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Cracking of *n*-Heptane on a CrHNaY Zeolite Catalyst. The Network of the Reaction

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The cracking of *n*-heptane has been studied at 400, 450, and 470°C over a CrHNaY zeolite catalyst using a tubular packed-bed reactor. The concept of "Optimum Performance Envelope" was used in order to identify which of the observed reaction products are primary and which are secondary. In this way the initial selectivity values for all primary products have been calculated and from such values we have seen that primary reactions other than cracking occur in this process. These reactions include isomerization and disproportionation of *n*-heptane. All the primary reactions which appear in the cracking of *n*-heptane can be explained as occurring on acid centers and consequently no direct catalysis by chromium ions in the first steps needs to be invoked to rationalize our results. Finally, a network for the "cracking" of *n*-heptane on the CrHNaY zeolite catalyst has been constructed on the basis of the observed behaviour of the selectivity curves.

INTRODUCTION

The cracking of paraffinic hydrocarbons has been extensively studied on zeolites containing ammonium, alkaline earth, and rare earth cations (*1–7*), but literature is scarce for reaction on transition metal cation-exchanged zeolites. Carbonium ion reactions on zeolites exchanged with transition metals have been studied and no clear correlation between activity and the concentration of acid sites was found (*8*). It has been suspected that other, more complex, factors related to the nature of the transition cations may play an important role. However, the interpretation of the kinetic results in cracking reactions is frequently muddled by the decay of catalyst activity. In most cases the data on catalytic cracking activity reported are instantaneous values measured at some definite reaction time, i.e., either after a few minutes from initiation of reactant flow (*2*), close to the initial value, or at a much longer time on stream (*3, 5*), when a pseudo-steady-state activity has been attained. All these results must be considered cautiously, since the activity and selectivity for the different products can change with time on stream. Therefore, only initial values should be considered to characterize adequately the intrinsic activity of a cracking catalyst and to provide information on the reaction mechanism. For this reason, pulse microreactor techniques have been frequently used in kinetics studies on cracking reactions; however, it has been pointed out (*9*) that such techniques can give distorted results due to the so-called chromatographic effect.

An alternative method which involves the analysis of samples taken at regular intervals of reaction time in a continuous flow system and the extrapolation of the values of conversion to time zero has been also used. It has recently been shown (*10*) that such a method can be quite inaccurate, especially when the decay of the catalyst is very fast. The most convenient method of treating data obtained with a catalyst whose activity decreases with time is to introduce a decay function into the kinetic rate equation, as has been proposed by several authors (*11–16*).

In the present work, the cracking of *n*-heptane was studied on a zeolite exchanged with chromium, an element which was expected to introduce dehydrogenation and

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cyclization properties to the zeolite. Then, the "Optimum Performances Envelopes" (OPE) (*16*), which represent the various selectivity behaviours in the absence of decay, were used to determine whether the observed products of the reaction are primary or secondary, stable or unstable, and to calculate the initial selectivities by determining the slopes of these curves at zero conversion. The values of these initial selectivities and their change with reaction temperature have been used to identify the various reactions taking place in the cracking of *n*-heptane on a CrHNaY zeolite.

EXPERIMENTAL METHODS

Materials

The CrHNaY zeolite catalyst used in this study was prepared by a conventional ion exchange technique. The starting material was NaY from Linde (SK-40). The final catalyst contained 32% of Na^+ replaced by Cr^{3+} and 13% replaced by H^+. The complete description of the preparation of this catalyst has been reported elsewhere (*17*). A HNaY sample with 23% of Na^+ replaced by H^+ by exchange with ammonium acetate solution was also used for comparison purposes as well as a NaY sample previously washed with sodium acetate.

The *n*-heptane was a high-purity reagent.

Procedure

Cracking experiments of *n*-heptane were carried out in a continuous flow fixed-bed reactor at atmospheric pressure and temperatures of 400, 450, and 470°C. Catalyst (particle size of 80/120 mesh) was placed into a Pyrex tubular reactor (12 mm i.d.) and pretreated in a helium stream at 350°C for 2.5 h, then the temperature was raised progressively to 500°C and held for 1 h. *n*-Heptane was fed to the reactor at constant space velocity by means of a positive displacement pump. Experiments at different space velocity were carried out by varying the weight of catalyst and the reactant flow rate. The effluent from the reactor was passed through a cooled water condenser. The liquid products condensed were collected and every 30 or 60 min were removed, weighed, and analyzed. The gaseous stream was introduced into gas burettes, where it was trapped by downward displacement of water saturated with NaCl. The total volume of gases recovered in each period of time was measured and their composition determined. The products, viz., liquids and gases, as well as the gases dissolved in the liquid fraction, were analyzed separately by gas chromatography, using the columns and conditions described elsewhere (*17*). Mass balance of not less than 95% was obtained on the basis of the liquid and gaseous products recovered. Coke deposited on catalyst was not determined.

The average yield of each product and the average total conversion were calculated from the chromatographic analysis data obtained for each sample of products accumulated every 30 or 60 min. Thus, the cumulative yields and total conversion at various constant catalyst/oil ratios (P) were calculated, as a running average of the half-hourly averages, from the above experimental results obtained at several constant space velocities (*10*). The ratio P at time on stream t_f was calculated by dividing the amount of catalyst by the total amount of *n*-heptane fed from time on stream zero to time t_f. The space velocity(s) was related to P and t_f by

$$S = \frac{1}{P \cdot b \cdot t_f},$$

where b is a proportionality constant.

Total conversion was calculated as the total number of carbon atoms of outlet hydrocarbons other than the feed divided by the number of carbon atoms in the *n*-heptane fed. The yield of a product was defined as moles of product divided by moles of *n*-heptane fed.

RESULTS

The products detected in a typical anal-

TABLE 1

Reaction Products from the *n*-Heptane "Cracking" Reaction on CrHNaY Zeolite Catalyst

Product	Type
Methane	Secondary stable
Ethane	Primary + secondary stable
Ethylene	Primary + secondary unstable
Propane	Primary + secondary stable
Propylene	Primary + secondary unstable
n-Butane	Primary + secondary stable
i-Butane	Primary + secondary stable
Butenes	Primary + secondary unstable
C_5 fraction i-Pentane *n*-pentane 2-Methylbutene-2	Primary unstable
C_6 fraction i-Hexane 1-Hexene *n*-Hexane Methylcyclopentane Cyclohexane	Primary unstable
C_7 fraction i-Heptane 3-Methylhexane Methylcyclohexane	Primary unstable
Aromatics fraction Toluene Xylenes	Secondary stable
Traces of C_n, $n \geq 8$	

ysis of the reaction products of *n*-heptane on a CrHNaY-32 zeolite sample are shown in Table 1. Cracking of *n*-heptane is the major reaction occurring. This reaction is accompanied by some isomerization and dehydrocyclization of *n*-heptane. It is noted that some traces of hydrocarbons heavier than the reactant are also detected and reported as C_n, where $n \geq 8$. Due to the small amount of this fraction no further identification was carried out.

The product yields at constant catalyst/oil ratio versus the corresponding total conversions at 400°C are shown in Figs. 1A to M. Broken lines appear where necessary to distinguish parts of the various constant catalyst/oil loops. The solid lines enclosing such loops are the OPEs. The types of products which these OPEs represent are listed in Table 1 and the initial selectivities of all primary products are listed in Table 2. These initial selectivities have been calculated by measuring the slope of the tangent to the OPEs at zero conversion of each product given in Fig. 1. In Table 3 the zero-time extrapolated yields of the products in the cracking of *n*-heptane on HNaY and NaY zeolite catalysts are compared with those obtained on the CrHNaY-32 sample under the same reaction conditions.

DISCUSSION

Conversion and selectivity over a cata-

TABLE 2

Initial Slopes of the Primary Reaction Products of the *n*-Heptane "Cracking" Reaction on CrHNaY Zeolite Catalyst

Product	Type	Initial selectivity		
		400°C	450°C	470°C
Ethane	Primary + secondary stable	0.06	0.09	0.12
Ethylene	Primary + secondary unstable	0.03	0.05	0.11
Propane	Primary + secondary stable	0.27	0.27	0.19
Propylene	Primary + secondary unstable	0.14	0.21	0.21
n-Butane	Primary + secondary stable	0.13	0.15	0.12
i-Butane	Primary + secondary stable	0.40	0.35	0.27
Butenes	Primary + secondary unstable	0.09	0.18	0.24
C_5 fraction	Primary unstable	0.13	0.17	0.24
C_6 fraction	Primary unstable	0.16	0.15	0.13
(2 + 3) methylhexane	Primary unstable	0.17	0.11	0.10

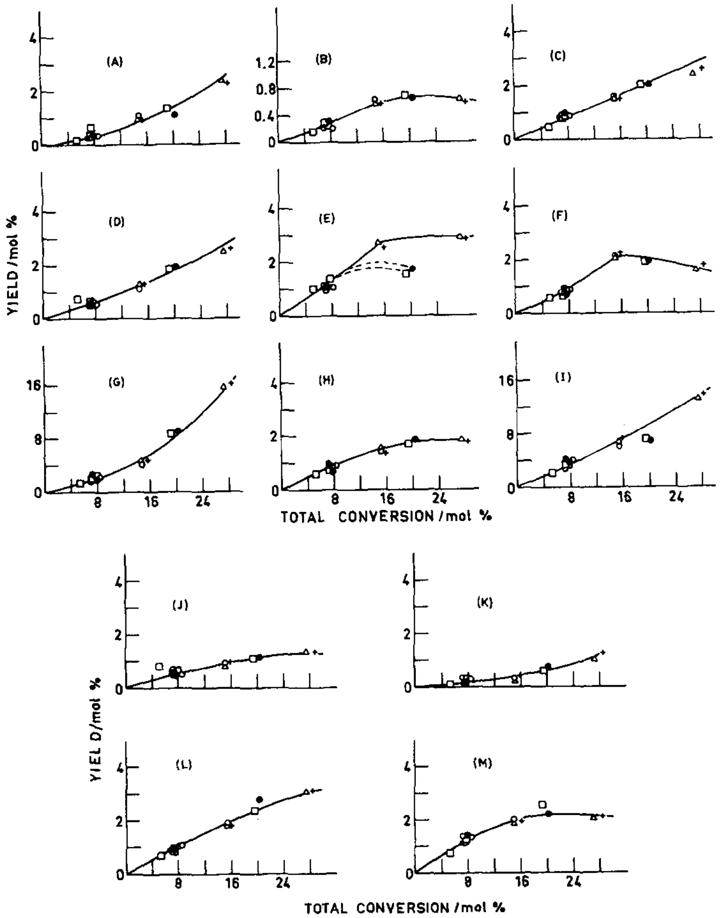

FIG. 1. Selectivity plots for products. Solid curves through the points represent the OPE at 400°C. The broken curves which appear are for different catalyst/oil ratios. The symbols represent the following catalyst/oil ratios: 0.36 (□); 0.52 (●); 0.69 (○); 0.77 (△); 1.35 (+). (A) Methane; (B) ethylene; (C) n-Butane; (D) ethane; (E) propylene; (F) butenes; (G) propane; (H) C_5 fraction; (I) i-butane; (J) C_6 non-cyclic; (K) aromatic fraction; (L) C_6 cyclic; (M) (2 + 3) methylhexane.

lyst which is subject to decay are dependent on the time on stream. Since this fact is not always taken into consideration, it is not surprising to find contradictory results in the literature describing cracking reactions. It is a fact in such systems that, depending on the time on stream at which the selectivities of the reaction products are compared, different conclusions can be reached. To avoid this problem in our work we have used the "Optimum Performance Envelopes" which represents the selectivity pattern for the same system in the absence of decay (*16*).

From the behaviour of the OPE curves shown in Figs. 1A to M it can be seen that ethane, propane, n-butane, and isobutane are primary plus secondary stable products, while ethylene, propylene, n- and isobutene are primary plus secondary unstable products. The C_5, the C_6, and the C_7 fractions contain primary unstable products. Finally, methane and the aromatic fraction appear as secondary, stable products. The same behavior was found at 450 and 470°C.

According to the carbonium ion theory, one would expect C_2 and C_5, and C_3 and C_4

TABLE 3

Conversion and Product Yields Extrapolated at Zero Reaction Time in "Cracking" of *n*-Hepane[a]

	Catalyst		
	CrHNaY-32	HNaY-23	NaY
Conversion, % C	12.7	35.4	3.4
Product yield, %			
Methane	1.17	5.50	0.44
Ethane	1.39	3.70	1.53
Ethylene	0.46	1.00	0.80
Propane	4.75	30.00	0.58
Propylene	3.02	1.25	0.90
n-Butane	1.75	8.02	0.57
iso-Butane	4.75	22.48	0.23
Butenes	2.20	2.50	1.00
C_5 fraction	1.39	0.60	1.80
C_6 noncyclic fraction	0.81	0.15	0.04
C_6 cyclic fraction	0.90	0.10	0.02
iso-Heptane	0.80	0.50	Traces
Aromatic fraction	0.50	0.30	Traces
C_n, $n \geq 8$	Traces	Traces	—

[a] n-Heptane flow, 18.4×10^{-3} mol · h^{-1}; W/F = 0.825 h; reaction temperature, 450°C.

to be the only primary cracking products in *n*-heptane cracking reactions. Also, the C_2 fraction should be equal to the C_5 fraction, and C_3 to C_4. Furthermore, the carbonium ion theory predicts a paraffin/olefin ratio of unity. The results presented in Table 2 show that not one of these conditions is fulfilled. Indeed, the ratios C_5/C_2 and C_4/C_3 are higher than unity at all temperatures and the ratio of paraffins/olefins is also greater than unity. It is also interesting to note that C_6 is found to be a primary product whereas C_1 appears as a secondary product. This means that C_6 does not proceed from a direct cracking reaction of *n*-heptane since it would imply the appearance of C_1 as a primary product, and according to Fig. 1A this is produced by secondary processes. Thus, the formation of C_1 on the CrHNaY-32 zeolite could be due to the cleavage of some primary products either thermally or catalytically on chromium ions, on sodium ions, or on the acid sites of the zeolite. In order to clarify the latter some additional experiments were carried out with a sodium and a decationated zeolite sample. The results presented in Table 3, although not corresponding to the same conversion level, induce us to believe that most of the C_1 is formed by acid catalysis and some by thermal cracking. Consequently, the contribution of chromium and sodium ions to the formation of C_1, if any, must be small. It is then reasonable to accept that the major part of the C_1 is produced by acid catalysis in secondary cracking. A relatively high amount of C_1 had also been found in cracking of paraffins on zeolite catalysts (*3*, *18*). The presence of C_1 could be explained by secondary reactions such as the cracking of an isopentyl carbonium ion or an isobutyl carbonium ion as suggested by Barthomeuf and Beaumont (*19*), and also by dealkylation of xylenes and toluene.

In order to explain the unexpected C_5/C_2 and C_4/C_3 ratios it is necessary to consider that C_4 and C_5 are generated not only by cracking but also by some other reaction. These results, as well as the appearance of C_6, suggest that the cracking of *n*-heptane over a chromium zeolite follows a somewhat different mechanism to the simple cracking of chains via carbonium ion intermediates. We believe that the additional initially occurring reactions present here involve the disproportionation of two heptane molecules, followed by the cracking of the long-chain products formed by this disproportionation, as is proposed in Fig. 2. Bolton and Bujalski (*4*), for example, also found that disproportionation occurs in the cracking of *n*-hexane on a NH_4Y zeolite. Taking into account such disproportionation reactions, it is possible to explain the appearance of C_6 as a primary product and to explain why the C_5/C_2, C_4/C_3 ratios are higher than unity.

The large number of reactions taking place via the disproportionation mechanism (Fig. 2) makes the quantitative determination of the initial selectivities of the various disproportionation products impossible. Here we have assumed as a first approximation, that reactions (1) and (2) will occur to a far greater extent than reactions (3), (4),

TABLE 4

Corrected Initial Selectivities for the Various Reactions in the Catalytic Cracking of *n*-Heptane on CrHNaY Zeolite Catalyst

Product	Type of reaction	Initial selectivity		
		400°C	450°C	470°C
$C_2^- + C_2^{2-}$	Cracking	0.09	0.14	0.23
C_5 fraction	Cracking	0.09	0.14	0.23
$C_3^- + C_3^{2-}$	Cracking	0.37	0.45	0.39
$C_4^- + C_4^{2-}$	Cracking	0.38	0.44	0.39
Total selectivity for cracking		0.47	0.58	0.62
C_6 fraction	Disproportionation	0.16	0.15	0.13
Total selectivity for disproportionation (bimolecular reaction)		0.32	0.30	0.26
C_7 fraction	Isomerization	0.17	0.11	0.09
Total selectivity for isomerization		0.17	0.11	0.09
Total initial selectivity for primary products		0.96	0.99	0.97

and (5) (*20*). Therefore the reactions we have considered are

$$2\ C_7 \rightarrow [C_{14}] \rightarrow 2\ C_7 \quad (6)$$

$$\rightarrow C_6 + 2\ C_4 \quad (7)$$

$$\rightarrow C_5 + C_3 + C_6 \quad (8)$$

$$\rightarrow C_2 + 2\ C_6. \quad (9)$$

From Table 2 one can see that, especially at the lower temperatures, the initial selectivity for C_2 is much smaller than the initial selectivities for C_3 and C_4. This observation leads us to assume that reaction (9) will occur to a much lesser extent than reactions (6), (7), and (8). With this assumption, the only disproportionation reactions which need be considered are reactions (7) and (8), since reaction (6) simply regenerates the initial reactants. Therefore, taking into account reactions (7) and (8) in Fig. 2, the initial selectivities presented in Table 2 can be thought of in the following ways. If reactions (7) and (8) occur in parallel with

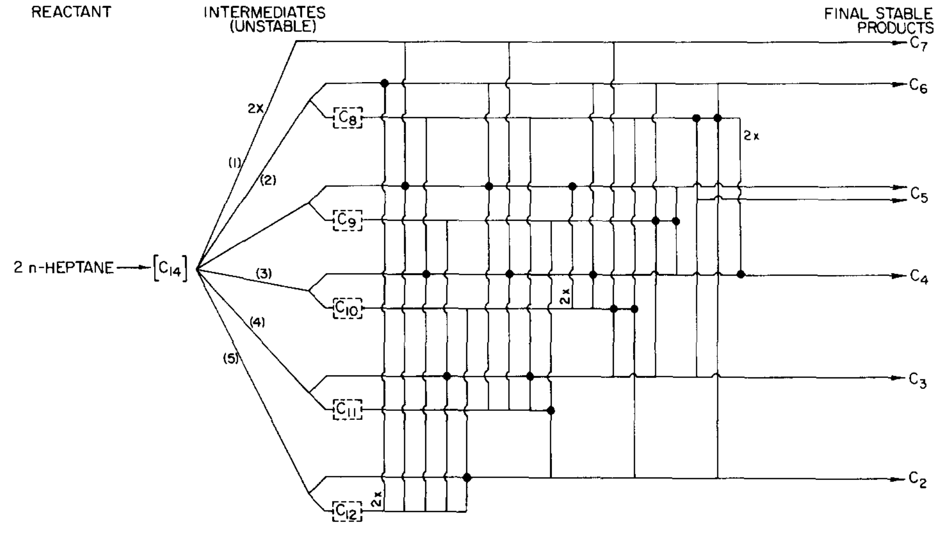

FIG. 2. Network of the reactions involved in the disproportionation of *n*-heptane.

the cracking reactions, and if C_2 is purely a product of cracking, the difference between the initial selectivities of C_5 and C_2 must represent the initial selectivity for C_5 via reaction (8), and consequently the selectivity for C_6 and C_3 formed by reaction (8). If we now subtract from the total initial selectivity for C_6 the selectivity due to reaction (8), the remaining selectivity corresponds to the C_6 formed through reaction (7). Then, from the stoichiometry of reaction (7), the initial selectivity for the C_4 must be twice the initial selectivity of the C_6 formed by reaction (7). By such considerations it is possible to calculate the initial selectivities (I.S.) for the C_3 and C_4 coming directly from the cracking of *n*-heptane:

$$\text{I.S. } C_3 \text{ cracking} = \text{Total I.S. } C_3 - \text{I.S. } C_{5\,(8)}, \quad (10)$$

$$\text{I.S. } C_4 \text{ cracking} = \text{Total I.S. } C_4 - 2 \times \text{I.S. } C_{6\,(7)}. \quad (11)$$

In the above the following values are inserted:

$$\text{I.S. } C_{6\,(8)} = \text{I.S. } C_{5\,(8)} = \text{Total I.S. } C_5 - \text{I.S. } C_2, \quad (12)$$

$$\text{I.S. } C_{6\,(7)} = \text{Total I.S. } C_6 - \text{I.S. } C_{6\,(8)}. \quad (13)$$

In Table 4 the corrected initial selectivities are presented. From this table it is possible to see that the corrected initial selectivity for the C_4 fraction is practically the same as the initial selectivity of the C_3 fraction, as would be expected for a pure cracking reaction. Also, the sum of the initial selectivities of the various reactions is 100% within the limits of our experimental error. From all this we conclude that, to a first approximation, reactions (7) and (8) together with the cracking and isomerization reactions, explain the initial selectivity values presented in Table 2 and hence reveal the network of initial reactions. Since isomerization and disproportionation, as well as cracking, play an important role in the system, the disappearance of the reactant, especially at the lower temperatures, cannot be taken as a measure of the rate of cracking, as is commonly done in the literature (*2, 7*).

From Figs. 1A to M one can see that all the product olefins are unstable in this system. Since C_3 and C_2 olefins are unlikely to be cracked under our reaction conditions, the instability has to be related with reactions other than cracking. We note also that it is generally accepted (*22–24*) that olefins can be saturated by successive hydrogen transfer on acid catalysts. At the same time, from Table 2, one can see that the ratio paraffins/olefins is greater than unity for all chain lengths, whereas the carbonium ion theory predicts a paraffins/olefins ratio of unity for the products of paraffin cracking. For the products formed via disproportionation reactions (7) and (8), we have calculated on the basis of the carbonium ion theory that the ratios C_4^-/C_4^{2-} and C_3^-/C_3^{2-} are 0.45 and 0.44, respectively.

If we now consider the production of the total C_3's and C_4's as being due to disproportionation reactions as well as the cracking reactions, the paraffins/olefins ratio would be expected to be less than unity. From the initial selectivities in Table 2 one can see that the paraffin/olefin ratio is greater than the expected value. Bolton and Bujalski (*4*) have suggested that this may be due to the saturation of olefins by protons from the Brønsted acid sites. Such a mechanism would also explain the decrease in the activity of the catalyst with the time on stream. In our case, however, it seems unlikely that the only source of H_2 could be the Brønsted sites. Indeed, from Figs. 1A to M it is possible to see that the catalyst/oil loops are very close to the OPEs. This indicates that in our case, catalyst decay is very slow and consequently the loss of Brønsted acid sites would have to be so small that it would not explain the necessary saturation of olefins and the consequent high paraffin/olefin ratios. We believe that the high paraffin/olefin ratios are due also to hydrogen transfer reactions from coke precursors, as has been suggested by other authors (*7, 21, 22*). The proposal of such a hydrogen transfer mechanism to explain the high paraffin/olefin ratio is also consistent with the fact that isobutane has the highest initial selectivity of all C_4. This isobutane is believed to be formed by the hydrogenation of isobutene via a hydrogen transfer mechanism (*23*) and by cracking of isoheptane formed by isomerization of *n*-heptane.

From Table 2 it is possible to see that the paraffin/olefin ratio approaches unity as the temperature of reaction increases. Some authors (*4*) have proposed that the rate-controlling step in the hydrogenation of olefins by hydrogen transfer is the desorption of the olefins. Our experimental results are in agreement with this idea if increasing the temperature increases the ability of the olefins to desorb before the hydrogen transfer reaction can take place.

In Fig. 1L aromatics are seen to be secondary products; consequently no direct dehydrocyclization of *n*-heptane must occur either on the chromium ions or on the acid sites. However, we cannot neglect the possibility that the chromium ions can also be active in the formation of aromatics from the olefinic products obtained in the cracking reactions.

According to Fig. 1M isoheptane seems to be a primary unstable product. In this case we think that isomerization of *n*-heptane to isoheptane could occur through a mechanism involving the formation of a carbonium ion on a Lewis acid site (*3*), a Brønsted acid site (*9, 24, 25*), or also through a mechanism involving a bifunctional catalyst, where the hydrogenating–dehydrogenating function would be the chromium. From comparison of the yield to isoheptane obtained on the CrHNaY-32 and HNaY samples, it can be suggested that such a reaction is related with the acid sites of the catalyst rather than with the chromium ions, since the values are not very different. The small difference on isoheptane yield observed could be explained by considering that the level of total conversion on the HNaY sample is higher, and it means that more secondary cracking reactions would occur, with disappearance of the primary isoheptane formed. Furthermore, additional experiments for dehydrogenation of methylcyclohexane on CrNaY zeolite containing an even higher degree of chromium exchange (83%), at 450°C, atmo-

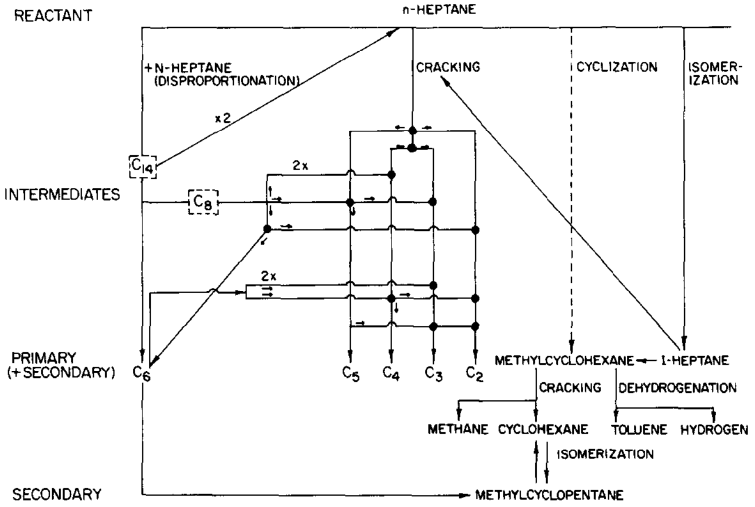

FIG. 3. Network of the reactions involved in the "cracking" of *n*-heptane.

spheric pressure, and a contact time of 2.6 h, gave yields to methylcyclohexene plus methylcyclohexadiene of 0.8 and to toluene of 0.4% at zero time on stream (*26*). This result shows the low hydrogenating–dehydrogenating activity of the chromium-exchanged Y zeolites. This is consistent with its low capacity as a bifunctional catalyst in the isomerization of *n*-heptane, and also with the fact that no aromatics have been obtained as primary products.

The cyclohexane and methylcyclopentane found in the products can be formed either by cyclization of C_6 or as intermediate cyclic products in the disproportionation reaction (*6*) as well as by the cracking of intermediate methylcyclohexane.

As a result of the above discussion we propose the network presented in Fig. 3 to measure the rate of the "primary" reaction involved in the catalytic cracking of *n*-heptane on a chromium-exchanged zeolite.

CONCLUSIONS

From the shapes of the selectivity curves for each product, as well as from the values of the initial selectivity of the various products observed, we conclude that in the "cracking" of *n*-heptane on a chromium acid Y zeolite catalyst, initial reactions other than cracking are taking place. Consequently the total rate of disappearance of the reactant cannot be used to measure the rate of the cracking reaction.

The primary reactions which we find to be taking place are isomerizations, disproportionations, and cracking, while the most important secondary reactions are cracking, hydrogen transfer, and dehydrocyclization. The formation of all the primary products obtained can be explained mainly due to acid catalysis and consequently no clear direct catalytic role has been found for the chromium ions in the primary reactions.

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