

Role of ZSM-5 and Ultrastable Y Zeolites for Increasing Gasoline Octane Number

ROSTAM J. MADON

Engelhard Corporation, Menlo Park, CN 40, Edison, New Jersey 08818

Received September 6, 1990; revised December 10, 1990

Octane number of gasoline made in a fluid catalytic cracker can be catalytically enhanced by using an ultrastable HY zeolite instead of one containing rare earth cations or by adding small amounts of ZSM-5 to a Y zeolite catalyst. ZSM-5 addition catalyzes both normal and branched olefin cracking to give mainly propylene, butenes, 2-methyl 1-butene, and 2-methyl 2-butene. Increase in octane number is mainly due to an increase in yields of C_5 hydrocarbons, an increase in aromatic concentration, and a decrease in yields of C_7^+ paraffins and straight olefins. The decrease in paraffin yield is due to the removal of olefins which would otherwise undergo secondary hydrogen addition. The USY zeolite gives a lighter gasoline with higher yields of C_5 and C_6 branched olefins than the REY zeolite which gives higher yields of C_7^+ branched paraffins. However, the USY catalyst, unlike the ZSM-5 addition case, does not decrease the yields of C_7^+ olefins. Reaction pathways that affect gasoline composition are different for the two cases; yet, in both cases, increases in C_5 hydrocarbons and decreases in C_7^+ paraffins contribute significantly to the increase in octane number. © 1991 Academic Press, Inc.

INTRODUCTION

Increasing gasoline octane number during fluid catalytic cracking (FCC) remains an important objective at most refineries. Two catalytic routes have been commercially successful. First the use of ultrastable HY (USY) catalysts instead of Y zeolites containing rare earth cations (REY); and second, the use of ZSM-5 in small amounts as an additive to a Y cracking catalyst. The first approach is dependent predominantly on the change in reaction chemistry due to the ready decrease in zeolite unit cell size (ucs) and the reduction in framework Al (Al_F) of a working USY catalyst compared to a working REY catalyst. The second approach is related to the unique shape selective property of the 10-membered ZSM-5 sieve (1). Discussions related to gasoline octane number increases with these two approaches have been given in Refs. (1-6).

This paper focuses on explaining reaction routes that result in forming and/or concen-

trating high octane number hydrocarbons in gasoline. It does not describe commercial strategies for ZSM-5 addition which have already been ably dealt with by Schipper *et al.* (2). To this end, our contribution draws upon and expands on earlier discussions (2-6). Although the paper concentrates on explaining the role of ZSM-5 for enhancing gasoline octane number, it also attempts to compare similarities and dissimilarities between the two routes for octane number enhancement: ZSM-5 addition to a Y catalyst versus the use of a USY catalyst by itself.

EXPERIMENTAL

All experiments were performed on an ARCO type FCC pilot unit containing a folded riser, disengager, stripper, and regenerator. A 2300-g catalyst charge was continuously circulated in the unit. At any time 21 g of catalyst were in the 0.4 m riser where gas oil cracking occurred. The temperature of the riser was kept isothermal at 794 K although a portion of the reaction occurred at a higher temperature as the catalyst en-

tered the riser from the hotter regenerator. Catalyst regeneration was done at 958 K with air. The residence time of the catalyst was about 10 s in the riser and about 20 min in the regenerator; hydrocarbon residence time in the riser was about 3 s. As catalysts REY and USY of similar activity were used, catalyst/oil weight ratios for all experiments only varied between 10 to 13.

Experiments were performed with (1) REY to which 1.1% ZSM-5 was added, (2) REY with 2.3% added ZSM-5, and (3) USY with 1.1% added ZSM-5. In further discussions, they are assigned Run numbers 1, 2, and 3, respectively. Conversions for all runs were between 69.8 and 73%; yields were corrected and compared at 70% conversion. Conversion is defined as the percentage weight of gasoline, gas, and coke made from gas oil.

Experiments were first done for 6 h with the base Y zeolite catalyst. Products were collected every hour and analyzed via gas chromatography and simulated distillation chromatography (ASTM D2887). The catalyst did not deactivate during the run. After 6 h, ZSM-5 was added to the unit and a second 6-h experiment was carried out, again with hourly product analyses and material balance checks. Results after the first and sixth hour were the same. At the end of the experiments, the hydrocarbon product was distilled (15/5 distillation-ASTM 2892), and the product that boiled below 489 K was collected as gasoline. We performed engine octane measurements to obtain both research octane number, RON, (ASTM D2699) and motor octane number, MON, (ASTM D2700) for the gasoline.

We obtained detailed analysis of the gasoline with a PIONA analyzer from Analytical Controls. This multidimensional chromatography technique has proven to be extremely useful for capturing the essence of product changes with catalyst change. In order to ensure the accuracy of the PIONA data, we prepared calibration standards and also obtained such standards from Alphagaz. PIONA parameters were tuned

TABLE 1
Catalyst Properties

	REY	USY
Surface area (m ² g ⁻¹)		
Total	153	157
Pores <2 nm diam	53	57
Zeolite (wt%)	7-9	7-9
Na ₂ O (wt%)	0.4	0.3
Unit cell size (nm)	2.436	2.431
Framework Al/unit cell ^a	13	7.7

^a Calculated from the unit cell size correlation given by Sohn, J. R., DeCanio, S. J., Lunsford, J. H., and O'Donnell, D. J., *Zeolites* 6, 225 (1986).

to resolve C₅ to C₉ hydrocarbons in detail and obtain C₁₀ and C₁₁ hydrocarbons as lumped totals. To look at gasoline structure in even greater detail, we used a 150-m Supelco Petrocol DH⁺ column in a Hewlett-Packard 5890A chromatograph.

Catalysts

Y zeolite catalysts were made via the Engelhard *in situ* crystallization technique (7, 8). Kaolin microspheres were first calcined at 1255 K, and then aged in sodium hydroxide for 6 h at 311 K. After aging, zeolite crystallization took place at 355 K. The microspheres containing the zeolite were first exchanged with ammonium nitrate and then rare earth exchanged to get the REY catalyst. The REY catalyst contained about 11 wt% rare earth as rare earth oxide on a zeolite basis. Exchange with rare earth was of course not done for the USY catalyst. After exchange, the catalysts were flash dried and calcined at about 800 K.

Both catalysts were steamed in 100% steam at atmospheric pressure and 1060 K. In order to obtain catalysts with equal activity, the REY catalyst was steamed for 6 h, whereas the USY catalyst was steamed for 2.75 h. Properties of the catalysts after steam treatment are given in Table 1. For later reference we note that the REY catalyst has a unit cell size 0.005 nm higher than that of the USY catalyst. Activity was mea-

sured by a microactivity test (MAT) similar to ASTM 3907. Our test was carried out with a catalyst to oil weight ratio of 5, using 6 g of catalyst and an oil delivery time of 48 s, and gave gas oil conversion values of 70% for both catalysts. Conversion, in a MAT just like that in the pilot unit, is defined as the percentage weight of gasoline, gas, and coke made from gas oil.

The ZSM-5 we used was not steam deactivated. It was used in a diluted form within a porous, inert matrix. This material is commercially available as Engelhard's Z100 additive. The diluted form is preferable to using pure ZSM-5 in order to obtain a uniform dispersion of the small amount of ZSM-5 in the catalyst-oil mixture.

Gas oil

A midcontinent gas oil with a specific gravity of 0.88 g/cc and an average molecular weight of 260 was used in all experiments. Paraffin, naphthene, and aromatic contents of the oil were 22, 33, and 45 vol%, respectively. The gas oil had a total Ni and V content less than 0.5 ppm, sodium content of 5 ppm, and basic nitrogen content of 250 ppm. The final boiling point obtained via simulated distillation chromatography was 812 K, with a 10% distilled value of 532 K.

RESULTS

The effect of adding ZSM-5 to a Y cracking catalyst is best noted by comparing the change in product yields as *weight percent on feed basis*. In this way, we can readily discern whether certain hydrocarbons or sets of hydrocarbons are formed or destroyed due to the presence of ZSM-5. Gasoline yield decreases by 4.4, 6.5, and 3.1 wt% for Runs 1, 2, and 3, respectively; while C₃ and C₄ hydrocarbon (LPG) yield increases by the same amount. Such an effect of ZSM-5 is well known and documented (2). We observe no change in hydrogen, methane, ethane, and coke yields even when 2.2 wt% ZSM-5 is added. In all cases, however, there is a small increase in ethylene formation. Changes in gasoline octane

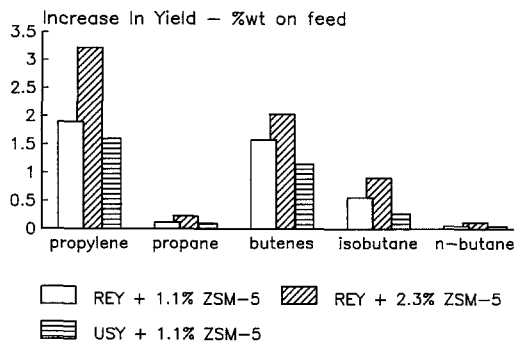


FIG. 1. Increase in yields of various LPG components. The yield increase is the difference in yields between yields obtained with the base case Y zeolite and after ZSM-5 was added to the Y catalyst. Yields are given as wt% on feed.

number are very dependent on feed properties and reaction conditions. Here, with REY and USY catalysts research octane numbers are 87.0 and 89.8, and motor octane numbers are 77.1 and 78.1, respectively. For Runs 1, 2, and 3 RON increased by 1.9, 3.9, and 1.9 numbers while MON increased by 0.7, 1.6, and 0.6 numbers, respectively. We note, comparing Runs 1 and 3, a slightly lower gasoline loss for the same RON increase with the USY catalyst. We also note that doubling the ZSM-5 content between Runs 1 and 2 doubled RON and MON increases but did not double the decrease in gasoline yield. We attempt later to explain these two observations when we discuss why octane numbers increase with concurrent decrease in gasoline yield.

As indicated in Fig. 1, yields of propylene and butenes show the largest increase in the LPG fraction. For Runs 1, 2, and 3, respectively, the relative increase in propylene is 58, 91, and 43%, and for butenes the increase is 36, 45, and 24%. Of the four butenes, isobutylene showed the largest yield increase. We also note an absolute increase in isobutane formation though not as large as for the olefins. Propane and butane, which have low yields with the base Y catalysts, do not show a large absolute increase with ZSM-5 addition. On a relative basis,

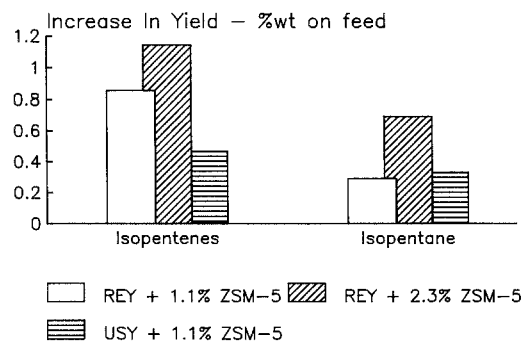


FIG. 2. Increase in yields of isopentenes and isopentane.

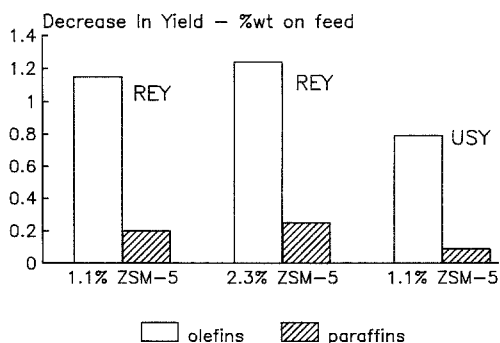


FIG. 3. Decrease in yields of C₆-C₉ straight chain olefins and *n*-paraffins.

alkanes do increase; for Run 2, for example, propane increases by 60% and butane by 40%.

Yields of branched pentenes and isopentane increase after ZSM-5 addition (Fig. 2). Details of C₅ hydrocarbon yields for Run 2 are given in Table 2. The formation of branched hydrocarbons increases substantially, whereas straight hydrocarbons are hardly affected. The concentration of all C₅

hydrocarbons in gasoline, however, is increased; for Run 2, we have a 50% increase of C₅ concentration in gasoline. C₆ hydrocarbons, except for the straight chain alkenes which decrease by 40%, remain relatively unchanged. The overall C₆ concentration in gasoline is not affected to the same extent as the C₅ hydrocarbon concentration.

Before discussing yield changes of heavier hydrocarbons, we recall that our PIONA analysis was tuned to give the most accurate information in the C₅ to C₉ hydrocarbon range. Hence in the following description only results up to C₉ hydrocarbons are given. However, there are relatively few aliphatic hydrocarbons in the C₁₀⁺ range in FCC gasoline, and we assume that C₁₀⁺ aliphatic hydrocarbon chemistry will mimic that of C₉ hydrocarbons. Therefore, all discussion for C₉ aliphatic hydrocarbons is assumed to hold for C₁₀⁺ aliphatic hydrocarbons.

The decrease in the yields of C₆ to C₉ straight chain aliphatics and C₇ to C₉ branched aliphatics is given in Figs. 3 and 4, respectively. These results are in accord with those given in Ref. (4). We see in Fig. 3 that the decrease in olefin yield is substantially higher than the corresponding decrease in *n*-paraffins. Branched aliphatics, on the other hand, show approximately equal decreases in olefin and paraffin yields. Like butane and propane, the yield of C₅ to C₁₀ *n*-paraffins is always very low in FCC

TABLE 2
C₅ and C₆ Hydrocarbon Yields^a

	REY	REY + 2.3% ZSM-5
C ₅		
<i>n</i> -Pentane	0.30	0.37
Isopentane	1.3	2.0
1-Pentene	0.25	0.28
<i>trans</i> -2-Pentene	1.2	1.2
<i>cis</i> -2-Pentene	0.66	0.62
3-Methyl-1-butene	0.05	0.07
2-Methyl-1-butene	0.53	1.0
2-Methyl-2-butene	1.7	2.4
C ₆		
<i>n</i> -Hexane	0.28	0.25
Branched alkanes	3.0	2.9
Straight chain alkenes	1.4	0.83
Branched alkenes	2.5	2.4

^a Wt% on feed basis.

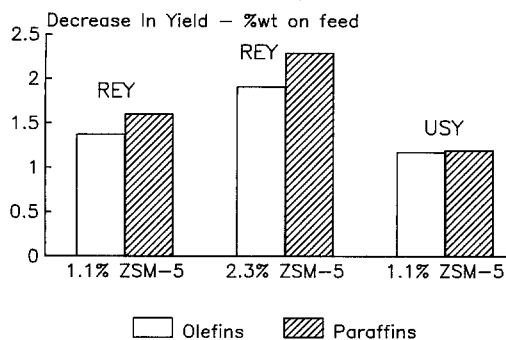


FIG. 4. Decrease in yields of C₇-C₉ branched olefins and branched paraffins.

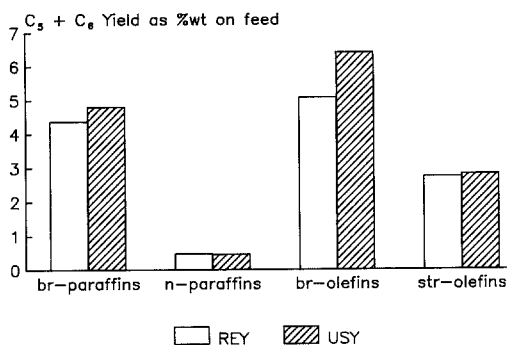


FIG. 6. Yields of straight (str) or normal, and of branched (br) C₅ + C₆ aliphatic hydrocarbons using REY and USY catalysts.

gasoline, with the total concentration of *n*-paraffins in all our cases being less than 2.5 wt%. Although the absolute changes for *n*-paraffins are small, there is a decrease of C₆ to C₉ *n*-paraffin yield in the presence of ZSM-5 by 20, 27, and 11% for Runs 1, 2, and 3, respectively. However, the main results to focus on are the large decreases in the yields of olefins. This, as we discuss later, is critical for understanding the role of ZSM-5 in FCC. Finally in Fig. 5 we show that there is no increase in aromatic formation. Note that doubling ZSM-5 addition from 1.1 to 2.3 wt% gives identical aromatic formation. The concentration of aromatics in gasoline increases by about 5% for all three runs. Similarly there is no increase in naphthene formation, and a small increase in naphthene concentration is observed.

Table 3, parts 1 and 2, offers a more detailed comparison for Run 2 by giving molar concentrations of hydrocarbons in gasoline. Gasoline yields are 55.7 wt% with the REY catalyst and 49.2 wt% with added ZSM-5. Note that though ZSM-5 addition increases the concentration of light hydrocarbons, C₅ to C₉ branched and *n*-paraffin concentrations, as well as total olefin concentrations, are similar in both cases.

So far we have given results of product yields affected by the addition of ZSM-5 to a USY and a REY catalyst. Let us now compare gasoline structure of a USY and a REY catalyst without any ZSM-5 addition. The unit cell size of the REY catalyst is

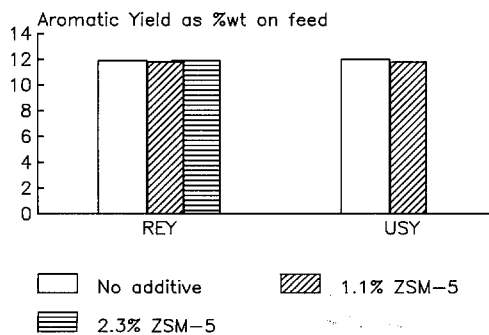


FIG. 5. Aromatic yields as wt% on feed.

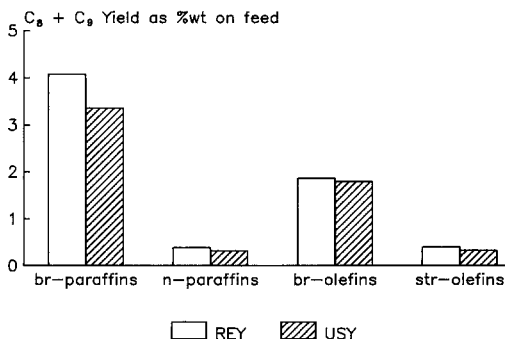


FIG. 7. Yields of straight (str) or normal, and of branched (br) C₈ + C₉ aliphatic hydrocarbons using REY and USY catalysts.

TABLE 3
Molar Concentrations of Hydrocarbons in Gasoline (Values in mol%)

	Saturates			Unsaturates			Aromatics
	Branched	Straight	Naphthenes	Branched	Straight	Naphthenes	
1. REY catalyst + 2.3% ZSM-5							
C ₅	6.0	0.76	0.16	10.4	4.3	0.55	—
C ₆	7.2	0.61	3.2	6.4	2.0	2.0	0.43
C ₇	3.6	0.29	4.2	2.1	0.31	2.0	2.7
C ₈	2.6	0.23	3.5	1.1	0.11	0.9	5.2
C ₉	1.9	0.23	2.5	0.5	0.05	0	7.3
Total	21.3	2.12	13.56	20.5	6.77	5.45	
C ₁₀ ⁺ = 10.1						C ₁₀ aromatics =	4.6
						Total	20.23
2. REY catalyst							
C ₅	3.6	0.54	0.13	6.4	3.8	0.48	—
C ₆	6.7	0.61	2.4	6.1	2.9	1.9	0.39
C ₇	5.0	0.45	4.0	3.8	1.2	1.9	2.3
C ₈	3.7	0.33	3.6	2.0	0.44	0.9	4.9
C ₉	2.6	0.29	2.6	0.93	0.17	0	7.2
Total	21.6	2.22	12.73	19.23	8.51	5.18	
C ₁₀ ⁺ = 11.3						C ₁₀ aromatics =	4.4
						Total	19.19
3. USY catalyst							
C ₅	4.4	0.55	0.13	8.5	4.2	0.47	—
C ₆	6.8	0.55	2.2	7.2	2.8	2.0	0.38
C ₇	4.6	0.37	3.7	4.0	1.1	2.1	2.3
C ₈	3.1	0.25	3.3	1.9	0.38	1.1	4.9
C ₉	2.1	0.23	2.2	0.9	0.15	0	7.0
Total	21.0	1.95	11.53	22.5	8.63	5.67	
C ₁₀ ⁺ = 9.7						C ₁₀ aromatics =	4.4
						Total	18.98

0.005 nm larger than the USY catalyst. Gasoline yield with the USY catalyst is 54.6 wt%; a yield 1.1 wt% lower than that with the REY catalyst, but with a 2.8 and 1.0 number increase in RON and MON, respectively. These results are directionally similar to those in Ref. (5).

Table 3, parts 2 and 3, gives the molar concentrations of hydrocarbons in gasoline obtained with REY and USY catalysts. The similarity of the gasoline concentrations is quite remarkable given the fact that the difference in research octane number is as high as 2.8. Aromatic contents are similar, and the total values of various saturated and unsaturated species are close. However, gasoline made with the USY catalyst gives higher

amounts of light branched aliphatic hydrocarbons. Figures 6 and 7 show these differences in aliphatic hydrocarbon formation by plotting yields as wt% on feed basis. Figure 6 shows that 26% more C₅ and C₆ branched olefins and 10% more C₅ and C₆ branched paraffins are made with the USY catalyst. On the other hand, 20% more C₈ and C₉ branched paraffins, Fig. 7, are made with the REY catalyst. Figure 7 also indicates that C₈ and C₉ branched and straight chain olefin yields with REY and USY catalysts are close.

DISCUSSION

The Role of ZSM-5

The effects of adding ZSM-5 to a Y cracking catalyst have been quantitatively de-

scribed in the previous section. We find, in agreement with others (2-4) that a small portion of the gasoline is cracked to give LPG and the octane number of the remaining gasoline is increased. In order to describe the reaction pathways via which the above events take place, we need to briefly review some important model compound studies carried out on ZSM-5; in particular, we refer to the work of Haag *et al.* (9).

Haag *et al.* (9) have shown that in ZSM-5 both straight and monomethyl branched olefins crack significantly faster than their paraffin counterparts and that cracking rates increase with chain length. For example, at 811 K, 1-hexene cracks 230 times faster than *n*-hexane; in fact, 1-hexene cracks 10 times faster than even *n*-dodecane. Branched 3-methyl 2-pentene cracks 180 times faster than 3-methyl pentane, 130 times faster than *n*-hexane, and 5 times faster than dodecane. In this way, cracking with ZSM-5 is similar to that in a Y zeolite.

Haag *et al.* conclusively show that there are no intrinsic diffusional barriers for cracking straight and monomethyl aliphatic hydrocarbons in ZSM-5. They explain that any difference in cracking rates of normal and monomethyl branched paraffins, especially at temperatures lower than 773 K, is not due to a sieving effect of ZSM-5 but because the small channel of ZSM-5 exercises a steric constraint on large bimolecular transition states required by monomethyl branched paraffins before they crack. Such bulky complexes are not necessary for cracking *n*-paraffins or straight and monomethyl branched olefins. However, Haag *et al.* show that as one goes from a monomethyl to a dimethyl branched molecule, especially one containing quarternary C, diffusion and shape selective effects become important. Nevertheless, the intrinsic difference in olefin and paraffin cracking rates is so high that even a doubly branched olefin 3,3-dimethyl 1-butene cracks several times faster than *n*-hexane (9). Thus this model compound work reveals that not only do

straight and monomethyl branched olefins crack significantly faster than paraffins, but even dimethyl branched olefins crack faster than paraffins. Our observations also suggest that olefin cracking predominates under our more complex conditions with gas oil as the starting reactant.

Abbot and Wojciechowski (10) show that cracking an olefin results in forming predominantly light olefins with only traces of propane and isobutane at high conversions. Whereas, during cracking of a paraffin, *n*-heptane, Corma *et al.* (11) obtain substantial amounts of light paraffins in the products. The fact that we observe a significant increase in propylene and butenes and a much smaller increase in propane and butanes substantiates our premise that olefin cracking must predominate. Furthermore, Corma *et al.* (11) show that when *n*-heptane cracks on ZSM-5 methane is a primary product, and the propylene/propane ratio is lower than with HY. In our work, we do not observe an increase in methane formation and the propylene/propane ratio is significantly increased when ZSM-5 is used. These observations indicate that in our experiments paraffin cracking is not important.

All the above arguments favor olefin cracking. We note, however, that Refs. (2, 3) indicate that during gas oil cracking ZSM-5 addition catalyzes paraffin cracking. We suggest that in the presence of highly reactive olefins, paraffin cracking with ZSM-5 is minimal. Thus cracking readily explains the decrease in gasoline olefins. Next we rationalize the observed decrease in gasoline paraffin yields (Figs. 3 and 4).

Both straight chain and branched olefins are formed via carbenium ion cracking of large gas oil molecules. We postulate that gasoline range paraffins have at least two sources. A large carbenium ion in the Y zeolite cracks to give a smaller carbenium ion and a free olefin. The smaller carbenium ion remains associated with the Brønsted acid center. Among the various reactions that can take place, one reaction is the transfer of a hydride ion from a saturated mole-

cule to this carbenium ion to form a paraffin. We call a paraffin formed in such a way a primary paraffin, and its formation cannot be influenced by the presence of ZSM-5. There are several pathways available to the free olefin. It can be protonated at a Brønsted acid site in the Y catalyst. Again among the various reactions that can take place with this newly formed carbenium ion, the important one for us to consider is H^- addition to give a paraffin. Such paraffins are thus formed via a secondary process, i.e., readsorption of a free olefin. Another pathway giving secondary paraffins may be due to direct hydrogenation with labile hydrogen from coke; metal contaminants if present would accelerate such hydrogenation. The secondary formation of paraffins can be decreased by the presence of ZSM-5.

Some of the olefins instead of readsorbing in the Y zeolite escape from it and are captured by ZSM-5. As discussed above the olefins are readily cracked in ZSM-5 to give two smaller olefins. In this way, ZSM-5 captures and cracks olefins formed in the Y zeolite. Olefins which could have potentially reentered a Y zeolite and reacted via the secondary route to form paraffins are destroyed, and an important pathway to paraffins is thus strongly influenced by the presence of ZSM-5. ZSM-5 cracks substantial amounts of C_6^+ straight chain and C_7^+ branched chain olefins, and thus reduces the reactants for the formation of secondary paraffins in that size range. The overall paraffin content of gasoline decreases in the presence of ZSM-5; and we do not need to invoke the cracking of paraffins to explain this observation.

An explanation given in Ref. (3) suggests that ZSM-5 preferentially cracks carbenium ions rather than the less reactive paraffins. However, carbenium ions once formed in Y cannot escape to be later captured by ZSM-5. Carbenium ions are unstable intermediates and must be associated with Brønsted acid sites on which they are

formed. Only the resulting product hydrocarbons emerging from the Y catalyst can enter and react within ZSM-5. Hence carbenium ions in Y which are precursors to primary or secondary paraffins are not influenced by ZSM-5. We feel it is important to distinguish between primary and secondary pathways for the formation of paraffins, and the fact that ZSM-5 can only influence the formation of secondary paraffins by intercepting and cracking olefins that are able to escape from the Y catalyst.

When a C_7^+ straight chain olefin cracks, the resulting smaller secondary carbenium ion will readily rearrange to a more stable tertiary carbenium ion. Hence the presence of ZSM-5 increases methyl branched C_4 and C_5 isomers in the product. On the other hand, there is very little change in the C_6 fraction except for the straight chain hexenes, some of which crack to propylene. The cracking of branched hexenes, however, seems to be compensated by their formation via the cracking of C_9^+ olefins and skeletal rearrangement of straight chain hexenes. Abbot and Wojciechowski (10) indicate that facile skeletal rearrangement of straight chain hexenes takes place in ZSM-5. For the C_5 fraction there is no change in the yield of straight chain pentenes. However, the cracking of C_8^+ olefins significantly increases the formation of branched pentenes. We also note the increase in isopentane formation.

We can explain the increase in both isobutane and isopentane yields in the same way we explained the decrease in C_7^+ isoparaffins. Though it is possible that isobutane and isopentane can be formed in ZSM-5, it is more probable that they are formed when the C_4 and C_5 branched olefins escape from ZSM-5 and some are captured by the Y catalyst. Here these olefins are protonated, accept a hydride ion, and form their respective isoparaffins. This explanation also fits our observation that since there is no change in branched C_6 olefin yield, there is no change in the yield of isohexanes. The secondary

reaction of olefins to paraffins thus explains the results of aliphatic hydrocarbons in LPG and gasoline. In general we see that the addition of ZSM-5 increases the concentration of all C_5 and some C_6 aliphatic hydrocarbons in the gasoline while decreasing the C_7^+ aliphatic fraction.

So far we have concentrated on reactions with aliphatic hydrocarbons which dominate in the presence of ZSM-5. But before we discuss the effect of these reactions on octane number, we need to comment on the effect of ZSM-5 on the gasoline aromatic fraction. We see from Fig. 5 that there is no increase in aromatic yields in the presence of ZSM-5. It is well known (12-14) that under the right conditions small olefins can be reacted within ZSM-5 to give aromatics. Under conditions and residence times similar to fluid bed cracking, however, there is no incremental formation of aromatics. There is also no increase in the yields of naphthenes. However the concentration of both aromatics and naphthenes in gasoline is increased.

The change in gasoline octane number is due to a balance between favorable and unfavorable events that occur when ZSM-5 is present. Except for 3-heptene, C_7^+ straight chain olefins have low octane numbers; however, 2- and 3-hexenes have RON values greater than 90. Several monomethyl branched C_7 and C_8 olefins have high octane numbers especially when the double bond is in internal positions. For example 2-methyl 3-hexene has a RON of 98 and a MON of 81. ZSM-5 plays a useful role when it removes C_7^+ straight chain olefins, but it hurts octane values by cracking 2- and 3-hexenes and certain branched olefins. Indeed, if ZSM-5 is added to a process, which, due to run conditions, feed, and catalyst type, makes substantial amounts of branched olefins, and if ZSM-5 cracks most of these molecules, the gasoline RON and MON may not increase noticeably and may even decrease.

Though C_7 and C_8 monomethyl branched

olefins have high octane numbers, the corresponding monomethyl branched paraffins have relatively low values; for example, 2-methyl heptane has a RON of only 27. Since monomethyl branched paraffins, usually 2- and 3-methyl branched species, are the most abundant paraffin isomers, decreasing their formation, as discussed above, helps boost gasoline octane number significantly. The small decrease in *n*-paraffin formation similarly helps enhance octane number. The biggest increase in octane number is due to the increased yields of C_5 aliphatic hydrocarbons at the expense of C_7^+ paraffins and straight olefins. Indeed 2-methyl 1-butene and 2-methyl 2-butene have research and motor octane numbers greater than 98 and 80, respectively. Even isopentane has a RON of 92 and a high MON of 90. Another boost in gasoline octane number is due to the increase of the aromatic concentration in gasoline. However, the effect of similar increase in naphthene concentration is more difficult to rationalize, since small branched cyclopentanes and cyclopentenenes have high octane numbers but branched cyclohexanes have low octane numbers.

In the above discussion we have used known octane numbers of pure hydrocarbons. However, the octane number of gasoline depends on the blending octane numbers of individual hydrocarbons. Even though this will not change our discussion regarding the effect of reaction chemistry on gasoline octane number, we cannot explain the absolute relationship between gasoline loss and octane number increase. As we saw from the Results section, doubling the ZSM-5 addition doubled the octane number increases but did not decrease the gasoline yield by the same factor. Such differences are due to the balance, as we have already stated, between favorable and unfavorable events that take place in the presence of ZSM-5, and therefore depend on how blending octane numbers of resulting hydrocarbons affect the overall gasoline octane number.

Ultrastable Y Zeolites

As indicated in the Results section, the USY catalyst, when compared to the REY catalyst, gave a 1.1% lower gasoline yield but with a RON and MON increase of 2.8 and 1.0 numbers, respectively. Inspection of Table 3 reveals that though composition of the gasolines using USY and REY looks remarkably similar, there are two important differences. First the USY catalyst gives a lighter gasoline. Second the USY catalyst gives 26% higher yields of high octane value C_5 and C_6 branched olefins, whereas the REY catalyst gives higher yields of lower octane value C_7^+ branched paraffins. In either case we do not see a change in the paraffins that reflects the opposite change in the corresponding olefins. Indeed, USY even with the lower ucs makes slightly more C_5 and C_6 branched paraffins and about the same C_8 and C_9 branched olefins as the REY catalyst. This is interesting since increased hydride ion transfer in higher ucs catalysts is conventionally recognized (5) as being the key reaction that transforms high octane value olefins to lower octane value paraffins.

It has been proposed (5, 15, 16) that paraffin yields during FCC are increased by increasing the overall reaction of olefins with naphthenes to give paraffins and aromatics. We do not observe this in the C_5 to C_9 range we report; instead the naphthene yields are slightly larger for the REY catalyst and the aromatic yields as seen from Fig. 5 are very close. One could propose that larger naphthenes than those we observe are responsible for hydride ion transfer to carbenium ions. However, we believe it would be difficult for large naphthenes associated with one or more rings to enter deep within a zeolite and react with carbenium ions. Though the general reaction may be relevant in some cases, especially with model systems (17), when comparing very different acid systems (16) or comparing very different unit cell sizes, one must approach its general use for explaining octane number changes in FCC with caution.

In summary our data indicate that octane number differences are due to more than simple hydride ion transfer. Since the USY catalyst makes lighter products than the REY catalyst, we propose that differences in the overall cracking pattern on the two catalysts must play a role that determines gasoline composition. We speculate that hydride ion transfer influences the cracking pattern on the catalysts. Since hydride ion transfer plays such an important role in determining gasoline composition, we will discuss situations that influence the reactions.

Hydride Ion Transfer

Pine *et al.* (5) proposed that two Al sites that are next nearest neighbors are necessary for hydride ion transfer. This hypothesis has recently been questioned (18, 19) on the basis that as Al_F decreases well below 10/uc, hydride ion transfer continues to take place (5, 20). Furthermore, if the paired Al sites are associated with Brønsted acid centers, one would have an energetically unfavorable situation in which a positively charged carbenium ion must transfer H^- to an adjacent carbenium ion. A similar unfavorable situation for H^- transfer exists if paired Al sites are associated with a Brønsted and a Lewis acid center. If one of the Al sites is not associated with an acid site and is capable of adsorbing a saturated molecule then the paired site mechanism is viable. Though such a situation seems possible for catalysts with a high concentration of Al_F , it seems untenable when Al_F amounts are low and where hydride ion transfer still exists (19, 20). We therefore agree with Corma *et al.* (18) that hydride ion transfer occurs between a carbenium ion associated with a Brønsted acid site and a free saturated hydrocarbon: an Eley-Rideal type of reaction. Once hydride ion transfer takes place the new paraffin molecule desorbs and the newly formed carbenium ion takes its place at the vacated site. Carbenium ions on solid acids, unlike those in the liquid medium, must be associated closely with a Brønsted acid site.

Quite simply then decreasing Al_F decreases the number of sites where H^- transfer can take place, and this lowers the conversion of olefins to paraffins. Decreasing Al_F should similarly affect the cracking reaction. We, therefore, need to explain why at times cracking is not affected as markedly as hydride ion transfer. Corma *et al.* (18) argue that since the adsorbed hydrocarbon concentration decreases as Al_F decreases and since H^- transfer is a bimolecular reaction, it will be affected to a greater degree than a monomolecular cracking reaction. However, if H^- transfer as suggested earlier is an Eley–Rideal type of reaction with only one adsorbed reactant, change in concentration of adsorbed carbenium ions will affect H^- transfer and cracking reactions in the same way.

We offer a different explanation for differences in cracking and H^- transfer rates. To do this we need to note that after dealumination treatments the Si/Al ratio on the surface of Y will differ from that in the bulk (21, 22). Dwyer *et al.* (21) indicate that for dealumination via steaming or via $SiCl_4$, the surface of the zeolite is Al enriched. Such measurements, however, can be influenced by the presence of nonframework Al that migrates to the surface of the catalyst during dealumination. In any case, different types of dealumination treatments will give different Si/ Al_F gradients within the zeolite crystal.

Corma and co-workers (19, 20) show that cracking and H^- rates are different for Y catalysts dealuminated by steaming and by $SiCl_4$. Hydride ion transfer reactions are represented in Ref. (19) by the butene/butane ratio measured upon gas oil cracking. The catalysts show similar butene/butane ratios up to Al_F values of 10/uc. For Al_F values less than 10/uc, the steamed catalysts show a large increase in the ratio, whereas the $SiCl_4$ treated samples show a much smaller increase. We suggest that for severe dealumination, i.e., Al_F less than 10/uc, the two techniques give different Al_F distributions in the zeolite, and that the

Brønsted acid strength of steamed catalysts may be decreased by the influence of non-framework Al present at the outer surface of the zeolite.

We extend this reasoning to hydride ion transfer reactions in general. We propose that H^- transfer is a *location sensitive* reaction. Though crystallographically all framework aluminums in Y are equivalent, we speculate that the reaction takes place more readily when a Al_F is situated well within the Y supercage where influences such as those of nonframework Al are minimal. Since the overall concerted transfer process requires H^- donation and stabilization of the new carbenium ion formed, the site at the favorable location must be a sufficiently strong Brønsted acid to allow the transition state to proceed along the reaction coordinate in a facile manner. Stronger acid sites would more readily favor stabilization of the carbenium ion than weak acid sites.

By these arguments we do not imply that H^- transfer does not take place on other solid acids like silica–alumina. It just does not take place at some sites with the same facility as when acid strength and spatial requirements are favorable. Sometimes H^- transfer may be curbed in zeolites like ZSM-5 if spatial constraints limit the formation of bulky transition states (9, 23). Beta scission, on the other hand, being a simpler event, is probably not as sensitive to the acid site as long as a hydrocarbon can arrive at the Brønsted acid site without diffusional or spatial limitations. In summary, we suggest that H^- transfer reactions require stronger Brønsted acid sites than β scission, and that often the strength of such sites, as in steamed Y zeolites, depends on their location.

Finally, Rajagopalan and Peters (24) have shown that coke formation increases as Al_F increases. Hence another possible pathway for paraffin formation, especially on catalysts with Al_F greater than 10/uc, is the secondary hydrogenation of olefins with labile hydrogen from coke and coke precursors within the supercage.

Comparing Octane Number Increase with ZSM-5 Addition and USY Catalyst

Let us compare the results of increasing octane number by these two cases to a REY catalyst. In both cases increase in octane number is accompanied by a loss in the yield of gasoline. For a similar increase in octane number the gasoline yield loss is greater when ZSM-5 is used. Furthermore, gasoline composition is quite perceptibly altered when ZSM-5 is added to a REY catalyst. Comparatively, differences in gasoline composition for REY and USY catalysts are smaller. The reason for the larger variation in gasoline composition with ZSM-5 is as follows. ZSM-5 cracks mainly C_6^+ straight olefins and C_7^+ branched olefins. Since the removal of 2- and 3-hexenes and C_7 and C_8 branched olefins reduces octane number, as compensation, other events must take place for the octane number to increase. Thus ZSM-5 addition involves larger shifts in reaction pathways for increasing gasoline octane number, and hence we observe a significant change in gasoline composition. However, there are commercial advantages for using ZSM-5, and these have been discussed in Ref. (2).

Unlike the ZSM-5 addition case, a USY catalyst does not reduce the C_7^+ branched olefins. It is the change in the overall cracking pattern of both gas oil and gasoline rather than just gasoline that allows USY to make more C_5 and C_6 branched olefins than REY. It is indeed an interesting question as to why Y zeolites do not crack gasoline fraction olefins as readily as ZSM-5. We offer three possible reasons. First, there is more competition between various molecules for adsorption sites in the larger Y supercages, whereas mainly straight and monomethyl aliphatics are easily admitted into ZSM-5. Second, H^- transfer which is much more prevalent in Y than in ZSM-5 competes with β scission and converts olefins to the more refractory paraffins. Finally, a Y zeolite cokes more rapidly than ZSM-5 (25, 26); therefore sites that are needed to crack gaso-

line molecules, a secondary step after larger gas oil molecules are initially cracked, are reduced in number in a Y zeolite.

Before concluding, we wish to reemphasize that in both cases we obtain a lighter gasoline than with a REY catalyst. Though the reaction pathways that lead to changes in gasoline composition for the two cases are different, a significant increase in octane number in each case is due to an increase in C_5 hydrocarbons and a decrease in C_7^+ paraffins.

ACKNOWLEDGMENTS

We thank K. Mathur for supervising the FCC pilot unit, and J. Knarr for setting up and running the PIONA analyzer. We also thank R. Bradway, E. L. Moorehead, and S. J. Tauster for several fruitful discussions.

REFERENCES

1. Chen, N. Y., Garwood, W. E., and Dwyer, F. G., "Shape Selective Catalysis in Industrial Applications," Dekker, New York, 1989.
2. Schipper, P. H., Dwyer, F. G., Sparrell, P. T., Mizrahi, S., and Herbst, J. A., *ACS Symp. Ser.* **375**, 64 (1988).
3. Rajagopalan, K., and Young, G. W., *ACS Symp. Ser.* **375** (1988).
4. Biswas, J., and Maxwell, I. E., *Appl. Catal.* **58**, 1 (1990).
5. Pine, L. A., Maher, P. J., and Wachter, W. A., *J. Catal.* **85**, 466 (1984).
6. Scherzer, J., *Catal. Rev.-Sci. Eng.* **31**, 215 (1989).
7. Haden, W. L., and Dzierzanowski, F. J., U.S. Patent 3,506,594 (1970).
8. Haden, W. L., and Dzierzanowski, F. J., U.S. Patent 3,647,718 (1972).
9. Haag, W. O., Lago, R. M., and Weisz, P. B., *Discuss. Faraday Soc.* **72**, 317 (1981).
10. Abbot, J., and Wojciechowski, B. W., *Can. J. Chem. Eng.* **63**, 462 (1985).
11. Corma, A., Monton, J. B., and Orchilles, A. V., *App. Catal.* **16**, 59 (1985).
12. Garwood, W. E., *ACS Symp. Ser.* **218**, 383 (1983).
13. Derouane, E. G., and Vedrine, J. C., *J. Mol. Catal.* **8**, 479 (1980).
14. Dejaifve, E. G., Vedrine, J. C., Bolis, V., and Derouane, E. G., *J. Catal.* **63**, 331 (1980).
15. Venuto, P. B., and Habib, E. T., "Fluid Catalytic Cracking with Zeolite Catalysts," Dekker, New York, 1979.
16. Weisz, P. B., *Chemtech*, 498 (1973).
17. Cheng, W.-C., and Rajagopalan, K., *J. Catal.* **119**, 354 (1989).
18. Corma, A., Faraldos, M., and Mifsud, A., *Appl. Catal.* **47**, 125 (1989).

19. Corma, A., Faraldos, M., Martinez, A., and Mifsud, A., *J. Catal.* **122**, 230 (1990).
20. Arribas, J., Corma, A., Fornes, V., and Mello, F., *J. Catal.* **108**, 135 (1987).
21. Dwyer, J., Fitch, F. R., Qin, G., and Vickerman, J. C., *J. Phys. Chem.* **86**, 4574 (1982).
22. Scherzer, J., *ACS Symp. Ser.* **248**, 157 (1984).
23. Frilette, V. J., Haag, W. O., and Lago, R. M., *J. Catal.* **67**, 218 (1981).
24. Rajagopalan, K., and Peters, A. W., *J. Catal.* **106**, 410 (1987).
25. Rollmann, L. D., *J. Catal.* **47**, 13 (1977).
26. Rollmann, L. D., and Walsh, D. E., *J. Catal.* **56**, 139 (1979).