

## Prediction of Cracking Catalyst Behavior by a Zeolite Unit Cell Size Model

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An experimental and theoretical study of the behavior of metal, hydrogen-exchanged Y and USY zeolite cracking catalysts has been conducted. From the experimental program, data on zeolite stability as well as catalyst activity and selectivity were obtained. Using a new theoretical framework for zeolite acidity, it was found that these data could be correlated against a single parameter, the unit cell constant of the steam deactivated catalyst. The cell constant is a measure of the silica to alumina ratio actually in the zeolite crystal structure. This ratio is a measure of acid site density which determines the acid strength distribution and ultimately affects activity and selectivity. The data clearly show that activity and selectivity changes resulting from various zeolite pretreatments such as cation exchange, acid extraction, and hydrothermal conditioning can be explained in terms of their effect on the zeolite cell constant. A logical extension of the acid site distribution theory is demonstrated by the influence of soda level on the performance of catalysts having the same cell constant.

### INTRODUCTION

For many years now, the refining industry has relied on the catalytic cracking process for conversion of gas oil into lighter products, especially naphtha for motor gasoline blending. The key ingredient in the success of this process has been the application of zeolites, especially the faujasites, as the catalytically active component in cracking catalysts. Compared to the previously applied silica-alumina catalysts, zeolite catalysts have offered higher activity, more naphtha selectivity, and increased production rates. Because of the widespread use of zeolite cracking catalysts and the impact of catalytically cracked naphtha on the gasoline pool, an effort was begun in our laboratory to study the fundamental factors governing zeolite behavior and relate them to overall catalyst performance. Of particular interest were the effects of cation exchange and other zeolite treatments on the activity and selectivity of cracking catalysts.

### METHODS

#### *Catalyst Preparation*

All of the zeolites used in laboratory preparations listed in Table 1 were obtained from the Linde Division of Union Carbide. The USY was their low soda grade LZ-Y82 and the HY was their grade LZ-Y62. The sample called REY, used in the stability studies was made by ion exchanging LZ-Y62 with an excess of rare earth chloride solution. The sample was then washed, calcined 2 h in air at 538°C and given a second exchange treatment with excess of rare earth chloride solution. The rare earth chloride solution was a commercial mixture having the following rare earth distribution: 43.0% La<sub>2</sub>O<sub>3</sub>, 30.2% CeO<sub>2</sub>, 20.6% Nd<sub>2</sub>O<sub>3</sub>, 4.8% Pr<sub>6</sub>O<sub>11</sub>, and 1.4% other oxides. The analyses obtained on this sample of REY are compared in Table 4 with those obtained on a sample of LZ-Y82.

All of the catalysts were prepared by spray drying a slurry of the zeolite and a synthetic silica-alumina gel matrix. The

TABLE 1  
Catalyst Properties

Catalyst	Symbol	Type of catalyst	Zeolite (wt %)	Exchanged metal (wt %)	Steamed 16 h at 760°C		
					Na <sub>2</sub> O (wt %)	Surface area (m <sup>2</sup> /g)	Cell constant (Å)
A-1	●	RE <sub>2</sub> O <sub>3</sub> Postexchanged in USY	25	0	0.24	226	24.23
A-2	●	RE <sub>2</sub> O <sub>3</sub> Postexchanged in USY	25	0.17	0.19	224	24.24
A-3	●	RE <sub>2</sub> O <sub>3</sub> Postexchanged in USY	25	0.56	0.20	215	24.245 <sup>a</sup>
A-4	●	RE <sub>2</sub> O <sub>3</sub> Postexchanged in USY	25	0.89	0.16	222	24.26
A-5	●	RE <sub>2</sub> O <sub>3</sub> Postexchanged in USY	25	1.04	0.24	233	24.25
A-6	●	RE <sub>2</sub> O <sub>3</sub> Postexchanged in USY	25	1.34	0.19	227	24.28
A-7	●	RE <sub>2</sub> O <sub>3</sub> Postexchanged in USY	25	2.45	0.18	214	24.335 <sup>a</sup>
A-8	●	RE <sub>2</sub> O <sub>3</sub> Postexchanged in USY	25	2.46	0.13	225	24.32
B	○	RE <sub>2</sub> O <sub>3</sub> Postexchanged in USY	20	0.63	0.08	176	24.29
C	□	Pre-RE <sub>2</sub> O <sub>3</sub> -exchanged in USY	20	0.16	0.08	201	24.23
D-1	◇	RE <sub>2</sub> O <sub>3</sub> -exchanged HY	20	0.83	0.18	208	24.26
D-2	◇	RE <sub>2</sub> O <sub>3</sub> -exchanged HY	20	1.43	0.16	220	24.31 <sup>a</sup>
E	⊠	U <sup>++</sup> -exchanged USY	20	1.11	0.08	233	24.28
F	△	Th <sup>++</sup> -exchanged USY	20	1.13	0.08	202	24.305 <sup>a</sup>
G	▽	Th <sup>++</sup> -exchanged HY	20	1.74	0.13	206	24.28
H	×	Precalcined USY	20	0	0.08	219	24.27
I	+	Dealuminated USY	20	0	0.16	242	24.255 <sup>a</sup>
J	⊞	Dealuminated, precalcined USY	20	0	0.08	226	24.235 <sup>a</sup>

<sup>a</sup> Average of two analyses.

spray-dried catalysts were washed with 5 wt% solutions of ammonia sulfate to remove most of the soda. In the cases where the catalysts were postexchanged with rare earths, the exchange was carried out at this time by stirring the washed wet catalyst in a dilute solution of the same mixed rare earth chlorides described above for 1 h at room temperature. The catalyst was then dried in an oven, usually overnight, at 115°C. Prior to catalytic evaluation, all of the catalysts were hydrothermally deactivated to simulate an equilibrium catalyst from a commer-

cial fluid catalytic cracking unit. The hydrothermal treatment consisted of steaming the catalyst in a fluidized bed for 16 h at 760°C under 1 atm of steam. The surface area of the steamed catalyst was measured by nitrogen adsorption using the ASTM procedure D-3663-78. The unit cell dimension was determined using the ASTM procedure D-3942-80.

About half of the catalysts were prepared with zeolites that had been modified either by ion exchange or some other treatment prior to being incorporated into the cata-

lyst. Catalysts D-1 and D-2 contain zeolites prepared by exchanging LZ-Y62 with different amounts of the same commercial rare earth chloride used in making the post-exchanged catalysts. After exchange, these zeolites were calcined for 1 h at 816°C to partially stabilize the crystal structure. The zeolite for catalyst C was made by exchanging LZ-Y82 with a small amount of the commercial rare earth chloride solution. In this case the exchanged zeolite was calcined 2 h at 538°C prior to being incorporated into the catalyst.

The thorium-containing zeolites were prepared by exchanging with  $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$  solutions for 6 h at 80°C. The ThUSY was calcined 2 h at 538°C before being formulated into catalyst F. The thorium-exchanged LZ-Y62 used in catalyst G was calcined 1 h at 816°C to obtain partial stabilization. The uranium-exchanged USY used in catalyst E was made

using the same procedure as that for the ThUSY. Uranyl nitrate was used as the uranium source.

The zeolite for catalyst I was prepared by leaching LZ-Y82 for 3 h at 80°C with an aqueous solution containing 1.0 wt% HCl and 12.8 wt%  $(\text{NH}_4)\text{SO}_4$ . This treatment raised the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio, measured by chemical analysis, from 4.56 to 6.50. The zeolite for catalyst J was a sample of this same acid-leached USY that had been further stabilized by calcination for 1 h at 816°C. Catalyst H contains zeolite prepared by calcining LZ-Y82 for 1 h at 816°C.

#### Catalyst Evaluation

The catalyst evaluation data are given in Table 2. Gas oil cracking activities were measured using the microactivity test (MAT), originally described by Ciapetta and Henderson (1), modified to more closely resemble the ASTM D-3907-80. In

TABLE 2  
Catalyst Activity and Pilot Unit Results

Catalyst	MAT activity (%)	Values at 65 vol% conversion to product boiling below 221°C					
		Research octane No. <sup>a</sup>	Motor octane No. <sup>a</sup>	C <sub>3</sub> - gas yield (wt%)	Bromine No. (gm/cgm) <sup>a</sup>	Butylenes (wt%)	Naphtha yield (Vol%) <sup>a</sup>
A-1	66.1	93.9	80.0	5.6	86	7.7	58.2
A-2	69.7	93.7	79.9	5.0	75	6.0	60.0
A-3	70.6	92.5	79.2	5.1	72	5.6	60.3
A-4	71.4	92.8	79.5	4.7	70	5.9	61.2
A-5	71.2	92.6	80.1	5.1	82	6.8	59.1
A-6	75.4	91.8	79.1	4.6	61	6.6	60.3
A-7	78.9	90.2	78.2	4.2	73	6.8	60.2
A-8	80.6	90.3	78.2	4.2	66	5.4	62.1
B	71.4	92.7	79.7	4.6	75	6.4	62.0
C	69.1	93.9	80.2	5.7	79	8.0	56.5
D-1	69.6	92.5	80.0	5.0	78	6.2	60.0
D-2	74.9	89.6	78.3	4.1	69	5.8	62.5
E	71.6	92.5	79.8	4.9	71	5.5	60.1
F	71.3	91.6	79.0	4.7	75	5.8	58.4
G	73.2	91.9	79.5	4.9	68	6.5	60.5
H	76.4	92.7	79.9	4.6	73	7.4	59.0
I	71.8	92.7	79.9	4.9	69	8.0	58.5
J	67.8	93.5	79.7	6.1	89	8.0	53.0

<sup>a</sup> Values are for a naphtha boiling range 18–221°C.

order to obtain sufficient samples of cracked product for yields by distillation and engine octane tests, an ARCO type (2) circulating pilot plant was used. This is a fully integrated, continuously circulating fluidized bed unit containing separate reactor, stripper, and regenerator vessels. Nitrogen was used as both the reactor fluidizing gas and catalyst stripping gas. An air-nitrogen mixture was used in the regenerator. All data were taken at a constant catalyst to oil ratio of 4.0 and a reactor temperature of 496°C. Conversion was varied by changing space velocity. The regenerator was operated between 593 and 607°C with a large excess of oxygen in order to return a low carbon catalyst to the reactor. The feedstock was an Arabian Light vacuum gas oil boiling from 330 to 555°C. The cracked naphtha was separated from higher boiling material by a 15/5 distillation (ASTM D-2892). The research and motor octanes are unleaded engine octane numbers determined by ASTM 2699 and 2700. The bromine numbers were determined by ASTM D-1159.

### RESULTS

Steam stabilities of the USY and REY zeolites are presented in Table 3 and the

analyses of the untreated zeolites are given in Table 4. At low temperatures, there is little loss in surface area or crystallinity for either zeolite type. However, as severity is increased, the relative surface area loss for the two zeolites is marked. At 816°C, the USY still has an appreciable retention of surface area whereas the REY has essentially lost all integrity.

Companion steam deactivation data on (1) a laboratory catalyst prepared with USY and (2) a commercially prepared catalyst containing a highly rare earth exchanged Y zeolite are given in Table 5. Activity ratios are calculated assuming a pseudo-second-order rate constant for conversion from the microactivity test. At low severities, the rare earth-containing catalyst is much more active than the USY-containing catalyst. This is indicative of the lower tetrahedral aluminum site density in USY. In the intermediate severity range, the catalysts are quite close in activity. However, as high temperatures begin to degrade the rare earth containing zeolite, the USY-containing catalyst shows up as the more active one. The level of deactivation in USY catalysts can be controlled by exchanging with stabilizing cations such as rare earth oxides. As shown in Table 1, steam deactiva-

TABLE 3  
Results for Zeolite Steamings, REY vs USY

Steaming		REY		USY	
Temp (°C)	Time (h)	Surface area (m <sup>2</sup> /g)	Zeolite crystallinity (%)	Surface area (m <sup>2</sup> /g)	Zeolite crystallinity (%)
Calcined 6 h at 538°C		520	73	612	234
649	4	531	117	579	308
649	16	531	108	629	268
649	64	517	124	575	265
760	4	494	129	571	235
760	16	421	107	520	256
760	64	225	49	486	275
816	4	102	31	498	295
816	16	20	<5	496	286
816	64	—	<5	445	263

TABLE 4  
Zeolites Used for Steaming Study

Identification	Assay, wt%				Calcined 6 h at 538°C		Unit cell size, (Å)
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	RE <sub>2</sub> O <sub>3</sub>	Surface area, (m <sup>2</sup> /g)	Zeolite crystallinity (%)	
USY	75.4	23.5	0.12	0	612	234	24.51
REY	54.2	20.7	1.3	23.3	520	73	24.67

tion shrinks the unit cell size in inverse relation to the amount of RE<sub>2</sub>O<sub>3</sub> in the catalyst. This is also illustrated in Fig. 1 where all the catalysts contain 25% zeolite yet the level of rare earth exchange on total catalyst varied from 0 to 2.46 wt%. This series of catalysts represents the best group for direct comparisons, as the only variable is the level of rare earth exchange.

A similar plot, Fig. 2, for the remaining catalysts in Table 1 also shows the trend of higher activity with increasing unit cell size. Hence, a wide variety of catalysts have their activities correlated by the common parameter, unit cell size. This appears to be true no matter what method is used to change the unit cell size. Some of the selectivity data from these experiments are pre-

sented in Figs. 3 through 5. These figures show a decreasing C<sub>3</sub>- gas yield, and a substantial drop in clear research and motor octane as unit cell size is increased. The data in Table 2 show that both the yield of butylenes and the olefin content of the motor gasoline fraction, as measured by bromine number, also decrease as unit cell size is increased. The naphtha yield, however, increases as unit cell size is increased.

#### DISCUSSION

The data presented here suggest that a single zeolite property, the unit cell size, can be used to correlate both the activity and selectivity performance of gas oil cracking catalysts. The unit cell size provides a measure of the Si/Al ratio of the

TABLE 5

Relative Activities for REY and USY Catalysts after various Steaming Severities

Steaming		REY activity <sup>a</sup> USY activity
Temp (°C)	Time (h)	
704	64	1.65
732	4	1.05
732	30	1.31
760	1	1.00
760	4	0.90
760	16	0.99
760	30	0.74
760	64	0.66
816	1	0.75

<sup>a</sup> Activity ratios are calculated assuming pseudo-second-order rate constants from MAT conversion.

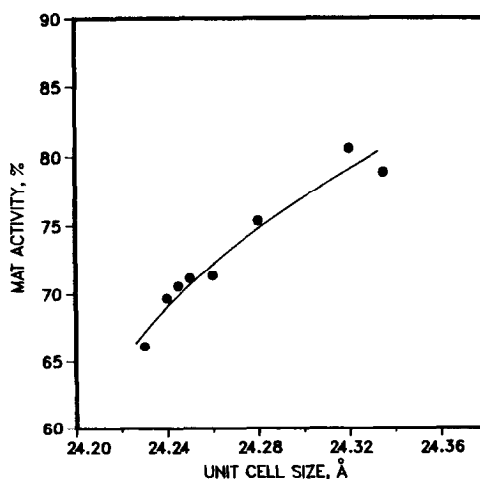


FIG. 1. Dependence of catalyst activity on zeolite unit cell size for catalysts containing 25% REUSY.

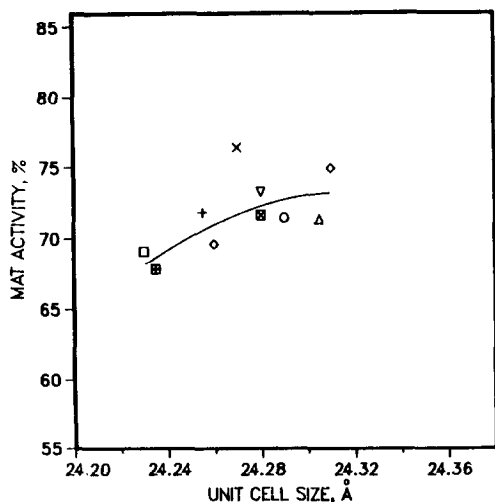


FIG. 2. Dependence of catalyst activity on zeolite unit cell size for catalysts containing 20% zeolite. See Table 1 for zeolite classifications.

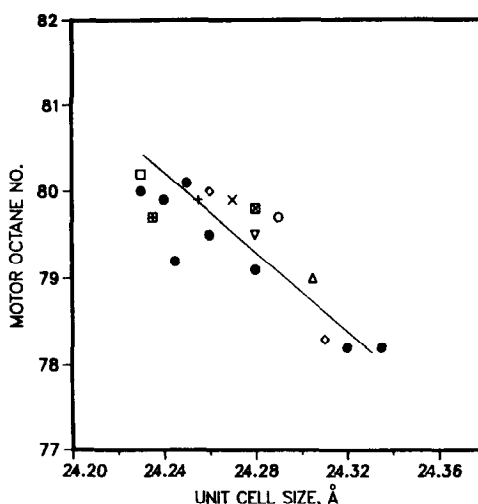


FIG. 4. Dependence of naphtha motor octane number on zeolite unit cell size. Naphtha boiling range is 18 to 221°C and values reported are unleaded octane numbers. See Table 1 for zeolite classifications.

zeolite in the steamed catalyst that is actually causing the gas oil to crack. It should be noted that all of the unit cell measurements given in Table 1 are for steamed catalysts so they are considerably lower than the unit cell sizes of the fresh zeolite added during the catalyst preparation. Since the unit cell is a measure of the Si/Al ratio of the zeolite framework (3) it also provides a

measure of the total number of tetrahedral aluminum sites per unit cell. These are usually considered to be equal to the total number of potential acid sites per unit cell. As the unit cell size decreases the number of acid sites per unit cell also decreases. This causes the site density to decrease and increases the probability of any given acid site becoming more isolated from other acid sites. If it is postulated that the acid

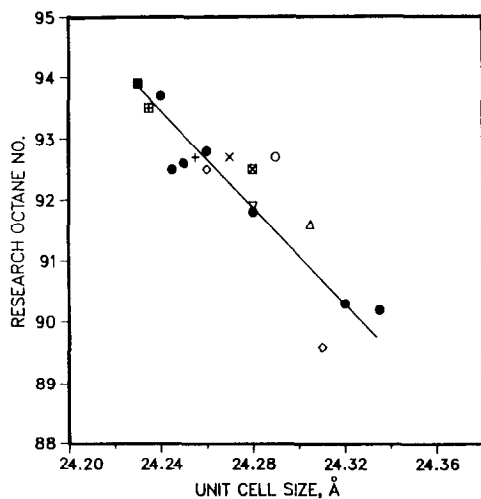


FIG. 3. Dependence of naphtha research octane number on zeolite unit cell size. Naphtha boiling range is 18 to 221°C and values reported are unleaded octane numbers. See Table 1 for zeolite classifications.

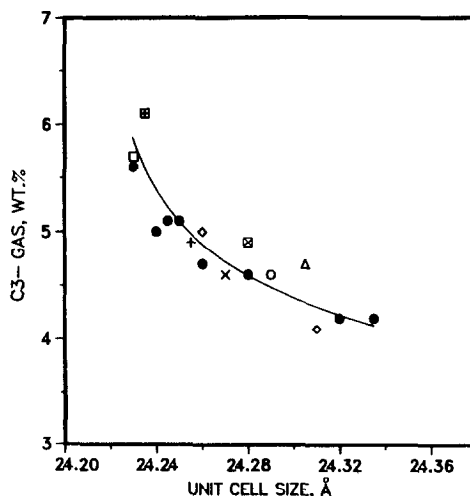


FIG. 5. Dependence of C<sub>3</sub>- gas yield on zeolite unit cell size. See Table 1 for zeolite classifications.

strength of a site is determined by its degree of isolation from its neighboring acid sites, the unit cell size becomes a measure of acid strength distribution as well as a measure of total acidity in the zeolite.

In the last few years there have been several papers on the distribution of silicon and aluminum atoms in the synthetic faujasite structures based on solid state NMR measurements (4-6). These authors have used solid state  $^{29}\text{Si}$  NMR to measure the relative concentrations of five nonequivalent silicon atoms in faujasites. These nonequivalent silicon atoms represent tetrahedrally coordinated silicon bonded to zero, one, two, three, or four O-Al groups in the zeolite framework. From these measurements it is possible, in some cases, to deduce complete zeolite structures. While there are some differences in opinion regarding the exact structures of low Si/Al ratio synthetic faujasites, the data generally support the conclusion that at the higher Si/Al ratios the distribution of aluminum is random within the constraints of Lowenstein's rule. Lowenstein's rule simply states that tetrahedral Al-O-Al linkages are not found in faujasite (7). More recently, the silicon distribution has been followed during the transition from Y to USY (8). As expected, the number of tetrahedral silicas bound to one or more alumina neighbors decreased while the number of silicas bound only to other silicas increased. It would be reasonable to assume on the basis of these measurements that the number of isolated aluminum sites must also be increasing as this transition to the lower unit cell material takes place. In a direct analogy of the different types of silicon tetrahedra detected by NMR, it can be postulated that there are different types of tetrahedral aluminum present in faujasite. Since Lowenstein's rule requires that each aluminum atom be bonded to four silicon atoms via an oxygen bridge, the different types will not be distinguished by their nearest neighbors as is the case with the silica tetrahedra. They can, however, be distinguished by their next

nearest neighbors (NNN). A completely isolated aluminum tetrahedron will have zero next-nearest alumina neighbors and is called a 0-NNN site. An alumina tetrahedra having one next-nearest alumina neighbor is called a 1-NNN site. This nomenclature can be carried out to the upper limit of 9-NNN sites in faujasite. While all of the aluminum sites are potentially strong acid sites, it is further postulated that the most isolated sites (0-NNN) are stronger than the 1-NNN sites and so on. This order of strength is consistent with the results of Beaumont and Barthomeuf who found that the effective acidity of zeolites X and Y increased as the number of sites per unit cell decreased (9). Kerr has reviewed similar findings by other workers (10).

Once it is accepted that different types of acid sites exist and that they are randomly distributed throughout the zeolite structure, it is possible to devise a simple statistical model to count the number and distribution of these sites. In the simplest form the only constraints that need to be met are (1) Lowenstein's rule, (2) no nonframework cations other than protons can be present, and (3) all tetrahedral sites must be crystallographically identical. These constraints combined with a binomial distribution resulted in the distribution shown in Fig. 6. A more general form of this same model is discussed by Wachter (11). It is apparent that the region of predominant strong acid sites is  $<24.31 \text{ \AA}$ . Peters has made a similar calculation for the silica tetrahedra using a log normal distribution (12).

For applications in commercial cracking catalysts, zeolite activity, and hydrothermal stability are both important issues. For zeolite activity, we would expect from the model that zeolites with high unit cell constants would make more active catalysts, due to the low Si/Al ratios and greater acid site densities. For hydrothermal stability, a relation between the density of acid sites and zeolite thermal stability has been proposed previously by Kühl and Schweizer

(13). In their analysis, stability requires  $(\text{SiO}_2 + \text{NaAlO}_2)/\text{HAlO}_2$  ratios of 5 or greater with lower values resulting in loss of zeolite integrity. Combining these two effects, one would then expect that catalysts formulated with high silica zeolite, such as USY, would initially be less active than a low silica analog, but would retain a better fraction of that activity under severe hydrothermal treatments.

These predictions are borne out with the data in Tables 4 and 5. Zeolite instability is seen for REY, a low Si/Al ratio zeolite, after exposure to steam at 760 or 816°C. Under these conditions, however, the USY zeolite retains a high fraction of surface area and crystallinity. Note that catalysts incorporating these zeolite types show a reversal in relative activities at the same conditions where REY instability becomes a significant factor. Thus, at low severities, REY gives a more active catalyst due to the high acid site density but this advantage is lost at high severities where the close proximity of acid sites causes destabilization of the zeolite structure and a resultant loss in cracking activity.

The acidity calculated from the model and the catalytic activity of a zeolite can be directly related. For gas oil cracking catalysts, the data in Figs. 1 and 2 can now be related to the zeolite acidity discussed above. As the unit cell constant increases, so does the zeolite acidity and thus catalyst activity. In the region of interest, only the stronger acid sites (0-NNN and 1-NNN) are present. The data in Fig. 2 indicate that it does not matter by what means the unit cell is changed. These data, as well as the selectivity data give in Table 2 and Figs. 3 through 5 clearly indicate that it is the acid distribution of the zeolite as measured by unit cell size that is the fundamental factor affecting catalyst activity and selectivity. The effect of rare earths on catalyst performance is an indirect effect in that different concentrations cause the zeolite in the catalyst to equilibrate to different unit cell sizes upon steaming. It does not matter whether

the rare earths are preexchanged or postexchanged into the zeolite or whether one starts with Y rather than a USY zeolite. After steaming, any differences due to preparative methods are gone. It is important to note that it is the characteristics of the steamed zeolite that are significant as these characteristics are representative of the catalyst in a commercial cracking unit. Since we see no difference between the actinides, thorium and uranium, and the mixed lanthanides used in the other catalyst preparations, we doubt that the Brønsted acidity attributed to the hydrolysis of rare earths ions (14) is important in commercial cracking catalysts. Changing the zeolite by non-iron exchange methods as was done in catalysts H, I, and J further points to the conclusion that it is the unit cell size and the acid distribution determined by that unit cell size that is controlling catalyst performance. The data from this study do not directly indicate whether Lewis or Brønsted sites are the most important in catalytic cracking under commercial conditions. However, the data do indicate that any changes in the ratio of these sites brought about by exchanging the zeolite with different cations are not of direct importance to either activity or selectivity.

Although the relationship between acid-

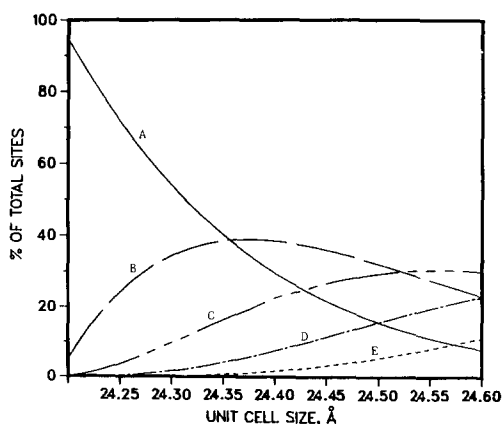


FIG. 6. Acid site type distribution as a function of zeolite unit cell size. (A) 0-NNN, (B) 1-NNN, (C) 2-NNN, (D) 3-NNN, (E) 4-NNN.



ity and activity for zeolites is well documented, there is little published information on the relationship between acidity and selectivity for zeolite-containing catalysts in gas oil cracking. In a study on the cracking of gas oil over catalysts containing USY and rare earth-exchanged USY, Scherzer and Ritter (15) found selectivity patterns similar to those reported in this study. They attributed the selectivity changes to an increase in hydrogen transfer brought about by the presence of the rare earth ions. Hydrogen transfer is clearly a concerted reaction (16) that should be enhanced by a high site density. Lowering the unit cell size of the zeolite lowers site density at the same time as it raises the percentage of strong acid sites. It is not always possible to separate the effects of these two phenomena. However, let us first consider site density.

In Fig. 7 a conceptual picture of the gas oil cracking process is presented. A carbonium ion adsorbed on the surface can either abstract a hydride ion from a coadsorbed molecule to form a paraffin or it can crack into an olefin and a smaller carbonium ion. When acid sites are isolated, hydride abstraction becomes more difficult and cracking to form olefins is preferred. When acid

sites are congested, hydrogen transfer predominates and thus paraffins are preferred. In terms of product qualities, this difference in reaction pathways can strongly influence naphtha octanes. Olefinic molecules have a much improved octane compared to the companion paraffinic species. This is shown in the research and motor octane response in Figs. 3 and 4 and by the bromine number and butylenes yield data in Table 2. Octanes in the low unit cell size region are quite good but drop substantially as this parameter is increased and isolated acid sites are lost. The decrease in hydrogen transfer, which leads to a more olefinic naphtha, also leads to more severe cracking and higher gas makes. Figure 5 shows how the  $C_3$ - gas yield increases markedly in the region of low unit cell size.

We have one example where the selectivity effects of two different types of acid sites could be separated. It was observed that there was a marked change in naphtha octane with soda level for a series of catalysts all made with USY (see Fig. 8). The variation in unit cell size for this data set is due to small variations in steaming conditions and is far too small to account for the sudden increase in octane observed at very

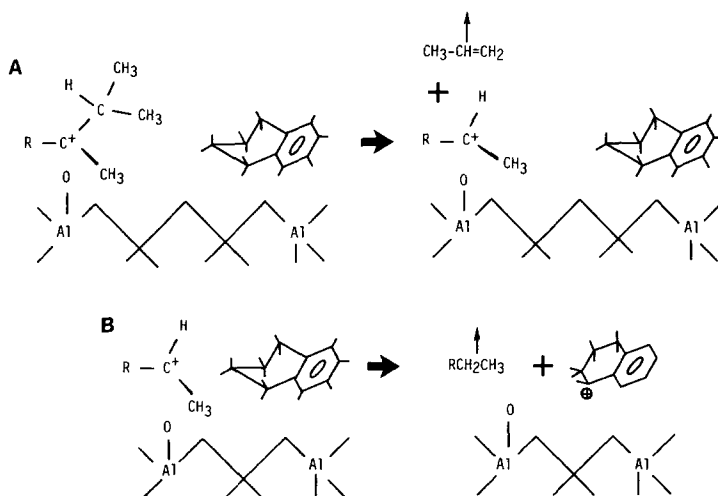


FIG. 7. Comparison of reaction products from isolated and congested acid sites. (A) Isolated acid sites allow for a more olefinic product. (B) Congested acid sites lead to hydrogen transfer and a more paraffinic product.

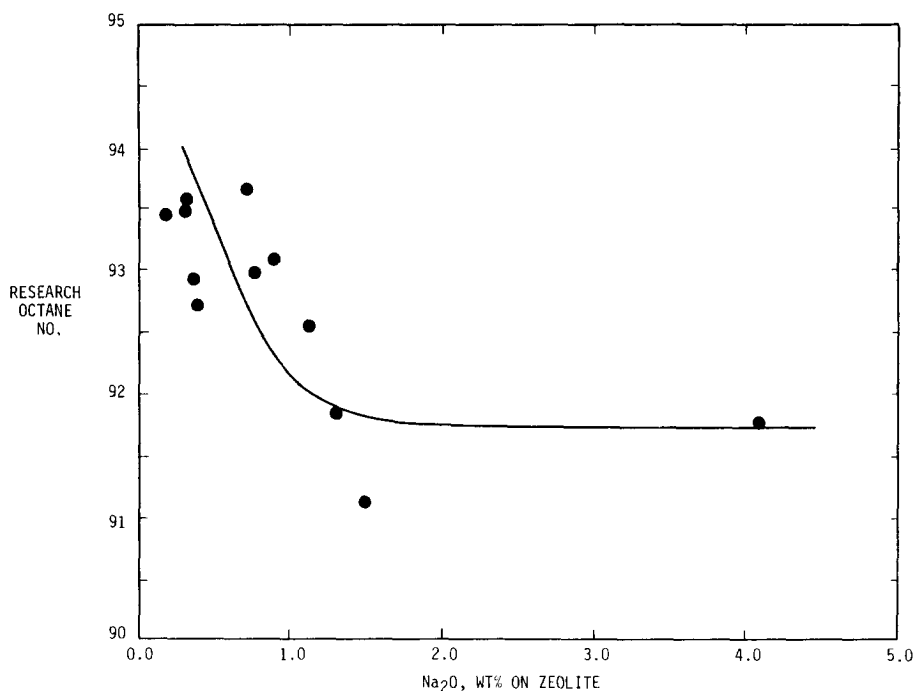


FIG. 8. Dependence of naphtha research octane number on soda content of zeolite. Unit cell size for the zeolite in these catalysts ranges from 24.22 to 24.25 Å. Naphtha boiling range is 18 to 221°C and values reported are unleaded octane numbers.

low soda levels. It should also be pointed out that the activities of the catalysts shown in Fig. 8 were about equal. It requires higher levels of soda to have a significant effect on catalyst activity. It is well known that soda is fairly mobile under catalytic cracking conditions. Conceptually it would be expected that the sodium ions would distribute themselves so as to preferentially neutralize the strongest (0-NNN) acid sites.

TABLE 6

Calculated Soda Levels for Complete Neutralization of Zero-Next Nearest Neighbor Sites

Cell constant (Å)	Average number of acid sites/unit cell	Na <sub>2</sub> O, wt% To poison 0-NNN sites only
24.22	3.5	0.80
24.23	4.6	0.99
24.24	5.8	1.23
24.25	7.0	1.33

A calculation can be made for neutralizing the 0-NNN sites by titrating them with sodium. For unit cell constants ranging from 24.22 to 24.29 Å, the results are given in Table 6. Note that the break in the octane curve in Fig. 8 is near the 1% Na<sub>2</sub>O on zeolite required to neutralize all of the 0-NNN sites for catalysts with this range of unit cell size. The inference is that 0-NNN sites have a much more profound effect on octane producibility than the 1-NNN sites that make up most of the remaining acid sites. While this still does not settle the question as to whether the difference is due to site isolation or acid strength, it probably explains a similar effect of soda level on octane described by Brown and co-workers (17).

#### CONCLUSIONS

In this work we have given experimental results for cracking catalysts containing a wide range of zeolites. As a unifying factor,

the unit cell constant can be used to correlate the acidity, activity, stability, and selectivity of these catalysts. The data show that the experimental method used to achieve a certain unit cell size in the steamed catalyst has no effect on catalyst performance. The unit cell size is an effective correlating parameter because it is a measure of the number and type of acid sites present in the zeolite crystal structure. A model has been developed for calculating the distribution of the different types of acid sites resulting from the different types of tetrahedral alumina. The most important factor affecting catalyst selectivity to high-octane naphtha is the suppression of hydrogen transfer reactions by highly separated acid sites in low unit cell size zeolites. The effect of low levels of soda on octane producibility can be suitably explained in terms of 0-NNN site neutralization.

#### REFERENCES

1. Ciapetta, F. G., and Henderson, D. S., *Oil Gas J.* **65**, 88 (1967).
2. Wachtel, S. J., Baillie, L. A., Foster, R. L., and Jacobs, H. E., *Oil Gas J.* **70** 104 (1972).
3. Breck, D. W., and Flanigen, E. M., in "Molecular Sieves" (R. M. Barrer, Ed.), p. 47. Society of the Chemical Industry, London, 1968.
4. Melchior, M. T., Vaughan, D. E. W., and Jacobson, A. J., *J. Amer. Chem. Soc.* **104**, 4859 (1982).
5. Ramdas, S., Thomas, J. M., Klinowski, J., Fyfe, C. A., and Hartman, J. S., *Nature (London)* **292**, 228 (1981).
6. Engelhardt, G., Lippmaa, E., and Magi, M. J., *J. Chem. Soc., Chem. Commun.* **1981**, 712.
7. Loewenstein, W., *Amer. Mineral.* **39**, 92 (1954).
8. Klinowski, J., Thomas, J. M., Fyfe, C. A., and Gobbi, G. C., *Nature (London)* **296**, 533 (1982).
9. Beaumont, R., and Barthomeuf, D., *J. Catal.* **26**, 218 (1972).
10. Kerr, G. T., in "Molecular Sieves" (W. Meier and J. B. Uytterhoeven, Eds.), p. 219. Amer. Chem. Soc., Washington, D.C., 1973.
11. Wachter, W. A., "Statistical and Topological Approach to Modeling Zeolite Acidity, Activity, and Stability." Sixth International Zeolite Conference, Reno, July 1983.
12. Peters, A. W., "Random Siteing of Aluminum in Faujasite." Symposium on Advances in Zeolite Chemistry, Division of Petroleum Chemistry, Amer. Chem. Soc. Mtg., Las Vegas, Nevada, March 1982.
13. Kühl, G. H., and Schweizer, A. E., *J. Catal.* **38**, 469 (1975).
14. Plank, C. J., "Proceedings, 3rd International Congress on Catalysis, Amsterdam, 1964," p. 727. North-Holland, Amsterdam, 1965.
15. Scherzer, J., and Ritter, R. E., *Ind. Eng. Chem. Prod. Res. Dev.* **17**, 219 (1978).
16. Gates, B. C., Katzer, J. R., and Schuit, G. C. A., "Chemistry of Catalytic Processes," p. 39. McGraw-Hill, New York, 1979.
17. Brown, S. M., Reagan, W. J., and Woltermann, G. M., U.S. Patent 4,325,813 (1982).