DETERMINATION OF THE CRACKING REACTION MECHANISMS ON THE BASIS OF THE INITIAL SELECTIVITY DATA.

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ABSTRACT

The cracking of 2-methylpentane on ultrastable HY zeolite catalyst has been studied at 573 K. It was found that this reaction leads to the formation of coke, paraffins, olefins and aromatics in the range of C_1 - C_9, *of which only* C_1 - C_6 *compounds and coke were found to be primary products. The yield of aromatics and other secondary products was relatively small and increased with conversion. An overall reaction mechanism for the reactions of 2-methylpentane has been constructed on the basis of the observed initial selectivity data and reaction pathway probabilities.*

Mechanistic considerations lead us to conclude that three main initial processes take place during 2-methylpentane cracking on ultrastable HY (i) Monomolecular Langmuir processes, i.e. adsorption and cracking of the 2-methylpentane molecules on pristine sites: (ii) Chain processes involving disproportionation and hydride transfer reactions between product carbenium ions on the catalyst surface and gas phase 2-methylpentane molecules followed by isomerization of the parent carbenium ion, and (iii) Coke formation. Monomolecular reactions account for about 8% of the total conversion, whereas chain reactions involving disproportionation and hydride transfer were dominant processes and accounted for about 90% of the total conversion of 2-methylpentane at 573 K.

INTRODUCTION

In recent years, considerable interest in the cracking of small parafin molecules has been developed. A variety of substrate molecules has been studied [1-7]. Reaction schemes and mechanisms obtained from cracking of such model hydrocarbon molecules can be used to determine the cracking patterns of the multicomponent feedstocks, e.g., in petroleum refining processes.

The mechanisms of catalytic cracking has been a matter of discussion for sometime [8-9]. Detailed mechanisms have been written starting from different hypotheses [1, 10-13]. Recent studies of the reactions of low-molecular weight paraffins indicate the occurrence of chemistry attribute to carbonium and carbenium ions under a variety of experimental conditions. These include observing the extent of isotopic exchange, isomerization and cracking as well as the effect of initiators or carbonium like precursors [1, 14, 15].

Recent studies indicate that paraffin reactions on aluminosilicate catalysts are initiated through the protonation of the reactant molecule across a C-H or C-C bond to form a pentacoordinated carbonium ion intermediate. This intermediate can either undergo dehydrogenation yielding molecular hydrogen and a parent carbenium ion or C-C bond rapture, producing a paraffin and a smaller carbenium ion [1, 5, 6]. A carbenium residing on an active site can either undergo isomerization, further cracking or act as a Lewis acid site and abstract a hydride from a gas phase reactant molecule. Then desorb as paraffin, and its place on the catalyst surface is taken by a carbenium ion of the gas phase molecule which denoted the hydride [13]. The newly formed carbenium ion can in turn undergo either beta-scission leading to the formation of an olefin and a smaller molecule carbenium ion or it can isomerize. Furthermore, any such carbenium ion can react with any other gas phase molecule via a hydride transfer reaction to form a new carbenium ion, which in turn repeats the process. Such intermolecular hydride transfer between carbenium ions and feed molecules propagate carbenium-ion-induced chain reactions. Termination of the chain involves the desorption of a carbenium as an olefin or its dehydrogenation to form coke or inactive surface products.

Our aim in this work is to provide an insight into a novel methodology for the determination of the reaction mechanism taking place during the cracking of hydrocarbons using initial selectivities obtained from optimum performance envelopes. Here we report on the detailed description of the cracking mechanisms of 2-methylpentane on ultrastable HY zeolite.

LITERATURE REVIEW (REACTION MECHANISM)

For the interpretation of the selectivity data and a quantitative discussion of reaction mechanisms, it is first necessary to select a list of cracking modes so as to ensure that all primary products can be accounted for. In the following discussion, we have selected such a list which assumes that: (i) the probability of cracking of C_3-C_5-species is insignificant; (ii) since the amount of initial coke is relatively small, the contribution of products from the formation of coke, e.g., H_2, is insignificant.

The course of 2-methylpentane (C_6H_{14}) cracking, based on the product distributions presented in Table 2 can be described such that the formation of hydrogen and C_1 to C_5 molecules via monomolecular processes is accounted for by the following initiation processes:

$$C_6H_{14} + H^+B^- \rightarrow C_6H_{15}^+B^- \xrightarrow{S_1} H_2 + C_6H_{13}^+B^- \quad (1)$$

$$C_6H_{15}^+B^- \xrightarrow{S_2} CH_4 + C_5H_{11}^+B^- \quad (2)$$

$$C_6H_{15}^+B^- \xrightarrow{S_3} C_2H_6 + C_4H_9^+B^- \quad (3)$$

$$C_6H_{15}^+B^- \xrightarrow{S_4} C_3H_8 + C_3H_7^+B^- \quad (4)$$

$$C_6H_{15}^+B^- \xrightarrow{S_5} C_4H_{10} + C_2H_5^+B^- \quad (5)$$

Where: H^+B^- = Bronsted site; $C_nH_{2n+1}^+$ = Carbenium ion with n-carbon atoms; and S_j = the probability that the j-th reaction pathway will be the one followed by the first molecule converted. We call this the reaction pathway probability, or RPP, in the succeeding discussion.

Examining results presented in Table 2 it can be seen that the ratios C_4-paraffins / C_2-olefins and propylene/propane are higher than unity A value close to unity would be expected if the source of all such species was simple monomolecular cracking of 2-methylpentane molecules as in reactions 1 to 5. This indicates to us that at least some C_4-paraffins and propylene are generated not only by the above monomolecular cracking reactions but also by other processes. This fact, as well as the appearance of primary C_5-paraffins species, lead us to suggest that in addition to monomolecular reactions cracking of 2-methylpentane over USHY proceeds via bimolecular processes. The following general bimolecular processes, involving disproportionation reactions is proposed to account for excess C_4 - C_5-paraffins:

$$C_6H_{14} + C_{2n+1}^{+}B^{-} \xrightarrow{S_j} C_mH_{2m+1} + C_kH_{2k+1}^{+}B^{-} \tag{6}$$

where 3 < m < 5 and 3 < k < 6. A complete set of possible disproportionation processes is presented in Table 5 (equations 7-9, 11-12 and 14). Desorption of C_kH_{2k+1} (k = 3 , 4) carbenium ions leads to the formation of the observed excess propylene. The above mentioned reactions account for the appearance of primary C_5-paraffins and the observed excess C_4-paraffins species over ethylene. The C_4-olefins, noted before, also seems to be explained. It remains to explain the presence of C_6-paraffin isomers in the initial products.

The initiation process takes place by protonation of a hydrocarbon molecule to form a carbonium ion. As mentioned earlier, the carbonium ion can decompose to form either H_2 and a parent carbenium ion or a smaller paraffin, leaving a small carbenium ion on the Bronsted site. Any carbenium ion can either participate in disproportionation reactions as in (Equation 6) or desorb as olefin or it can isomerize and carry on chain propagation reactions by abstracting a hydride ion from a feed molecule as shown in an overall equation 7.

$$C_6H_{14} + C_{2n+1}^{+}B^{-} \xrightarrow{S_j} C_nH_{2n+1} + C_6H_{13}^{+}B^{-} \tag{7}$$

The possible hydride transfer reactions are presented in Table 5 (equations 6, 10, 13, 15-16). Hydride abstraction by species which have undergone a number of methyl and hydride shifts leads to the formation of isomeric products of 2-methylpentane. The formation of 2-methylpentane isomeric products is described by an overall equation 16 in Table 5. The chain termination step involves donation of a proton to the Bronsted site base by a carbenium ion and its desorption as an olefin or, as in the case of , cracking to produce propylene and a propyl ion as indicated in equation 17. One more reaction mode must be taken into account, i.e., the formation of coke as indicated in equation 17.

Determination of the reaction pathway probabilities was made using the set of equations 1 to 18 presented in Table 5 and the molar selectivities of the initial products. For each product, its molar selectivity F_i can be expressed as a linear combination of the appropriate reaction pathway probabilities which lead to its formation. The resulting equation can be written in matrix form;

$$\underline{F} = \underline{A}.\underline{S} \tag{8}$$

Where:

$$\underline{F} = \begin{bmatrix} F_{H2}, F_{P1}, F_{P2}, F_{P3}, F_{P4}, F_{P5}, F_{P6_{SI}} \\ , F_{O2}, F_{O3}, F_{O4}, F_{O5}, F_{O6}, F_{Coke}, 1.0 \end{bmatrix}^T \tag{9}$$

Where

F_{H2}, F_{P1}, FP_{6SI}	molar selectivities of hydrogen, i-th product paraffin and 2-methylpentane isomers, respectively.
F_{Oi}, F_{Coke}	are molar selectivities of the i-th product olefin and coke, respectively;
$\underline{A}$	is 13 x 18 matrix of stoichiometric coefficients taken from equations 1 to 18 in Table 5.

In this reaction we lack five equations, relating the relative rates of parallel reactions for each of the surface species, in order to arrive at a unique solution. In order to proceed we have adopted the use of a constrained solution described in detail elsewhere [17].

Using a linearly constrained solution appproachh we have solved for the pathway probabilities S in equation 8 in terms of molar selectivities F_i of the initial products. A computer program LINDO (Linear Iterative and Discrete Optimizer) with the objective function Max and Min ($S_1 + S_2 + S_3 + S_4 + S_5$) was used for this purpose. The reaction pathway probabilities for cracking reactions of 2-methylpentane calculated in this way are presented in Table 6.

EXPERIMENTAL METHOD AND MATERIALS

The 2-methylpentane of 99.45% purity was obtained fromAldrich Chemical Co. Ltd and used without further purification. The main impurity was 3-methylpentane (0.55%). Ultrastable HY (USHY) was prepared from NaY obtained from BDH Chemicals by repeated exchange with 0.5 M NH_4NO_3 solution at approximately 293 K for 24 h. Between exchanges, the catalyst was dried at 383 K for 24 h and then calcined in air at 773 K for 2 h. After ten such exchanges the catalyst was steamed at 573 K for 24 h. The samples were pelletized, crushed and sieved to obtain the 60-80 mesh material for our runs. On analysis, the catalyst was found to be 99.8% Na^+ exchanged. Bulk Si/Al ratio was determined by X-ray Fluorescence while frame work Si/Al ratio was determined by ^{29}Si MAS-NMR. Crystallinity was checked by X-ray diffraction. The physical properties of our catalyst are summarized in Table 1.

Table 1: Physicochemical properties of the catalysts used in the cracking of 2-methylpentane

	Catalyst	
	NaY	**USHY**
Na^+ (a)	10.28%	<230 ppm
a_0(Å) (b)	24.69	24.58
Si/Al (bulk)(c)	2.42	3.30
Si/Al (framework)(d)	2.61	6.00
Al atoms/UC(framework)(e)	53.13	40.24

a - determined by Neuteron activation energy.
b - determined by X-ray diffraction.
c - determined by X-ray fluorescence.
d - determined by ^{29}Si MAS-NMR
e - determined according to the equation $N_{Al} = 112.1\ (a_o - 24.222)$ in reference [16],where a_o is the unit cell constant.

The conversion of 2-methylpentane was carried out in an isothermal, plug flow, glass reactor (60 x 2 cm I.D.). The catalyst was diluted with sand in order to minimize thermal effects in a bed 11 cm long. Prior to each experiment the catalyst was purged with nitrogen for 30 minutes. Next, 2-methylpentane was pumped through the reactor at an appropriate rate and temperature. At various times the catalyst-to-reactant ratios between 0.001 - 0.0291 were used. This was achieved by changing the amount of catalyst in the reactor, the weight of the feed being kept constant. The shematic diagram of the experimental set-up used is shown in Figure 1.

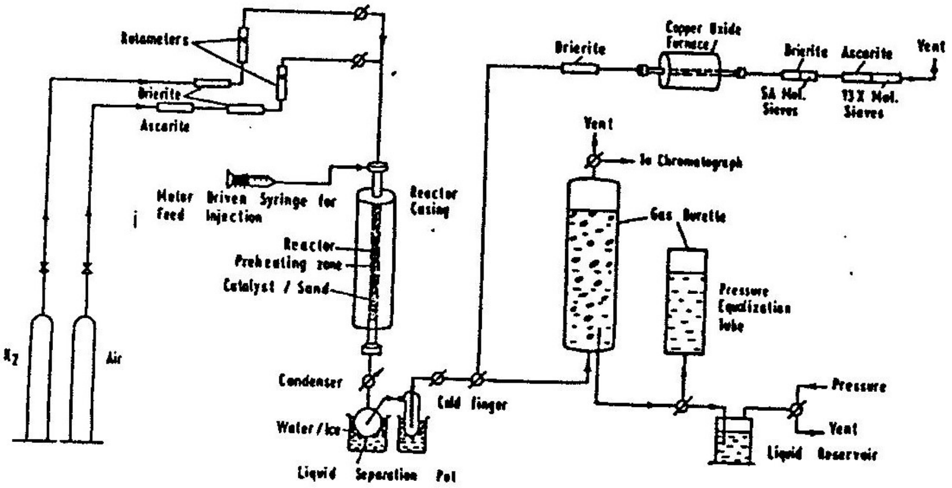

Fig. 1 Schematic diagram of the experimental set-up

Time on stream (TOS) was varied between 1 and 20 minutes by changing the feed rate of the reactant but keeping the weight of the total feed constant. During the reaction, the liquid products were collected in a glass pot and a cold finger immersed in a water-ice mixture. The gaseous products were trapped in a gas a burette by the downward displacement of water At the end of each run, the reactor was purged with nitrogen (150 cm^3/min, 40 min) and the purged gases were also collected in burette. Regeneration gases were then passed through a reactor containing copper oxide as an oxidation catalyst to ensure their complete combustion to carbon dioxide and water. Any water produced was trapped inAscarite and 13X molecular sieves. The amount of coke produced during the reaction was calculated from the weight of water and carbon dioxide trapped during regeneration.

Gaseous products in the range C_1-C_4 were analyzed by a Carle SX-1156 gas chromatograph which also allowed for H_2 determination. Liquid products were analyzed by a Varian 6000 gas chromatograph with a 60 m SE54 capillary column and a flame ionization detector Products up to C_7

were eluted at 273 K followed by a temperature program of 278 K/min up to 573 K. The identification of the liquid products was performed using a Finnigan 1020 automated GC/MS.

RESULTS

Blank runs were performed in order to determine the extent of thermal cracking. They were carried out by pumping 2-methylpentane through a reactor packed with inert silica which was thoroughly cleaned with 36% hydrochloric acid solution and rinsed with distilled water Thermal cracking of 2-methylpentane at 573 K was found to be negligible.

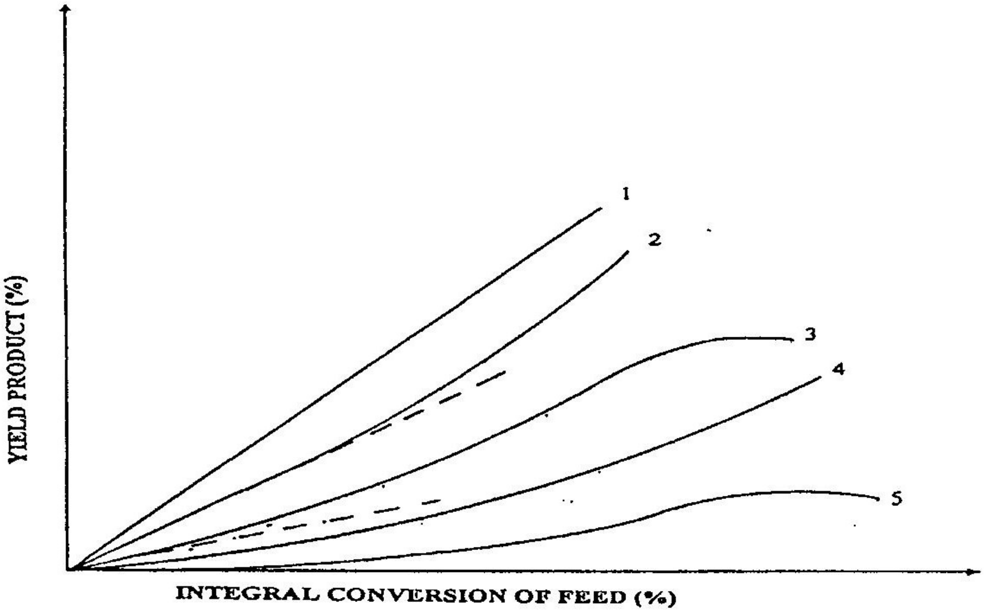

Fig. 2: **Theoretical optimum performance envelope (OPE) curves of various products. The OPEs shown refer to the products: (1) stable primary product (2) stable primary plus secondary product (3) unstable primary product (4) stable secondary product and (5) ustable secondary product**

The product distribution obtained during the catalytic cracking of 2-methylpentane is presented in Table 2 to 4. The products include paraffins, olefins, aromatics in the range of C_1-C_9 atoms and coke. For each reaction product, the time-averaged yield sampled from t = 0 to t_f, the run duration, can be plotted against the integral conversion of the feed. These plots at various catalyst-to-reactant ratios, can be enveloped by a single curve, the optimum performance envelope, which describes the selectivity behaviour of products to be described by characteristic curves as illustrated in Figure 2. The initial selectivity of a product, given by the slope of the optimum performance envelope at zero conversion is non zero for a primary product and zero for secondary or subsequent products. Figure 3 shows examples of yields of primary products versus corresponding average conversion of 2-methylpentane. Initial selectivities and product types were obtained by determining the selectivity behaviour at zero conversion as explained above. Products types and initial weight and molar selectivities for primary products are listed in Table 2.

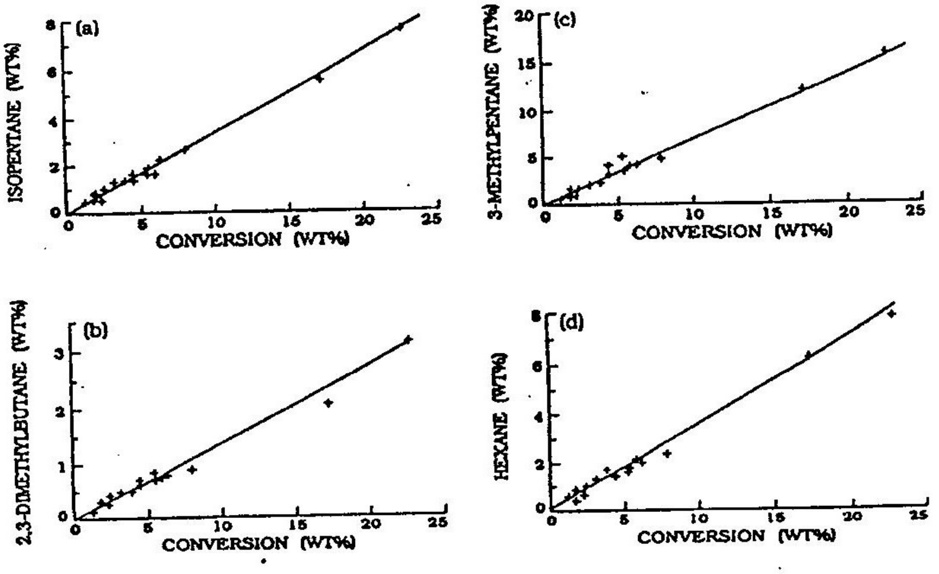

Fig. 3: Optimum perfformance envelopes for products of reaction of 2-methylpentane on USHY at 573 K (a) isopentane (b) 2,3-dimethylbutane (c) 3-methylpentane (d) n-hexane. catalyst to reactant ratio 0.0077-0.0291

As can be seen in Table 2 the primary products consisted mostly of 2-methylpentane skeletal isomers, i.e., 3-methylpentane, 2,3-dimethylbutane and n-hexane, which made up about 90% of all initial products. Other significant products include propane, 2-methylpropane and 2-methylbutane. Relatively small amounts of methane, ethylene, C_4 and C_5-olefins, and C_6-olefins were also present. The C_5-olefins consisted mainly of 2-methyl-2-butene and trans-2-pentene. The C_6-olefins consisted largely of 2-methyl-2-pentene, cis-3-methyl-2-pentene as shown in Table 3. Others like cis- and trans-2-hexene, cis-and trans-3-hexene, 2,3-dimethyl-1-butene and 2,3-

dimethyl-2-butene were detected in the products in trace amounts by mass spectrometric analysis. It is interesting to note that C_6-olefinic products have similar skeletal structures as initial 2-methylpentane isomeric products. It is worth noting that hydrogen and ethane were not detected in the products.

Table 2: Initial weight and molar selectivities for products from reaction of 2-methylpentane on USHY zeolite

Product	Type[a]	Weight selectivity[b]	Molar selectivity[c]
Hydrogen	-	-	-
Methane	IS	0.0017	0.0091
Ethane	-	-	-
Ethylene	IS	0.0006	0.0018
Propane	IS	0.0120	0.0235
Propylene	IS	0.148	0.0303
iso-Butane	IS	0.0147	0.0218
n-Butane	IS	0.0040	0.0039
iso-Butene	IS	0.0040	0.0061
trans-2-Butene	IS	0.0030	0.0046
iso-Pentane	IS	0.0300	0.0358
n-Pentane	IS	0.0010	0.0012
C_5-Olefins	IS	0.0100	0.0012
2,3-Dimethylbutane	IS	0.1400	0.1400
3-Methylpentane	IS	0.7116	0.7116
n-Hexane	IS	0.0384	0.0384
C_6-Olefins	IS	0.0140	0.0143
Coke	IS	0.0110	0.0110
TOTAL		1.0018	1.0568

[a] 1:primary, S: stable. Product types are designed according to the shapes of their optimum performance envelope.

[b] The initial weight selectivity is determined by the initial slope of the corresponding yield-conversion plot see Figure 2.

[c] Initial molar selectivities were calculated from the initial weight selectivities in using the relationship:

$$\text{molar selectivity} = \text{weight selectivity}\,\frac{\text{feed molecular weight of feed}}{\text{product molecular weight product}}$$

Table 3: Initial Molar Selectivities for C_6-Olefins from reaction of 2-Methylpentane over USHY

Product	Initial Molar Selectivity
2-Methyl-1-pentene	0.0013
2-Methyl-2-pentene	0.0039
cis-3-Methyl-2-pentene	0.0038
trans-3-Methyl-2-pentene	0.0014

In addition to primary products, the cracked products contained secondary products. The secondary products consisted largely of 2,2-dimethyl butane, methylcyclopentane, C_7-olefins, toluene, C_8-olefins and C_7 - C_9 aromatics as depicted in Table 4. Aromatics with carbon numbers greater than 9, mainly alkylated benzenes and naphthalenes, were relatively minor products. The C_7 paraffins consisted essentially of 2-methylhexane, 3-methylhexane and heptane. Aromatization led mainly to the formation of toluene, dimethylbenzenes and trimethylbenzenes. The aromatics were detected in the liquid products at conversion higher than 5% and their yield increased sharply with increasing conversion. On the other hand, the yield of 2,2-dimethylbutane, methyl-cyclopentane, C_7 paraffins and olefins increased linearly with increasing conversion and in general levelled off at conversions greater than 20%. This suggests that such products are unstable under reaction conditions and react to form subsequent products, perhaps coke and aromatics.

Table 4: Yield of secondary products from the reaction of 2-Methylpentane at 25% conversion.

Product	Yield wt %
2,2-Dimethylbutane	0.117
Methylopentane	0.067
C_7-Paraffins	0.437
C_7-Olefins	0.133
Toluene	0.041
C_8-Olefins	0.047
Dimethylbenzenes	0.010
Trimethylbenzene	0.004

DISCUSSION

Examination of Table 6 shows that the contribution of conversion by pure monomolecular process (entries 1-3) is small. Protolysis on pristine sites accounts for only about 8%, of the total conversion. The most favoured protolytic reactions are: (i) the fragmentation of a ion to produce propane and propyl ion (entry 3) and (ii) the production of a C_4-paraffin and an ethyl ion (entry 4). Another significant protolytic process is the cracking of the ion to methane and a C_4-olefin. Note that protolyis of a ion to produce C_4-paraffin and an ethyl ion (entry 3) is a more favoured reaction than that of the production of ethane and a butyl ion which does not occur A similar cracking behaviour was observed in 2-methylbutane and n-heptane reactions. [15,18]

Table 5: Initial processes occurring on USHY fo the reaction of 2-methyl entane

Monomolecular processes		
	$C_6H_{14} + H^+B^- \xrightarrow{S_0} H_2 + C_6H_{13}^+B^-$	(1)
	$C_6H_{14} + H^+B^- \xrightarrow{S_1} CH_4 + C_5H_{11}^+B^-$	(2)
	$C_6H_{14} + H^+B^- \xrightarrow{S_2} C_2H_6 + C_4H_9^+B^-$	(3)
	$C_6H_{14} + H^+B^- \xrightarrow{S_3} C_3H_8 + C_3H_7^+B^-$	(4)
	$C_6H_{14} + H^+B^- \xrightarrow{S_4} C_4H_{10} + C_2H_5^+B^-$	(5)
Bimolecular processes		
	$C_6H_{14} + C_2H_5^+B^- \xrightarrow{S_5} C_2H_6 + C_6H_{13}^+B^-$	(6)
	$C_6H_{14} + C_2H_5^+B^- \xrightarrow{S_6} C_3H_8 + C_5H_{11}^+B^-$	(7)
	$C_6H_{14} + C_2H_5^+B^- \xrightarrow{S_7} C_4H_{10} + C_4H_9^+B^-$	(8)
	$C_6H_{14} + C_2H_5^+B^- \xrightarrow{S_8} C_5H_{12} + C_3H_7^+B^-$	(9)
	$C_6H_{14} + C_3H_7^+B^- \xrightarrow{S_9} C_3H_8 + C_6H_{13}^+B^-$	(10)
	$C_6H_{14} + C_3H_7^+B^- \xrightarrow{S_{10}} C_4H_{10} + C_5H_{11}^+B^-$	(11)
	$C_6H_{14} + C_3H_7^+B^- \xrightarrow{S_{11}} C_5H_{12} + C_4H_9^+B^-$	(12)
	$C_6H_{14} + C_4H_9^+B^- \xrightarrow{S_{12}} C_4H_{10} + C_6H_{13}^+B^-$	(13)
	$C_6H_{14} + C_5H_{12}^+B^- \xrightarrow{S_{13}} C_5H_{12} + C_5H_{11}^+B^-$	(14)
	$C_6H_{14} + C_5H_{11}^+B^- \xrightarrow{S_{14}} C_5H_{12} + C_6H_{13}^+B^-$	(15)
	$C_6H_{14} + iso-C_6H_{13}^+B^- \xrightarrow{S_{15}} iso-C_6H_{14} + C_6H_{13}^+B^-$	(16)
ß-Cracking		
	$C_6H_{13}^+B^- \xrightarrow{S_{16}} C_3H_6 + C_3H_7^+B^-$	(17)
Coke Formation		
	$C_6H_{14} \xrightarrow{S_{17}} Coke$	(18)

Where: = 2-methylpentene; Sj = Reaction Pathway Probability of j-th reaction; and = Carbenium ion

Entries 4 to 7 in Table 6 present a set of RPP's representing disproportionation reactions between product carbenium ions on the catalyst surface and gas phase 2-methylpentane molecules. This set of probabilities shows that, at this temperature the overall probability for a transition state complex, formed from a gas phase 2-methylpentane molecule and - ions, to undergo disproportionation is small in comparison with other reaction modes.

In Table 6 it can also be seen that, in addition to disproportionation, chain reactions also consist of processes involving hydride transfer Two hydride transfer reactions were found to be active: (i) hydride abstraction by ions from the feed molecules to form C_5-paraffins and ions (entry 8) and (ii) hydride abstraction by ion to form 2-methylpentane skeletal isomers and a parent 2-methylpentyl ion (entry 9). As can be seen in Table 6 hydride transfer is the dominant reaction mode. These reactions account for about 90% of the total conversion of 2-methylpentane at 573 K.

Table 6: Reaction Pathway Probabilities (RPP) for the reactions of 2-Methylpentane over USHY at 573 K

Entry No.	RPP	Reaction Pathway Probability
1.	S_1	0.0091
2.	S_3	0.0235
3.	S_4	0.0223
4.	S_7	0.0025
5.	S_8	0.0180
6.	S_{10}	0.0029
7.	S_{11}	0.0083
8.	S_{14}	0.0108
9.	S_{15}	0.8900
10.	S_{17}	0.0110
	TOTAL	0.9984

* All RPPs not listed here are equal to zero.

The formation of secondary aromatic products probably involves the cyclization of large carbenium ions followed by the formation of the aromatic structures through the monomolecular elimination of small paraffins and hydrogen. The formation of the aromatics and the other secondary products increased with increasing conversion, since the higher the conversion, the higher will be the concentration of olefin product species which can participate in secondary dimerization reactions with carbenium ions. These same reactions can lead to coke formation if the cyclized dehydrogenated species become undesorbable.

CONCLUSION

It has been shown in this study that the cracking reaction mechanism can be determined, with appreciable accuracy, on the basis of the initial weight and molar selectivity data. The results show that conversion of 2-methylpentane at 573 K proceed via three main initial processes:

(i) monomolecular processes; (ii) chain processes involving disproportionation and hydride transfer and; (iii) coke formation.

Chain reactions played a dominant role in the conversion of 2-methylpentane at this temperature. It was also shown that product skeletal isomers of 2-methylpentane are a result of hydride transfer chain reactions between a ion and gas phase feed molecules. Further work is under way to determine the kinetics of this process by using a model that accounts for monomolecular and bimolecular processes.

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The manuscript was received on 28th July 1995 and accepted for publication after revision on 25th August 1996.