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Transition-State Selectivity in the Cracking of *n*-Heptane over Modified ZSM-5 Catalysts

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The rates of cracking of *n*-heptane on Ni-, Zn-, and H-ZSM-5 incorporated with a silica binder were in the order of Ni-ZSM-5 > Zn-ZSM-5 > H-ZSM-5. Transition state selectivity, dehydrogenation and classical carbonium ion chemistry were used to explain the relative activities of these catalysts. Activation energy for cracking of heptane over Ni-ZSM-5 was found to be 32 ± 3 kcal/mol. © 1986 Academic Press, Inc.

INTRODUCTION

Several of the shape selectivity studies on ZSM-5 have dealt with the differences in reactivity of paraffin isomers due to the diffusional transport resistances encountered by the more highly branched isomers. Chen and Garwood (*1*) studied the molecular sieving effect of ZSM-5 on the reactivity of C_5 to C_7 paraffin isomers. They found that the higher the degree of branching of an isomer the smaller its reaction rate would be compared to the reaction rate of the *n*-paraffin of the same carbon number. Anderson *et al.* (*2*) obtained similar results in their study of hexane isomers reacting over H-ZSM-5.

Haag *et al.* (*3*) in their study of C_6 to C_9 hydrocarbons found that "the selective cracking of *n*-paraffins compared to monomethyl paraffins (from C_6 to C_9) is due to a higher intrinsic rate constant of the *n*-paraffin, with diffusional mass transport playing no appreciable role." They attribute the monomethyl paraffin/*n*-paraffin selectivity to steric constraints resulting from a larger carbonium ion intermediate for the monomethyl paraffin as compared to the *n*-paraffin. They also found that the structural selectivity was not present for the corresponding olefins because sterically hindered intermediate complexes did not occur. Thus, separate mechanisms for olefins and paraffins are occurring.

For many years metals have been added to acid-cracking catalysts for the purpose of hydrocracking. In the cracking of paraffins, the metals perform two functions. First, they increase the lifetime of the catalyst by retarding the formation of coke; and second, they increase the activity of the catalyst by converting paraffins into olefins. Olefins are easier to crack than paraffins and they also form the surface carbonium ions that serve as initiators for cracking the paraffins. Since the size of the intracrystalline cages of ZSM-5 severely retards the formation of coke (*9*), the main effect of adding a dehydrogenation metal to ZSM-5 is to improve the activity.

In this study, by using bifunctional catalysts of different dehydrogenation characteristics (Ni-ZSM-5, Zn-ZSM-5, and H-ZSM-5), we have examined the role played by transition-state selectivity on the cracking of *n*-heptane.

EXPERIMENTAL

Catalyst preparation and analysis. The three catalyst were prepared as follows: 1 g of the NH_4-ZSM-5 was slurried with 200 ml of a solution containing 12.7% Ni $(NO_3)_2 \cdot 6H_2O$ and refluxed at 361 K for 4 h. The exchanged catalyst was then filtered and

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dried at 381 K for 13 h. The catalyst was then mixed with a solution of Ludox 40, extruded, dried, and calcined at 811 K for 7 h. The Ni-ZSM-5 extrudates were then crushed to particles in the size of 100 to 400 μm with a density of approximately 0.75 g/ml. Therefore, the Ni-ZSM-5 catalyst referred to contained 69% silica binder and 31% zeolite. An analysis of this material by ICP indicated the following: Ni = 0.078% and Al = 1.64%. An analysis by XPS indicated that the nickel was on the external surface of the particles. Hence, during the calcination the nickel migrated from inside of the pores of the catalyst to the external surfaces.

The Zn-ZSM-5 was prepared in a similar manner except the ion exchange solution contained 38% $Zn(NO_3)_2 \cdot 6H_2O$. The final catalyst used in the experiments contained 42% zeolite and 58% SiO_2 binder. An ICP analysis yielded Zn = 1.11%, and Al = 1.4%. In an XPS analysis of the particle surface the zinc was not seen. The bulk density of the 100- to 300-μm particles was 0.62 g/ml.

The hydrogen form of the ZSM-5 was prepared in a similar fashion as the Ni-ZSM-5 except an 11% solution of NH_4Cl was used. The final catalyst contained 20% zeolite and 80% binder. Particles of 100 to 300 μm with a bulk density of 0.79 g/ml were used in the reactor. An XPS analysis of the catalyst did not detect any Al on the surface of the particles. Hence, only the binder could be seen. All three catalysts were reduced prior to reaction by flowing a stream of pure hydrogen through the catalyst bed at 823 K.

The reactions were studied using a 316 SS microreactor system designed to operate up to 21 atm (1 atm = 1.01×10^5 N/m^2) and 775 K. The microreactor was immersed in an isothermal eutectic salt bath. The products were collected at atmospheric pressure using cold traps and were analyzed using separate chromatographs for the vapor and liquid products.

The experiments lasted between 15 min and 1 h depending on how long it took to collect a sufficient liquid sample for weighing and subsequent GC analysis. Outlet vapor samples and flow rates were taken three times per run to certify that a steady state had been achieved. Generally five runs could be made before any loss of activity occurred with Ni- and Zn-ZSM-5 whereas H-ZSM-5 started to show loss of activity after three runs. The catalysts were regenerated with air until neither CO or CO_2 were present in the outlet stream. The experimental procedure has been described in greater detail by Riley (*4*).

DISCUSSION AND RESULTS

Cracking Mechanism and Transition-State Selectivity

The cracking of *n*-heptane on modified ZSM-5 catalysts as subsequently discussed and illustrated in Tables 1, 2, and 3 occurred at vastly different rates. To account for these differences two separate mechanisms are proposed. For the H-ZSM-5, the least active catalyst, a carbonium ion mechanism is proposed whereas for Ni- and Zn-ZSM-5 a metal dehydrogenation/carbonium ion mechanism is postulated. These mechanisms are described in detail by Anderson *et al.* (*2*), Haag *et al.* (*3*), and Chester (*5*).

The carbonium ion mechanism is a result of the Brønstead acidity of the catalyst. The mechanism is as follows.

$$C_7H_{16} + H^+_{(s)} \rightarrow C_7H^+_{15(s)} + H_2 \qquad (1)$$

then

$$C_7H^+_{15(s)} \rightarrow C_7H_{14} + H^+_{(s)} \qquad (2)$$

or

$$C_7H^+_{15(s)} \rightarrow C_4H^+_{9(s)} + C_3H_6 \qquad (3)$$

$$C_4H^+_7 \rightarrow C_4H_8 + H^+_s$$

More favorably, the bimolecular reaction with a carbonium ion occurs,

$$C_7H_{16} + R^+_{(s)} \rightarrow C_7H^{\delta^+}_{15} - H - R^{\delta^+} \qquad (4)$$

Then

$$C_7H_{15}^{\delta+} - H - R^{\delta+} \rightarrow C_7H_{15}^+(s) + HR \quad (5)$$

and

$$C_7H_{15}^+(s) \rightarrow C_3H_{7(s)}^+ + C_4H_8 \quad (6)$$

$$C_3H_{7(s)}^+ \rightarrow C_3H_6 + H_{(s)}^+$$

The preceding carbonium ion mechanism shows only the initial cracking steps. Subsequent reaction steps to account for the formation of aromatics are presented by Vedrine *et al.* (*6*) and Dejaifve *et al.* (*7*).

The metal dehydrogenation/carbonium ion mechanism is very similar to the simple carbonium ion mechanism and differs only in the type of intermediate formed. The first step is the metal catalyzed dehydrogenation of *n*-heptane to form heptene as shown in

$$\text{Heptane} \xrightarrow[\text{metal}]{} \text{Heptene} + H_2 \quad (7)$$

Though not as good as Pt or Pd, Ni is a good dehydrogenation catalyst whereas Zn is a weak one (*10*).

The heptene then reacts with a Brønstead acid site to give a carbonium ion which cracks to produce propylene and butylene as shown in the reactions

$$C_7H_{14} + H_{(s)}^+ \rightarrow C_7H_{15}^+(s) \quad (8)$$

$$C_7H_{15(s)}^+ \rightarrow C_3H_{7(s)}^+ + C_4H_8 \quad (9)$$

$$\hookrightarrow C_3H_6 + H_s^+$$

The C_3 and C_4 olefins are then partially hydrogenated to form the paraffins or they are converted to higher molecular weight products. The heptene does not need to form a bulky intermediate complex as heptane does (Eq. (4)) in order to crack. It is the bulk intermediates formed by alkanes which give rise to the transition-state selectivity.

Transition-state selectivity as discussed by Haag *et al.* (*3*) pertains to the relative cracking rates of a *n*-paraffin to a monomethyl paraffin with the same number of carbons. This ratio, called the constraint index (CI), is given for *n*-hexane/3-methyl pentane on H-ZSM-5 by Meisel and Weisz (*9*). They report CI values for *n*-hexane/3-methyl pentane of 1.52 at 811 K and 8.33 at 588 K. Guisnet *et al.* (*11*) report the CI for *n*-hexane/3-methyl pentane at 673 K of 4.0 for H-ZSM-5 and 15.5 for Pt-H-ZSM-5. The increase in the CI on Pt-H-ZSM-5 was attributed to formation of C_6^+ cations whereas on H-ZSM-5, C_3^+ cations would lead to transition complexes with greater steric hinderances.

The ratio of the cracking rates of olefins to paraffins over acid-cracking catalysts has been studied by many researchers. Haag *et al.* (*3*) found that the ratio of first-order rate constants for 1-hexene and *n*-hexane on H-ZSM-5, $K_{1\text{-hexene}}/K_{n\text{-hexane}}$, to be 260 at 811 K. In another publication, Haag *et al.* (*12*) report a value of 784 at 727 K for $K_{1\text{-hexene}}/K_{n\text{-hexane}}$ on H-ZSM-5. Nace (*13*) reports the ratio of olefin to paraffin cracking rates at 756 K for n-C_8, n-C_{12}, and n-C_{16} over 46-Al-silica-alumina and REHX zeolite to be between 2 and 50.

Relative Reactivities and Product Distributions

A summary of the range of run conditions and conversions obtained for each of the three catalysts is given in Table 1. Ni-ZSM-5 was clearly the most active cracking catalyst of the three catalysts tested and H-ZSM-5 was clearly the least active. Table 2 compared the temperature required with each catalyst to achieve roughly the same conversion of heptane. As can be seen from Table 2, the stronger the dehydrogenating functionality of the catalyst the lower the required reaction temperature. The product distributions and run conditions of each run are listed in Table 3.

The product distributions obtained by cracking *n*-heptane on Ni-ZSM-5 consisted of 75 to 80 wt% C_3 to C_5 hydrocarbons and between 1 and 5 wt% C_1 to C_2 hydrocarbons. The remaining products were C_6–C_8 aliphatics and C_6–C_9 aromatics. The C_6–C_8 aliphatics were more prevalent in the runs at 620 K whereas the C_6–C_9 aromatics were

TABLE 1

Reaction Conditions for *n*-Heptane Decomposition

Catalyst	Temp. (K)	Pressure (atm)	CT[a] (s-g/cm^3)	WHSV[b] (h^{-1})	Conversion (%)
Ni-ZSM-5	620–680	4.30–15.46	0.99–3.18	4.00–37.15	22.6–97.2
H-ZSM-5	789	16.15	2.19	14.91	48.8
Zn-ZSM-5	644–686	5.49–7.53	1.41–1.81	4.07–16.63	30.0–73.62

[a] Contact time (grams catalyst/volumetric flow rate at reactor *T*, *P*).

[b] Weight hourly space velocity (grams fed per hour per gram of catalyst).

more prevalent at 680 K. The product distribution for the Zn-ZSM-5 runs were very similar to the low temperature (620 K) runs made with Ni-ZSM-5. H-ZSM-5 required a much greater temperature (789 K) than either of the two metal exchanged catalysts to obtain a significant extent of heptane cracking. The product distribution for the H-ZSM-5 run was also unlike the metal exchanged catalysts runs in that the C_1–C_2 compounds were 15 wt% of the total products. These results for H-ZSM-5 are qualitatively similar to those of Miale *et al.* (*8*) in that they also observed no aromatics in the products. Our results were comparable to those of Anderson *et al.* (*2*) where they observed similar amounts of C_1 and C_2 compounds. Both Miale and Anderson used *n*-hexane as the feed and Miale used several zeolites whereas Anderson only used H-ZSM-5.

The differences in the activity of the three modified ZSM-5 catalysts as previously discussed can be explained using transition-state selectivity theory and other known properties of ZSM-5. First nickel and zinc are known to be hydrogenation/dehydrogenation catalysts. Of the two metals zinc is the weaker catalysts, i.e., it does not catalyze hydrogenation of aromatic rings but does catalyst hydrogenation of olefins (*10*). Chester (*5*) in his paper titled "Dehydrogenation of *n*-Hexane by Highly Dispersed Platinum in Zeolite Y," has found that hexenes were common intermediates which further reacted to form aromatics, isohexanes, and light gases. Guisnet *et al.* (*11*) in their work as previously discussed found traces of C_6 olefins with Pt-H-ZSM-5 but not with H-ZSM-5. In the analysis of the *n*-heptane cracking products for Ni- and Zn-ZSM-5 trace amounts of heptenes where obtained. In light of the extremely high ratios of the rates of cracking of olefins to paraffins over ZSM-5, almost all of the olefins that are formed are lost by secondary reactions. In fact Haag (*14*) has shown that, at least for ZSM-5, olefins are common intermediates regardless of the feed.

TABLE 2

Temperatures for Comparable Conversion

Catalyst	Ni-ZSM-5	Zn-ZSM-5	H-ZSM-5
T (K)	621	667	789
Conversion	45.33	36.10	48.8
Contact time (s-g/cm^3)	1.37	1.55	2.19

The fact that metals make acid-cracking catalysts more active in paraffin cracking cannot fully explain the increase in activity that metals impart to ZSM-5. Yan (*10*) presents data for the cracking of naptha over rare earth exchanged Linde Y zeolite. He states that the reactor temperatures required to achieve 60% conversion for REY, ZnREY, PdREY, and PdZnREY were 606, 603, 575, and 578 K, respectively. The temperatures required to achieve similar con-

TABLE 3

Heptane Cracking over Ni-, Zn-, and H-ZSM-5

Catalyst/run	Ni/1	Ni/2	Ni/3	Ni/4	Ni/5	Ni/6	Ni/7	Ni/8	Ni/9
Temperature (K)	650	650	649	649	650	621	621	620	621
Pressure (atm)	5.52	12.80	6.35	8.47	4.30	5.83	12.35	12.00	11.49
Conversion[a] (%)	88.53	54.42	65.11	58.00	76.25	45.33	25.39	22.57	32.28
Mass closure[b] (%)	94.3	95.9	99.8	100.4	99.7	92.9	94.1	95.1	97.9
Contact time[c] (s-g/cm^3)	2.35	0.99	1.97	1.54	3.18	1.37	1.06	1.13	1.22
H_2/feed (mol/mol)	3.22	2.07	0.86	1.29	0.55	3.04	4.43	1.47	1.55
WHSV[4] (h^{-1})	4.00	29.55	11.93	16.71	5.97	7.88	16.53	31.32	26.78
Product distribution (wt%)									
C_1–C_2	3.96	1.87	1.20	1.35	1.24	1.54	5.12	2.09	1.29
C_3	29.82	18.27	19.71	20.03	21.41	13.99	23.23	19.31	13.39
C_4	33.37	33.69	35.81	38.05	34.06	39.65	39.04	39.22	45.15
C_5	15.12	30.72	22.43	25.07	19.18	32.06	17.14	20.96	33.16
C_6–C_8[e]	6.24	6.85	8.73	6.21	9.61	7.84	13.51	18.42	7.01
Benzene	0.71	0.71	0.79	0.76	0.79	0.00	1.97	0.0	0.0
Toluene	2.80	1.01	1.65	1.10	3.10	0.0	0.0	0.0	0.0
Xylenes	4.18	3.58	4.51	3.93	5.05	2.86	0.0	0.0	0.0
Et-benzene	0.84	1.01	0.96	0.84	1.06	0.0	0.0	0.0	0.0
C_9 aromatics	2.97	2.31	4.20	2.65	4.50	2.05	0.0	0.0	0.0

versions between Ni-ZSM-5 and H-ZSM-5 differed by about 150 K.

The difference in the size of the transition state for heptene and *n*-heptane accounts for much of the increase in activity. Paraffins like *n*-heptane crack through a bimolecular mechanism but the olefins like 1-, 2-, and 3-heptene crack through a monomolecular mechanism. Even though the steric hinderance for *n*-paraffin transition complexes is smaller than that of monomethyl paraffin transition complexes, a steric hinderance does exist. Whereas there is no steric hinderance for normal olefin transition complexes because they are monomolecular. This explains why the ratio of $K_{\mathrm{olefin}}/K_{\mathrm{paraffin}}$ is so much higher in H-ZSM-5 than on large pore zeolites (REHX) or amorphous silica–alumina catalysts (46-AI).

Thus dehydrogenation metals have a synergistic effect when added to ZSM-5. By producing olefin intermediates the metals on ZSM-5 enhance the cracking rates of normal paraffins on ZSM-5 to a greater extent than metals on catalysts not exhibiting transition-state selectivity toward the cracking reaction.

Kinetic Parameter Estimation

The experimental data obtained allowed the calculation of the activation energy and rate constant for *n*-heptane cracking on Ni-ZSM-5. A first-order rate equation was used to model the reaction and the activation energy and rate constant were calculated by nonlinear parameter estimation. The activation energy was found to be 32 ± 3 kcal/gmol which is in good agreement with 30 kcal/gmol reported by Miale *et al.* (*8*) for cracking *n*-hexane over various zeolite catalysts. The first-order rate constant at 650 K was 0.20 ± 0.02 s^{-1}.

SUMMARY AND CONCLUSIONS

The differences between the size of the transition states and the pore sizes, which has been called transition-state selectivity, was used to explain the differences in the rate of cracking of *n*-heptane over bifunctional ZSM-5 catalyst of different dehydrogenation capabilities. A heptene intermedi-

TABLE 3—*Continued*

Catalyst/run	Ni/10	Ni/11	Ni/12	H/1	Zn/1	Zn/2	Zn/3	Zn/4	Zn/5
Temperature (K)	680	679	680	789	667	667	667	644	686
Pressure (atm)	15.46	13.45	9.42	16.15	7.53	5.49	9.69	6.26	7.50
Conversion[a] (%)	92.92	95.13	97.20	48.82	36.10	29.99	73.62	26.46	32.48
Mass closure[b] (%)	99.4	98.8	95.9	94.6	92.0	95.6	96.4	94.7	94.4
Contact time[c] (s-g/cm^3)	1.07	1.17	1.60	2.19	1.55	1.84	1.42	1.77	1.47
H$_2$/feed (mol/mol)	1.68	2.36	2.49	1.85	2.94	4.23	1.81	1.93	2.70
WHSV[4] (h^{-1})	37.15	23.12	11.38	14.91	8.56	4.07	16.63	8.52	9.30
				Product distribution (wt%)					
C$_1$–C$_2$	2.82	3.33	3.63	15.04	2.83	4.45	0.62	1.82	3.38
C$_3$	20.39	23.25	26.44	28.11	25.02	28.00	6.20	18.53	23.08
C$_4$	35.15	36.14	33.38	33.22	32.16	33.29	42.36	33.18	41.18
C$_5$	25.12	19.09	16.05	23.63	21.94	25.83	40.36	36.97	24.87
C$_6$–C$_8$[e]	4.52	2.97	1.73	0.0	12.59	8.43	10.46	9.51	7.49
Benzene	0.0	0.0	0.0	0.0	2.89	0.0	0.0	0.0	0.0
Toluene	0.93	1.46	1.37	0.0	1.02	0.0	0.0	0.0	0.0
Xylenes	5.73	6.30	8.50	0.0	1.55	0.0	0.0	0.0	0.0
Et-benzene	1.19	1.16	1.50	0.0	0.0	0.0	0.0	0.0	0.0
C$_9$ aromatics	4.15	6.30	7.41	0.0	0.0	0.0	0.0	0.0	0.0

[a] Conversion is grams heptane converted to products/grams heptane fed.

[b] Mass closure (mass fed/mass collected) · 100%.

[c] Contact time (grams ZSM-5/volumetric flow rate at reactor *T*, *P*).

[d] Weight hourly space velocity (grams fed per hour per grams of ZSM-5).

[e] Excludes heptane fed.

ate was postulated to participate in the cracking of *n*-heptane over Ni-ZSM-5. This work gives further support to the classical carbonium ion cracking mechanism.

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