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A Kinetic Model for the Hexane Cracking Reaction over H-ZSM-5

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A kinetic model for the *n*-hexane cracking reaction over H-ZSM-5 has been developed. This model describes hydrocarbon transformations in the following reaction steps: protolytic cracking of *n*-hexane, hydrogen transfer between *n*-hexane and light olefins, oligomerization, and cracking of olefins. The activation energy of the protolytic cracking steps is 75.6–152.4 kJ/mol, depending on the reaction products, and that of the hydrogen transfer steps is 4.1–8.9 kJ/mol, depending on the olefin involved in the reaction step. It is demonstrated that a considerable contribution from hydrogen transfer to *n*-hexane cracking manifests itself in the autocatalytic character for the reaction at 400°C. At 538°C (the temperature of the α-test) hydrogen transfer does not play an appreciable role in hexane cracking over H-ZSM-5 zeolites.

INTRODUCTION

The paraffin cracking reaction over zeolite catalysts is of prime importance in gas oil cracking and catalyst dewaxing processes. This reaction has also been used for the characterization of the catalytic properties of various zeolites by the α-test (cracking of *n*-hexane) (1–4) and the Constraint Index (cracking of *n*-hexane and 3-methylpentane) (5).

The mechanism of the paraffin cracking reaction has been extensively investigated (for a review see Refs. (6–8) and papers cited therein). Most recent studies (6–15) have demonstrated that the reaction proceeds via two mechanisms:

Mechanism A. Monomolecular paraffin cracking via nonclassical pentacoordinated carbonium ions RH_2^+,

$$RH + H^+ \rightarrow RH_2^+ \rightarrow \text{reaction products.}$$

Mechanism B. Hydrogen transfer steps followed by β-scission of tricoordinated carbenium ions R^+,

$$RH + R_1^+ \rightarrow R^+ + R_1H$$
$$R^+ \rightarrow \text{reaction products,}$$

where RH = original paraffin, R_1^+ = smaller carbenium ion.

Investigation of the product selectivities during the cracking reactions of *n*-hexane and 3-methylpentane, performed by Haag and Dessau (6), has shown that mechanism B predominates when the reaction is carried out over the large pore zeolite Y, whereas mechanism A is more important with the medium pore H-ZSM-5 zeolite. It has also been shown (6) that the ratio between the contributions of mechanisms A and B to the overall conversion is a strong function of temperature, paraffin partial pressure, and conversion level.

In the present paper we report on a kinetic model for the *n*-hexane cracking reaction over H-ZSM-5 based on the above mechanisms. The kinetic model is used in conjunction with experimental data for (1) quantitative characterization of the contributions of mechanisms A and B to hexane conversion over H-ZSM-5 under various reaction conditions, and (2) analysis of the α-test based on a simple first order kinetic model.

EXPERIMENTAL

The conversion of *n*-hexane was studied at 400, 450, 500, and 538°C in a flow system using a quartz microreactor. The initial concentration of *n*-hexane in the mixture with nitrogen was 40 mol%. The reaction products were analysed by gas chromatography 7 min after the beginning of the reaction. It has previously been shown (14) that experimental data obtained in this way characterize the catalytic properties of the fresh zeolites under stationary conditions of the reaction. The data were obtained at relatively low hexane conversions ($x < 30\%$) in

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the absence of secondary olefin aromatization process. Three H-ZSM-5 zeolites with SiO_2/Al_2O_3 ratios (R) of 34, 240, and 280 (samples defined as Z-34, Z-240, and Z-280, respectively) were used. Details of the catalyst preparation and catalytic measurements are reported elsewhere (14).

RESULTS AND DISCUSSION

Kinetic Model

In order to describe the pathways of the hexane cracking reaction over H-ZSM-5 zeolites we developed a kinetic model which included 16 group components: nine olefins $C_2^=$–$C_{10}^=$, six paraffins C_1–C_6, and hydrogen H_2. The kinetic model was developed on the basis of the following reaction scheme, where Z is a zeolite catalytic site:

1. Protolytic cracking of the C–H bond in the n-hexane molecule,

$$C_6 + Z \xrightarrow{k_{CH}} C_6^=Z + H_2.$$

2. Protolytic cracking of the C–C bond in the n-hexane molecule,

$$C_6 + Z \xrightarrow{k_{CC}(n)} C_n^=Z + C_{6-n} \quad 2 \leq n \leq 5.$$

3. Hydrogen transfer between n-hexane and light olefins,

$$C_6 + C_n^=Z \xrightarrow{k_{HT}(n)} C_6^=Z + C_n \quad 2 \leq n \leq 5.$$

4. Olefin oligomerization and cracking,

$$C_n^= + C_m^=Z \underset{k_o^-(n,m)}{\overset{k_o^+(n,m)}{\rightleftharpoons}} C_{n+m}^=Z$$

$$2 \leq n,\ m \leq 8,\ 4 \leq n + m \leq 10.$$

5. Olefin adsorption and desorption,

$$C_n^= + Z \overset{K_a}{\rightleftharpoons} C_n^=Z \quad 2 \leq n \leq 10.$$

The kinetic model was developed with the following assumptions:

(a) adsorption equilibrium is established;

(b) the adsorption constant K_a is independent of the olefin molecular weight.

In this case the rates of the reaction steps are as follows:

Protolytic cracking of the C–H bond,

$$r_{CH} = k_{CH}P_{C_6}[Z];$$

Protolytic cracking of the C–C bond,

$$r_{CC} = k_{CC}(n)P_{C_6}[Z];$$

Hydrogen transfer,

$$r_{HT} = K_a k_{HT}(n)P_{C_6}P_{C_n^=}[Z];$$

Olefin oligomerization and cracking,

$$r_o = K_a k_o^+(n,\ m)P_{C_n^=}P_{C_m^=}[Z] - K_a k_o^-(n,\ m)P_{C_{n+m}^=}[Z].$$

In these equations k_{CH} and $k_{CC}(n)$ are the rate constants for protolytic cracking of C–H and C–C bonds, respectively; $k_{HT}(n)$ is the rate constant for hydrogen transfer; $k_o^+(n,\ m)$ and $k_o^-(n,\ m)$ are the rate constants for olefin oligomerization and olefin cracking, respectively; [Z] is the concentration of vacant catalytic sites; and P_{C_6} and $P_{C_n^=}$ are the partial pressures of C_6 and $C_n^=$, respectively. The dependence of the rate constants on the number of carbon atoms in olefin molecules reflects (1) the change of the reactivities of olefins (hydrogen transfer steps, olefin oligomerization and cracking steps) with an increase in olefin molecular weight, and (2) the different probabilities of formation of $C_2^=$–$C_5^=$ olefins in hexane protolytic cracking steps.

The kinetic model for hexane cracking reaction consists of a set of 16 equations describing the rates of transformation of 16 components in 25 reaction steps,

$$r_i = \sum_{s=1}^{25} \nu_{is}r_s \quad 1 \leq i \leq 16,$$

where r_i is the rate of transformation of the ith component, ν_{is} is the stoichiometric coefficient of the ith component in the sth reaction step, and r_s is the rate of the sth reaction step. Steady-state concentration of vacant catalytic sites is calculated using the following equation:

$$[Z] = 1\Big/\left(1 + K_a \sum_{n=2}^{10} P_{C_n^=}\right).$$

In the present work the rate constant values were determined for the steps of protolytic cracking of n-hexane and for the steps of hydrogen transfer. This procedure was carried out by comparison of the mathematical modeling results with the experimental dependence of the product distribution on contact time ($WHSV^{-1}$) for n-

hexane conversion over various catalysts at 400, 450, 500, and 538°C. The values of the rate constants of olefin oligomerization and cracking steps were determined earlier (16) on the basis of experimental results on ethene and propene conversions.

Figure 1 shows that good agreement was attained between simulated and experimental data on the *n*-hexane cracking reaction over Z-240 zeolite. It should be noted that the agreement was practically the same for the description of this reaction over all three zeolites used in this study.

Rate Constants

In order to define the effect of the aluminum content on HZSM-5 activity in the steps of protolytic cracking of the C–H and C–C bonds in the *n*-hexane molecule and in the steps of hydrogen transfer between *n*-hexane and light olefins, we compared the values of the rate constants of these steps determined at 500°C for Z-34, Z-240, and Z-280 zeolites. The comparison has shown that zeolite activity in all the above reaction steps is strictly proportional to the zeolite aluminum content. Such a dependence was reported previously (16) for the steps of olefin oligomerization and cracking. These results further support the conclusion, made in a number of papers (3, 4, 14, 17, 18), that HZSM-5 of different SiO_2/Al_2O_3 ratios, when prepared in the absence of water vapor, contains catalytic sites of only one type: bridging hydroxyl groups associated with framework aluminum atoms.

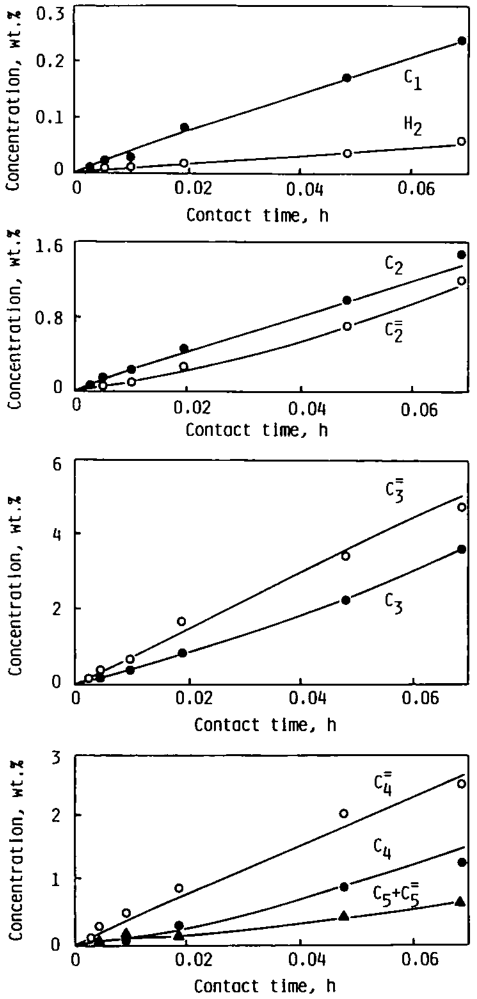

FIG. 1. Cracking of hexane over Z-240 zeolite at 500°C. Experimental data (points) and simulated curves for the concentrations of reaction products as function of contact time.

TABLE 1

Activation Energy and Relative Values of the Rate Constants of Protolytic Cracking Steps on Z-240 Zeolite at 500°C

Reaction step	Relative rate constant value	E_a, kJ/mol
$C_6 + Z \rightarrow C_{6}^{=}Z + H_2$	1	99.8
$C_6 + Z \rightarrow C_{2}^{=}Z + C_4$	0.20	75.6
$C_6 + Z \rightarrow C_{3}^{=}Z + C_3$	1.39	96.7
$C_6 + Z \rightarrow C_{4}^{=}Z + C_2$	1.66	109.4
$C_6 + Z \rightarrow C_{5}^{=}Z + C_1$	0.54	152.4

Note. Rate constant value for C–H bond cracking step has been taken as unity (absolute value of this rate constant is 12.6 mmol · $g^{-1}h^{-1}$).

Table 1 demonstrates the values of the rate constants for protolytic cracking of *n*-hexane over Z-240 zeolite. The presented data indicate that the most probable event is the cracking of C–C bonds with formation of C_2 and C_3 paraffins and $C_4^{=}$ and $C_3^{=}$ olefins, respectively. The relatively high probability of hydrogen formation in the C–H bond cracking step should be also noted.

Rate constant values presented in Table 2 show that the rate of hydrogen transfer between *n*-hexane and olefins increases sharply from ethene to butenes and does

TABLE 2

Activation Energy and Relative Values of the Rate Constants of Hydrogen Transfer Steps on Z-240 Zeolite at 500°C

Reaction step	Relative rate constant value	E_a, kJ/mol
$C_6 + C_{2}^{=}Z \rightarrow C_{6}^{=}Z + C_2$	1	8.9
$C_6 + C_{3}^{=}Z \rightarrow C_{6}^{=}Z + C_3$	48.3	7.4
$C_6 + C_{4}^{=}Z \rightarrow C_{6}^{=}Z + C_4$	73.3	4.1
$C_6 + C_{5}^{=}Z \rightarrow C_{6}^{=}Z + C_5$	73.3	4.1

Note. Rate constant value for the step of *n*-hexane interaction with adsorbed ethene has been taken as unity (absolute value of this rate constant is 8.8 mmol · $g^{-1}h^{-1}$).

not change with further increase of olefin molecular weight. We suppose that such a dependence is due to the difference in the probabilities of existence of primary, secondary, and tertiary carbenium ions, which are generally accepted (6, 7, 19) to be intermediate species in hydrogen transfer reactions. Using the data of Table 2 we come to the conclusion that the relative probabilities of existence of primary, secondary, and tertiary carbenium ions are 1, 48.3, and 73.3 respectively. It should be noted that $C_4^=$ olefins (*n*-butene and isobutene) were treated as one component. Thus, the value 73.3 should be considered as the lower estimation of the relative probability of the existence of *tert*-butyl carbenium ions.

Using the kinetic model for the analysis of the experimental data on hexane conversion at different temperatures, we have been able to estimate quantitatively the activation energy of hydrogen transfer steps. Table 2 shows that for the steps of *n*-hexane interaction with the adsorbed ethene, propene, and $C_4^=$–$C_5^=$ olefins, the activation energy is 8.9, 7.4, and 4.1 kJ/mol, respectively. The activation energy of protolytic cracking steps is in the range 75.6–152.4 kJ/mol (Table 1), depending on the reaction products. It is shown below that such an essential difference in the temperature dependence of protolytic cracking and hydrogen transfer is the reason for the sharp decrease of the contribution of hydrogen transfer steps in hexane conversion with increasing temperature.

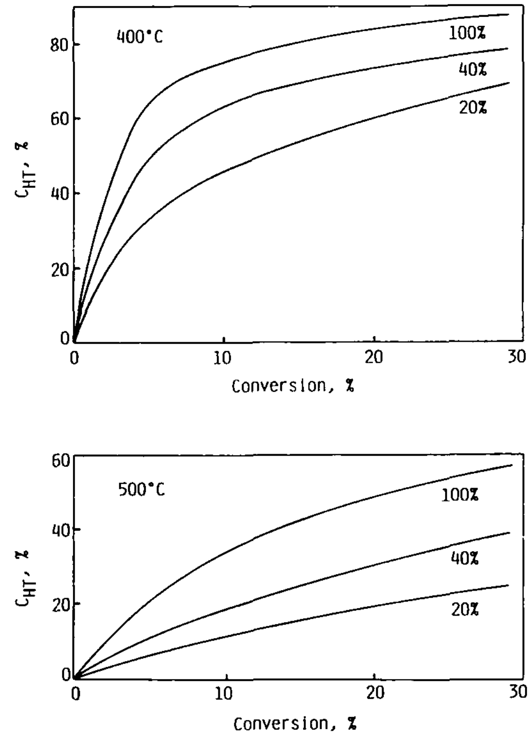

FIG. 2. Effect of conversion and initial *n*-hexane concentration (mol%) on the contribution of hydrogen transfer steps in the conversion of *n*-hexane at 400 and 500°C.

Contribution of Hydrogen Transfer to Hexane Cracking

In order to estimate quantitatively the contribution of hydrogen transfer steps in the overall hexane conversion, we used the results of mathematical modeling performed in the following manner. At first, the hexane cracking reaction was simulated using the rate constant values corresponding to the real catalyst (Z-240). In that way the simulated dependence of the reaction rate r_1 on hexane conversion was obtained. After that, the rate constants of hydrogen transfer steps were equated with 0, and the simulated dependence of the reaction rate r_2 on hexane conversion was obtained. The contribution of hydrogen transfer steps C_{HT} (%) was defined as the ratio $100(r_1 - r_2)/r_1$, using the values of r_1 and r_2 corresponding to the same hexane conversion.

Figure 2 indicates that with increasing initial hexane concentration and conversion level, and with decreasing temperature, the contribution of hydrogen transfer steps in the overall hexane conversion increases appreciably. Table 3 shows that the quantitative estimates obtained on the basis of the proposed kinetic model are in reasonable agreement with the estimates obtained previously by Haag and Dessau (6).

The contribution of hydrogen transfer steps in hexane transformation manifests itself in the autocatalytic character of the reaction (see Fig. 3). In agreement with the aforementioned data, the magnitude of the autocatalytic effect decreases sharply with increasing temperature.

α-Activity

The reaction of *n*-hexane cracking has been used (1–4) as a test reaction (α-test) for the catalytic activity of zeolite catalysts. In the modified α-test (3, 4), catalytic activity was evaluated by determining the first-order rate constant of cracking *n*-hexane at 538°C and initial *n*-hexane concentration of 13 mol%.

The results of the previous (6, 12–15) and present studies demonstrate that *n*-hexane cracking proceeds via two reaction mechanisms. A question arises as to the nature of the catalytic activity measured in the α-test: it could be activity in protolytic cracking steps, or activity in hydro-

TABLE 3

Contribution of Hydrogen Transfer Steps to *n*-Hexane Cracking over H-ZSM-5 at 450°C (conversion 10%)

Initial hexane concentration, mol%	10	20	100
C_{HT}, % (data from Ref. (6))	21	40	78
C_{HT}, % (data of this work)	15	24	54

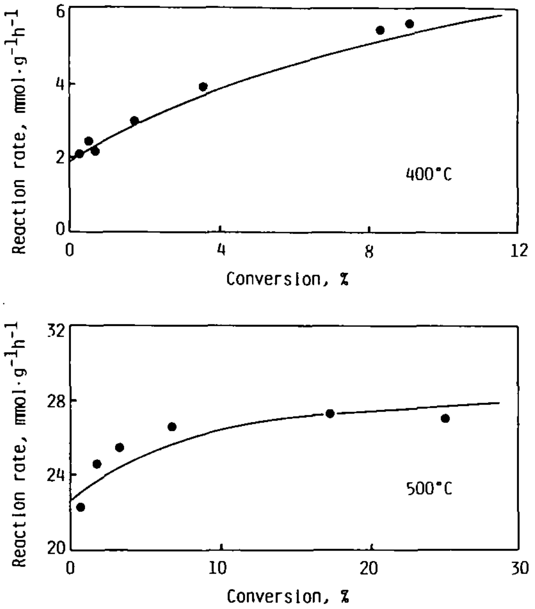

FIG. 3. Effect of n-hexane conversion on the rate of the reaction over Z-240 zeolite at 400 and 500°C: Experimental data (points) and simulated curves.

gen transfer steps, or a combination of these two activities.

In order to solve this question we performed mathematical modeling of the n-hexane cracking reaction over real Z-240 catalyst and two hypothetical Z-240(1) and Z-240(2) catalysts (activities of these catalysts are characterized by the data shown in Table 4). Simulations were carried out under the conditions of the α-test, and the dependence of n-hexane conversion on contact time (WHSV^{-1}) was obtained for the three mentioned catalysts. After that simulated data were plotted in coordinates of the first-order kinetic equation (see Fig. 4), where contact time was determined as the ratio between the catalyst sample weight and the feed molar rate. Figure 4 shows that the n-hexane cracking reaction, which proceeds via two mechanisms, can be described (under the chosen conditions) by first-order kinetics, as has been already reported previously (4). From Figure 4 it follows that for Z-240 catalyst the first-order rate constant k_α is equal to 135 mmol · g^{-1}h^{-1}. This value coincides practically with the sum of the rate constants of protolytic cracking steps over this catalyst (at 538°C this sum is equal to 133 mmol · g^{-1}h^{-1}).

TABLE 4

Relative Values of the Rate Constants of Protolytic Cracking Steps and Hydrogen Transfer Steps, and the First Order Rate Constant (k_α) for Z-240, Z-240(1), and Z-240(2) Catalysts

Rate constant	Relative value		
	Z-240	Z-240(1)	Z-240(2)
k_{CH}	1	5	1
k_{CC}	1	5	1
k_{HT}	1	1	5
k_α	1	4.7	1.3

Note. Rate constant values for Z-240 catalyst have been taken as unity.

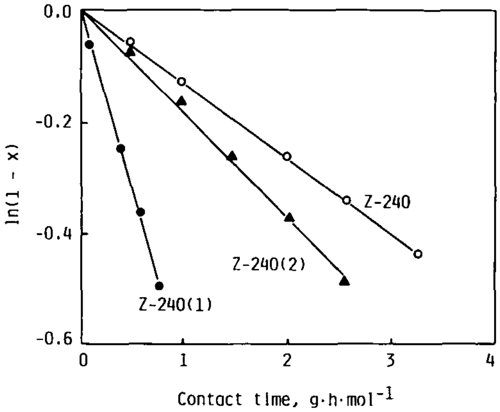

FIG. 4. First-order plots for simulated n-hexane conversion (T = 538°C, $C^0_{C_6}$ = 13 mol%) over Z-240, Z-240(1), and Z-240(2) catalysts. Points correspond to the kinetic modeling results.

Table 4 compares the first-order rate constants corresponding to Z-240, Z-240(1), and Z-240(2) catalysts with the rate constants of different reaction steps over these catalysts. From the presented data it is clear that α-activity is governed by the activity in protolytic cracking steps, and slightly depends on the activity in hydrogen transfer steps. This finding, as well as the correctness of the first-order kinetics for n-hexane cracking under the conditions of the α-test, can be explained by the low contribution of hydrogen transfer steps to overall hexane conversion under such reaction conditions (high temperature and low n-hexane concentration in the feed).

REFERENCES

1. Weisz, P. B., and Miale, J. N., *J. Catal.* **4,** 527 (1965).
2. Miale, J. N., Chen, N. Y., and Weisz, P. B., *J. Catal.* **6,** 278 (1966).
3. Olson, D. H., Haag, W. O., and Lago, R. M., *J. Catal.* **61,** 390 (1980).
4. Haag, W. O., Lago, R. M., and Weisz, P. B., *Nature* **309,** 589 (1984).
5. Frillette, V. J., Haag, W. O., and Lago, R. M., *J. Catal.* **67,** 218 (1981).
6. Haag, W. O., and Dessau, R. M., *in* "Proceedings, 8th International Congress on Catalysis, Berlin, 1984," Vol. 2, p. 305. Dechema, Berlin, 1984.
7. Corma, A., Planelles, J., Sanchez-Marin, J., and Thomas, F., *J. Catal.* **93,** 30 (1985).

8. Khadzhiev, S. N., Gairbekov, T. M., Topchieva, K. V., and Rossinski, A. M., *Dokl. Acad. Nauk SSSR* **281,** 864 (1985).
9. Lombardo, E. A., Pierantozzi, R., and Hall, W. K., *J. Catal.* **110,** 171 (1988).
10. Lombardo, E. A., and Hall, W. K., *J. Catal.* **112,** 565 (1988).
11. Abbot, J., and Wojciechowski, B. W., *J. Catal.* **115,** 1 (1989).
12. Abbot, J., *Appl. Catal.* **57,** 105 (1990).
13. Santilli, D. S., *Appl. Catal.* **60,** 137 (1990).
14. Luk'yanov, D. B., *Zeolites* **11,** 325 (1991).
15. Wielers, A. F. H., Vaarkamp, M., and Post, M. F. M., *J. Catal.* **127,** 51 (1991).
16. Luk'yanov, D. B., and Shtral', V. I., *in* "Preprints of ACS Symposium on Alkylation, Aromatization, Oligomerization and Isomerization of Short Chain Hydrocarbons over Heterogeneous Catalysts," Vol. 36, No. 4, p. 693. ACS Division of Petroleum Chemistry, New York, 1991.
17. Jacobs, P. A., and von Ballmoos, R. J., *Phys. Chem.* **86,** 3050 (1982).
18. Lago, R. M., Haag, W. O., Mikovsky, R. J., Olson, D. H., Hellring, S. D., Schmitt, K. D., and Kerr, G. T., *in* "Proceedings of the 7th International Zeolite Conference" (Y. Murakami, A. Iijima, and J. W. Ward, Eds.), p. 677. Kodansha, Tokyo, 1986.
19. Chen, N. Y., and Haag, W. O., *in* "Hydrogen Effects in Catalysis" (Z. Paál and P. G. Menon, Eds.), p. 695. Dekker, New York, 1988.