Cracking of n-Heptane on Metal-Free H-ZSM-5 Zeolite at High Hydrogen Pressure

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The cracking of n-heptane in the presence of hydrogen on metal-free H–ZSM-5 was investigated. Under certain conditions it was possible to combine the processes of cracking and hydrogenation. The product distribution was attributed to the bimolecular cracking mechanism whether hydrogen was present or not. However, the relative amount of saturated reaction products depended on the hydrogen partial pressure. This was interpreted by hydrogen transfer reactions and direct hydrogenation. The hydrogenation of alkenes counteracts the coke formation and/or controls the number of vacant acid sites. The rate of cracking increases with increasing hydrogen partial pressure according to be apparent first order kinetics. The apparent activation energy (70 ± 2 kJ/mol) of n-heptane cracking was found to be independent of hydrogen partial pressure. © 1994 Academic Press, Inc.

INTRODUCTION

Catalytic cracking of alkanes is frequently used as a test reaction to assess the acidic properties of zeolite catalysts. It is generally accepted that alkane cracking proceeds via a bimolecular carbenium ion mechanism or the monomolecular carbonium ion mechanism (1). The effect of alkenes formed during reaction on the catalyst activity in the primary cracking step should depend on the route of the cracking. Unsaturated hydrocarbons are able to interact with acid sites. They can form carbenium ions and initiate the bimolecular chain reaction mechanism (2–4). Otherwise, these carbenium ions act as Lewis acid sites and restrict the formation of carbonium ions by protonation of alkanes in the monomolecular route. Bimolecular cracking prevails at high alkene concentrations. Monomolecular cracking is favoured at low alkene site coverage (1, 5, 6).

The adsorbed alkenes can undergo consecutive condensation reactions which finally result in coke formation. This process can block the catalytic active sites from further interaction with molecules and inhibit the reaction in both pathways (7).

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The hydrogenation ability of H–ZSM-5 was demonstrated by conversion of ethene (8, 9). Assuming that the alkene hydrogenation reaction can be catalyzed by the zeolite, increasing hydrogen partial pressure permits the maintenance of a high stationary concentration of alkanes and control of the concentration of alkenes. Furthermore, one can visualize that the hydrogen can counteract the coke formation at the acid sites. This could force up the cracking activity in the presence of hydrogen as already described for bifunctional reforming catalysts (10).

The aim of the present work was to study the cracking of n-heptane in the presence of hydrogen on metal-free H–ZSM-5 zeolite and to show the possibility of directing the cracking and the hydrogenation processes under certain conditions.

EXPERIMENTAL

Reactions

Catalytic reactions were carried out using a tubular quartz reactor mounted inside a stainless steel tube. The n-heptane was added continuously. The flows of hydrogen and nitrogen were controlled by a mass flow controller. The characteristic conditions of reaction used in this study are summarized in Table 1. The reaction products were analyzed by on-line gas chromatography using a 50-m PLOT Al_2O_3 column, deactivated with KCl. The zeolite was used as pressed powder with a mesh size of 0.315 to 0.4 mm.

Catalyst

H–ZSM-5 zeolite was synthesized template-free in the Bitterfeld Chemie AG. A silicon to aluminum ratio of 24 was determined by ^{27}Al MAS NMR. The IR-spectra of the sample prior to and after adsorption of pyridine are shown in Fig. 1. We determined the ratio of Brønsted to Lewis acid sites to be 4, based on the intensities of the bands at 1540 cm^{-1} and 1460 cm^{-1}. The amount of metal impurities was checked by Proton-Induced X-Ray Emis-
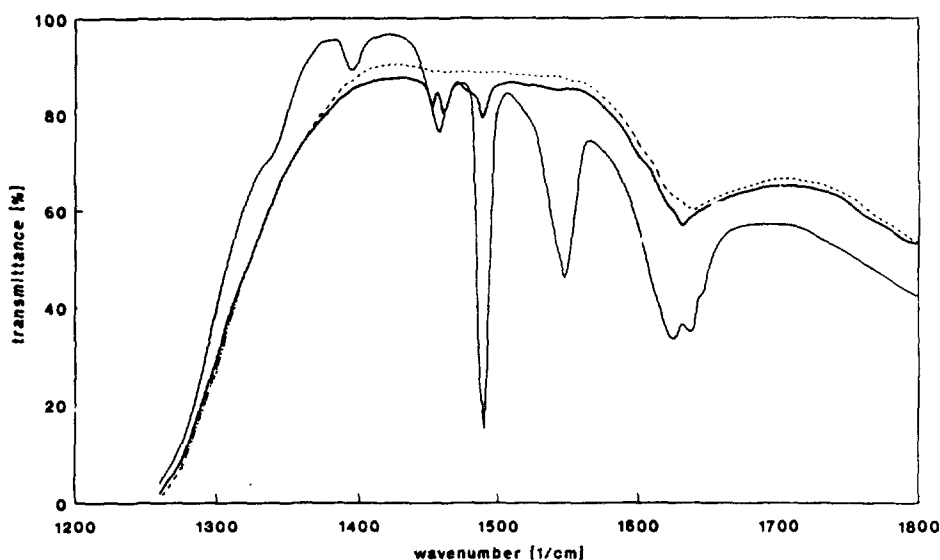
FIG. 1. IR-spectra of H–ZSM-5 sample after ultra-high-vacuum activation at 773 K for 2 h (---), after adsorption of pyridine (—), and after desorption (━). Adsorption conditions: $p = 10$ mbar (1 bar $= 10^5$ Pa); $T = 473$ K.

sion Spectrometry (PIXE) according to Ref. (11). Only traces of the following elements were found: Fe (537 ppm), Ca (285 ppm), Ti (380 ppm), and Zr (83 ppm).

RESULTS AND DISCUSSION

The partial pressure of n-heptane was kept constant in all experiments, whereas the partial pressure of hydrogen was varied by mixing it with nitrogen. Under the given reaction conditions the conversion of n-heptane was lower than 5 mol%. The rate of isomerization did not exceed 15% of the total conversion. No systematic dependence on the applied hydrogen partial pressure was found. Hence the investigation was focused only on the cracking reaction.

The *rate* of cracking on H–ZSM-5 was calculated from the rates of formation of hydrocarbons with one to six carbon atoms r_{C_i},

$$\text{rate} = 1/7 \cdot (r_{C_1} + 2 \cdot r_{C_2} + 3 \cdot r_{C_3} + 4 \cdot r_{C_4} + 5 \cdot r_{C_5} + 6 \cdot r_{C_6}).$$

TABLE 1

Conditions of Reaction

Temperature	543 K
Pressure	25 bar (1 bar $= 10^5$ Pa)
Partial pressure	
Hydrogen	0–21.7 bar
Nitrogen	0–21.7 bar
n-Heptane	3.3 bar
Ethene	0.2 bar
Amount of catalyst	100 mg
WHSV	109 h^{-1}

The rate of cracking decreased with increasing time on stream (Fig. 2). We assume a linear correlation between the cracking rate and time on stream (lines in Fig. 2) as described in the literature (12). The loss in activity during the reaction was found to be nearly constant for different partial pressures of hydrogen.

The higher the value of the hydrogen partial pressure the higher the cracking activity. In contrast to Giannetto *et al.* (13) a direct proportionality between the initial cracking activity (extrapolation of the rate of cracking to zero time on stream using the linear equation) and the hydrogen partial pressure was evident (Fig. 3). The markers indicate the limits of errors in estimating the initial rates.

The carbon content of the catalyst was determined after 120 min time on stream and flushing the catalysts with nitrogen for another 30 min at reaction temperature. The
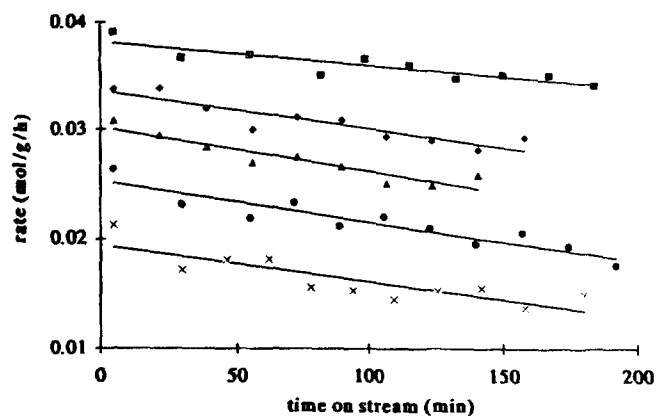

FIG. 2. Rate of n-heptane cracking in dependence on time on stream and hydrogen partial pressure (■ 21.7 bar; ◆ 16.3 bar; ▲ 10.8 bar; ○ 5.4 bar; × 0 bar).
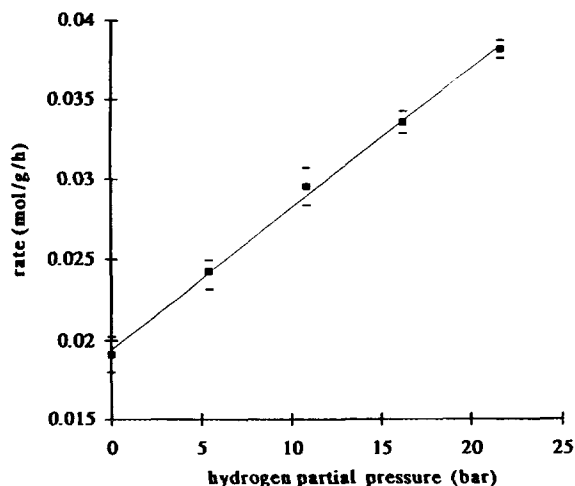
FIG. 3. Initial rate of *n*-heptane cracking in dependence on hydrogen partial pressure.

FIG. 5. Product distribution at 5 min time on stream and different hydrogen partial pressures ($\blacksquare$ C_3-, $\boxminus$ C_4-, $\square$ C_5-, $\square$ C_6-hydrocarbons).

amount of carboneous deposits on H-ZSM-5 zeolite decreased with increasing hydrogen partial pressure (Fig. 4).

The distribution of cracking products after 5 min time on stream and at different hydrogen partial pressures is summarized in Fig. 5. We did not observe methane, ethane, and ethene cracking products under the experimental conditions given. The main products of reaction were propane, *n*-butane, and iso-butane. Saturated hydrocarbons dominated over unsaturated products of reaction. With increasing hydrogen partial pressure the relative amount of alkenes decreased. The initial molar ratio of alkanes to alkenes diminished at lower values of the hydrogen partial pressure (Fig. 6). The ratio of paraffins to olefins did not change significantly with time on stream.

To estimate the apparent energy of activation, cracking was investigated over a temperature range of 533 to 573 K. The distribution of products did not change significantly with temperature. A value of 70 ± 2 kJ/mol was found both in the absence and in the presence of hydrogen. This value suggests a dominant bimolecular carbenium
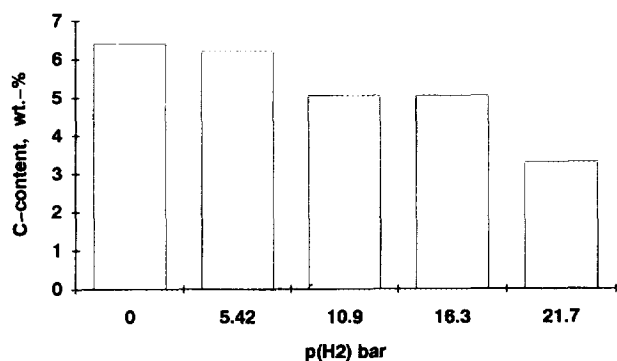
ion mechanism (14) and is close to the value given by Giannetto *et al.* (13).

Reaction network

The main reaction products are hydrocarbons with three (C_3), four (C_4), five (C_5), and six (C_6) carbon atoms. The absence of methane and ethane indicates that the cracking is mostly attributable to the carbenium ion mechanism. Furthermore, the cracking products are not balanced pairs, e.g., C_1 + C_6 or C_3 + C_4.

To explain the lack of light cracking products we assume in agreement with the literature the formation of a C_7 dimer (C_{14}*) at the surface of the zeolite (13, 15, 16). This intermediate could undergo further cracking reactions:

$$0.357\,C_7 \rightarrow 0.357\,C_3 + 0.357\,C_4 \qquad [1]$$
$$0.643\,C_7 \rightarrow 0.3215\,C_{14}{}^*$$
$$0.1055\,C_{14}{}^* \rightarrow 0.211\,C_4 + 0.1055\,C_6 \qquad [2]$$
$$0.0791\,C_{14}{}^* \rightarrow 0.0791\,C_3 + 0.0791\,C_5 + 0.0791\,C_6 \quad [3]$$
$$0.1366\,C_{14}{}^* \rightarrow 0.2732\,C_5 + 0.1366\,C_4. \qquad [4]$$

FIG. 4. Carbon content of H-ZSM-5 catalyst after cracking of *n*-heptane in dependence on hydrogen partial pressure.

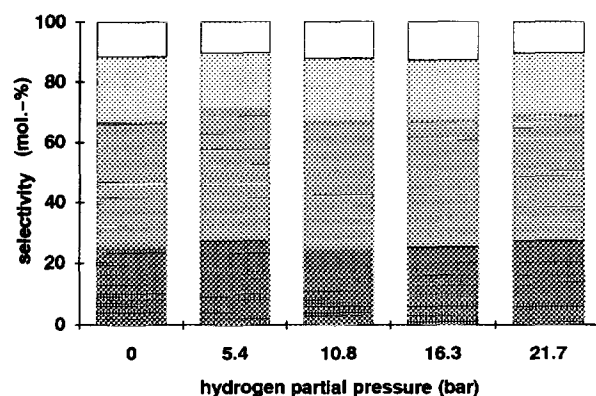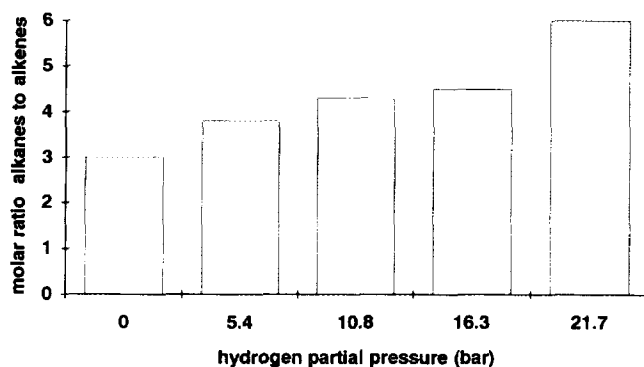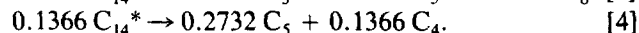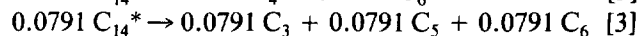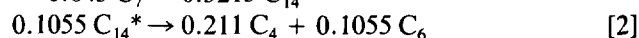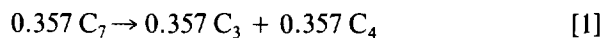FIG. 6. Molar ratio of alkanes to alkenes depending on hydrogen partial pressure.

Reactions between n-heptane and the cracking products were not considered because of the low conversion. Assuming the reactions [1]-[4], (j), one can formulate a system of linear equations

$$\text{rate}_{C_7} = \sum_j \sum_i p_{i,j} C_i,$$

where $p_{i,j}$ are the unknown stoichiometric parameters, C_i are the rates of formation of the products with i C atoms, and rate_{C_7} is the total rate of cracking of n-heptane. Including the chemical background of the chemical equations, one can calculate the values for the parameters. Trials with further chemical reactions did not yield arithmetically and chemically meaningful solutions. This given set of formal reactions can describe the observed selectivity of cracking n-heptane. The stoichiometric values given in Eqs. [1]-[4] were calculated from the selectivities of cracking at 21.7 bar hydrogen partial pressure at 5 min time on stream. Only the carbon balance was considered, not the differences between alkanes and alkenes. The way in which these reactions can explain the product distribution at the beginning of the reaction in hydrogen is shown in Fig. 7. The relative importance of reactions 2, 3, and 4 is demonstrated. The change of the gas atmosphere has little influence on the distribution of products with respect to their C-numbers (Fig. 5). The high partial pressure of the n-heptane favours dimerization. This process seems to be nearly independent of the hydrogen partial pressure. On the other hand, the initial molar ratio of alkanes to alkenes within the reaction products decreases with decreasing hydrogen partial pressure (Fig. 6).

Hydrogen transfer

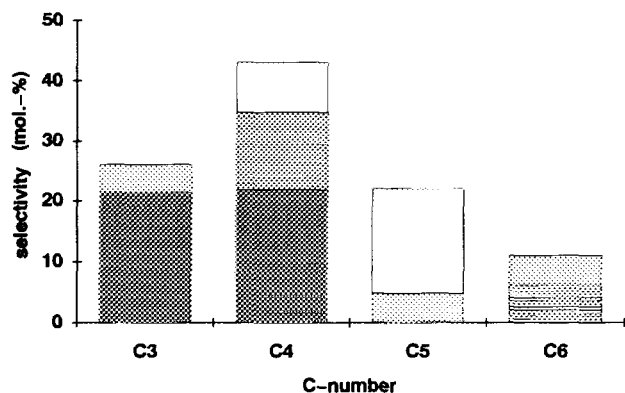The stoichiometry of alkane cracking requires the formation of 1 mol of alkanes per mole of alkanes cracked

FIG. 7. Attribution of postulated reaction network to product distribution at 5 min time on stream and hydrogen partial pressure of 21.7 bar (□ reaction 1; ▤ reaction 2; ▨ reaction 3; □ reaction 4).

in the primary cracking. The number of moles of alkenes produced depends on the number of secondary reactions, e.g., cracking or polymerization/oligomerization. Values of the molar ratio of alkanes to alkenes higher than one can be the result of hydrogen transfer reactions between the olefinic products. This reaction produces alkanes and polyalkenes, aromatics, and coke by disproportionation (2, 17).

Under the given experimental conditions we found only traces of products with C-numbers higher than 7. Therefore, we concluded that the dehydrogenated products corresponding to the alkane excess would be adsorbed on the surface of the zeolite. The degree of this hydrogen transfer reaction seems to be constant during reaction because of the constant ratio of saturated and unsaturated cracking products with time on stream. During cracking hexene-1 on HY zeolite the carboneous deposits become more and more dehydrogenated as the conversion decreases, whereas on H-ZSM-5 the C/H ratio of the coke does not change (18).

The constant ratio of alkanes to alkenes during cracking in nitrogen atmosphere could reflect the behaviour mentioned above. Despite the high partial pressure of n-heptane, there seems to be a restricted hydrogen transfer from the steric point of view.

H-ZSM-5 forms very small amounts of coke, partly because the structure of the pore system does not allow the formation of large molecules inside the zeolite structure (19). However, the amounts of the carbonaceous deposits on the catalyst were surprisingly high (Fig. 4) and may be attributed to the reaction conditions (partial pressure of the hydrocarbon was 3.3 bar). The increase of the cracking activity with increasing hydrogen partial pressure was accompanied by a diminution of the amount of carbon on the catalyst.

In order to clarify the effect of hydrogen on the total amount of these deposits we continued with the following experiments. The reaction was carried out in nitrogen atmosphere for 2 h. Then the hydrocarbon feed was stopped, the catalyst was flushed with hydrogen or nitrogen for 30 min, and the reaction was started again. The activity after the hydrogen treatment was higher than that found after 2 h time on stream. In the case of nitrogen application the former activity was restored. Furthermore, we determined the carbon content of the catalyst after the flushing with nitrogen and hydrogen. The amounts of carbon-containing deposits were 4.2 wt.% (hydrogen treatment) and 6.3 wt.% (nitrogen treatment). This indicates that the hydrogen hydrogenates unsaturated species, which are strongly adsorbed at the surface of the catalyst and cause the loss in activity with time on stream. A relation between the amount of deposits and the observed cracking rate was evident. However, if one assumes, that only hydrogen transfer (disproportionation)

is responsible for the excess of alkanes, one could not completely explain the differences in the experiments in the nitrogen and the hydrogen atmosphere with respect to the changes of the alkane to alkene ratio. The distinct increase of the overall molar ratio of alkane to alkenes with increasing hydrogen partial pressure could be accounted for by the fact that a direct hydrogenation of cracking products takes place additionally.

Influence of Ethene on Cracking Activity

In accordance with the literature (8, 9) we observed a hydrogenation of ethene in presence of hydrogen on H–ZSM-5 without combination with any metal (Fig. 8). The nature of the active sites of zeolites responsible for hydrogenation is still under debate. To explain the correlation between the initial cracking rate and the hydrogen partial pressure we made the following hypothesis: that intermediate and product alkenes can be hydrogenated by acid zeolite in the presence of hydrogen and that the coverage of the zeolite surface with alkenes influences the cracking activity.

To test the above hypothesis we decided to investigate the cracking of n-heptane in the presence of an olefin and hydrogen. To distinguish between cracking products and the conversion of the alkenes, ethene was added to the n-heptane feed at a hydrogen partial pressure of 21.7 bar. After the reaction was started in hydrogen atmosphere the ethene was added at 60 min time on stream for a further 60 min. The ethene feed was then interrupted (Fig. 9). The carbon content of the catalyst was determined after the reaction was run in ethene and values similar to the experiments without the ethene were found. The results show a reversible inhibiting influence of the olefin. At 543 K and a partial pressure of the reactants of 3.5 bar the adsorption of ethene is probable. In the literature it was shown (20, 21) that the ethene adsorbs very strongly on Brønsted acid sites on HY zeolites even at low temperatures. Palekar and Rajadhyaksha estimated the isosteric
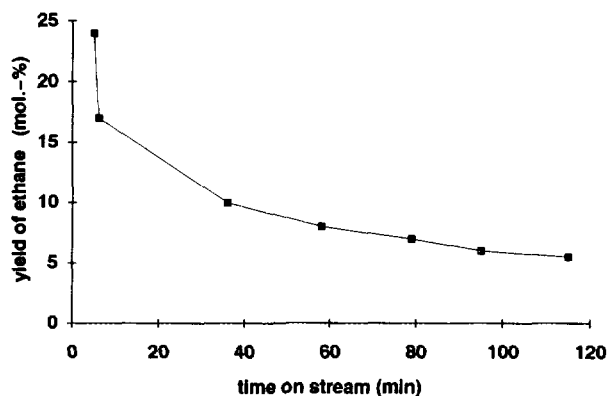

FIG. 8. Yield of ethane in ethene conversion versus time on stream. Reaction conditions: $T = 543$ K; $p = 25$ bar.
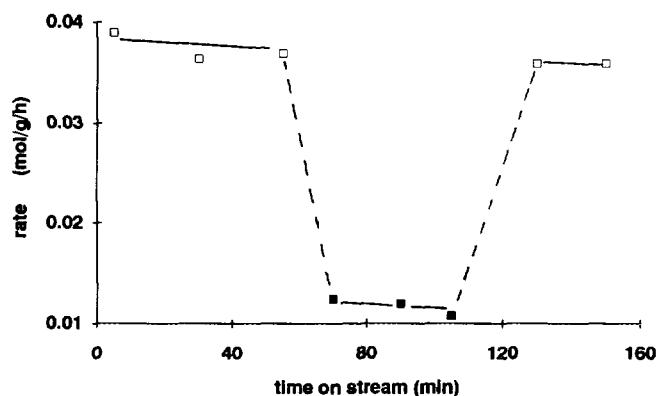

FIG. 9. Rate of n-heptane cracking in hydrogen atmosphere at 21.7 bar in the absence (□) and presence of ethene (■).

energy of adsorption of ethene on H–ZSM-5 to be 54.2 kJ/mol (22). This adsorption of ethene results in a lower number of vacant acid sites.

A remarkable conversion of ethylene into oligomers (formation of deposits which hinder the access of n-heptane molecules to the acid sites) can be excluded since the carbon content (3.3 wt%) was not influenced by the presence of ethene. Similar results were shown by Gielen and Palekar, who found that ethene does not affect the rate of coking during cracking of n-hexane at 773 K and 0.74 bar partial pressure of the reactants (23). The cofeed of ethene directs the system in the same way as the decrease in hydrogen partial pressure, without changing the activity for formation of carbon-containing deposits on the catalysts.

Reactions Influenced by Hydrogen

The interaction of an alkene (C_nH_{2n}) with a Brønsted acid site (H^+Z) results in an intermediate carbenium ion ($C_nH_{2n}H^+Z$). We assume that this species can participate in hydride abstraction reactions (4, 6). Usually, alkanes (C_mH_{2m+2}) act as the source of the hydride ions:

$$C_nH_{2n}H^+Z + C_mH_{2m+2} \rightarrow C_mH_{2m}H^+Z + C_nH_{2n+2}. \quad [i]$$
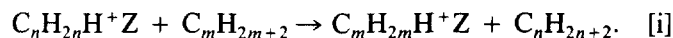
In cracking according to the bimolecular reaction mechanism, this is the rate determining step.

In the presence of excess hydrogen it seems probable that hydride abstraction from a molecular of hydrogen could occur:

$$C_nH_{2n}H^+Z + H_2 \rightarrow C_nH_{2n+2} + H^+Z. \quad [ii]$$

Molecular orbital calculations have shown that this reaction should be possible (24). Hence the hydrogen partial pressure could control the state of the equilibrium and thus the number of available acid sites (H^+Z).

This transformation represents an acid-catalyzed hydrogenation of adsorbed unsaturated hydrocarbons. Despite the concurrence of both reactions, the regeneration of acid sites during reaction [ii] could initiate new chains and therefore force up the cracking activity. Furthermore, the interaction of the carbenium ion with unsaturated molecules (C_iH_{2i}) can take place (25) and would lead to dehydrogenated products $(C_nH_{2n-2}H^+Z)$ adsorbed on the surface and saturated product molecules:

$$C_nH_{2n}H^+Z + C_iH_{2i} \rightarrow C_nH_{2n-2}H^+Z + C_iH_{2i+2}. \quad [iii]$$
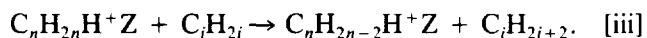
The rate of this coke formation [iii] depends on alkene concentration. The equilibrium of the hydrogenation reaction [ii] controls the surface concentration of unsaturated hydrocarbons. The chance of interaction between alkenes and adsorbed species decreases with increasing hydrogen partial pressure.

An apparent formal first order of n-heptane cracking was found with respect to the hydrogen partial pressure (Fig. 3). This agrees with the first order kinetics of acid-catalyzed hydrogenation of ethene on metal-free H-ZSM-5 (18).

The hydrogenation ability could be the reason for the initiating effect of hydrogen observed and the excess of paraffinic reaction products. The similar values of apparent energy of activation 70 ± 2 kJ/mol suggest that the rate determining step during cracking was not changed by varying the ratio of nitrogen to hydrogen in the reaction mixture.

CONCLUSIONS

Under certain reaction conditions H-ZSM-5 is able to hydrogenate alkenes. This hydrogenation ability influences the acid-catalyzed cracking of n-heptane. The cracking of n-heptane is mostly ascribed to the bimolecular cracking mechanism under the investigated reaction conditions. The product distribution with respect to the C-numbers of products cannot be explained by simple carbon–carbon bond scissions in a heptylcarbenium ion whether hydrogen is present or not. We propose that cracking proceeds over a dimerization step, too.

Selectivity in favour of alkanes depends on hydrogen partial pressure. Under nitrogen atmosphere the high value of the ratio of alkanes to alkenes was related to

hydrogen transfer reactions and coke formation. In the presence of hydrogen, hydrogenation reactions can occur in addition to hydrogen transfer reactions. The initial ratio of alkanes to alkenes and the initial rate of cracking of n-heptane was directly proportional to the hydrogen partial pressure.

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