Over 25 years ago, two Grace researchers wrote a compelling paper for the American Chemical Society demonstrating that the use of a ZSM-5 additive in Fluid Catalytic Cracking (FCC) was more effective than increasing temperature for maximizing propylene in the FCC process. Grace first described the commercialization of ZSM-5 in *Catalagram* No. 72 in 1985, together with Mobil Corporation as an avenue to achieve higher gasoline octane. In this paper from 1999, Xinjin Zhao and Terry G. Roberie examined the effect of varying levels of ZSM-5 additives versus reactor temperature for maximizing light olefins in FCC products and the implications for gasoline olefins. Most of the tests were conducted in the Grace DCR™ Pilot Plant. While the effect of ZSM-5 on gasoline olefins varies with different systems, the work by Zhao and Roberie proved that ZSM-5 additives reduced C6+ olefins under all the conditions studied.

Employing a catalyst additive approach allows FCC units to accommodate a variety of operational needs without hardware changes or capital investment. Today, ZSM-5 additive technology has become instrumental in producing propylene from the FCC. Grace has continued to innovate in this space and recently launched game-changing catalytic technology with the highest propylene activity and best activity retention in the industry. Grace's ZAVANTI™ ZSM-5 additive is specifically designed for max propylene FCC units and incorporates best-in-class ZSM-5 zeolite, manufacturing techniques, and binding chemistry.

Michael Hawkins
Regional Marketing Manager
W. R. Grace & Co.

ZSM-5 Additive in Fluid Catalytic Cracking

Effect of Additive Level and Temperature in Light Olefins and Gasoline Olefins

Xinjin Zhao, Terry Roberie

Originally published in ***Industrial and Engineering Chemistry Research*** **in 1999 (38 3847-3853)**

The effects of ZSM-5 additive and riser reactor temperature on the product selectivity in fluid catalytic cracking of gas oil were systematically investigated in an adiabatic circulating riser reactor. In addition to the fact that ZSM-5 can substantially increase propylene and butene, it is found that ethylene yield linearly increases with the amount of ZSM-5 in the system. The ethylene is likely from the overcracking of C5 and C6 olefins. The effect of ZSM-5 on gasoline range olefins was clarified. In the temperature range of 794-839 K (970-1050ºF) studied in the current work, ZSM-5 additive always reduces C6 + olefins. The effect of ZSM-5 on C5= is different. C5 olefin increases at 794 K, but decreases at 839 K. Since C5 olefins account for about one-third to one-half of the gasoline olefins, the overall gasoline olefin contents were dominated by the behavior of C5 olefins. Compared with the effect of ZSM-5, the effects of temperature on light olefins are relatively small. Most of the olefin increases with increasing temperature were due to the increased conversion at higher temperature, rather than a selectivity shift. The yields of diolefins increase with temperature. The effect of ZSM-5 on gasoline diolefins was found to be minimal.

Introduction

The use of a variety of additives has significantly improved the flexibility and operation of fluid catalytic cracking (FCC) units over the years.[1,2] Without hardware change, the catalyst additive approach allows FCC units to accommodate a variety of operational needs. In fact, there are probably few commercial FCC units that do not use some kinds of additives for various applications. Although various zeolites have been studied, ZSM-5 remains the only known commercially used zeolite in FCC units other than faujasite. ZSM-5 was first introduced into the fluid catalytic cracking process as an additive for improving gasoline octane in the 1980s.[3] As the current primary role of fluid catalytic cracking as a gasoline fuel producer is shifting toward being a producer for light olefins and other petrochemical feedstocks in many refiners, ZSM-5 is now used primarily to increase the yields of C3 and C4 olefins for alkylations, oligomerization, and other petrochemical processes. With the ever-increasing demands for high proportions of propylene and butene, greater propylene production in refineries will be required. Propylene demand was approximately 39 million tons in 1995 and this is forecast to increase to almost 90 million tons by 2015.[4] The other incentive for propylene production in FCC is to balance the increasing gap between C3=/C2= demand and the C3=/C2= yield ratio from steam naphtha cracking.

There have been numerous studies on the effect of ZSM-5 additive on FCC product selectivity.[5-7] Most of the earlier studies were focusing on octane enhancement and gasoline composition change. For example, Young et al.[8] reported the effects of ZSM-5 additive on gasoline composition and octane levels for various different base catalysts. It was showed that ZSM-5 reduced heavy gasoline olefins (C6+) while increased light olefins (C5-). Much of the earlier work on ZSM-5 application in FCC has been summarized in the book by Chen et al.[9] The most comprehensive studies on the effects of high levels of ZSM-5 additive on light olefins and gasoline compositions were reported by Mobil researchers.[10,11] In those studies, a commercial ZSM-5 additive was used to study the effect of various additive levels at various temperatures. It was found that addition of ZSM-5 additive was much more effective than simply increasing riser temperature for maximizing LPG olefins in fluid catalytic cracking operations. The study also provided detailed analyses of the effect of ZSM-5 on gasoline compositions.

In this paper, we will examine the effect of high levels of ZSM-5 additives vs high temperature for (i) maximizing light olefins in FCC products and (ii) the implications for gasoline olefins. The current study uses a ZSM-5 additive with high crystal content and covers a wide range of ZSM-5 vs faujasite cracking and more systematic data on the additive level. Other than propylene, we will also compare the two different strategies: ZSM-5 additive vs temperature on butene and ethylene levels. The effect of ZSM-5 on FCC gasoline range olefins, the major source of gasoline pool olefins, will also be examined in detail. The effect of temperature and ZSM-5 on gasoline diolefins will also be discussed.

The effects of ZSM-5 on branching, isomerization, etc. have been studied extensively in the literature.[6,8,12] We will focus on the issues that have not been fully explored.

Experiments

Most of the tests were conducted in the Davison circulating riser (DCR). A schematic of the unit is shown in Figure 1. A more detailed description of the unit features and capabilities can be found in the literature.[13] The DCR is a simulated laboratory scale fluid catalytic cracking unit equipped with an adiabatic circulating riser reactor (as in commercial FCC units) and a continuous regenerator. The riser feed rate is controlled at 1000 g/h. The catalyst circulation rate is adjusted by changing the feed preheater temperature to achieve the set reactor outlet temperature. The catalyst circulation rate varies between about 5000 to 9000 g/h for a typical catalyst. For each catalyst and feed combination, we typically obtain four different conversion levels with four different catalyst-to-oil ratios, achieved by adjusting the different feed preheating temperatures from 422 to 644 K (from 300 to 700°F). The experiments were conducted at riser outlet temperatures of 794 K (970°F), 816 K (1010°F), and 839 K (1050°F). Since the riser is adiabatic, the reactor bottom mixing temperature is significantly higher than the reactor top control temperature. A typical temperature gradient from the reactor top to the reactor bottom mixing temperature is about 50 K. The total unit pressure is controlled at 273.7 kPa. As in typical commercial FCC operations, about 3 wt% of steam is used for feed atomization. The vapor phase residence time in the riser is about 1.5-2 s. The liquid and gaseous products were analyzed by gas chromatographs. The liquid effluent products were also analyzed by using GC-simulated distillations for conversion and yield calculations. The conversion was defined as 100% less the weight percent amount of light cycle oil (494-644 K) and heavy cycle oil (>644 K) obtained by GC-simulated distillation. Carbonaceous deposits on the catalyst were analyzed by carbon analyzer (Leco, Corp., St. Joseph, MI). The gasoline composition was analyzed by a Grace-Davision's proprietary octane calculation software based on detailed GC analyses of the gasoline potion of the liquid products. The GC (HP6890) was equipped with a 100 m capillary column. The GC identified typically about 350 components of the gasoline and condensed them into structural groups for data analyses. Some description of the software can be found in the literature.[14,15]

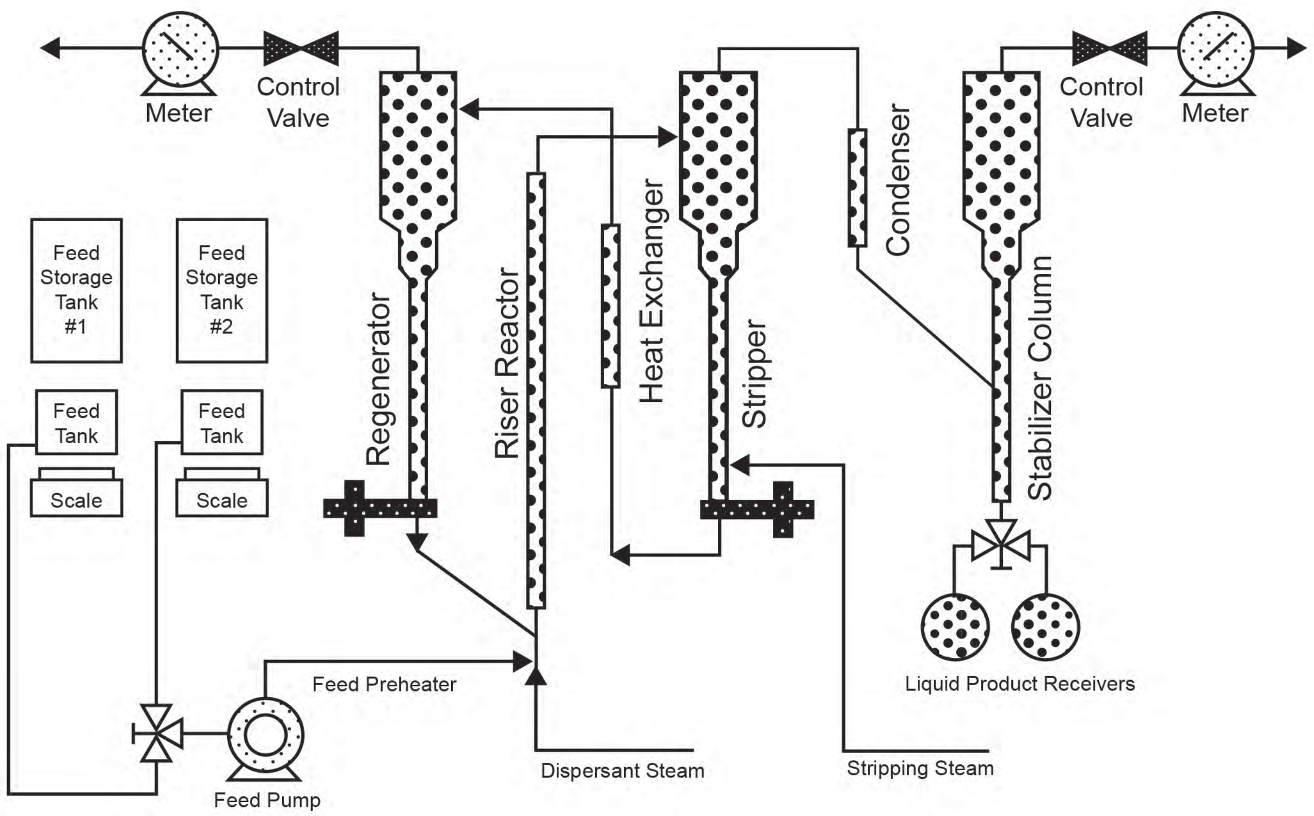

Figure 1. DCR pilot plant schematic.

Description	GCVGO F96-579
API gravity at 60°F	23.9
aniline point,°F	198
sulfur, wt%	0.73
total nitrogen, wt%	0.1
basic nitrogen, wt%	0.042
Conradson carbon, wt%	0.33
average mol wt	388
simulated distillation for vol %, °F	
IBP	464
10	637
50	806
90	977
FBP	1152
K factor	11.81
Cp	59.8
Cn	20.6
Ca	19.6

Table 1. Feed Properties

A commercial FCC gas oil feedstock from a U.S. Gulf Coast refinery was used for the DCR testing. The properties of the feed are shown in Table 1. The feed contains 0.33 wt% of Conradson carbon and has an average molecular weight of about 388. It has a UOP K factor of 11.81. The n-d-M analysis (ASTM D3238) results on the carbon types are also shown in Table 1. It has a feed naphthenic carbon content of 20 wt%.

The base cracking catalyst used in the study was a commercially deactivated equilibrium catalyst originally supplied by Grace Davison. The catalyst properties are shown in Table 2. The catalyst consists of ultrastable Y-zeolites and modified hydrosol matrixes for matrix activity,[16] and balanced with Kaolin clay. The amount of rare earth oxide on catalyst was about 0.75 wt%. The deactivated unit cell size was 2.425 nm. The levels of contaminant nickel and vanadium on the equilibrium catalyst were about 1164 and 1560 ppm. Overall, both the feed and the catalyst used in the current study are representative of a typical commercial FCC system in a current refinery. As a follow up to this work, the effect of base cracking catalyst and feedstocks on the catalytic performance of ZSM-5 in FCC will be systematically investigated and the results will be reported separately.[17]

Continued on Page 9

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	Base Catalyst EQ97-17	ZSM-5 Additive C96-285
	Chemical Analysis	
Al_2O_3, wt%	32.0	32.4
SiO_2, wt%	63.4	45.2
RE_2O_3, wt%	0.75	0.02
P_2O_5, wt%	0.73	16.81
Physical Properties (Thermal, 3h/811K)		
surface area, m²/g	171	
ZSA, m²/g	139	
MSA, m²/g	32	
unit cell size, Å	24.26	
Properties After Deactivation (4h/1089K, 100% stm)		
surface area, m²/g		94
ZSA, m²/g		77
MSA, m²/g		17

Table 2. Catalyst Properties

The ZSM-5 additive was a commercially available ZSM-5 additive manufactured by Grace Davison. The additive contains 25% of ZSM-5 zeolite. It contains phosphorus for ZSM-5 stabilization. The additive was hydrothermally deactivated at 4 h/1500°F to simulate a commercial deactivation process. The chemical analyses and physical properties of the ZSM-5 additive are shown in Table 2. The effect of the deactivation procedure on the performance of the ZSM-5 additive will be reported separately.[18] The ZSM-5 additive was steam deactivated separately and then blended with the base catalyst to the desired level. Additive levels were adjusted to achieve ZSM-5 crystal levels of 0.5, 1, 2, 4, 8 wt% in the overall catalyst inventory. As a reference, a typical commercial FCC unit today operates at about 1 wt% of ZSM-5 crystal or less.

Experimental Results

Table 3 shows the conditions we studied. For each condition, we obtained full mass balance yields at four different conversion levels to allow data interpretations under constant conditions or conversion levels. Most of the data reported are interpreted at a constant conversion level to allow a more meaningful comparison. The detailed yield distribution will not be the main focus of the paper. The current paper will mostly discuss the results on olefin products ranging from ethylene to gasoline range olefins.

temp, K	0 wt%	0.5 wt%	1 wt%	2 wt%	4 wt%	8 wt%
794	X	X	X	X	X	X
816	X		X		X	
839	X		X		X	X

Table 3. ZSM-5 (wt%) Riser Testing Study Conditions

Propylene Yields

The effects of varying ZSM-5 level and temperature on propylene yield are shown in Figure 2. Propylene increases with conversion. As shown by Wojciechowski et al., it is considered a primary, stable product.[19] For the yield data at 794 K, propylene yield at an interpolated constant conversion of 72.5 wt% [second-order kinetic conversion x/(1 - x) of 2.64] is shown in Figure 3. The first 2 wt% of additive provided a 30% increase in propylene yield from the base case without ZSM-5. With up to 32 wt% of additive, propylene yield increased from 4.6 to 11.1 wt%, an increase of 150%. The propylene yield continuously increases with the additive level. However, it is clear that the incremental propylene yield from ZSM-5 decreases rapidly with increasing level. The incremental propylene yield from 10 to 32 wt% of additive is equivalent to the incremental propylene yield from the first 4 wt% of additive.

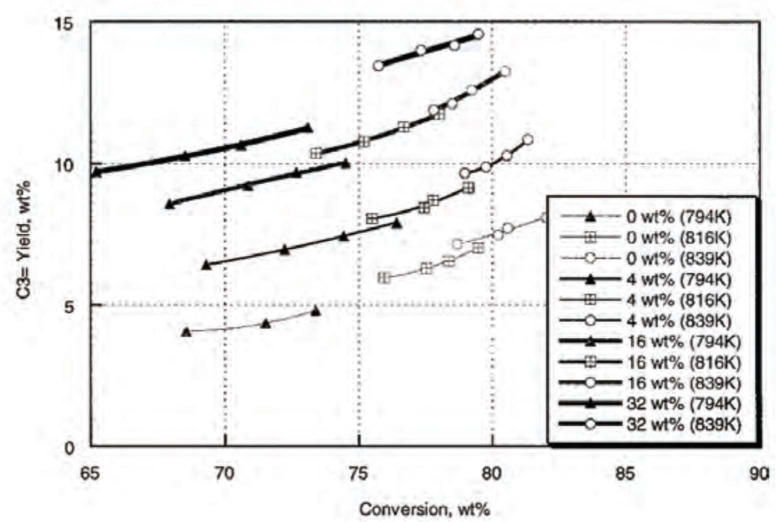

Figure 2. Effect of ZSM-5 additive/temperature on C3= yield.

Figure 3. Effect of ZSM-5 additive on C3= yield.

At constant conversion, the effect of temperature increase on propylene yield is very small. Although higher temperature does provide higher propylene, the increase is mostly due to the increased conversion level. At high conversion, the overcracking of gasoline starts to significantly contribute to the yields of propylene and butene products. Comparison of the two different approaches for maximizing propylene clearly favors the use of ZSM-5 over increasing temperature. In fact, a temperature increase from 794 to 839 K only gave a propylene increase equivalent to about 4 wt% of the ZSM-5 additive from the current study. In a commercial FCC unit, 4 wt% of additive is certainly much easier to cope with than a reactor temperature increase of 45 K (80°F).

The trend of C3 olefinicity is worth noting. ZSM-5 naturally increases C3 olefinicity due to the high C3= yield. However, C3 olefinicity actually decreases with increasing temperature. Since propane is a thermal cracking product, the low olefinicity with increasing temperature indicates the increasing contribution of thermal cracking at higher temperature.

Butene Yield

Both hydrogen transfer and isomerization reactions can significantly affect the distribution of C4 olefin products. Figure 4 shows the butene yield change with varying levels of ZSM-5 additive at three different temperatures. Unlike the propylene yield, butene yield typically goes though a maximum with varying conversion. At high conversion, butene tends to get saturated to butane. As in the case of propylene, butene also increases monotonically with increasing additive level. The first 4% of additive gave a 25% increase in butene yield. Within the range of additive levels studied, there is no indication that butene reached a maximum, though the incremental yield after 10 wt% of additive is relatively small. Due to the high isomerization activity of ZSM-5, a large fraction of the butene increase comes from an increase isobutene in Figure 5.

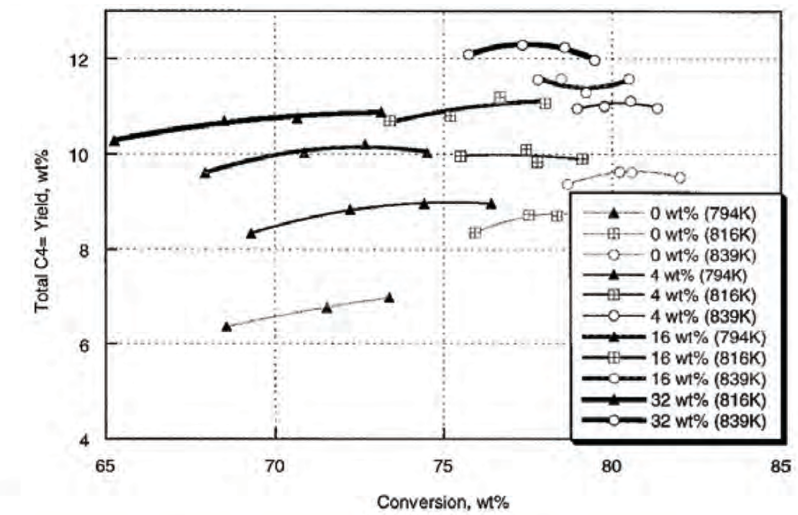

Figure 4. Effect of ZSM-5 additive/temperature on C4= yield.

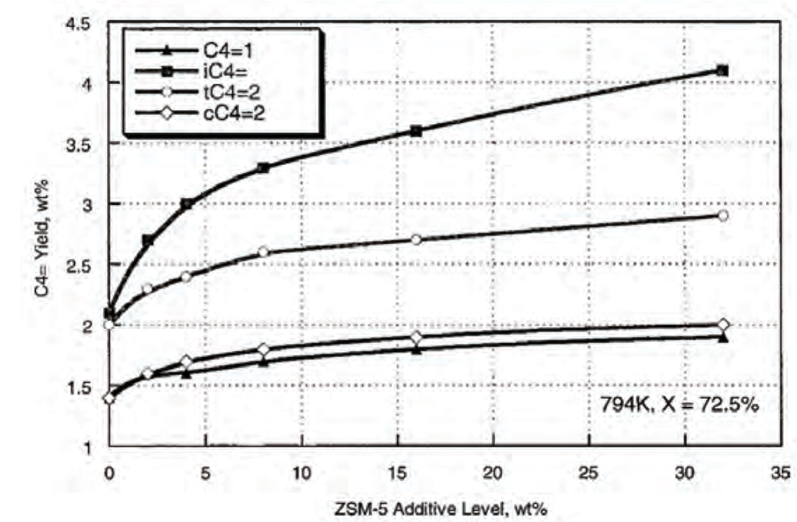

Figure 5. Effect of ZSM-5 additive on butylene yields.

Isobutene selectivity increases drastically with the increasing of ZSM-5 level. It indicates that a major portion of the C4= made by ZSM-5 is isobutene, which is the most desired product. ZSM-5 has very little effect on either nC4 or iC4 (Figure 6). As a result, the C4 olefinicity improves drastically with increasing ZSM-5 additive level. Literature work has also shown that ZSM-5 increases the branching of gasoline range olefins.[8] Temperature increases affect the relative rate of cracking vs hydrogen transfer reaction. At higher temperature, the rate of cracking increases faster than the rate of hydrogen transfer due to its higher activation energy.[10,20] As a result, the fraction of iC4= which is converted to isobutane is substantially less at higher temperature. The sums of isobutane and butene are relatively temperature independent (Figure 7).

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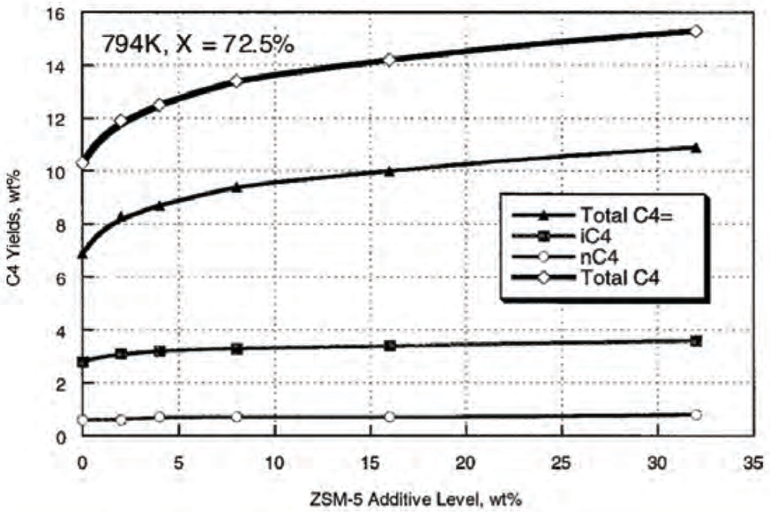

Figure 6. Effect of ZSM-5 additive on C4 yields.

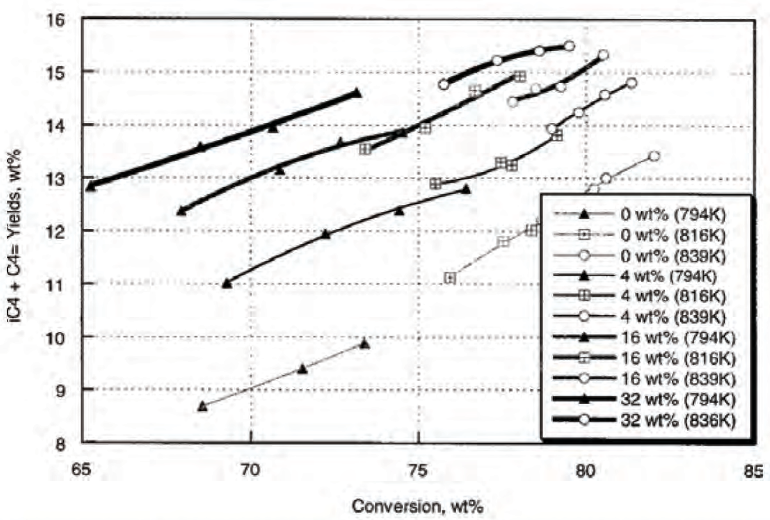

Figure 7. Effect of ZSM-5 additive/temperature on iC4 + C4= yields.

Ethylene Yield

It is generally not economical to separate ethylene from FCC products due to its low concentration. Therefore, ethylene yield from FCC is typically not a major concern. However, it has been noted that ethylene yield increases with use of ZSM-5.[10] The effects of ZSM-5 additive level and temperature on ethylene yields from the current study are shown in Figure 8. Both ZSM-5 addition and temperature increases can substantially increase ethylene yield. The highest level of ethylene we obtained was about 3 wt%. More significantly, the increase of ethylene at constant conversion is linearly proportional to the amount of ZSM-5 in the system (Figure 9). Therefore, a high level of ZSM-5 significantly increases ethylene yield from FCC. Extrapolation of the yield to 100% of ZSM-5 catalyst indicates about 7 wt% of

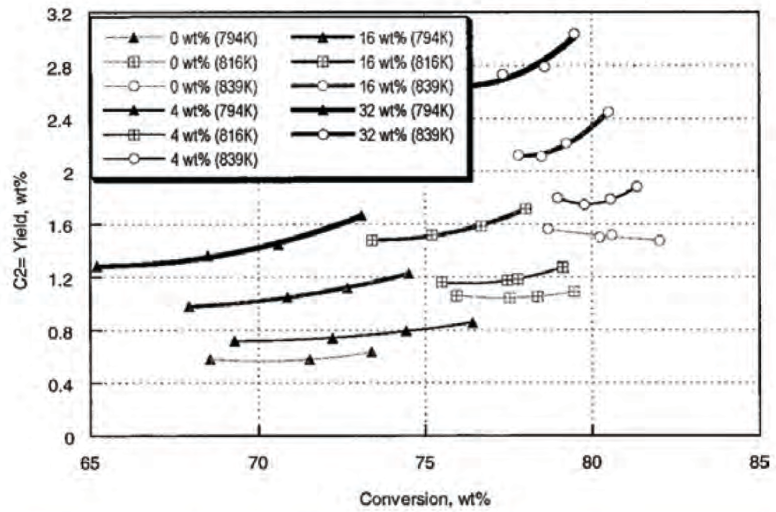

Figure 8. Effect of ZSM-5 additive/temperature on C2= yield.

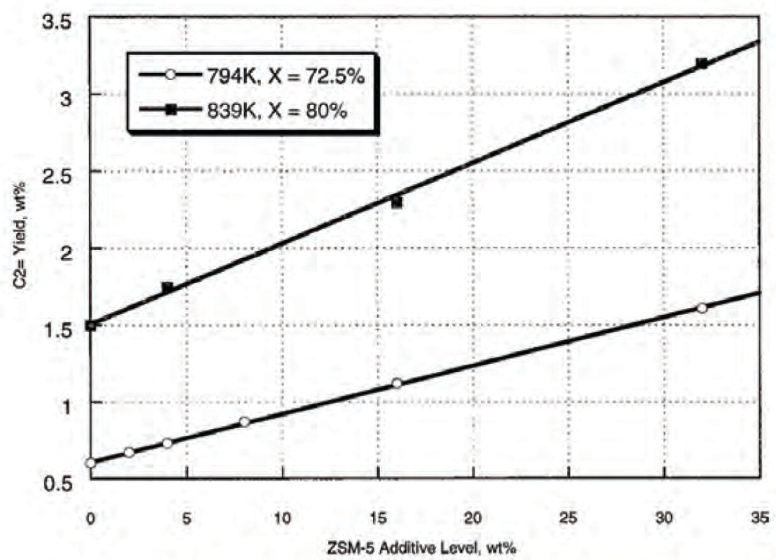

Figure 9. Effect of ZSM-5 additive on ethylene yield.

ethylene at a riser temperature of 839 K. Recovery of ethylene at the high concentration is expected to be more economical. It certainly becomes more economical to recover this high level of ethylene. The fact that ethylene levels linearly correlated with ZSM-5 levels indicates that faujasite contributes very little to the ethylene yield. It is probably an overcracking product of C5+ gasoline range olefins or disproportionanation of C6=. It has been reported that olefins smaller than C6 are stable with respect to direct cracking and must dimerize before a species is formed which is unstable enough to crack.[21] At the temperature range we used in the current study, especially at 839 K, the production of ethylene is probably associated with the cracking of pentenes or even butenes. It should be pointed out that dimerization and recracking reactions play a significant role in the product olefin distribution.[22,23]

Figure 10 shows the effect of ZSM-5 and temperature on ethane production. Higher temperature yielded more ethane due to the incremental thermal cracking. However, ZSM-5 additive did not contribute to ethane production. It is indicative of the mechanism for ethylene production from olefins cracking rather than free radical mechanism.

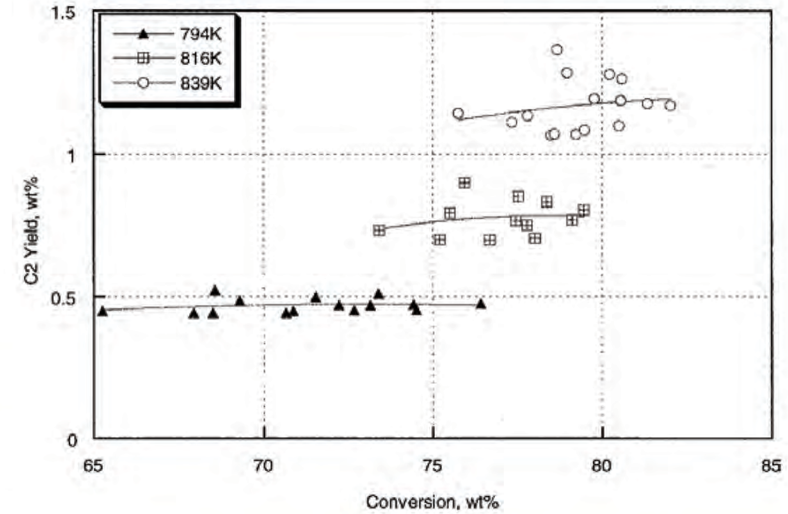

Figure 10. Effect of temperature on C2 yield.

Gasoline Olefins

Due to the environmental concerns, gasoline olefin content is increasingly regulated in the United States. It has been shown that ZSM-5 reduces the heavier olefins while increasing C5 olefins in gasoline.[8] However, the effect of ZSM-5 catalyst on total FCC gasoline olefins has been somewhat mixed. In the current study, Figure 11 shows the gasoline olefin variations with increasing ZSM-5 additive at two different temperatures. At 794 K, ZSM-5 increases gasoline olefins by about 2-3 wt%. At the higher riser temperature of 839 K, gasoline olefins had an initial increase with ZSM-5 but then decreased significantly with further increase of ZSM-5 level.

To rationalize the different trends for gasoline olefins, we summarized all the olefin yields ranging from gas to gasoline products (Figures 12 and 13). It is clear that ZSM-5 converts the gasoline range olefins (from C6= to C9=+) to light olefins (from C2= to C4=). With increasing ZSM-5 level, more heavy olefins (C6=+) are converted to light olefins (C4=-). C5 olefin is at the crossover point of this process. Depending on the specific system, C5 olefin can either increase or decrease with increasing ZSM-5. In the two examples, we have C5 olefin levels increasing with ZSM-5 at 794K (Figure 12), while they decrease with ZSM-5 at 839K (Figure 13). A possible explanation is that C5= cracking has a higher activation energy than heavier olefins. Since C5 olefins consist of 30-50 wt% of the total gasoline olefins (Figure 14), the trend of C5 olefins can dominate the direction of total gasoline olefins one way or another. Although the two current examples are based on a change in riser temperature, it is expected that different feeds or catalysts or other change could also affect where exactly the crossover is. As a result, the effect of ZSM-5 on gasoline olefins can be different for different systems. The effect of operating temperature, C/O, and feed effect on gasoline olefin can be found in the literature.[24]

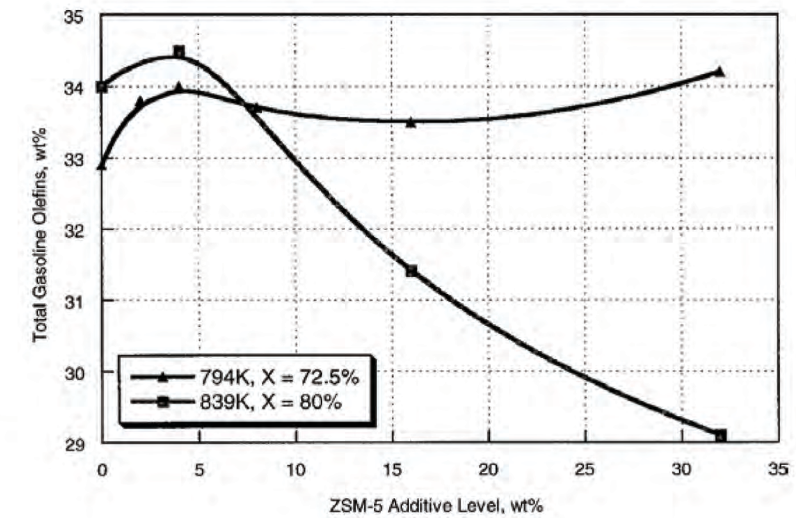

Figure 11. Effect of ZSM-5 additive on gasoline olefins.

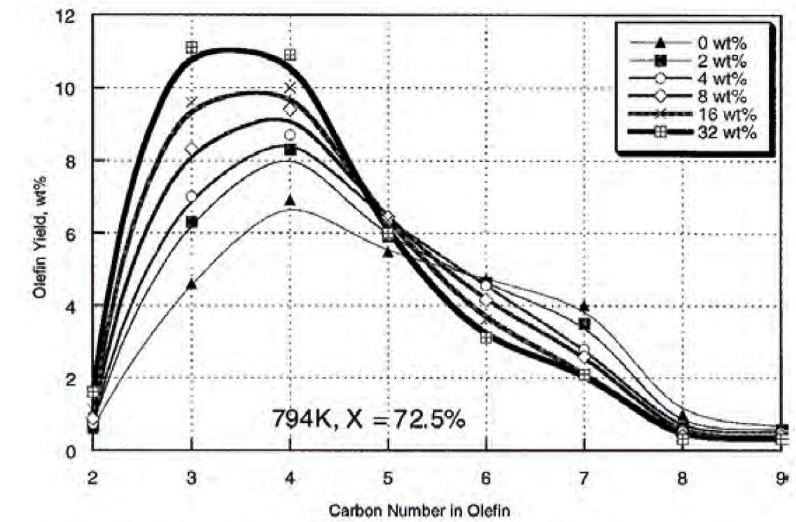

Figure 12. Effect of ZSM-5 additive on olefin distribution.

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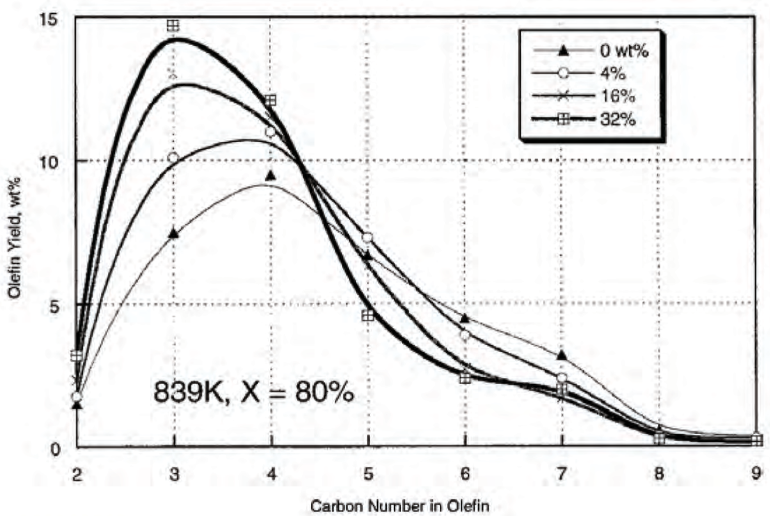

Figure 13. Effect of ZSM-5 on olefin distribution.

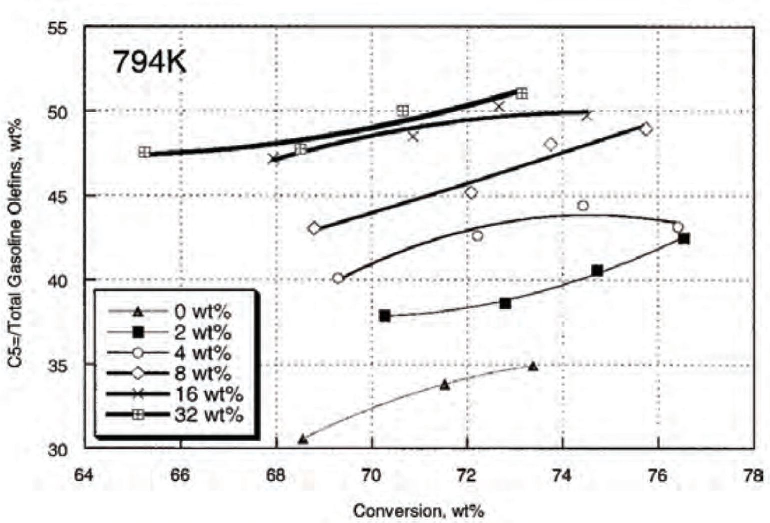

Figure 14. Total C5= olefins in gasoline olefin.

Figure 15 shows the effect of ZSM-5 on isoamylene at 794K. Since C5 olefins increase with ZSM-5 addition, one can expect that isoamylene also increases with ZSM-5 additive level. Certain commercial FCC units are expected to separate C5 olefins from the gasoline stream in order to obtain feedstocks for TAME production. In those cases, ZSM-5 can have a double benefit: increasing isoamylene yield and reducing gasoline olefins.

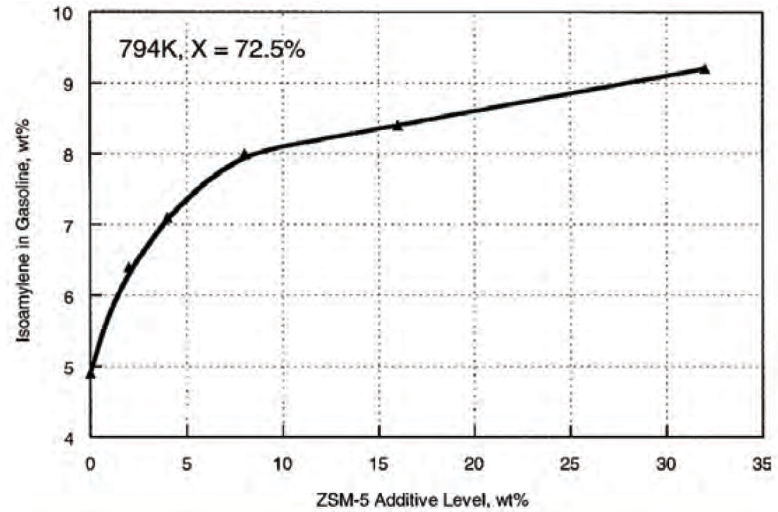

Figure 15. Effect of ZSM-5 additive on isoamylene yield.

Gasoline Diolefins

The existence of diolefins in gasoline can significantly affect the stability of the gasoline due to the highly reactive nature of diolefins. Light diolefins in the LPG stream can also significantly impact the down stream alkylation economics by increasing the acid consumption. Figures 16 and 17 show the effect of ZSM-5 vs temperature on the gasoline diolefin concentrations. Increasing the temperature from 794 to 839 K almost tripled the amount of diolefins in the gasoline from about 0.6 about 1.7 wt%. Although there were some scattering in the data, the addition of ZSM-5 additive seems to have very little effect on the diolefins concentration, another advantage of using ZSM-5 over temperature for maximizing propylene yield. In the current study, we did not detect a significant amount of butadiene under the conditions we used.

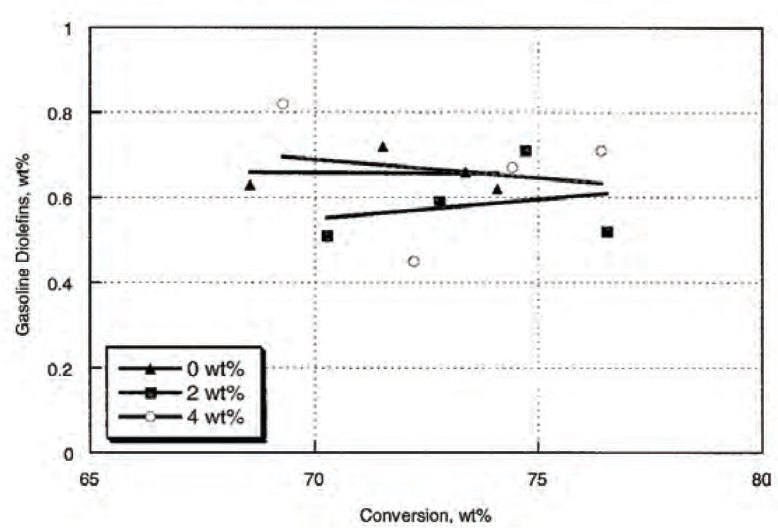

Figure 16. Effect of ZSM-5 additive on gasoline diolefins yields.

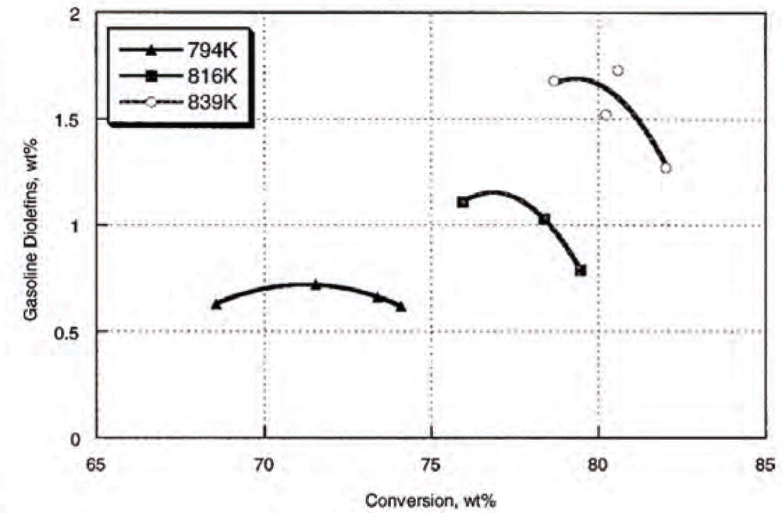

Figure 17. Effect of temperature on gasoline diolefins yields.

Discussion

The current work provided similar results to that of Buchanan et al.[10,11] for the light olefins. For example, both studies showed that very high propylene yield can be obtained with ZSM-5, while increasing the riser temperature is not nearly as effective for maximizing propylene. However, there are some minor differences in some of the observations. Within the additive levels we studied (32 wt%), we did not observe a maximum yield for the light olefins (e.g., propylene or butene). Judging from the zeolite surface areas, the additive used in the current study contains more than twice as much ZSM-5 crystal in the additive. Therefore, the current study in effect covers a wider range of ZSM-5 levels than the previously reported study.
It is not clear to us why the production of olefins should go down with higher additive level. Since the reported work was not compared at a constant conversion level, the observed effect could be due to the lower activity of ZSM-5 for overall conversion. At a very high ZSM-5 level, the overall conversion goes down, which could result in lower olefins yields.

Another minor difference between the two studies is the effect of temperature. The effect of temperature was reported to be different for the base case and the case with ZSM-5.[10] The authors observed that increasing temperature did not result in an olefin increase when high levels of ZSM-5 additive were present. In the current work, the effect of temperature on propylene yield is relatively small, but the effect is the same with or without additives (Figure 2). On the other hand, temperature does have a significant effect on butene yield. The effect of temperature is mostly due to the different activation energy of cracking vs hydrogen transfer.

Another point worth mentioning is the effectiveness of ZSM-5 at different temperatures. Figures 18 and 19 compare the percentage increase of all the olefins due to ZSM-5 at two different temperatures: 794K vs 839K. At 794K, 8 wt% of ZSM-5 crystal provided a 145% increase of propylene and 58% of butene increase. At 839K, the same level of ZSM-5 only increases the yield of propylene by 95% and of butene by about 25% at 839K. Higher temperature typically means more gasoline olefins. The greater gasoline olefins did not result in more LPG olefins. Careful examination of the gasoline composition shows that higher temperature increases the production of light gasoline olefins (e.g. C5=) versus the heavier gasoline olefins. The lighter gasoline olefins are more difficult to crack than the heavier olefins. The cracking of the lighter gasoline olefins does make a substantial amount of ethylene, which was observed in the current study.

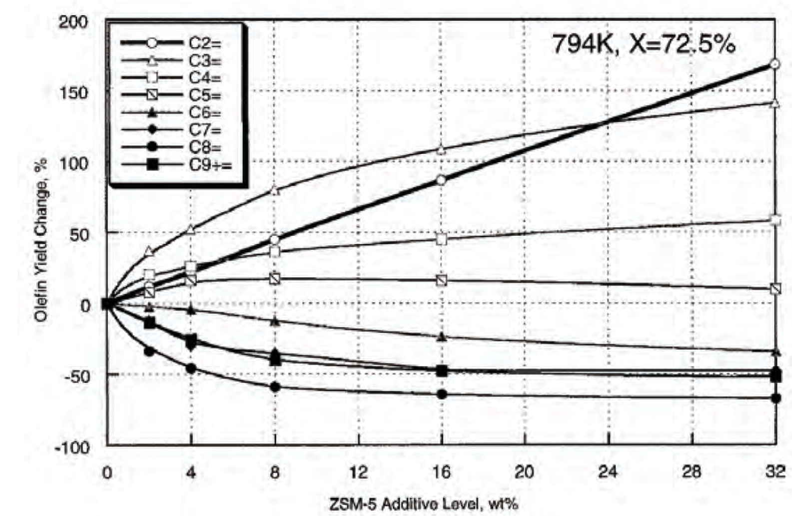

Figure 18. Olefin yield change with ZSM-5 additive level.

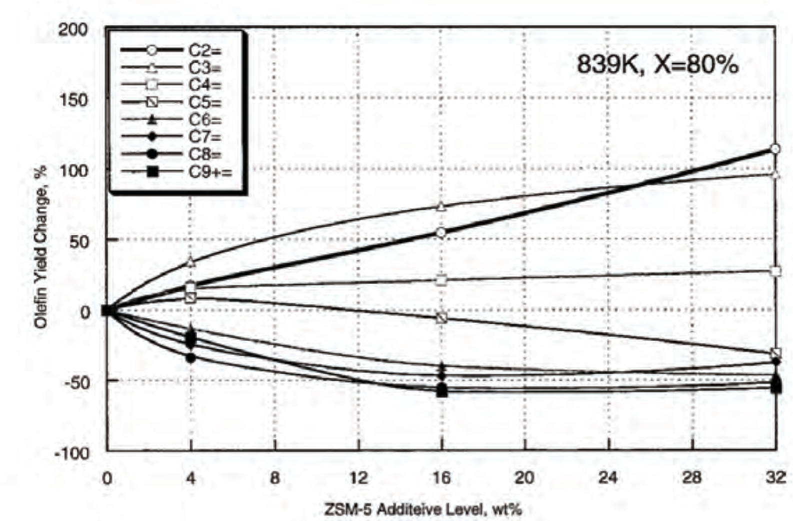

Figure 19. Olefin yield change with ZSM-5 additive level.

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Conclusions

Using ZSM-5 additive is more effective than increasing temperature for maximizing propylene in the FCC process. Ethylene yield increases linearly with the level of ZSM-5 additive, indicating that faujasite contributes little to the formation of ethylene. The effect of ZSM-5 on gasoline olefins varies with different systems. ZSM-5 reduces C6+ olefins under all the conditions we studied. However, the effect of ZSM-5 on C5 olefins is dependent on the temperature. ZSM-5 increases C5= under typical FCC operating conditions, while it reduces pentenes at higher temperatures. The increase of ethylene yield is correlated with the reduction in pentene yield at high temperature. Increasing riser temperature increases diolefins in both the C4 and gasoline range. No appreciable effect of ZSM-5 on diolefins was observed.

Acknowledgment

The authors thank N. Dale McCrary for his assistance in the experimental work, and Dr. W.-C. Cheng for many helpful discussions. The authors also thank Grace Davison for permission to publish this work.

Literature Cited

1. Cheng, W.-C.; Kim, G.; Peters, A. W.; Zhao, X.; Rajagopalan, K.; Ziebarth, M.; Pereira, C. *Catal. Rev. Sci. Eng.* **1998**, *40* (1-2), 39-79.
2. Krishna, A. S.; Hsieh, C. R.; English, A. R.; Pecoraro, T. A.; Kuehler, C. W. *Additives Improve FCC Process, in Hydrocarbon Processing.* **1991**, 59-66.
3. Schipper, P. H.; Dwyer, F. G.; Sparrell, P. T.; Mizrahi, S.; Herbst, J. A. *Zeolite ZSM-5 in Fluid Catalytic Cracking: Performance, Benefits, and Applications, in Fluid Catalytic Cracking: Role in Modern Refining*, M. L. Occelli, Editor. 1988, American Chemical Society: Washington, D. C. p 64-86.
4. Manning, T. J. *Hydrocarbon Process.* **1997**, 76 (5), 85-88.
5. Biswas, J.; Maxwell, I. E. *Appl. Catal.*, **1990**, 58, 1-18.
6. Hsing, L. H. In *International Symposium on Advances in Fluid Catalytic Cracking*; ACS Meeting, 1993, Chicago, IL, August 22-27, 1993.
7. Madon, R. J. J. *Catal.* **1991**, 129, 275-287.
8. Young, G. W.; Suarez, W.; Roberie, T. G.; Cheng, W.-C. In *1991 NPRA Annual Meeting*; San Antonio, TX, 1991.
9. Chen, N. Y.; Degnan, J. T. F.; Smith, C. M. *Molecular Transport and Reaction in Zeolites*; VCH Publishers: New York, 1994.
10. Buchanan, J. S.; Adewuyi, Y. G. *Appl. Catal. A: Gen.* **1996**, 134, 247-262.
11. Adewuyi, Y. G.; Klocke, D. J.; Buchanan, J. S. *Appl. Catal. A: Gen.* **1995**, 131, 121-133.
12. Adewuyi, Y. G. *Appl. Catal. A: Gen.* **1997**, 163, 15-29.
13. Zhao, X.; Weatherbee, G. D.; Rajagopalan, K. R. In *The Fifth World Congress of Chemical Engineering*; San Diego, CA, 1996.
14. Haas, A.; McElhiney, G.; Ginzel, W.; Nuchsbaum, A. *Petrochem./Hydrocarbon Technol.* **1990**, 43, 21-26.
15. Cotterman, R. L.; Plumlee, K. W. *ACS Meeting*; Miami Beach, FL, 1989.
16. Rajagopalan, K.; Habib, E. T. Understanding FCC Matrix Technology. *Hydrocarbon Process.* **1992**, 43-46.
17. Zhao, X.; Harding, R. H. Ind. Eng. Chem. Res. 1999, 38, 3854-3859 paper in this issue).
18. Zhao, X.; Roberie, T. G., in preparation.
19. Wojciechowski, B. W.; Corma, A. *Catalytic Cracking*; Marcel Dekker: New York, 1986.
20. Venuto, P. B.; Habib, E. T. *Fluid Catalytic Cracking with Zeolite Catalysts*; Marcel Dekker: New York, 1979.
21. Abbot, J.; Wojciechowski, B. W. Can. J. *Chem. Eng.* **1985**, 63 (June): 462-469.
22. Smirniotis, P.; Ruckenstein, E.; *Ind. Eng. Chem. Res.*, **1994**, 33, 800-813.
23. Buchanan, J. S.; Santiesteban, J. G.; Haag, W. O. J. Catal. 1995, 158 279-287.
24. Mott, R. W.; Roberie, T.; Zhao, X. 1998 NPRA Annual Conference, 1998.

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