimolecular process:

$$C_6 + C_6 \rightarrow [C_{12}] \rightarrow C_5 + [C_7] \rightarrow C_5 + C_4 + C_3 \quad (6)$$

As C_7 species were not detected as initial products, (Table 3) further cracking of this fragment must occur before desorption. Cracking of C_7 to produce C_3 and C_4 fragments is considered more probable than C_2 and C_5 (*8*). Calculation of the total molar initial selectivity for C_2 and C_5 shows that this is less than the initial molar selectivity for C_4 (Table 4). The remaining C_4 species can be accounted for by the bimolecular process

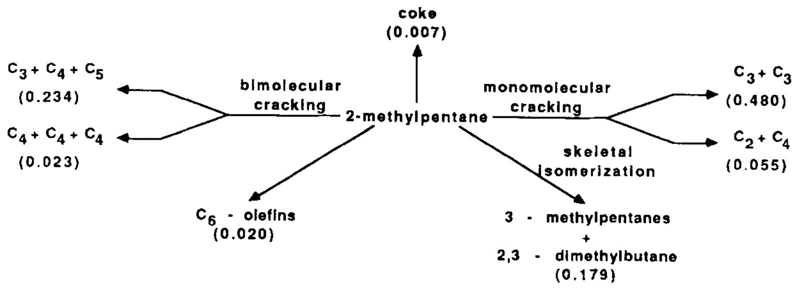
$$C_6 + C_6 \rightarrow [C_{12}] \rightarrow C_4 + [C_8] \rightarrow C_4 + C_4 + C_4 \quad (7)$$

No C_8 species are detected initially, so that further cracking must occur before desorption. The C_8 species can also crack to produce $C_3 + C_5$, but the overall process would be indistinguishable from Eq. (6).

The initial selectivity for formation of C_3 species by monomolecular cracking (Eq. (1)) can now be calculated by subtracting the molar selectivity for C_3 formed by reaction (6) (i.e., by subtracting the selectivity for C_5) from the total observed selectivity for C_3. The remaining initial processes are skeletal isomerization to C_6 paraffins, formation of C_6 olefins, and coke production. The initial C/H ratio for coke produced at this temperature was ~0.5, indicating mainly adsorbed feed. Table 4 shows that, as in the case of 2,2,4-trimethylpentane, a hydrogen balance is maintained for initial products.

Figure 6a shows the initial selectivities calculated for all reaction modes of 2-methylpentane on HY at 500°C. Reaction processes for *n*-hexane under the same conditions are presented for comparison in Fig. 6b. It is apparent that initial bimolecular processes occur to a greater extent for the branched C_6 paraffin, as the initial se-

(a) **2-methylpentane**



(b) **n - hexane**

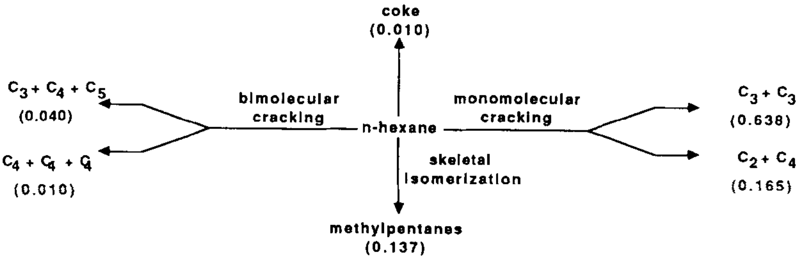


FIG. 6. Networks for initial reactions of 2-methylpentane and *n*-hexane on HY at 500°C. Numbers in parentheses indicate initial selectivities.

lectivity for these reactions exceeds that for the linear isomer by a factor of 5.

A significant difference between the initial reaction processes for *n*-hexane and 2-methylpentane shown in Fig. 6 is that C_6 olefins are produced only from the branched isomer. Interaction of the "tertiary" hydrogen atom of 2-methylpentane with a Brønsted site can lead to formation of molecular hydrogen and a residual C_6 carbenium ion (*1*). This ion can either desorb as a C_6 olefin or crack further, to form C_3 or $C_2 + C_4$ fragments. The possibility of further cracking explains why the initial molar selectivity for molecular hydrogen (0.086) in Table 4 exceeds that for C_6 olefin production (0.02), showing that cracking is more probable than direct desorption by a factor of 4.

The linear C_6 paraffin molecule may also undergo initial reaction at Brønsted sites, but, in the absence of tertiary hydrogen atoms in the structure, no molecular hydrogen is formed. C_6 olefins are not detected as initial products and reaction is limited to protolysis, yielding a smaller paraffin and an adsorbed carbenium ion. The proposed reaction modes from the two C_6 paraffins are illustrated in Fig. 7.

We have already noted that, although 2,2,4-trimethylpentane has a tertiary hydrogen atom in its structure, molecular hydrogen is not produced in the initial reaction. This is now seen to be consistent with the

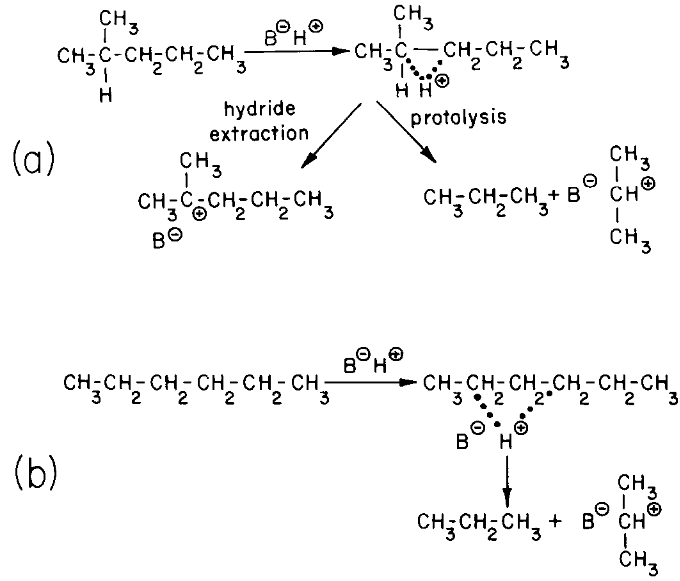


FIG. 7. Mechanisms for reactions of *n*-hexane and 2-methylpentane at a Brønsted site.

observation that no C_8 olefins are found as initial products in that system.

Kinetics

We have shown that Eq. (1) can be used to fit experimental results for reactions of *n*-paraffins on HY zeolite in the temperature range 300–500°C (*3*, *5*, *7*). Optimum values of kinetic parameters obtained are presented in Table 5. Figure 8 shows that experimental conversions of the branched paraffin 2,2,4-trimethylpentane on HY can also be fitted by Eq. (1). At temperatures of 400°C and above, we find that the value of parameter *B* is negative for all linear paraffins studied so far, and its magnitude is close to −1. This has been shown to reflect strong inhibition by product olefin mole-

TABLE 5

Kinetic Parameters for Reaction of Linear and Branched Paraffins on HY Zeolite

Paraffin	Temperature (°C)	Kinetic parameters[a]			
		A (mol/g cat/min)	B	N	G (min^{-1})
n-Hexadecane	300	156	10.2	0.75	348
n-Hexadecane	400	1.72	−0.998	0.42	1.52
n-Dodecane	400	0.62	−0.996	0.88	1.43
n-Octane	400	0.22	−0.994	0.80	1.11
n-Hexane	500	1.36	−0.900	1.06	0.88
2,2,4-Trimethylpentane	300	12.6	−0.63	0.96	42.1
2,2,4-Trimethylpentane	400	287	−0.998	0.81	2010

[a] Kinetic parameters were obtained by fitting experimental conversion results using Eq. (1). All reactions were carried out in a plug flow reactor at 1 atm pressure.

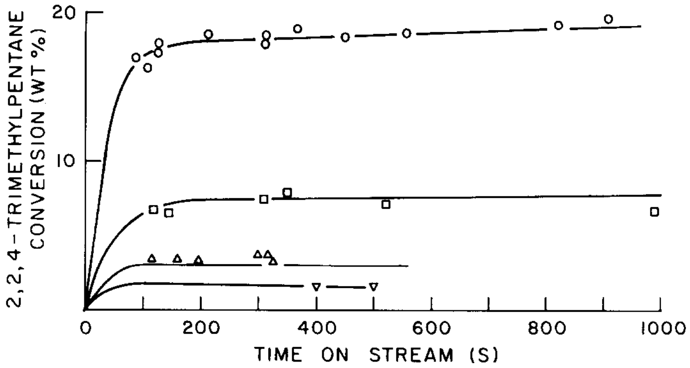


FIG. 8. Experimental points and theoretical curves for reaction of 2,2,4-trimethylpentane on HY at 300°C fitted by Eq. (1). Catalyst-to-reactant ratios: ○, 0.338; □, 0.111; △, 0.037; ▽, 0.0148.

cules. From Table 5, it is clear that the value of this parameter is also close to -1 for reaction of 2,2,4-trimethylpentane at 400°C, showing that the major olefinic product, isobutene, is more strongly adsorbed at the active sites than the feed molecule. At 300°C, for reaction of 2,2,4-trimethylpentane on HY, parameter B is also negative, but its value is now -0.60. The tendency for this parameter to become more positive as the temperature is decreased from 400 to 300°C has also been observed for reaction of *n*-hexadecane (Table 5), and we have explained this (*7*) in terms of the decreasing selectivity for olefinic products as hydrogen transfer reactions become more dominant and paraffinic products are produced instead of the olefins which otherwise compete for adsorption on the active sites.

CONCLUSION

Molecular hydrogen can be formed as an initial product during catalytic cracking of paraffins, if the feed molecule contains an unshielded hydrogen atom bonded to a tertiary carbon atom. However, three distinct sources of molecular hydrogen in the products can be present. These are (a) thermal processes, (b) hydrogen produced in association with coke and aromatics, and (c) dehydrogenation resulting from interaction of a tertiary hydrogen atom with a Brønsted site. The tendency to produce hydrogen increases with temperature in each of these processes.

In contrast, the tendency to form more unsaturated coke decreases with temperature for both branched and linear paraffin feedstocks. Such unsaturated coke can be produced in the absence of aromatic product molecules, showing that the two species can be formed by independent routes. The formation of mononuclear aromatics as intermediates on the route to coke does not appear to be necessary.

Here as well as for reactions of *n*-paraffins, consideration of selectivities for all primary products shows that an overall hydrogen balance is maintained. Catalytic activity can be fully restored by appropriate regeneration procedures showing that hydrogen is not irreversibly lost from the catalyst.

The kinetic model previously applied to linear paraffins is also valid for a branched paraffin such as 2,2,4-trimethylpentane. The kinetic parameters obtained show that for both linear and branched paraffins, the reaction is inhibited by product olefins.

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