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The Comparison of Cracking Activity, Product Selectivity, and Steam Stability of ZSM-5 to Other Cracking Catalysts

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A modified "α-test" method was adopted to examine the new type zeolite ZSM-5 which was synthesized in our laboratory. The results show that HZSM-5 has superb activity on *n*-hexane cracking, lower aging rate, and better steam stability than other zeolite-type catalysts. HZSM-5 has good selectivities of C_3 and C_4 paraffin at low temperatures and ethylene and aromatics at high temperatures.

INTRODUCTION

ZSM-5 is a new type of synthetic zeolite (*1*) having a wide Si/Al ratio from 20 to ∞ and straight channels with a pore diameter between 5 to 7 Å. Because of its specific structure, this zeolite has been suggested as a high potential catalyst for fuel and petrochemical processing, such as gasoline from methanol (*2–4*), olefin aromatization (*5*), benzene–ethylene alkylation, selective production of para-xylene (*6*), hydrodewaxing (*7*), etc. Thus, it is worthwhile to compare the reaction activity, product selectivity, steam stability, and aging rate of this new zeolite to other well-known zeolite-type catalysts.

In 1966, Miale *et al.* (*8*) found that most cracking catalysts have the same activation energy of 30 kcal/mol for *n*-hexane cracking, which can be used as a quantitative comparison of relative magnitudes of cracking activities of crystalline aluminosilicate zeolites. In this paper, we will adopt their method (α-test) with slight modifications to examine the ZSM-5 which has been synthesized in our laboratory (*9*).

EXPERIMENTAL

Conversion data on *n*-hexane cracking were obtained in a quartz tubular flow reactor holding 3 g (~5 cm^3) catalyst. The catalyst was pelleted, crushed, and sized to 12 ~ 20 mesh. As shown in Fig. 1, a stream of nitrogen at a 300 cm^3/min flow rate was metered through an *n*-hexane saturator at room temperature (~30°C). The saturated N_2 gas was passed continuously through the reactor, resulting in an apparent contact time of 1 sec. The cracked stream was collected and injected into a Varian 3700 FID gas chromatograph to obtain the conversion and the product distribution data.

At a given temperature, the apparent first order reaction rate constant is

$$k = \left(\frac{1}{\tau}\right) \ln\left(\frac{1}{1 - x}\right) \qquad (1)$$

where x is the observed fractional con-

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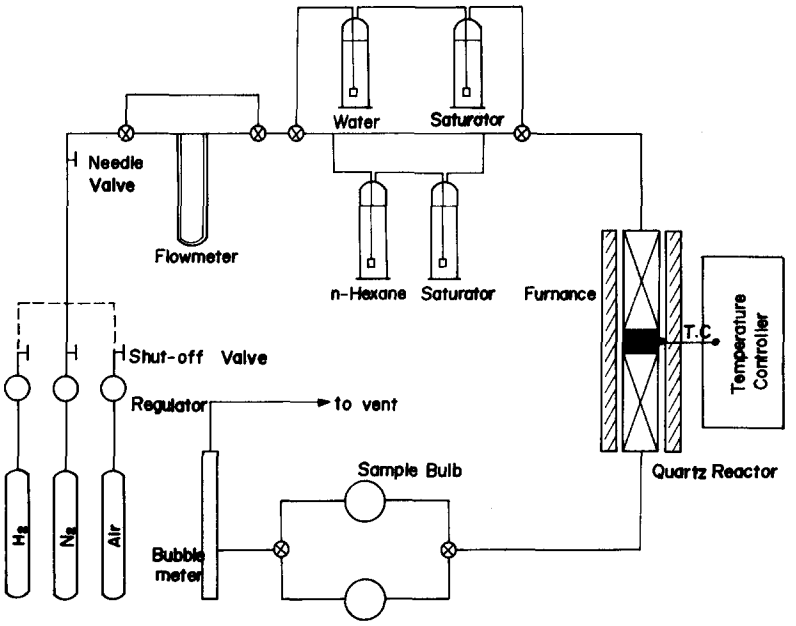

FIG. 1. The flow diagram of catalyst activity test unit.

version and was considered meaningful only at low conversion levels on n-hexane cracking and τ is the apparent contact time. To avoid the competition of secondary reactions the designed conversion range is 5 $\sim$ 20% in this experiment.

Since several order of magnitudes of activity was encountered, reaction temperature of each catalyst had to be different from each other to keep the conversion in the designed range. The reaction rate constant can be extrapolated to the same reference temperature by using the following equation:

$$k_{cat} = ke^{(E/R)(T_r - T/T_r T)} \qquad (2)$$

TABLE 1

Composition of ZSM-5 and Their Properties

Zeolite product	A	B	C
SiO_2/Al_2O_3	122	60	30
Na_2O/Al_2O_3	0.60	0.60	0.74
TPA evolution[a] temperature (°C)	———	450	———
Decomposition temperature (°C)	———	>950	———
Particle size	———	90% 10 $\sim$ 15 μm	———
Adsorption (g/g)			
n-C_6H_{14}/C-C_6H_{14}	5.93	5.55	3.52
n-C_6H_{14}	0.129	0.123	0.066
H_2O	0.111	0.101	0.139

[a] DTA heating rate: 30°C min^{-1}. Carrier gas-N_2 (300 cm^3/min).

TABLE 2

Degree of Cation Exchange of Various Catalysts

Catalyst	Degree of cation exchange (%)
NH_4ZSM-5(30)	The maximum degree of cation exchange[a]
NH_4ZSM-5(60)	The maximum degree of cation exchange[a]
NH_4ZSM-5(120)	The maximum degree of cation exchange[a]
LaY	60
NH_4Y	100
NH_4M	57
MgX	55

[a] Catalysts are exchanged with 1 N NH_4Cl solution about 10 $\sim$ 12 times (80°C, 4 hr for each time), then the last exchanged solution, which is determined by atomic adsorption spectroscopic meter, is filtered to ensure that there is no Na^+ content. At this time, the degree of cation exchange is what we called the maximum degree of cation exchange.

where

T = reaction temperature (K)
T_r = reference temperature (K)
k_{cat} = first order reaction rate constant at reference temperature (T_r) (sec^{-1}).

The relative rate constant α is defined as

$$\alpha = \left(\frac{k_{cat}}{k_{ref}}\right) \text{at } T_r \qquad (3)$$

where k_{ref} is the first order rate constant of n-hexane cracking of the reference catalyst. In this paper we chose a commercial cracking catalyst (TCC-DB-1) as the general reference catalyst. The reference temperature was 540°C. From our study the measured activation energies of ZSM-5 and other cracking catalysts for n-hexane cracking is in the range of 15 ~ 30 kcal/mol. Since the pore size and cracking activity of each catalyst is different from each other, the magnitude of diffusion disguise on activation energy is not the same. The measured activation energy may not reflect the true chemical activation energy. In this study we chose an activation energy of 30 kcal/mole for calculation of the α-value.

In this experiment, the ZSM-5 catalysts were synthesized in our laboratory. The nature of crystalline product were examined by X-ray powder diffraction, differential thermal analysis, and gravimetric adsorption measurement. Some physical properties and chemical composition of ZSM-5 zeolite are summarized in Table 1. Other zeolite-type catalysts such as faujasite X, faujasite Y, and mordenite were bought from Strem Chemicals. All the zeolites were ion exchanged to proper forms. The extent of ammonium ion exchange of each catalyst is listed in Table 2. Prior to testing, each catalyst sample was treated with a water saturated air stream (P_{H_2O} $\simeq$ 22 mm Hg) at 540°C for 2 hr, then the catalyst sample was purged by a N_2 stream for 30 min at 540°C and then cooled to the reaction temperature.

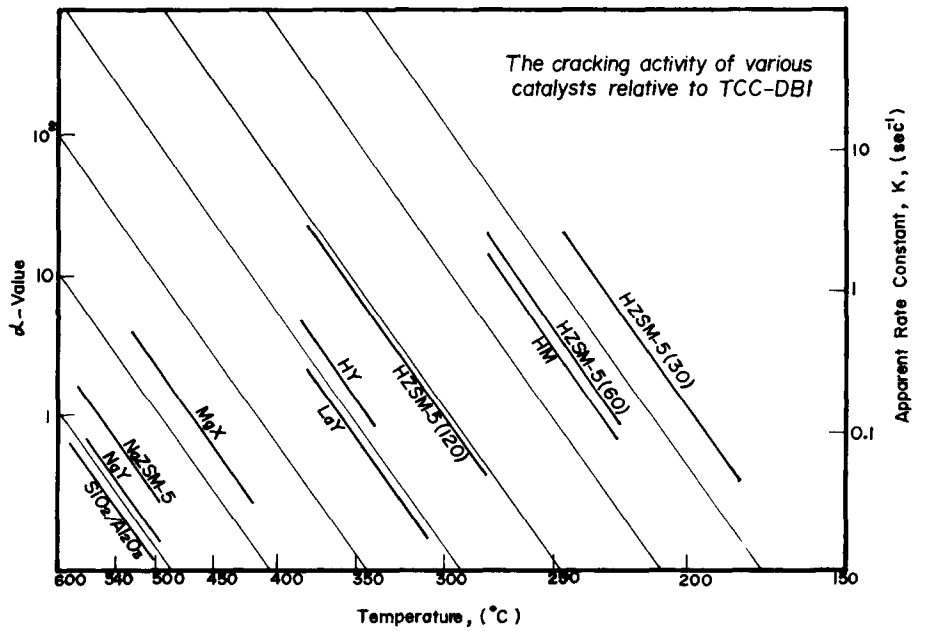

FIG. 2. The n-hexane cracking activities of various catalysts relative to TCC-DB-1.

TABLE 3

α-Values and Product Selectivities of Various Catalysts at 5 $\sim$ 20% Conversion Levels[a]

	SiO_2/Al_2O_3	TCC	NaY	NaZSM-5[b]	MgX[b]	LaY	HY	HZSM-5 (120)	HM	HZSM-5 (60)	HZSM-5 (30)
Reaction temperature (°C)	540	540	540	540	450	340	360	320	230	240	200
Conversion (wt%)	2.9	3.7	4.8	8.8	7.5	6.2	21.4	26.2	13.1	19.0	14.2
α-Value	0.8	1.0	1.3	2.5	20.6	700	1200	7600	←	>100,000	→
Product selectivity											
CH_4	7.8	7.9	10.3	11.3	6.4	0.2	0.8	0.2	—	—	—
C_2H_6	8.4	7.4	11.2	4.7	4.8	0.6	1.1	1.8	0.05	0.1	0.04
C_2H_4	17.8	20.3	24.7	37.7	19.9	1.5	4.9	4.5	0.4	0.4	0.1
C_3H_8	8.5	3.5	2.5	1.1	3.9	43.6	37.8	40.9	24.4	26.0	22.4
C_3H_6	40.5	35.5	26.6	33.2	36.2	9.1	15.2	9.1	0.1	1.5	0.3
i-C_4H_{10}	4.4	1.3	—	—	—	21.1	18.6	12.7	32.8	24.3	27.5
n-C_4H_{10}	3.0	1.3	0.3	0.2	0.8	0.7	5.4	18.0	14.1	25.3	25.1
C_4H_8	6.8	12.1	15.8	10.5	25.5	13.0	13.3	8.2	20.2	15.2	11.1
C_5H_{12}	1.2	0.9	0.7	0.3	0.4	—	1.5	4.0	6.1	11.2	11.7
C_5H_{10}	—	2.2	3.9	0.4	1.4	2.8	0.7	0.1	—	0.6	—
C_6H_{12}	1.4	7.6	5.9	0.4	0.6	1.1	0.7	0.3	1.9	0.6	1.8

[a] Pretreatment, 2 hr in air + steam at 540°C; catalyst time on stream, 3 min; apparent contact time, 1 sec.

[b] Catalyst time on stream, 1 min.

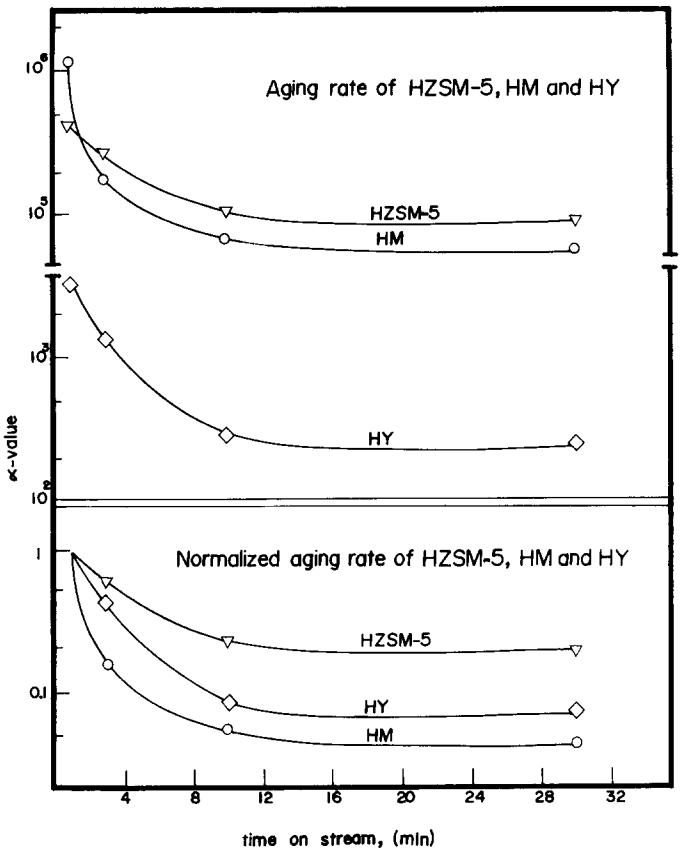

FIG. 3. The comparison of aging rate of HZSM-5, HM, and HY at meaningful low conversion level.

RESULTS AND DISCUSSION

The relative magnitude of cracking rate constant (α-value) of each catalyst at a time on stream of 3 min is given in Fig. 2 and Table 3. The relative activity increases in the order as

$$SiO_2/Al_2O_3 < \text{TCC-DB-1} \ (\alpha = 1) < \text{NaY} < \text{NaZSM-5} < \text{MgX} < \text{LaY} < \text{HY} < \text{HZSM-5(120)}^+ < \text{HM} < \text{HZSM-5(60)}^+ < \text{HZSM-5(30)}^+ + SiO_2/Al_2O_3 \text{ ratio.}$$

As shown in Fig. 2, the *n*-hexane cracking activity of HZSM-5 is much higher than the cracking activity of HY and the α-value of HZSM-5 increases as the Si/Al ratio decreases. Data on reaction temperature, conversion, and product selectivity of each catalyst on *n*-hexane cracking are given in Table 3. According to the "α-value," the catalyst in Table 3 can be grouped into three classes as:

Class I

$\alpha \geq 100{,}000$ high-activity catalyst

Class II

$700 \leq \alpha \leq 7600$ median-activity catalyst

Class III

$\alpha \leq 20.6$ low-activity catalyst

As shown in Table 3, the higher the "α-value" of the catalyst, the higher the average molecular weight of hydrocarbons in the product stream.

Due to the coke formation, the activity of the cracking catalyst decreases as the cata-

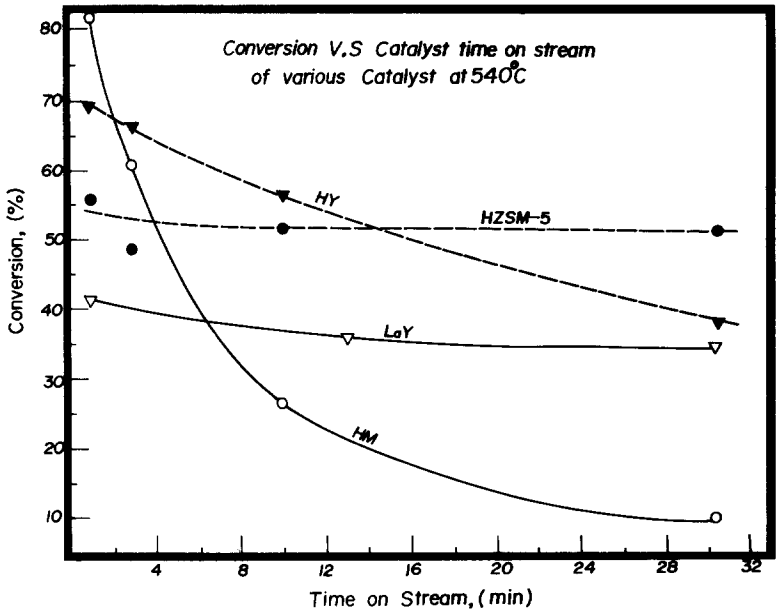

FIG. 4. The comparison of steam stability of HZSM-5 and HY at meaningful low conversion level.

lyst time on stream increases. In Fig. 3, the α-values of several zeolites were plotted against the catalyst time on stream. As shown in the figure HZSM-5 has the lowest rate of decay and H-mordenite has the highest rate of decay. The low aging rate of ZSM-5 suggests that the specific pore structure and electrostatic field of ZSM-5 may hinder the coke formation.

When zeolites are subjected to steam and heat, their structures will be gradually destroyed, resulting in an irreversible loss

TABLE 4

Conversions and Product Selectivities of Various Catalysts at 540°C[a]

	—	SiO_2/Al_2O_3	TCC	NaY	NaZSM-5	HY	HM	HZSM-5	LaY
Conversion (wt%)	1.63	3.95	5.84	7.62	8.77	69.55	81.87	55.65	40.90
Product selectivity									
CH_4	13.7	9.3	8.7	10.1	11.3	2.1	8.7	5.7	2.6
C_2H_6	12.0	8.5	6.1	11.4	4.7	3.7	8.9	13.6	4.8
C_2H_4	32.8	23.3	23.3	24.5	37.7	8.1	10.1	19.4	8.6
C_3H_8	2.1	4.6	2.2	2.3	1.1	36.0	51.3	23.4	28.0
C_3H_6	23.2	39.7	32.6	27.3	33.2	25.0	8.3	23.1	36.8
i-C_4H_{10}	0.5	1.9	0.4	—	—	9.2	2.9	1.7	4.4
n-C_4H_{10}	1.6	1.8	0.7	0.2	0.2	6.6	3.2	3.3	6.1
C_4H_8	6.9	8.7	13.2	16.7	10.5	4.9	2.0	6.9	7.9
C_5's$^+$	7.2	2.2	12.8	7.5	1.3	4.4	4.6	3.0	0.8
C_2^-/C_3^-	1.4	0.6	0.7	0.9	1.1	0.3	1.2	0.8	0.2
C_3/C_3^-	0.1	0.1	0.1	0.1	0.03	1.4	6.2	1.0	0.8
i-C_4/C_3^-	0.02	0.05	0.01	—	—	0.4	0.3	0.1	0.1
i-C_4/n-C_4	0.3	1.1	0.6	—	—	1.4	0.9	0.5	0.7

[a] Pretreatment, 2 hr in air + steam at 540°C; catalyst time on stream, 1 min; apparent contact time, 1 sec.

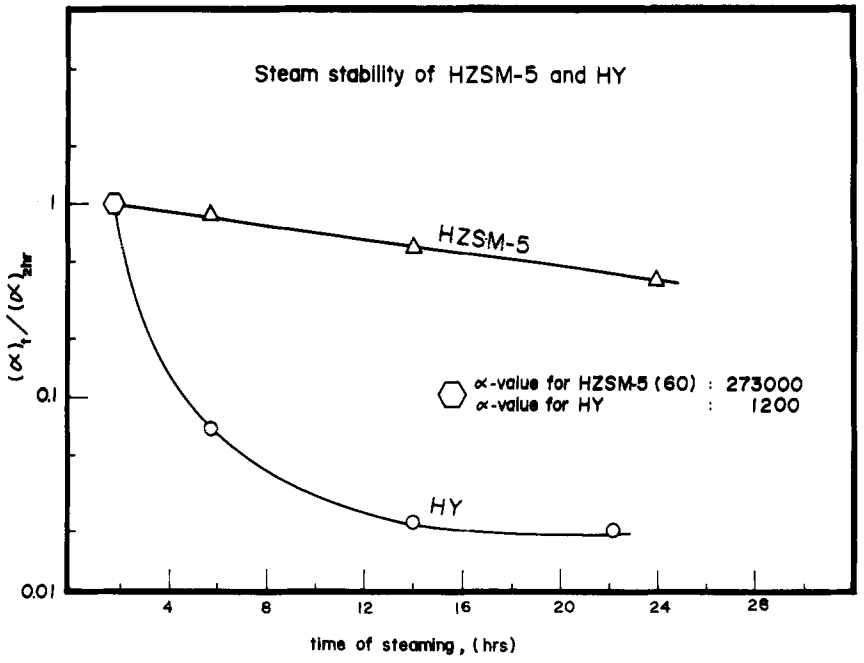

FIG. 5. The comparison of aging rate of HZSM-5, LaY, HM, and HY at 540°C.

of activity. During the methanol to hydrocarbon processing water is one of the major product. Nevertheless, Mobil has confirmed that the catalyst system is the ZSM-5 version. Figure 4 gives the results of the comparison of steam stability of HZSM-5 to HY. Both the HZSM-5 and the HY were steamed from 2 to 24 hr with a steam partial pressure of 22 mg Hg at 540°C. After 24 hr steam the crystallinity of ZSM-5 was about 70% of the fresh catalyst. In Fig. 4, the normalized α-values vs time of steaming was constructed on a semi-log paper. Figure 4 shows that a straight decay line was obtained for HZSM-5 and a rapid decay curve was obtained for HY. These results suggest that the mechanisms of deactivation of HZSM-5 and HY by steaming might be different from each other. The differences will be further investigated by X-ray diffraction and acidity analysis.

Conversions and product selectivities of various catalysts at the same operating temperature of 540°C are given in Table 4. As shown in Table 4, ethylene and propylene are the major products for class III catalyst ($\alpha < 20.6$) and in contrast propane is the most important product for class I and II catalysts. Among the class III catalysts, the product distribution of NaY and NaZSM-5 was similar to the result of thermal cracking (column 1 in Table 4), and Strem's SiO_2/Al_2O_3 gave a product

TABLE 5

Product Selectivities of Various Catalysts at 90% Conversion Levels[a]

	HY	HM	HZSM-5	LaY
Conversion (wt%)	88.5	90.3	96.3	91.3
Product selectivity				
CH_4	6.8	42.1	13.3	17.3
C_2H_6	6.9	29.5	10.4	14.8
C_2H_4	12.8	11.6	21.1	14.3
C_3H_8	37.5	11.6	9.3	19.9
C_3H_6, i–C_4H_{10}, n–C_4H_{10}	31.2	4.9	22.8	24.2
C_4H_8	4.9	0.2	8.3	4.6
C_5's	—	0.2	0.4	0.3
C_6H_6	—	—	10.7	3.7
C_7H_8	—	—	3.8	—

[a] Pretreatment, 15 min in air at 540°C; temperature, 500°C; apparent contact time, 10 sec; catalyst time on stream, 5 min.

spectrum similar to TCC-DB-1. In both class III and class I and II catalysts, NaZSM-5 and HZSM-5 produce greater amounts of ethylene than other catalysts.

Figure 5 gives the aging rate data of HY, HZSM-5, H-modernite, and LaY at 540°C. Because the conversions were outside the meaningful range of α-test, the conversion was plotted directly against the catalyst time on stream in Fig. 5. Figure 5, like Fig. 2, also shows that HZSM-5 and H-modernite have the lowest and the highest aging rate, respectively.

As the conversion increased, the differences on product selectivity between HZSM-5 and other catalysts in class I and II increased. Table 5 gives the product selectivity of HZSM-5, HY, H-modernite, and LaY at 90% conversion level. Among the catalysts in Table 5, HZSM-5 produces greater amounts of ethylene and aromatics. This indicates that HZSM-5 is a good potential catalyst for basic petrochemical manufacturing.

NOMENCLATURE

k first order reaction rate constant (sec^{-1})

k_{cat} first order reaction rate constant (sec^{-1})

k_{ref} first order reaction rate constant of reference catalyst at reference temperature (sec^{-1})

T reaction temperature (K)

T_r reference temperature (K)

x conversion

α relative magnitude of cracking activity

τ contact time (sec)

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