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Hydrogen Formation, Chain Reactions, and Inhibition during Cracking Reactions of Hydrocarbons

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Relationships between formation of hydrogen and molecular structure of the feed hydrocarbon have been studied for cracking processes on aluminosilicate catalysts. Saturated hydrocarbons with a hydrogen atom bonded to a tertiary carbon are generally more susceptible to yielding molecular hydrogen as an initial product, through interaction with a Brønsted site. However, exceptions to this trend can arise when steric interactions become important, as in some branched molecules. Good correlations were obtained for relative ease of hydrogen formation by comparing experimental data with results from simulations using molecular orbital calculations. Further correlations exist between production of molecular hydrogen and the observation of either inhibition or acceleration of the cracking reaction following initiation, which can be explained by considering hydride ion abstraction from the feed molecule as the common mechanistic feature.

INTRODUCTION

Cracking reactions of saturated hydrocarbons have been observed to be accompanied by formation of molecular hydrogen, both for reactions in liquid superacid media (*1–4*) and also for reactions on solid acid catalysts at elevated temperatures (*5–8*). In liquid superacids, hydrogen formation has been attributed to protonation of the C–H bond, leading to bond cleavage and formation of a carbenium ion, although the mechanism of the process is still unclear (*1*, *2*). For reactions of paraffins and cycloparaffins on solid acids, including zeolites, three distinct sources of hydrogen have been identified (*8*). Two can be attributed to processes involving free radicals—thermal cracking (*9*, *10*), and reactions leading to coke and aromatics (*11–13*). The third process involves interaction of the hydrocarbon with Brønsted sites on the catalyst surface and appears to proceed through protonation of the reactant molecule (*6*, *14*). Many of the characteristics of this process parallel hydrogen formation in liquid superacids, including preferential reaction for hydrogen bonded at a tertiary carbon atom (*2*, *6*). Inhibition of hydrogen formation in highly branched molecules due to steric factors (*2*, *6*) as well as for reactions of paraffins with hydrogen bonded only at primary carbon atoms (*15*) has also been observed in both types of system.

This study examines the catalytic formation of hydrogen during cracking of saturated hydrocarbons on aluminosilicates. Computer calculations have been performed to simulate hydrogen production at an active site, and relationships between hydrogen formation, inhibition by product species, and acceleration through chain reactions have been reported.

THEORY

It has been shown previously that reactions of various saturated hydrocarbons on aluminosilicate catalysts can be described by a four-parameter kinetic model (*6*, *7*, *16–20*). Parameters A and B have been related to the rate constant for individual cracking and isomerization process and the Langmuir adsorption constants for reactant and products. The parameters N and G are related to the rate of aging of the catalyst under particular reaction conditions.

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EXPERIMENTAL

The cracking and isomerization experiments were carried out using a plug flow reactor system. The experimental equipment and techniques used have been described previously (*17*). Liquid and gaseous products were analyzed by gas chromatography (*17*). All experiments were performed under 1 atm.

The HY zeolite (97.3% exchanged) was prepared from NaY (Si/Al = 2.4) (Linde Co., Lot 45912, SK 40) by repeated exchange with 0.5 *N* ammonium nitrate solution. The catalyst was washed with deionized water and calcined at 500°C after each stage of the exchange process. The catalyst was steamed for 24 h at 200°C before use.

HZSM-5 (Si/Al = 105) was provided by SNAM Progetti, S.p.A., Milan, Italy, and was also exchanged with ammonium nitrate solution prior to use (*7*).

TABLE 1

Initial Product Selectivities for Reaction of 2,2,4-Trimethylpentane on HY at 500°C

Product	Type[a]	Initial weight selectivity
Hydrogen	(Not observed)	0
Methane	1S	0.0103
Ethane	2S	0
Ethylene	2S	0
Propane	(1+2)S	0.0017
Propylene	(1+2)S	0.041
Isobutane	(1+2)S	0.455
n-Butane	(1+2)S	0.0027
Isobutene	1U	0.405
trans-2-Butene	(1+2)S	0.026
cis-2-Butene	(1+2)S	0.019
3-Methyl-1-butene	(1+2)S	0.00084
2-Methyl-1-butene	(1+2)S	0.0010
2-Methyl-2-butene	(1+2)S	0.0081
cis-2-Pentene	(1+2)S	0.00229
trans-2-Pentene	(1+2)S	0.00124
Isopentane	(1+2)S	0.0114
n-Pentane	(1+2)S	0.00458
C_6 olefins	2S	0
C_7 olefins	2S	0
C_8 olefins	2S	0
Toluene	2S	0
C_8 aromatics	2S	0
C_9	2S	0
Coke	(1+2)S	—
	Total	0.990

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

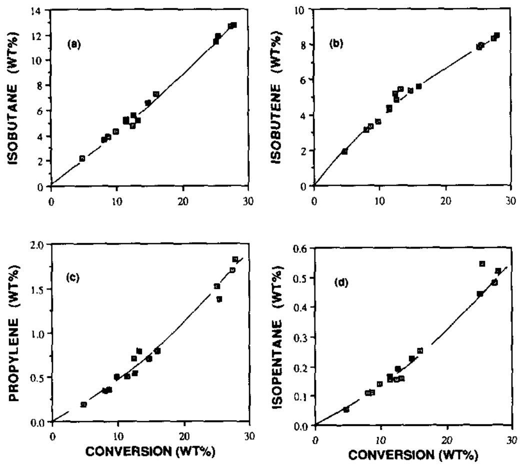

FIG. 1. Plots of yield against conversion for products formed from reaction of 2,2,4-trimethylpentane on HY at 500°C: (a) isobutane, (b) isobutene, (c) propylene, (d) isopentane.

RESULTS AND DISCUSSION

Selectivity and kinetic phenomena for reaction of paraffins (*6–9, 16–20*) and cycloparaffins (*21, 22*) on aluminosilicate catalysts have been reported previously. The general approach to obtaining initial product selectivities is illustrated here for reaction of 2,2,4-trimethylpentane on HY at 500°C. Figure 1 shows examples of plots of yield against conversion for various products from this reaction. The total conversion was varied by changing both the levels of catalyst/feed and also the time on stream for a particular experiment. Initial selectivities can be obtained from the slopes of each curve approaching zero conversion. These selectivities are given in Table 1, where product types are also designated as previously described (*23*). The initial weight selectivity for hydrogen for reaction of 2,3-dimethylbutane on HY at 500°C has been reported as 0.0036 (*24*). Although molecular hydrogen is an initial product from reaction of 2,3-dimethylbutane, it was not observed at any conversion level from reaction of 2,2,4-trimethylpentane under similar reaction conditions. It is apparent that molecular structure of the feed hydrocarbon must have a significant influence on hydrogen formation, and this is discussed in more detail below.

Formation of Molecular Hydrogen

It has been reported that there can be three distinct sources of molecular hydrogen during cracking reactions of saturated hydrocarbons on aluminosilicate catalysts (*8*). Two of these processes can probably be attributed to free radical processes and would lead to thermal cracking of the feed (*9*, *10*) and dehydrogenation to produce coke and aromatic species (*8*, *21*). The third process, which can be considered to proceed through ionic intermediates, occurs when a hydride ion is abstracted from the paraffin or cycloparaffin at a Brønsted site located on the surface of the catalyst (*6*, *14*). The presence of any thermal cracking of the feed hydrocarbon can be detected by examining its behavior in the absence of catalyst (*9*) at the reaction temperature. In general, it has been found that thermal cracking becomes important only at temperatures in excess of 500°C (*9*, *10*). Molecular hydrogen was not detected as a product of thermal cracking in the present studies.

Evolution of molecular hydrogen in association with formation of coke and aromatics is particularly apparent when hydrogen is detected only as a secondary reaction product, and its formation can be linked to a corresponding dehydrogenation during formation of highly unsaturated products (*21*). This has been observed for reaction of *n*-hexane and cyclopentane on HY at 500°C (*8*). It should be noted that these feedstocks contain hydrogen atoms bonded only at primary or secondary carbon atoms.

Formation of molecular hydrogen through hydride abstraction from the feed molecule at a Brønsted site is revealed when hydrogen appears as an initial product as shown in Fig. 2 for reaction of 3-methylpentane on HY at 500°C. This has also been found for reactions of 2,3-dimethylbutane (*24*) and methylcyclopentane (*8*) under the same conditions. It will be noted that these feedstocks all have a hydrogen atom bonded at a tertiary carbon. It is this mechanism for hydrogen formation which will be the focus of attention in the present study. The reaction can be considered to occur through hydride ion abstraction at a Brønsted site identified with a surface hydroxyl group leading to a molecule of hydrogen and a residual carbenium ion. This process can also be considered to proceed through a carbonium ion intermediate, in which C–H bond cleavage is favoured over C–C bond rupture, as described for reactions in liquid superacid media (*1–3*).

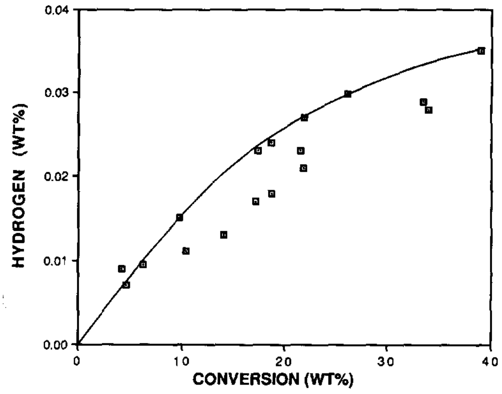

FIG. 2. Plot of yield against conversion for formation of molecular hydrogen on HY at 500°C for reaction of 3-methylpentane.

In general, there appears to be a significantly higher tendency to produce molecular hydrogen from reaction of saturated hydrocarbons containing a hydrogen atom bonded to a tertiary carbon atom. This has been observed for cracking reactions of paraffins on zeolites (*5–7*) at high temperatures (*2*, *3*). It is possible to measure the tendency of a particular hydrocarbon molecule to produce molecular hydrogen via hydrogen ion abstraction through the rate constant for this process. This can be obtained from the over-

TABLE 2

Calculated Activation Energies and Experimental Rate Constants for Hydrogen Formation from Reactions of C_6 Paraffins on HZSM-5

Paraffin	Experimental rate constant[a] for hydrogen formation (mol/g cat/min)	Calculated activation energy (kcal/mol)
n-Hexane	1.22	19.8
2,3-Dimethylbutane	1.82	17.7
2-Methylpentane	4.57	16.2
3-Methylpentane	9.31	12.9

[a] Reaction conditions: 500°C, 1 atm.

TABLE 3

Initial Selectivities for Hydrogen Formation for Reaction on HY at 500°C

Paraffin	Type[a]	Initial molar selectivity
n-Hexane	2S	0
Cyclopentane	2S	0
2-Methylpentane	1U	0.0860
3-Methylpentane	1U	0.108
2,3-Dimethylbutane	1U	0.155
2,4-Dimethylpentane	2S	0
2,2,4-Trimethylpentane	(Not detected)	0
Methylcyclohexane	(1+2)S	0.049

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

all initial kinetic rate constant for catalytic reactions of the feed, provided the initial selectivity for hydrogen formation is also known (*7*). While it is usually possible to obtain an initial selectivity value from yield–conversion plots, an overall rate constant can be obtained only when there is an adequate kinetic model for the process (*16*).

Cracking reactions of C_6 paraffins on HZSM-5 have been studied in some detail (*7, 14, 25*) and rate constants for formation of molecular hydrogen (*7*) are shown in Table 2. It should be noted here that molecular hydrogen is an initial product on HZSM-5, whereas hydrogen is observed only as a secondary product on HY. This has been attributed to the presence of Brønsted sites with higher acidity on the pentasil (*7*). Overall initial rate constants have been reported previously, as well as values for initial hydrogen selectivity obtained from yield–conversion plots (*7*). This shows that rates of hydrogen formation are indeed higher for the branched paraffins than for the linear molecule, but there must be other influences beyond simply characterizing the molecule according to whether a hydrogen atom is bonded to a tertiary carbon atom. This also becomes apparent by examination of the initial selectivities for hydrogen formation on HY at 500°C presented in Table 3. There is a measurable initial selectivity for hydrogen from the C_6 branched paraffins, whereas this was not the case for 2,4-dimethylpentane (Fig. 3) or 2,2,4-trimethylpentane (Table 1).

In order to understand some of these influences, some preliminary attempts have been made to simulate the hydrogen formation process by theoretical calculations. There have been other attempts to study cracking phenomena through molecular orbital calculations (*26, 27*) which have provided useful insight when combined with experimental observation. The present calculations compared the relative ease of ab-

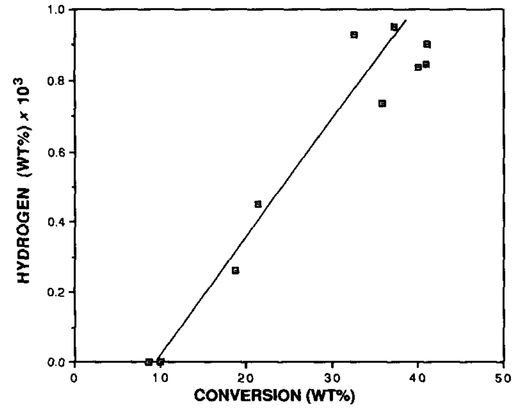

FIG. 3. Plot of yield against conversion for formation of molecular hydrogen during reaction of 2,4-dimethylpentane on HY at 500°C.

stracting a hydride ion from various hydrocarbon molecules. The geometry of each hydrocarbon was first optimized by finding the conformation of the molecule which corresponded to an energy minimum. A free proton (H_b) was then positioned at a fixed distance (3 Å) from the carbon atom bearing the hydride undergoing abstraction (H_a), so that a linear $C–H_a....H_b^{\delta+}$ configuration was maintained. Linear configurations have been suggested previously for the approach of a proton to a saturated hydrocarbon molecule (*2*, *28*). Linear $C–H...H^+$ transition state configurations have also been discussed for hydride ion transfer to an alkyl carbenium ion (*29*). Angular configurations with three-center two-electron bonds have also been proposed (*2*, *27*, *30*). The linear configuration was assumed for the purpose of the present study as this simplified calculation. Energies were calculated using ZINDO (*31*) corresponding to each configuration as the central H_a was moved toward $H_b^{\delta+}$. As the $C–H_a$ distance was increased incrementally, the $H_a–H_b$ distance decreased, so that the total configuration tended toward that of a carbenium ion and molecular hydrogen. The charge on the overall structure was assigned as +1, so that there were partial charges on all atoms including the "free proton" and the "hydride ion" undergoing abstraction.

TABLE 4

Calculated Activation Energies for Hydride Abstraction Leading to Formation of Molecular Hydrogen

	Hydrocarbon	C–H type	ΔE (kcal/mol)
	n-Butane	Primary	28.0
	n-Butane	Secondary[a]	20.8
	n-Pentane	Secondary[a]	20.3
	n-Hexane	Secondary[a]	19.8
	n-Octane	Secondary[a]	19.2
	n-Nonane	Secondary[a]	19.3
	n-Dodecane	Secondary[a]	19.1
	n-Hexadecane	Secondary[a]	19.0
	2-Methylpentane	Tertiary	16.2
C_6	3-Methylpentane	Tertiary	12.9
	2,3-Dimethylbutane	Tertiary	17.7
	2-Methylhexane	Tertiary	14.3
C_7	2,2,3-Trimethylbutane [*t*-Bu]$CH(CH_3)_2$	Tertiary	14.8
	2,4-Dimethylpentane	Tertiary[b]	14.0, 29.1
	2-Methylheptane	Tertiary	14.5
C_8	2,2,4-Trimethylpentane [*t*-Bu]–$CH_2CH(CH_3)_2$	Tertiary	30.8
C_9	2,2,5-Trimethylhexane [*t*-Bu]$CH_2CH_2CH(CH_3)_2$	Tertiary	17.2
C_{10}	[*t*-Bu]$_2CHCH_3$	Tertiary	10.8
C_{12}	([*t*-Bu]$CH_2)_2CHCH_3$	Tertiary	39.8
C_{13}	[*t*-Bu]$_3CH$	Tertiary	6.1
C_{16}	([*t*-Bu]$CH_2)_3CH$	Tertiary	44.4

[a] In each case the central carbon atom in the chain was used.
[b] Two values are given for ΔE, depending on the conformation of the molecule.

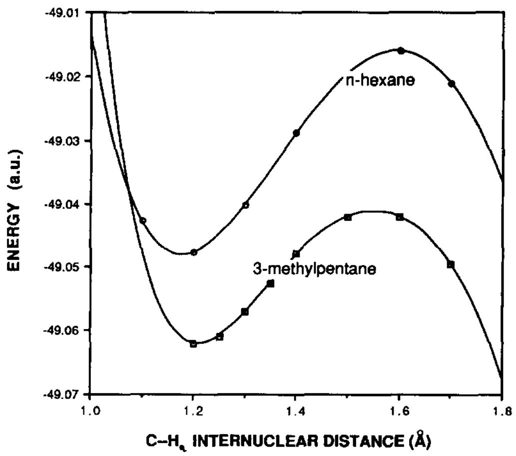

FIG. 4. Potential energy profiles for hydride abstraction from C_6 paraffins.

Typical potential energy profiles obtained in this way are illustrated for reaction of *n*-hexane and 3-methylpentane in Fig. 4. Although these calculations represent a simplified system, particularly regarding the isolation of the hydrocarbon and proton from other influences which could perturb overall change distribution, it is interesting to associate the magnitude of the calculated energy barriers with an activation energy for the process. Calculated values for these "activation energies" are given in Table 4 for a number of paraffins undergoing the process described. For the linear paraffins, the H_a atom removed was located on a central carbon atom. In order to simplify calculation, the conformation of the hydrocarbon chain was also fixed as the C–H$_a$ bond was extended.

Table 4 shows that hydrogen formation by abstraction of H$_a$ from a secondary carbon in a linear paraffin is generally more difficult than removal of H$_a$ from a tertiary carbon in a branched molecule. It also shows that there is little influence of chain length in the linear hydrocarbons, once a certain size has been reached. Abstraction of hydrogen from a primary carbon atom, as expected, also has a higher calculated activation energy than that for abstraction from a secondary carbon atom. Values for calculated activation energies for reaction of the C$_6$ paraffins are shown in Table 2 together with observed rate constants for reaction on HZSM-5 at 500°C (*7*). The experimentally observed trend in rate of formation of hydrogen is in good agreement with the calculated activation energies.

The calculated activation energy corresponding to reaction of 2,2,4-trimethylpentane in Table 4 is seen to be much higher than for other paraffins with tertiary carbon atoms. Indeed the calculated value of 30.8 kcal/mol is significantly higher than that for hydrogen formation from the corresponding linear paraffin (19.2 kcal/mol). This high energy barrier arises because of the steric interactions between the proton H$_a$ and protons on methyl groups associated with C$_1$ and C$_2$ corresponding to the most favorable conformation of the molecule. Olah (*2, 3*) has also noted that hydrogen formation may not be favored for reaction of certain highly branched alkanes, and steric reasons are also cited. Other studies in liquid superacid media (*4*) have reported that reaction of 2,2,4-trimethylpentane leads to C–C bond cleavage, rather than to formation of molecular hydrogen. Our calculations show that this effect is associated with the presence of a neopentyl group as substituent at a tertiary carbon atom. Further replacement of one or both of the methyl substituents in 2,2,4-trimethylpentane by neopentyl groups at the tertiary carbon enhance this effect further as seen in Table 4, corresponding to activation energies of 39.8 and 44.4 kcal/mol, respectively. On the other hand, replacement of neopentyl substituents by *t*-butyl groups should promote ease of hydrogen formation, as there is no associated calculated steric effect in these cases. It is also interesting to note that similar apparently anomalous trends have been noted for substitution reactions (S_n^1 or S_n^2) involving alkyl halides in solution when neopentyl groups are present as substituents (*32, 33*).

The case of 2,4-dimethylpentane also presents an interesting example. As for reaction of 2,2,4-trimethylpentane, molecular hydrogen was not observed as an initial product during reaction of this hydrocarbon on HY at 500°C (Fig. 3). Examination of the geometry of this molecule in its lowest energy conformation shows that the two tertiary hydrogen atoms are not equivalent. One should be easily removed, corresponding to an activation energy of 14 kcal/mol, while the other is subject to steric interaction and gives a calculated activation energy of 29.1 kcal/mole. The former hydrogen atom should behave in a manner similar to the tertiary C–H in 2-methylpentane, while the latter is expected to resemble the tertiary C–H in 2,2,4-trimethypentane. We can conclude that only the second type of C–H is presented for interaction at the Brønsted site, perhaps due to local steric constraints at the site.

Cracking Reactions: Inhibition or Acceleration

There is significant evidence to show that initiation of cracking reactions for paraffins and cycloparaffins on zeolite catalysts occurs at Brønsted sites (*14, 23, 34–36*). Although initiation can occur through formation of molecular hydrogen with concurrent generation of a carbenium ion, initial selectivity values show that this is not the dominant mode, particularly for reaction of linear paraffins (*6, 7*). For example, results in Table 3 show that for reaction on HY, initiation by this process would account for 10.8% of the total for 3-methylpentane, and only 8.6%

for reaction of 2-methylpentane (*24*). The alternative initiation process can occur via protonation of a C–C bond rather than in C–H bond, leading to a paraffin fragment and a carbenium ion. In either case, following initiation there will be a high probability that the original Brønsted sites will be occupied by adsorbed carbenium ions, which can function as Lewis centers, leading to propagation of the cracking process through chain reactions via a hydride abstraction process (*18, 23*).

The relative ease with which this chain process can occur will depend on the ease of hydride abstraction from feed molecules, and should show an obvious parallel with the hydrogen formation process already discussed. Reactant hydrocarbons which easily form molecular hydrogen as an initial product would be expected to favor the chain propagation process and this may lead to an observed acceleration in cracking rate (*18*). Reactants which do not easily yield molecular hydrogen would participate in the chain process with much more difficulty, leading to possible inhibition of reaction (*16*).

TABLE 5

Values of Parameter *B* for Reactions of Paraffins

Reactant	Catalyst	Temperature (°C)	*B*
n-Hexane	HY	500	−0.89
n-Hexane	HZSM-5	500	−0.61
n-Octane	HY	400	−0.994
n-Dodecane	HY	400	−0.996
n-Dodecane	LaY	400	−0.98
n-Dodecane	Silica–alumina	400	−0.80
n-Dodecane	H-mordenite	400	−0.69
n-Dodecane	HZSM-5	400	−0.79
n-Hexadecane	HY	400	−0.998
2-Methylpentane	HZSM-5	500	−0.58
2,3-Dimethylpentane	HZSM-5	500	−0.93
2,2,4-Trimethylpentane	HY	300	−0.63
2,2,4-Trimethylpentane	HY	400	−0.998
2,2,4-Trimethylpentane	HY	500	−0.96

The four-parameter kinetic model described under Theory has been successfully applied to reaction of linear paraffins on zeolites and amorphous silica–alumina under various conditions (*7, 16, 19*). One of the advantages of this model is that it gives a quantitative estimate of the degree of inhibition through the *B* parameter (*19*). This parameter approaches a limiting value of −1 when there is strong product inhibition and approaches a large positive value in the absence of inhibition. Table 5 shows values of this parameter from previous application of the kinetic model to a number of systems (*6, 7, 16–20*). For reactions at 400–500°C, all linear paraffins studied give a negative value for *B*, approaching −1 in most cases (*16*). This correlates well with the relatively poor propensity toward formation of molecular hydrogen for these feedstocks, as shown in Tables 2, 3, and 6, as well as high calculated activation energy. The kinetic model can also be applied to reaction of branched paraffins, but is successful only in some cases (*6, 7*). Results from reactions of 2,2,4-trimethylpentane (*6*) in the range 300–500°C can be fitted by the model, as shown in Fig. 5, and parameter *B* (Table 5) indicates strong inhibition. Again, this correlates well with the absence of hydrogen formation (Tables 3 and 6) and the high calculated value for activation energy. Fitting of kinetic results for reactions of the branched C_6 paraffins on HZSM-5 at 500°C (*7*) also indicates inhibition (Table 5). This may appear to contradict the apparent ease of formation of molecular hydrogen for the methylpentanes on this catalyst, as well as the low calculated activation energy in Table 2. However, these observations can be explained in terms of the pore structure of this catalyst giving rise to shape-selective effects (*37*). Formation of molecular hydrogen can be represented as a monomolecular process which is not subject to severe steric constraints. For the chain process to occur, however, two hydrocarbon species must be brought into close proximity at the active site for hydride transfer to occur. The resultant bimolecular process is restricted by pore dimensions (*25*) within the catalyst, and inhibition is observed.

In contrast, there is no shape-selective influence for reaction of the methylpentanes or 2,3-dimethylbutane on HY or on amor-

TABLE 6

Reaction of Paraffins on HY Zeolite at 500°C

Paraffin (reaction temp °C)	Initial hydrogen formation	Inhibition	Acceleration via chain mechanism	Calculated activation energy (kcal/mol)
n-Octane (400)	No	Yes	No	19.2
n-Dodecane (400)	No	Yes	No	19.1
n-Hexadecane (400)	No	Yes	No	19.0
n-Hexane (500)	No	Yes	No	19.8
2-Methylpentane (500)	Yes	No	Yes	16.2
3-Methylpentane (500)	Yes	No	Yes	12.9
2,3-Dimethylbutane (500)	Yes	No	Yes	17.7
2,2,4-Trimethypentane (500)	No	Yes	No	30.8
2,4-Dimethylpentane (500)	No	No	Yes	14.0, 29.1

phous silica–alumina. As a result, not only do we observe molecular hydrogen as a primary product (Table 3), but the cracking process is no longer inhibited. Instead, the rate of reaction is actually accelerated by creation of Lewis centers which are available to participate in the chain process (*18*, *23*). Under these conditions, the kinetic model described above fails, and a new type of kinetic behavior is observed. This is reflected in the plots of conversion against time which now show an induction effect (*18*).

It should be noted that kinetic results for reaction of 2,4-dimethylpentane do not fit the kinetic model in contrast to those for 2,2,4-trimethylpentane during reaction on HY at 500°C. Figure 6 shows curves characteristic of an acceleration via chain reaction rather than inhibition although the effect is less pronounced than for the branched C_6 paraffins. It will be recalled that this molecule has two distinct tertiary C–H bonds in

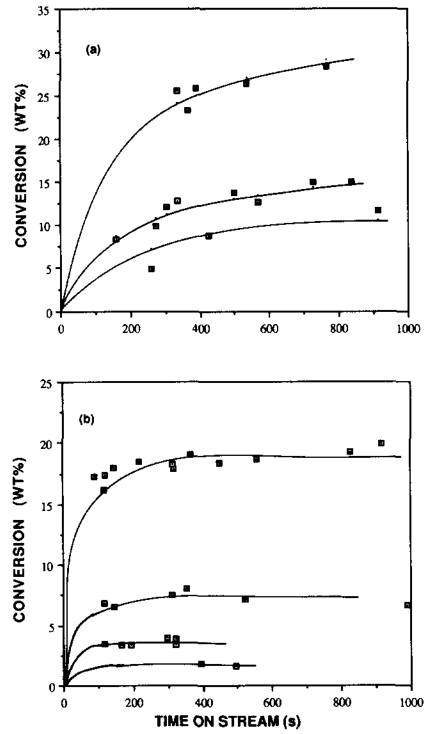

FIG. 5. Theoretical curves and experimental points for reactions of 2,2,4-trimethylpentane on HY at (a) 500°C, catalyst/feed ratios: 0.0154, 0.0038, 0.0020; (b) 400°C, catalyst/feed ratios: 0.103, 0.0345, 0.0138.

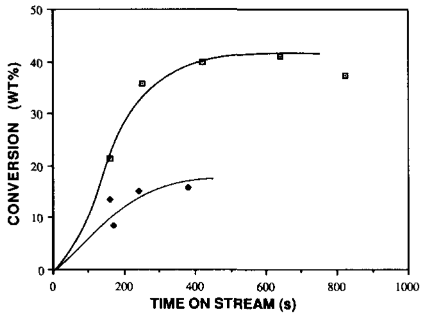

FIG. 6. Plots of conversion against time for reactions of 2,4-dimethylpentane on HY at 500°C: catalyst/feed ratios, 0.0204, 0.0102.

the lowest energy conformation, corresponding to low and high calculated activation energy. As molecular hydrogen was not observed initially, we concluded that only the latter was available due to local steric constraints at the site. From the observation of acceleration rather than inhibition of the cracking process we must now conclude that the former type of C–H is available for hydride transfer to a carbenium ion. This suggests that the steric factors influencing potential hydride abstraction at the original Brønsted site and those for an adsorbed carbenium ion may differ.

Table 6 shows a summary of the observed behavior of various hydrocarbons on HY, which illustrated the correlations between formation of molecular hydrogen, product inhibition, and acceleration of reaction on this catalyst.

CONCLUSION

This study shows how the relative ease of formation of molecular hydrogen via hydride abstraction is related to the structure of the feed hydrocarbon. Hydrogen atoms bonded to tertiary carbon atoms are, in general, more reactive than those bonded to secondary carbon. Exceptions occur when removal of hydrogen is sterically hindered, as observed for neopentyl substituents at a tertiary carbon atom. Observed experimental trends can be correlated with activation energies from molecular orbital calculations. There are also correlations between the relative ease of hydrogen formation and kinetic phenomena reflecting either inhibition or acceleration of the overall cracking reaction. This can be understood by considering the common mechanistic basis for each of these processes.

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