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Catalysis Today 55 (2000) 207–212

CATALYSIS TODAY

www.elsevier.com/locate/cattod

The chemistry of olefins production by ZSM-5 addition to catalytic cracking units ☆

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Abstract

The addition of ZSM-5 to fluidized catalytic cracking (FCC) units can greatly increase yields of C_3–C_5 olefins, which are key intermediates in the manufacture of clean fuels such as ethers and alkylate.Understanding how ZSM-5 functions in catalytic cracking helps in optimally applying this zeolite, and can provide guidance in developing next-generation catalysts. Here, the results of model compound studies are presented, which elucidate the changes in reaction pathways that occur in the FCC unit upon ZSM-5 addition. The observed increase in C_{5-} and decrease in C_{7+} olefins and paraffins can be accounted for by ZSM-5's interception of heavy olefin intermediates that would otherwise undergo hydrogen transfer over the base faujasitic catalyst. Interpretations are also offered for the high $C_3{=}/C_4{=}$ratio seen for high activity ZSM-5 additives, and for the high gasoline selectivity associated with high Si/Al ZSM-5 additives. ©2000 Elsevier Science B.V. All rights reserved.

Keywords: ZSM-5; Zeolites; Catalytic cracking; Clean fuels; Olefins

1. Introduction

A number of 'clean' fuels are typically made from light olefins such as propylene or butene. The fluid catalytic cracking (FCC) units in petroleum refineries are a major source of these olefins. In this paper we will discuss the chemistry involved when the catalyst ZSM-5 is added to cracking units to make more olefins.

Clean fuels are generally fuels that burn cleanly and that do not inhibit the functioning of catalytic converters for engine exhaust. Also, government regulations have defined acceptable fuel characteristics, such as oxygen content. Clean fuels typically have little or no olefins, aromatics or sulfur. Two common examples of clean fuels are alkylate and methyl *tert*-butyl ether (MTBE).

Olefins are useful building blocks for making clean fuels, because olefins are relatively reactive. It is relatively easy to oligomerize them, alkylate them, or add alcohol or water to make various oxygenates. To increase the amount of these clean fuels, it is necessary to increase the supply of olefins used to make them. Adding ZSM-5 to catalytic crackers has been found to be an effective means of increasing olefins production.

Fig. 1 shows some of the major processing units commonly found in gasoline-oriented refineries. The units shown in dashed outline are less common. Crude oil is distilled into fractions that are processed in various units downstream. The C_3–C_4 stream may be used directly as LPG, which is considered a type of clean fuel. The C_6–C_{10} naphtha is fed through a reformer that converts low octane naphthenes and paraffins into

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☆ This is a write-up of talk #1596 presented in November 1997 as part of the Symposium on Environmental Catalysis at the 5th Chemical Congress of North America. This write-up is to be included in the published proceedings of the Symposium.

PII: S0920-5861(99)00248-5

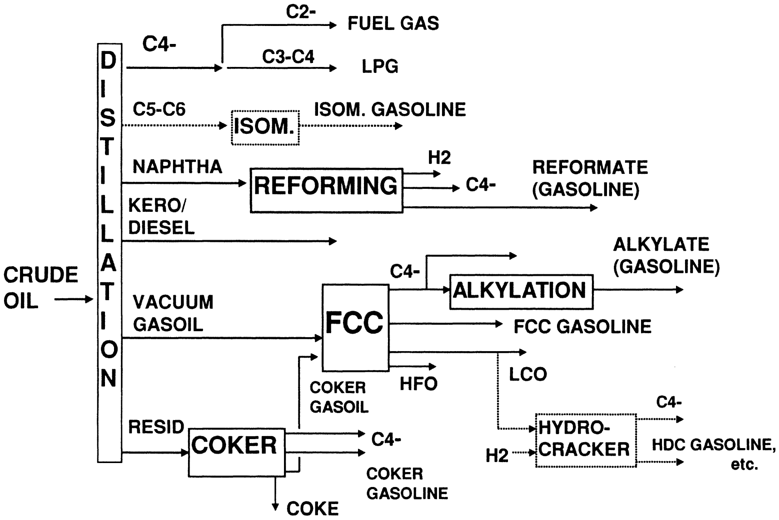

Fig. 1. Processing units in a fuels refinery.

high-octane aromatics. The vacuum gasoil (roughly C_{25}–C_{40}), is fed to the FCC unit, where it is cracked to smaller molecules.

The straight run C_3–C_4 stream and the C_3–C_4 byproducts from reforming or hydroprocessing units are largely paraffinic. The FCC is the major producer of olefins in the refinery, with a smaller contribution from thermal cracking processes like coking. Most FCC units have an alkylation unit downstream to make premium alkylate fuel from the C_3–C_4 olefins, and isobutane.

In an FCC unit, the powdered catalyst continuously circulates between a riser-type reactor, and a regenerator. The base FCC catalyst is a stabilized Y zeolite, bound in a spray-dried matrix such as silica–alumina. Liquid feed is introduced at the base of the riser, where is vaporized by red-hot catalyst. The oil vapors sweep the catalyst up a tall reactor tube, while the cracking reaction goes on. At the top of the riser, catalyst is separated out with cyclones, stripped with steam, and flows to the regenerator, where coke is burned off the catalyst.

The reaction products are sent through an elaborate train of distillation towers to separate them into useful fractions. Usually, the C_{2-} stream is used as fuel gas. The C_{2-} contains a significant amount of ethylene, but it is a challenge to recover the ethylene economically. The yield of gasoline is around 50% by weight. Our main interest here is the C_3–C_4 stream, which can be used for making clean fuels. The propylene is also in demand for petrochemicals such as polypropylene.

2. Role of ZSM-5 in the FCC

Table 1 shows some of the yield shifts that occurred when a large amount (25% of the total catalyst charge) of ZSM-5 containing additive was added to a pilot FCC unit [1]. The first column lists the products with the base catalyst alone, while the second column shows the changes in yield when ZSM-5 was added. The gasoline research octane increased from 91.3 to 93.4. Adding ZSM-5 had little effect on the heavier components such as heavy fuel oil. This is not surprising, because the pores in ZSM-5 are only 5–6 Å wide, which is not large enough for these large molecules to enter.

The main effects of adding ZSM-5 are an increase in the gasoline octane rating, a decrease in gasoline (typically C_5–C_{12} hydrocarbons) and an increase in C_{4-} gas products, especially C_3–C_4. The C_{5+} species that drop are mainly the paraffins and olefins, not the aromatics. C_7–C_8 paraffins and olefins drop by about half. On the surface, this may seem like a simple case of an acid catalyst which is cracking paraffins and olefins to make smaller paraffins and olefins. That chemistry

Table 1
FCC light ends yield shifts upon addition of 25% ZSM-5 additive at 538°C and 67 wt.% conversion [1]

	Base	ZSM-5 added
Product yields (wt.%)		
Methane	1.16	−0.20
Ethane	0.97	−0.21
Ethylene	0.87	+0.84
Propane	0.81	+0.56
Propylene	3.49	+5.77
n-Butane	0.41	+0.24
i-Butane	1.60	+1.04
n-Butenes	3.48	+1.46
i-Butene	1.70	+1.64
n-Pentane	0.29	+0.04
Br. Pentanes	1.84	+0.33
n-Pentenes	2.38	−0.68
Br. Pentenes	2.41	+0.67
Hexanes	1.78	−0.59
Hexenes	3.88	−1.18
Heptanes	1.35	−0.74
Heptenes	2.38	−1.86
Octanes	1.00	−0.53
Octenes	1.47	−1.14
C_{5+} gasoline	47.85	−11.62

would be consistent with the behavior of ZSM-5 in other systems. For instance, it is generally accepted that commercial processes for dewaxing distillate and lubes over medium pore zeolites like ZSM-5 operate by cracking out the waxy straight chain paraffins.

However, a different pattern of conversions appeared when some model paraffins and olefins were run over ZSM-5 at the space velocities that might be encountered in an FCC reactor, as shown in Table 2 [2]. Here we tried to match the conditions that might obtain for gasoline-range aliphatics reacting over ZSM-5 in the riser. In the riser, the solids density is low, and not much of the catalyst is actually ZSM-5, so there is not much ZSM-5 in the reactor; therefore, the effective residence time (gas volumetric flow per volume of ZSM-5 crystal) is typically less than 0.01 s. Furthermore, the catalyst in an FCC unit is severely deactivated by steaming in the regenerator.

Table 2
Conversion of C_6–C_{10} paraffins and olefins over ZSM-5 in fixed-bed reactor at simulated riser conditions (538°C) [2]

Feed	Conversion (wt.%)
Hexane	0.3
Octane	0.4
Decane	0.6
Hexene	26.0
Octene	77.0
Decene	83.0

Table 2 shows that the reactivity of paraffins is much lower than for olefins. Paraffin conversion at these conditions is almost negligible, whereas olefins conversion is substantial. Also, the reactivity of olefins increases very greatly with the size of the olefin. More refined experiments at low conversion show that the cracking rate constant increases by nearly an order of magnitude in going from hexene to heptene; also, the rate of olefin isomerization is typically even faster than the rate of olefin cracking, for olefins up to about C_8. These trends in olefin reactivity can be understood in terms of the beta-scission mechanism [3].

The results reported in Table 2 (almost no paraffin conversion over ZSM-5 at FCC riser conditions) appear to be at odds with the results shown in Table 1 (substantial reduction in paraffins as well as olefins). To understand these results, it is necessary to understand how the base catalyst works. Fig. 2 is a simplified diagram of the main pathways for the formation of gasoline-range paraffins in the FCC unit, over the base catalyst. Some paraffins are formed by the cracking of higher paraffins or alkylaromatics. This cracking process also makes gasoline-range olefins.

Through processes which are still not understood in detail, hydrogen from hydrogen donor hydrocarbons can be transferred to these olefins to make paraffins. The base faujasite catalyst is very good at promoting these bimolecular hydrogen transfer reactions. This is a major pathway for making gasoline-range paraffins. Gasoline paraffins are relatively stable, so they do not

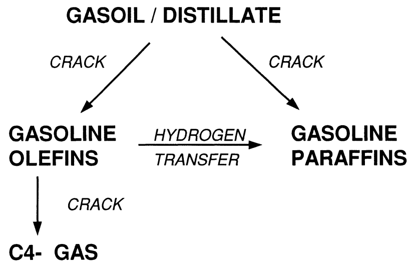

Fig. 2. Dominant pathways for FCC paraffin production.

usually undergo much further cracking, compared to gasoline olefins, which are prone to crack to C_4- gas. Thus, the hydrogen transfer mechanism is a means of increasing gasoline yields, and this was a significant advantage of the faujasite cracking catalysts when they were introduced in the 1960s.

If ZSM-5 acts to accelerate the cracking of the gasoline-range olefin pool, fewer gasoline-range olefins will be available for conversion to paraffins, and the net result will be a reduction in both C_{6+} paraffins and C_{6+} olefins. This proposed reaction pathway was tested by running a hexene feed over beds of ZSM-5 additive and faujasite-containing base catalyst, and over beds of the two catalysts in series [2]. Over the base catalyst, about 27% of the hexene was converted to hexane, via hydrogen transfer reactions. Over the ZSM-5 catalyst, 47% of the hexene was converted, but nearly all by cracking to smaller paraffins; less than 2% went to hexane. When the ZSM-5 bed preceded the base catalyst bed in the reactor, the hexane yield dropped from 27 to 16%, indicating that conversion of higher olefins to lower olefins over ZSM-5 can indeed decrease the production of higher paraffins in the FCC reaction system.

Our understanding, then, is that when ZSM-5 is added to the FCC unit, it mainly just cracks and isomerizes C_{5+} olefins. This general framework has proven useful in understanding some specific issues that have come up in catalyst formulation and application.

3. Effects of ZSM-5 activity on propylene/butene product ratio

Propylene and butene from the FCC have different values at different refineries, depending on the downstream processing equipment and the local markets. Control of the propylene/butene ratio is important in maximizing refinery profits.

Fig. 3 shows propylene/butene product ratios for C_5–C_{10} alpha olefin feeds, cracked over ZSM-5 at 538°C. The propylene/butene (weight/weight) product ratio for cracking of pure hexene over ZSM-5 is well over 2, whereas for C_7–C_{10} olefins, it is less than 1. The C_3/C_4 ratio falls off for the C_5–C_6 feeds at higher partial pressure, because of secondary reactions. These product ratios can be explained by the carbenium ion cracking mechanism [3]. On the other hand, hexene is less reactive than the higher olefins. For small amounts of ZSM-5, or for low-activity ZSM-5 additive, the amount of hexene cracked, relative to the higher olefins, will be small, and the propylene/butene ratio of the incremental products will be small. As the amount of ZSM-5 added to an FCC unit increases, more hexene will be cracked, and therefore the propylene/butene product ratio will increase.

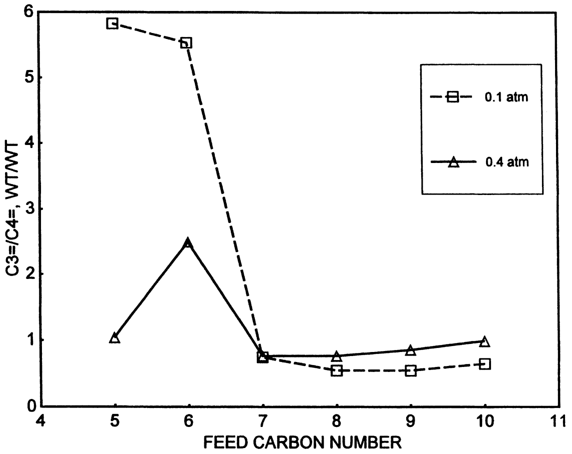

Fig. 3. C_3/C_4 olefin product ratio for cracking C_5–C_{10} olefins over ZSM-5 at 538°C.

A 1 : 1 hexene/octene feed mixture was used to explore this concept [4]. Fig. 4 shows the propylene/butene product ratio for this model feed for nine FCC additives containing ZSM-5. All runs were made

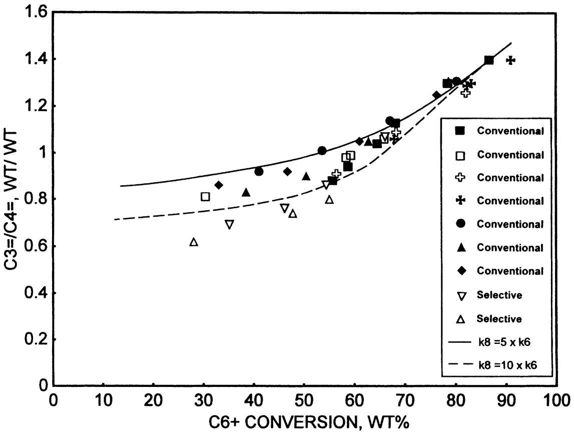

Fig. 4. C_3/C_4 olefin product ratio for hexene/octene feed over steamed bound and unbound ZSM-5 at 538°C, with calculated C_3/C_4 for two ratios of k_8/k_6 [4].

at 538°C and 1 atm. Reaction severity, indicated by C_{6+} conversion, was varied by changing flow rates.

Earlier experiments [4] had shown that, for typical ZSM-5 additives, the ratio of first-order rate constants for octene and hexene cracking (k_8/k_6) lay between 5 and 10. Propylene selectivities of about 70 and 22 wt.%, respectively, were observed for hexene and octene feeds, and butene selectivities of 17 and 40 wt.%. Two curves of expected propylene/butene ratios were calculated, using these selectivities and using $k_8/k_6=5$ and $k_8/k_6=10$. It was expected that the results for all of the ZSM-5 catalysts would fall between these two curves. This was largely true for the 'conventional' ZSM-5 additives, where the silica/alumina ratio of the ZSM-5 was less than about 100 : 1. The selectivity of all these additives appears to be about the same. Thus, the results from a small amount of a highly active ZSM-5 additive should be comparable to the results with a larger amount of a less-active additive. The overall ZSM-5 activity (taking into account both additive activity and amount) is a primary means of controlling the propylene/butene product ratio.

4. Effects of ZSM-5 Silica/Alumina Ratio

The propylene/butene ratios for the two 'gasoline selective' catalysts, however, were significantly lower than seen for the conventional additives, even at comparable C_{6+} conversions. These results indicate a fundamental difference in selectivity between the high silica and low silica ZSM-5 for these reactions. Gasoline selective FCC additives are believed to contain ZSM-5 which has been synthesized with silica/alumina ratios much greater than 100 : 1. For a given amount of gasoline octane boost, these additives have been shown to reduce C_{4-} make, thus increasing gasoline yields [5,6].

Reaction patterns over two unbound ZSM-5 catalysts, with 55 : 1 and 450 : 1 silica/alumina ratios, were studied, in order to gain more insight into the effects of silica/alumina [4]. It was found that, for pure hexene and pure octene feeds, the selectivies to propylene and octene were the same for the two catalysts. However, the ratio k_8/k_6 was around 8 for the 55 : 1 catalyst, but around 13 for the 450 : 1 catalyst at 538°C. As a result, the propylene/butene ratio for the 450 : 1 ZSM-5 in cracking of a hexene/octene feed was significantly lower than for the 55 : 1 ZSM-5, as shown in Fig. 5.

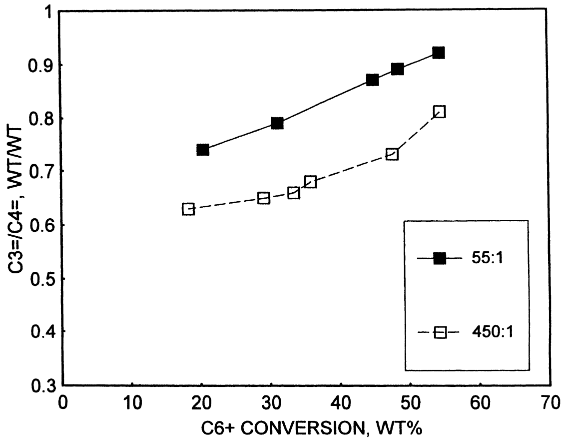

Fig. 5. C_3/C_4 olefin product ratio for hexene/octene feed over steamed 55 : 1 and 450 : 1 ZSM-5 at 538°C [4].

Fig. 6 shows the degree of skeletal isomerization versus cracking for a 1-hexene feed over the two ZSM-5 catalysts. For a given degree of cracking, the hexene is more highly isomerized over the 450 : 1 catalyst. Isomerization is much faster here than cracking. These results, and the higher k_8/k_6 ratio for the 450 : 1 catalyst, suggest that the 55 : 1 catalyst may be more mass-transfer limited than the 450 : 1 catalyst.

For hexene cracking, the activation energy over the 55 : 1 catalyst was about 15.3 kcal/mol, and 20.5 kcal/mol over the 450 : 1 catalyst. For octene

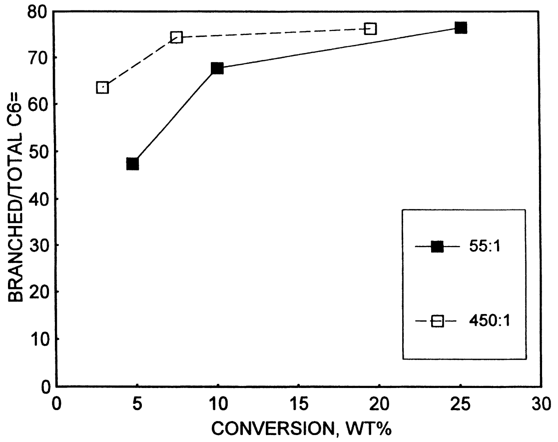

Fig. 6. 1-Hexene skeletal isomerization versus cracking over steamed 55 : 1 and 450 : 1 ZSM-5 at 538°C [4].

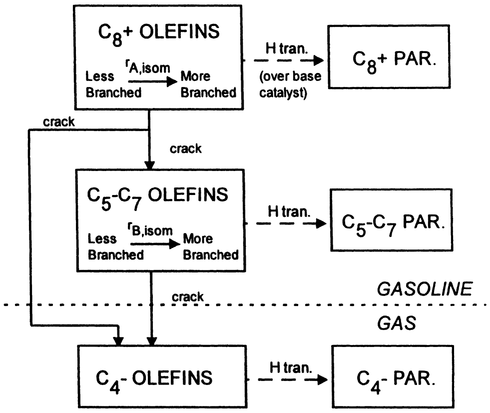

Fig. 7. Reactions of olefins in FCC unit.

cracking, activation energies were 2.8 kcal/mol for the 55 : 1 catalyst, and 4.1 kcal/mol for the 450 : 1 catalyst. The lower activation energies for the 55 : 1 ZSM-5 are consistent with mass transfer limitation over this catalyst.

A summary of key reaction paths is shown in Fig. 7. The hydrogen transfer reactions (dashed arrows) are promoted almost exclusively by the base catalyst. The other reactions (isomerization and cracking), shown with solid arrows, are significantly accelerated by the addition of ZSM-5. All the reactions which are promoted by ZSM-5 tend to increase gasoline octane numbers, but only the cracking to C_{4-} reduces gasoline yields. The results presented here indicate that the ratio of this type of cracking to the other ZSM-5-catalyzed reactions is lower for the 450 : 1 catalyst than for the 55 : 1 catalyst.

5. Conclusions

When ZSM-5 is added to the FCC unit, the main reactions it catalyzes are C_{5+} olefin isomerization and cracking. The yield and octane shifts observed upon ZSM-5 addition can be explained in terms of these olefin reactions. Hexene is less reactive than the higher gasoline-range olefins, but hexene cracking gives a higher propylene/butene product ratio. For small amounts of ZSM-5, or a use of a low-activity ZSM-5 additive, relatively little hexene is cracked in the FCC unit. With increasing amount or activity of ZSM-5, more hexene is cracked, and the propylene/butene ratio can increase dramatically.

In general, compared to reactions over the 55 : 1 ZSM-5, the rates of the fastest reactions (which tend to boost octane with little or no gasoline yield), are accelerated over the 450 : 1 ZSM-5 relative to slower reactions, which tend to reduce gasoline yield with less gain in octane. These reactivity patterns, which suggest diffusional limitation of reaction rates over the lower silica/alumina ZSM-5, can explain the higher gasoline selectivity observed for the ZSM-5 FCC additives prepared with higher silica/alumina ratios.

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