

Chapter 1

INTRODUCTION

Backgrounds

The first commercial catalytic cracking process was developed by Eugene Houdry in the 1920s. This process was an out growth of his experiments on catalysts for removing sulfur from oil vapors. These catalysts became deactivated due to buildup of a carbonaceous deposit from the oils. Houdry discovered that this deposit could be burnt off with air, and the catalyst activity restored. This discovery made a commercially viable process possible. The fluid catalytic cracking (FCC) process continues to play an important role as gasoline producing unit in most oil refineries. Several FCC and catalysts are currently being developed and the maximized the production of light olefins for petrochemical usage while maintaining high gasoline yield. The objective of the FCC unit is to convert low value, high boiling point feed stocks into more valuable products such as gasoline and diesel.

The introduction and commercialization of the zeolite catalysts in the 1960s was a major milestone in the development of fluid catalytic cracking. Compare to synthetic amorphous catalyst, zeolite catalyst offered improved activity retention as well as superior yield distribution. To take full advantage of this improved performance, the FCC process quickly moved from bed cracking to all riser cracking. The zeolite are the primary catalytic ingredient in all FCC catalyst formulations. Zeolite technology has moved from the early X faujasites used in the 1960s to wide range of variations on the more stable Y faujasite crystal. The zeolite catalyst contains several other components. These include active aluminas, binders, fillers, metals, traps or materials intended to catalyze reactions other than cracking. Each of these components plays a role in the overall functioning of the catalyst. In making catalyst decisions, the FCC engineer must weigh the effect of each and estimate the performance of various combination of ingredients.

In the present the worldwide phasing out of lead and increase in demand for unleaded gasoline necessitate actions by the refiners in order to achieve the high gasoline octane numbers. In addition to improvements due to modifications in the process operation, much hope is place on improvements in the octane by new catalyst formulations. The introduction of ZSM-5 as an octane enhancing FCC catalyst additive was one of the most interesting accomplishments during the recent years. However, there are only a few studies regarding the behavior of individual hydrocarbon over zeolite mixtures.

In the present study we prepare and examine the performance of mixed zeolite catalyst in the cracking of n-Octane. The laboratory evaluation of the catalytic performance of mixed zeolite catalyst using a microactivity test unit (MAT).

Previous Reseaches

Lungstein et al., (1999) stated that the hydrocarcking and hydroisomerization of n-octane, 2,5-dimethylhexane and 2,2,4-trimethylpentane on Ni-containing ZSM-5, mordenite and beta catalysis was investigated at 20 bar hydrogen pressure and a temperature of 533 K. The acidity decreased in the sequence ZSM-5 > BETA \approx MOR for the n-octane conversion and increased in this sequence for the conversion of 2,5-dimethylhexane and 2,2,4-trimethylpentane. The selectivity for isomerization of n-octane and 2,5-dimethylhexane was the highest on NiHBETA and the lowest on NiHZSM-5. The trends in the acidity and selectivity were explained by the accessibility of the acid sites, estimated by adsorption of probe molecules followed by IR spectroscopy, and by a simulation of the space available in the pores of these zeolites.

Corma et al., (1999) reported that a large variety of zeolite topologies including: large pore tridirectional (Beta), large pore unidirectional (Mordenite, SSZ-24), bidirectional 10 memberring pore (MRP) (ZSM-5), bidirectional 10 \times 8 MRP (Ferrierite), tridirectional with connected 12 and 10 MRP (CIT-1), bidirectional with 12 connected by 10 MRP (NU-87), tridirectional with 10 \times 11 \times 12 MRP (NU-86), and finally 10 MRP, and independent 12 MR cavities connected by 10 MR windows (MCM-22), have been studied as catalysts for the cracking of gasoline range model molecule (n-heptane). Kinetic and decay constants as well as selectivity parameter

such as paraffin/olefin, $i\text{-C}_4/n\text{-C}_4$, $i\text{-C}_5/n\text{C}_5$, C_3/C_4 , and C_2/C_5 have been used to discuss the behaviour of the above zeolite structures as potential FCC additives.

Mao et al., (1999) claimed that ZSM-5 zeolite, when doped with fluorine species in relatively low concentration using ammonium fluoride as precursor, and subsequently activated stepwise at high temperature, show an enhance surface acidity because of : (i) the formation of new Bronsted acid site; and (ii) the strengthening of some acid sites of the parent zeolite. This is ascribed to the proton attack of the zeolite surface by the chemisorbed $\text{H}^+ \text{F}^-$ ion pair. Under these preparation conditions, the zeolite structure is fully preserved. Such enhanced acid properties are traduced by a significant increase in the yield of methyl tert-butyl ether (gas phase reaction).

Dzikh et al., (1999) mentioned that the effect of mixing of an ultrastabilised acid form of Y zeolite (USHY, $\text{Si}/\text{Al}=4.5$) with two different HZSM-5 zeolites, synthesised by different methods, with template (CVN, $\text{Si}/\text{Al}=45$) and without template (CVM, $\text{Si}/\text{Al}=26$), and presenting quite different acidic properties, is studied using as model reaction the transformation of n-heptane at $350\text{ }^\circ\text{C}$. The results obtained point to the existence of some interactions between the processes occurring in the two zeolites, and are helpful in the understanding of the known ZSM-5 addition effect in the cracking catalysts. There is a clear enhancement in the formation of ramified C_4 products for the USHY:ZSM-5 mixtures (75:25, wt%) and (50:50), relative to the additive linear predictions, this effect being significantly more extensive for the mixtures with the ZSM-5 sample presenting the highest acid strength. In the mixtures (90:10) there is also an increment in the ramified/linear products ratio. The initial olefin/paraffin products ratio registered a slight increase, relative to the expected values, in all the mixtures with CVN. In the case of CVM there was also an increase of this parameter, but only for the mixture with 10% of ZSM-5, a significant reduction being observed in all the other cases.

Adewuyi et al., (1995) wrote that the effect of the addition of high levels of ZSM-5 to streamered rare earth ultra-stabilized fluid catalytic cracking (FCC) catalysts has been studied in an isothermal, bench scale, once-through riser pilot plant. Catalyst mixtures consisting of RE-USY blended with ZSM-5 at additive levels 12.5, 25, 50 and 75 wt. % were examined. Results indicate yields of light alkenes could be maximized by operating with large amounts of ZSM-5. For the particular gas oil used

in this study, a maximum of light alkenes yield occurs at an additive level of about 25 wt. %, other feeds can show a different response. At the 25 wt. % additive level we observed maximum yield increases of about 150 % in propene and isobutene and 120 % in n-butenes. At lower additive levels (<25 wt. %) conversion of reactive gasoline range species (mainly alkenes) is not complete. Above 25 wt. %, conversion of these species is essentially complete and the effect of ZSM-5 is dilution of the base cracking catalyst with concomitant loss in overall conversion. The FCC naphtha octane (both RON and MON) also increased with additive up to 25 wt. % and also observed an increased in ethylene yield, along with suppression of some undesirable products such as methane. In the presence of 25 wt. % ZSM-5 additive, there were no significant shifts in bottoms (or HCO, heavy crude oil) and light cycle oil (LCO) at constant conversion and only slight decrease in coke yield at constant cat/oil ratio.

Aitani et al., (2000) declared that the effects of high severity operation and ZSM-5 addition on the FCC product yield structure have been studied in a MAT unit. VGO cracking at high reaction temperature of 500-650 °C increases the yield of light olefins (propylene and butenes) with a corresponding loss in gasoline yield and increase dry gas formation. Similar behavior is observed with the addition of 0-20 wt.% ZSM-5 additive, however, with no increase in dry gas. The combination of the two effect (high severity and ZSM-5 addition) makes the FCC unit and excellent source of light olefins for downstream petrochemical and alkylation units. A novel downer reactor FCC configuration is proposed to suppress thermal cracking reactions and dry gas formation during high severity operation.

Degnan et al., (1999) proposed that ZSM-5 has found widespread application as a fluid catalytic cracking additive for both propylene production and gasoline octane improvement. This paper traces its development by Mobil from the laboratory evaluation stage through its full-scale commercialization. Correct laboratory testing and an elucidation of reaction chemistry were critical to the successful commercialization of this catalyst. This review focuses not only on the historical development and refinement of the ZSM-5 additive concept within Mobil, but also on lessons learned in the effective evaluation of this catalyst in progressing it from laboratory- to commercial-scale catalytic cracking units.

Eila et al., (1990) contented that the effect of the addition of ZSM-5 to an ultra-stabilized RE-USY fluid catalytic cracking (FCC) catalyst has been studied in a DCR (Davidson continuous riser) pilot plant, that closely matches a commercial unit. The lower gasoline yield obtain after ZSM-5 addition is consequence of selective cracking of most the low octane number components, rendering a highly olefinic LPG. Our study, at two different severities (505 and 520 °C), revealed that the octane boost in the gasoline fraction can be explained by three reasons: the previously mentioned selective removal, a concentration effect of naphthenes and aromatics and particularly, the increase of specific light C₅-C₆ components. This last effect depends on cracking severity. Rather than being due to a concentration effect, the increase of light branched and olefinic high octane number components is more intense at lower severities.

Biswas and Maxwell (1990) insisted that addition of ZSM-5 to an ultra-stabilized fluid catalytic cracking (FCC) catalyst leads to significant losses in gasoline yield, the gasoline being cracked preferentially to propylene, iso-butane and butylene. The octane boost resulting from ZSM-5 addition is due to an increase in gasoline aromatics concentration as well as a decrease in molecular weight. Rather than being due to a particular reaction mechanism, the increase in aromatics concentration is in essence a concentration effect resulting from preferential removal of the non-cyclic gasoline components through cracking. No increase in gasoline component branching is observed on ZSM-5 addition. Of particular importance is the effect of ZSM-5 addition on the octane potential of the low-octane gasoline heart-cut (b.p. 70-130 °C) from the FCC unit. A boost in motor octane number (MON) is observed due to cracking of low-MON components, e.g. olefins, to gas. However, no effect on heart-cut research octane number (RON) is seen, since these olefins have a significant RON contribution. A comparative study has been made of the effects of ZSM-5 addition and operation at higher reactor temperatures on gasoline octane enhancement in fluid catalytic cracking. Higher FCC reactor temperatures give rise to higher research octane levels than ZSM-5 addition does due to the catalytic formation of gasoline aromatics and preservation of olefins; the latter are preferentially cracked out in the presence of ZSM-5. Hence, a higher gasoline yield is realized, even at high motor octane levels. One detrimental factor, however, is the increased production of dry gas.

Nalbandian et al., (1993) asserted that a commercial ZSM-5 containing additive was tested at a MAT unit and the derived results concerning product distribution as well as gasoline composition shifts have been interpreted by means of changes in the rates of certain secondary reactions occurring during catalytic cracking. The most important results of the ZSM-5 addition are gasoline yield decrease, LPG alkenes increase and RON gain. The gasoline composition changes include a significant decrease of the C₆-C₉ alkanes yield, lighter gasoline formation through increase of the C₅ hydrocarbons yields, increased branching in the light alkenes and a small decrease in the naphthenes and aromatics yields. Most of the above effects have been interpreted by taking into account the enhanced alkenes reactivity on ZSM-5. A comparison of the present results with those from pilot plants and commercial units reveal that the shifts imposed by ZSM-5 either to the product yield distribution or to gasoline composition are in very good agreement, despite the significant differences of the absolute yields.

Buchanan and Adewuyi (1996) claimed that FCC yields were quantified for operation under conditions that maximize the production of light olefins. These conditions include high reaction temperatures, use of low unit cell size base catalysts (USY and RE-USY), and addition of large amounts of ZSM-5. Adding 25% ZSM-5 additive nearly tripled propene yields, and increased butenes by about 60%. The fraction of isobutene in the butenes rose from 32-35 wt.-% to its equilibrium value of about 40%. For the base catalysts alone, increasing the reaction temperature from 811 K to 852 K gave a modest increase in C₃-C₄ olefins, but this effect was largely absent for the ZSM-5/base catalyst mixture. This suggests that raising temperature loses effectiveness as a means of increasing light olefins yield, in the presence of large amounts of ZSM-5. Addition of 25 % ZSM-5 additive had effects on C₂- species and butadiene which have not generally been observed with lower levels of ZSM-5. Ethylene yields increased, and methane and ethane yields decreased, while butadiene yields were halved. Increasing temperature gave significant increases in the yields of butadiene, all C₂- species, and a decrease in butanes; these trends are the opposite of those seen with ZSM-5 addition. PIONA analysis of selected gasoline samples showed that raising temperature gave a more olefinic gasoline. ZSM-5 addition increased olefin branching and shifted olefins and paraffins to lower carbon numbers.

Most yield shifts could be understood in terms of how changing temperature and adding ZSM-5 affect the relative rates of cracking versus hydrogen transfer for the gasoline-range olefins.

Buchanan (2000) mentioned that the addition of ZSM-5 to fluidized catalytic cracking (FCC) units can greatly increase yields of C₃–C₅ 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 C₅- and decrease in C₇₊ 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 C₃=/C₄= ratio seen for high activity ZSM-5 additives, and for the high gasoline selectivity associated with high Si/Al ZSM-5 additives.

Morsi and Shokry (2000) report that conversion of n-octane over ZSM-5 zeolite are greatly enhanced by incorporation of 0.35 wt.% Fe, Zn, Zr metals. Hydroconversion rates were conducted at temperature range of 350-500 °C, W/F of 14.8 g. of catalyst/g.mole of feed/h, and hydrogen/feed=5:1 (mole:mole). The product selectivity with total conversion was examined at the temperature range under study. The catalyst Zr/H25 M-5 gave the highest selectivity toward aromatization and production of xylenes.

Smirniotis and Ruckenstein (1994) claimed that the cracking of n-octane, 2,2,4-trimethylpentene and 1-octene was examined over ZSM-5, β zeolite, Y, USY and the composites of any of the two former zeolite as additives to the latter two traditional cracking zeolites, under high-severity conditions, namely relatively high temperature (500 °C) and high conversions. The behaviours of these catalysts under the above conditions are very different from those already studied in the literature, which have been at low conversion and lower temperature. While for the latter condition the selectivities for olefins were higher and for aromatics lower over ZSM-5 than over Y faujasite, in the present conditions the above trends are invert. The shifting in the rate of primary cracking, hydrogen transfer, oligomerization and

bimolecular condensation cracking reactions produced by the changes in the zeolite employed and conditions are responsible for this behaviour. For the composite of Y faujasite with either ZSM-5 or β zeolite the C_3 and C_4 paraffin selectivities can be calculated as the weight averages of those for the individual zeolites. In contrast, for the USY zeolite base composites, the additivity rule is not always obeyed and the selectivities for the C_3 and C_4 paraffins can be larger than those over the individual zeolites.

Objectives

1. To prepare the NaY, REY, USY and ZSM-5 zeolite.
2. To evaluate the performance of additive ZSM-5 zeolite on fluid catalytic cracking catalyst.

Possible Achievements

The possible achievements is to produce NaY, REY, USY and mixed ZSM-5 catalysts. The influence of ZSM-5 additive on fluid catalytic cracking catalyst can be more clarified. The knowledge from this work can be applied to further fluid catalytic cracking study.

Contents of Research

1. Synthesis of NaY zeolite
2. Preparation of REY, USY and ZSM-5
3. Preparation of catalysts
 - 3.1 Variation of zeolite contents
 - 3.2 Variation of mixed zeolite contents
4. Characterization and evaluation of catalysts
5. Comparison of the performance of a mixed zeolite catalyst