A STUDY OF CATALYTIC CRACKING OF *n*-HEPTANE OVER CHROMIUM-EXCHANGED ZEOLITES

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N-heptane cracking over a chromium-exchanged Y-zeolite was studied in a flow system at 400°, 450° and 470 °C. The initial catalytic activity indreases with the extent of chromium-exchange. The primary product distributions obtained suggest the occurrence of cracking through the classical carbonium ion mechanism, accompanied by a bimolecular disproportionation reaction. The relative contribution of these two reaction pathways seems to depend on reaction temperature.

Introduction

The cracking of paraffinic hydrocarbons has been extensively studied on zeolites containing ammonium, alkaline earth and rare earth cations [1—7], but on transition metal cation-exchanged zeolites the literature is scarce. It is generally accepted that the catalytic activity of zeolites is strongly associated with surface protons and that the reaction proceeds by a carbonium ion mechanism [8—9]. However, in those cases in which the selectivity to cracking products was examined in detail, significant differences between the experimental results and the products predicted by the conventional carbonium ion mechanism were found. In an earlier work [10] we reported some preliminary data showing that in the decomposition of *n*-heptane over CrY zeolites, cracking is the major reaction while isomerization and dehydrocyclization only occur to a minor extent. In this study we present a more detailed investigation of *n*-heptane cracking over the same series of catalysts. The composition of the cracking products and the variation of the selectivities with the extent of cation exchange are examined with respect to the mechanism of the reaction.

Experimental methods

Materials

The catalysts used were prepared from a NaY zeolite (SK—40) obtained from Linde (lot. no. 3607-411). The original zeolite was previously purified by treatment with 0.1 M sodium acetate solution followed by the necessary washings with deionized water. A series of four samples with different chromium content were prepared by repeated exchange of the purified zeolite with 0.2 M aqueous solution of chromium

acetate at 55 °C. During the exchange the pH of the slurry was fixed at 4.5 by adding 0.1 M HNO_3 solution. In following this procedure all the zeolite samples suffered an approximately similar degree of decationation (1—13%) in addition to the chromium exchange. After the exchange, the samples were thoroughly washed with deionized water until no acetate or nitrate ions were detected in the filtrate. They were later dried at 110 °C, pelleted, crushed and sized to 80—120 mesh.

The degree of exchange was determined by analysis of the remaining sodium and exchanged chromium in the solid zeolite, and by measuring the extracted sodium in the filtrate. Table I shows the composition of the catalyst samples. All chemicals were at least of reagent grade purity.

Table I

Composition of Catalysts

Catalyst	Cations			
	per unit cell		% Na+ replaced by:	
	Na^+	Cr^{3+}	H^{+*}	Cr^{+3}
CrHNaY-24	35.9	4.4	12	24
CrHNaY-32	30.7	6.0	13	32
CrHNaY-52	19.4	9.7	13	52
CrHNaY-58	18.2	10.8	9	58

* Calculated from the difference of Na^+ in the parent NaY zeolite and $Na^+ + Cr^{3+}$ in the solid after the exchange.

Procedure

The catalytic activity was measured in a flow reactor at atmospheric pressure and temperatures of 400° to 470 °C. For each experiment a fresh portion of hydrous-form catalyst (1—3 g) was placed in a Pyrex tube (12 mm i.d.) between two plugs of quartz wool. Prior to use, the catalysts were pretreated under a flow of dry helium as follows: raising the temperature up to 350 °C over a period of 1 h period, and holding at that temperature for 2.5 h. The reactor was then cooled to the reaction temperature while maintaining the helium stream. Liquid n-heptane was introduced into the system by a small displacement pump at a feed rate varing from 2.7 to 11.0 ml/h. Samples of both liquid and gas products were taken at 30 min intervals during 3 to 4 h runs.

The liquid products were analyzed by GLC, using a 4.3 m column with silicone gum rubber (SE-30) on Chromosorb P at a temperature program of 35°—150 °C, and the gas products with a 2 m column of silica gel and Porapak Q at a temperature program of 35°—180 °C.

Results and discussion

Some blank experiments were performed in order to evaluate the thermal decomposition of *n*-heptane. At the higher reaction temperature, 470 °C, and the smaller flow rate of *n*-heptane, 2.7 ml/h, used in this study, the conversion was ~ 3%. Since the contribution of thermal cracking was usually less than 10% of the total conversion, we have not attempted to make any corrections when reporting the catalytic data.

Additional experiments were carried out to look at the catalyst deactivation. On samples with a high chromium content we found a linear decay of the activity [10]. However, on samples with less chromium the activity was almost constant over a period of several hours. Thus, the initial values of the activity and product selectivity were determined by extrapolation back to zero reaction time. The results were satisfactorily reproduced and the material balance was generally greater than 94%.

Measurements were performed at different reaction temperatures over a wide range of conversions on the CrHHaY-32 sample. The results obtained are shown
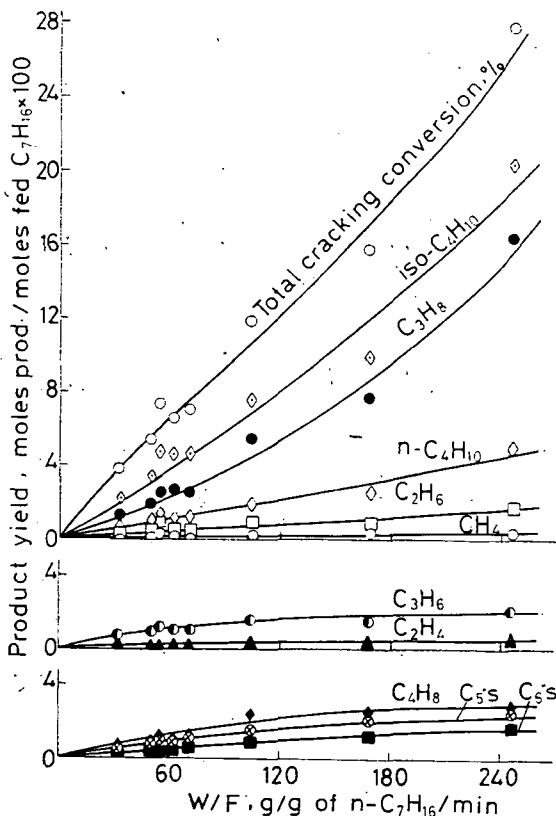

Fig. 1. Dependence of cracking conversion and product yield of CrHNaY-32 zeolite on contact time at 400 °C.
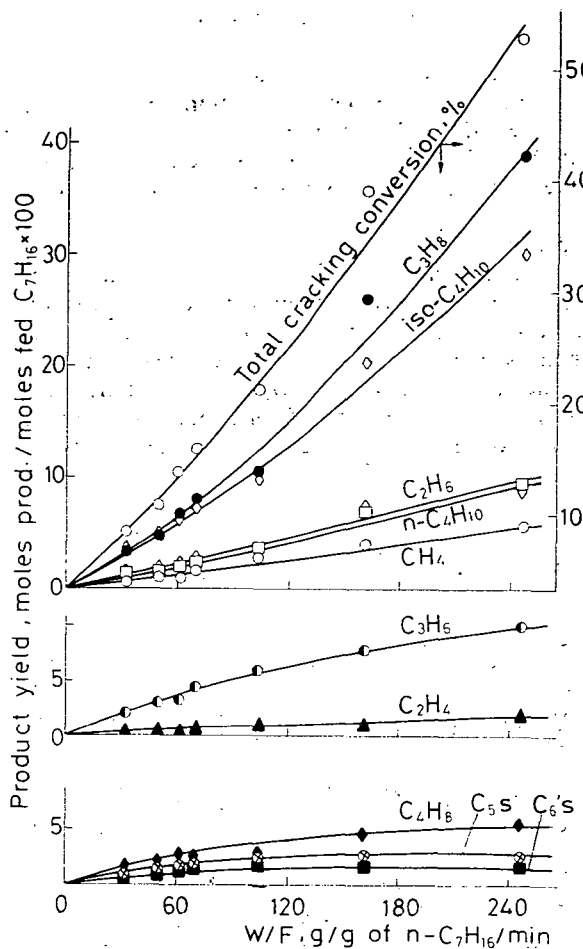
Fig. 2. Dependence of cracking conversion and product
yield of CrHNaY-32 zeolite on contact time at 450 °C.

in Figs. 1, 2 and 3. The total cracking conversion has been calculated on the basis
of a carbon balance in the products, by referring to the number of carbon atoms in
the n-heptane feed. We can see that the yields to the different products increase con-
tinuously with increasing contact time and that all of them appear to be primary pro-
ducts of the reaction. This is confirmed in Fig. 4, where a typical plot of product
selectivities versus cracking conversion at 450 °C shows positive values for the
different selectivities at zero conversion. Using similar plots for the other temperatu-
res, we have determined the corresponding initial product distribution, which are
summarized in Table II. The large production of C_3's and C_4's and the relatively small
quantities of CH_4 and C_2's observed, specially at 400 °C, together with iso/normal
ratios of the C_4, C_5 and C_6 alkanes higher than 1, are typical characteristics of n-
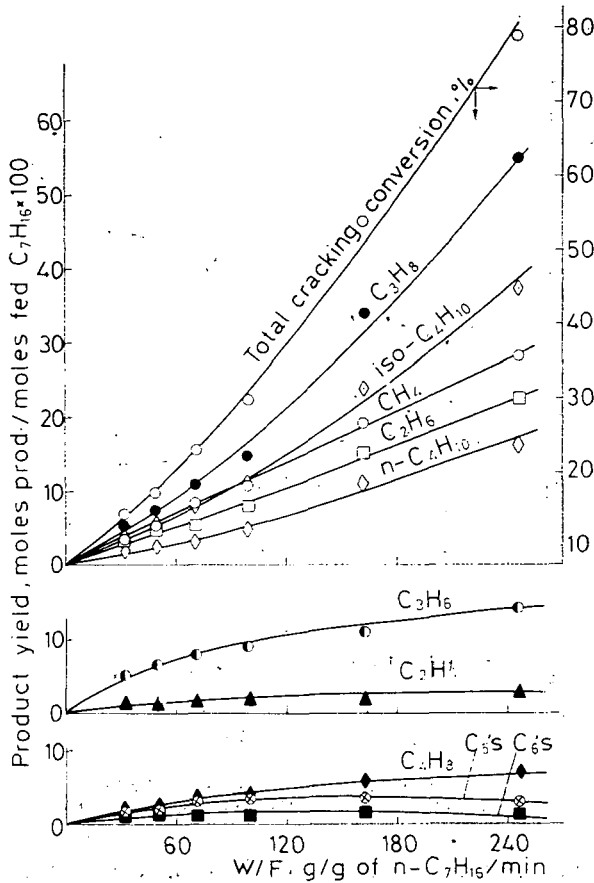
Fig. 3. Dependence of cracking conversion and product yield
of CrHNaY-32 zeolite on contact time at 470 °C.

heptane cracking by carbonium ion intermediates. However, other reaction features
noted in Table II, *e.g.*, C_1, C_2 and C_3 fractions not equal to C_6, C_5 and C_4, respecti-
vely, and saturate-to-unsaturate ratio in each fraction generally greater than one, can
not be easily explained by a carbonium ion mechanism.

These results suggest therefore, that the cracking of n-heptane over chromium
zeolites partially follows a different mechanism from the classical one involving car-
bonium ion intermediates. In our opinion such an additional mechanism would
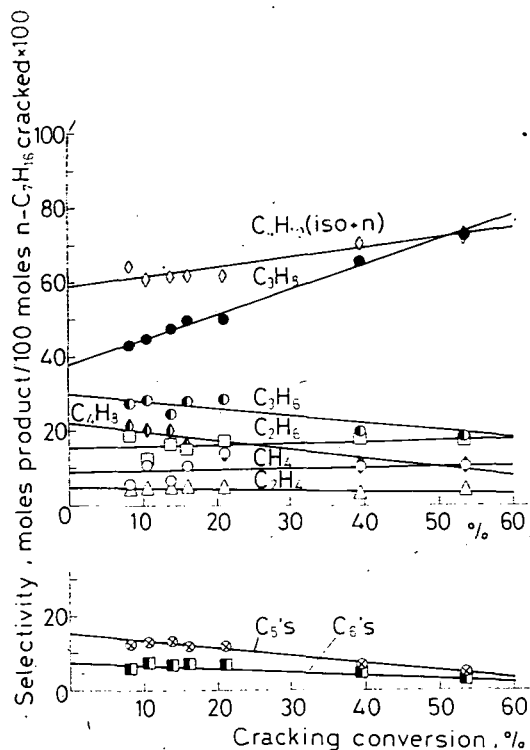involve the following disproportionation reactions:

$$2 C_7 \rightarrow [C_{14}] \rightarrow 2 C_4 + C_6$$

$$2 C_6 \rightarrow [C_{12}] \rightarrow 3 C_4$$
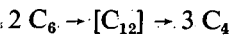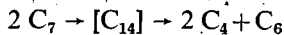
Fig. 4. Typical plot of product selectivity *vs.*
cracking conversion with CrHNaY-32 zeolite at 450 °C

which would explain the great amount of C_4's formed. A similar disproportionation mechanism has been put forward for *n*-heptane cracking on ammonium-exchanged Y zeolites [6]. The suggestion of radical and carbonium ion mechanism taking place simultaneously [7] does not seem very probable in our case, because the results obtained, particulary at 400 °C, show a high relative concentration of *iso*butane to C_1 and C_2 hydrocarbons. However, the proposal of a monomolecular mechanism of direct scission of carbon-carbon bond simultaneously with a bimolecular disproportionation [6] seems to be more consistent with the results of Table II, particulary at 400 °C.

At a higher temperature it seems necessary to accept a decrease in the relative contribution of the disproportionation mechanism to the overall reaction, in order to explain the decrease of the C_4/C_3, C_4/C_2 and C_4/C_1 ratios. On the other hand, the decrease of paraffins to olefins ratio in the products with reaction temperature may well result from the lower contribution of the disproportionation reactions mentioned above, together with a greater facility of the olefins to desorb from the catalyst and the fewer hydrogen transfer reactions.

The effect of the extent of cation exchange on the cracking activity and on the product distribution has been studied at three different temperatures. The results

Table II

Initial Product Distribution for the Cracking of n-heptane on HNaYCr-32 zeolite at Different Reaction Temperatures (mole of cracked products per 100 moles of C_7 cracked)

Product	400 °C	450 °C	470 °C
Methane	1	9	34
Ethane	14	15	26
Ethylene	3	5	11
Total C_2's	17	20	37
Propane	29	38	36
Propylene	20	30	43
Total C_3's	49	68	79
Iso-Butane	66	42	27
n-Butane	18	17	13
Butenes	18	22	18
Total C_4's	102	81	58
Total C_5's*	13	15	15
Total C_6's**	8	7	7
C_4/C_3	2.1	1.2	0.7
C_4/C_1	102.0	9.0	1.7
C_4/C_2	6.0	4.0	1.6
Paraf./Olef.***	3.3	2.0	1.4

* Predominantly isopentane and decreasing amounts of n-pentane and 2-methyl 2-butene.
** Predominantly 2-methyl pentane and 3-methyl pentane, followed in decreasing order of n-hexane and 1-hexane.
*** In fractions C_2 to C_4.

Table III

Distribution of Cracked Products on Several Catalysts at Different Reaction Temperatures. (Moles of cracked products per 100 moles of C_7 cracked)

Catalyst Temp. °C	CrHNaY-24			CrHNaY-32			CrNHaY-52			CrHNaY-58		
	400	450	470	400	450	470	400	450	470	400	450	470
Conversion, % cracking	2.4	7.6	12.7	5.4	10.6	16.9	10.7	23.6	37.0	12.2	32.8	49.2
Methane	+	15.3	27.5	1.1	10.9	32.5	7.0	25.4	46.0	7.4	39.6	50.8
Ethane	21	16.4	23.5	11.6	13.1	29.0	9.9	13.9	21.6	11.1	14.1	26.4
Ethylene	+	7.9	7.1	2.2	4.3	8.8	1.9	3.9	4.1	2.7	4.5	4.5
Propane	39.6	49.7	47.2	35.8	44.8	44.0	49.5	52.2	51.7	46.3	58.2	54.4
Propylene	21.0	41.2	43.3	18.5	28.5	38.7	15.9	26.0	31.6	20.5	28.5	30.0
Isobutane	55.4	31.7	29.9	63.7	44.8	33.4	68.4	52.3	43.9	66.9	46.5	40.1
n-Butane	17.5	15.7	15.0	21.9	16.5	13.9	17.6	16.9	15.7	16.7	12.9	13.9
Butenes	34.6	26.3	21.2	14.9	20.7	16.1	6.0	12.7	13.5	8.0	13.7	14.2
Total C_5's	16.6	9.7	10.6	12.7	13.1	10.7	11.7	9.5	7.3	12.3	9.5	6.8
Total C_6's	5.0	3.9	4.4	8.0	7.6	6.4	8.2	5.1	4.1	9.0	4.9	4.5

obtained, summarized in Table III, show firstly that the cracking activity of the zeolites increase with the degree of chromium exchange and, secondly that all catalysts present similar product distribution patterns, which resemble the one obtained with the CrNHaY-32 sample. Although some gradual changes in the selectivities are noted as the chromium content in the zeolite increases, that may be due to differences in conversion level. Comparison of the product selectivities for CrHNay-24, CrHNaY-52 and CrHNaY-58 zeolites with the corresponding values of CrHNaY-32 at equal conversion, obtained from Fig. 4 and similar figures for 400° and 470 °C (not included here), reveals that the selectivities do not sensibly change with the percentage of chromium exchange, suggesting a similar cracking mechanism for all the CrHNaY samples.

    In conclusion, the results obtained in n-heptane cracking on chromium-exchanged Y zeolite show that the activity increases as chromium content is increased. The cracking product distributions obtained suggest, in accordance with other studies [5—7], that the reaction takes place by two types of mechanisms, which involve carbonium ion intermediates and disproportionation reaction, and that their relative contributions to the overall reaction depend on temperature.

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