FLUID CATALYTIC CRACKING (FCC), CATALYSTS AND ADDITIVES

1. Introduction

Fluid catalytic cracking (FCC) is a central technology in modern refining (1,2) and is used to upgrade a wide variety of gas, oil, and residual feedstocks to gasoline, diesel fuel, and light gases. The first FCC unit, PCLA-1, came on stream in 1942 and though considered a mature technology, both hardware and catalyst developments continue to be made. A brief history of the important events in the development of FCC catalysts is shown in Table 1. In the 1960s, the introduction of zeolite Y revolutionized the process by increasing gasoline selectivity, adding almost $2 of value per barrel of feed processed (3). Before this breakthrough, amorphous silica-alumina catalysts were used that had poor gasoline selectivity and made much coke and gas compared with zeolite-based catalysts. More than 40 years later, zeolite Y, or more precisely, modified versions of zeolite Y, continues to be at the heart of the modern FCC catalyst.

In the 1980s, the introduction of a second zeolite, ZSM-5, dramatically improved the ability of refiners to increase both gasoline octane number and the yields of light olefins (propylene and butylenes). Originally employed to improve gasoline octane, the focus of ZSM-5 additive use has switched more toward the production of propylene as the demand for FCC propylene has increased significantly to supply the growing petrochemicals industry.

In the early 1990s, the introduction of new alumina technologies with a higher tolerance to the contaminant metals Ni and V further increased the flexibility of the FCC unit to process heavier crude sources (4).

In this chapter, we focus on developments in FCC catalyst technology and the driving forces behind them. Although the FCC process has been used for more than one-half of a century, new and important developments continue to be made in several areas. Some of these new developments are a direct response

Table 1. **Important Dates in FCC Catalyst Development**

	Development year
aluminum chloride catalyst	1915
activated clay catalysts (Houdry)	1928
silica/alumina catalyst (Houdry)	1940
first commercial production of FCC catalyst (Davison)	1942
commercial production of microspheroidal catalysts (Davison)	1948
synthetic high alumina catalyst (Davison)	1955
commercial production of zeolite Y (Union Carbide)	1959
introduction of zeolitic FCC catalyst (Mobil)	1962
introduction of USY and REUSY zeolites (Davison)	1964
silica-sol bound catalysts (Davison)	1973
introduction of Pt combustion promoter (Mobil)	1974
feed-added Ni passivation technology (Phillips)	1975
alumina-sol bound catalysts (Davison)	1981
commercialization of spinel SO_x additive (ARCO)	1982
introduction of ZSM-5 (Mobil)	1984
coke-selective, deep bottoms cracking matrices (Davison)	1986
introduction of Ni-tolerant matrix technologies (Davison)	1990
commercialization of V-trapping technology (Davison)	1992
introduction of additives for gasoline sulfur reduction (Davison)	1995
introduction of CSSN/Z-17 high activity zeolites (Davison)	1996
commercialization of NO_x control additive technologies (Davison)	1997
introduction of catalyst for sulfur reduction (Davison)	2001
introduction of Z-28 and Z-30 high activity zeolites (Davison)	2003
introduction of Tunable Reactive Matrices (Davison)	2004

to environmental regulation. Another important driving force is the goal to process heavier crude sources with higher levels of contaminants. Changes in hardware, such as the increasing use of advanced riser termination technology to further reduce catalyst/oil contact time have also resulted in significant changes in FCC catalyst technology. With the increasing integration of petroleum refining and chemicals production, the value of specific molecules in the product spectrum is driving FCC catalysts toward specific selectivities. Each of these trends has long-term implications for the development of future catalysts and hardware for the FCC unit.

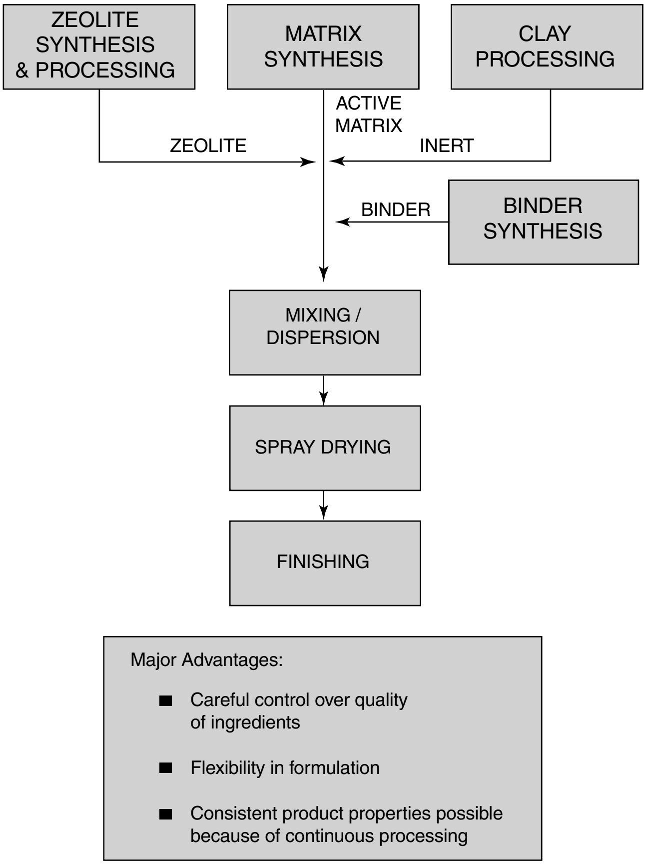
2. FCC Catalyst Design Fundamentals

FCC catalysts are generally comprised of zeolite, clay, active-matrix, and binder. The primary source of cracking activity comes from the zeolite component. Zeolite Y (faujasite) has been used in FCC catalysts since the early 1960s, however, a tremendous amount of R&D effort over the years has led to the continuous introduction of zeolite Y derivatives with a wide variety of performance-enhancing properties.

The principle modifications involve zeolite ultrastabilization and rare-earth ion exchange. In the ultrastabilization process, steam calcination is used to increase the framework Si/Al ratio of the zeolite Y. Not only does this process result in an increase in the intrinsic stability of the zeolite, it also results in the development of a secondary mesoporous network of pores that enhance the bottoms upgrading activity of the zeolite.

Rare earth ion exchange increases the activity of the zeolite and retards crystal destruction and dealumination in the hydrothermal environment of the regenerator. The higher the degree of rare-earth exchange of the zeolite, the higher the unit-cell size of the equilibrated zeolite in the equilibrium catalyst. Increasing the degree of rare earth exchange increases the gasoline selectivity of the FCC catalyst.

Most fluid cracking catalysts, especially those used in resid applications, are manufactured with an *active-matrix* component usually based on specialty aluminas. Active-matrix contributes a catalytically active surface that derives its activity (and selectivity) predominantly from porous silica-alumina that may have undergone chemical or physical modification to enhance activity as well as other aspects of its performance. Of importance is the maximization of pores in the range 100–600 Å, since these pores are known to be important for coke-selective bottoms upgrading (5). Recently, new FCC catalyst technology



Major Advantages:

- Careful control over quality of ingredients
- Flexibility in formulation
- Consistent product properties possible because of continuous processing

Fig. 1. Typical FCC catalyst manufacturing flow scheme.

was introduced based on the ability to tune pore size distribution and matrix acidity (6).

Clay is an important component that fulfills the remaining catalyst particle performance requirements. Clay serves as a heat sink and transfer medium. It can also serve as a sink for sodium, improving the catalyst's resistance to sodium poisoning. Clay provides little or no activity to the catalyst, but it does provide mechanical strength and density to the particle for optimum fluidization properties.

The binder is the "glue" that holds all catalyst components together and provides particle physical integrity. Some binders, such as alumina-sol polymers, have intrinsic cracking activity and thus aid in bottoms cracking.

Figure 1 shows the principle steps in the manufacture of FCC catalysts.

3. Residual Oil Processing

In today's highly competitive market, refiners are under increasing pressure to maximize profits in an environment where they, not only must operate their FCC units to meet increasingly stringent environmental regulations, but also have to produce products that meet tighter quality specifications. Nevertheless, with declining demand for fuel oil many refiners have found that processing larger amounts of lower cost resid feedstocks in the FCCU or RFCCU can substantially increase profitability (7).

Resid feedstocks have a higher boiling range compared with vacuum gas oil's and are characterized by high concentrations of polynuclear naphthenes, aromatics, and asphaltenes as well as high levels of contaminant metals, notably nickel and vanadium and high Conradson Carbon residue. Not surprisingly, proper design of the FCC catalyst is crucial for units operating with such feedstocks.

For units processing resid feeds where performance is impacted by high levels of contaminant metals and high feed Conradson Carbon residue, catalyst coke selectivity is the most important performance characteristic. Catalyst stability and metals tolerance are also very important features of a catalyst designed for resid applications. To facilitate the cracking of the large hydrocarbon molecules found in resid feeds, the catalyst must be designed to maximize diffusion of these bulky species to the active acid sites (5,8). Zeolitic and matrix activity must be optimized for each application and is dependent on feedstock properties along with the dominant bottoms cracking mechanisms characteristic of the feed. Resistance to less common catalyst poisons such as iron is critical for an increasing number of refiners and can be addressed by the correct choice of matrix technology. Finally, catalyst physical properties must be optimized to ensure maximum unit retention (8). The influential effects of metals tolerance is described below.

3.1. Contaminant Metals (Ni, V, and Fe).

In the 1990s, a wide range of technologies were developed to improve the tolerance of FCC catalysts to contaminant metals in the feed, primarily vanadium, and nickel (4). The dearomatization function of nickel is responsible for an increase in coke yield as the Ni level increases on the equilibrium catalyst. Moreover, the dehydrogenation

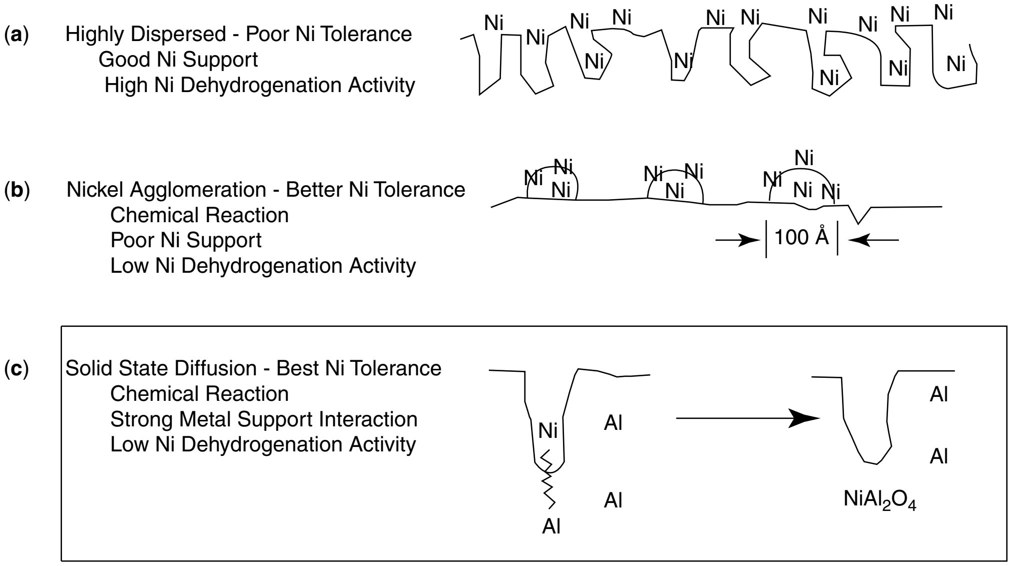


Fig. 2. Matrix technology passivates Ni by strong metal–support interactions.

activity of the Ni leads to the formation of molecular hydrogen. Since hydrogen is the most difficult gas to compress, an increase in the FCC unit can quickly limit the wet gas compressor. In order to increase the tolerance of FCC catalysts to Ni contamination, special matrix alumina technologies were developed. These react with contaminant Ni, removing it from the surface and forming stable Ni–aluminate phases in the bulk of the alumina (Fig. 2). Oxygen TPD measurements provide evidence for the solid-state diffusion of Ni into the alumina away from the surface and therefore the reactants.

Vanadium is particularly harmful to catalyst performance because it deactivates the zeolite component and causes yields to deteriorate (9). Vanadic acid is believed to form from vanadium oxides in FCCU regenerators in the presence of steam:

$$V_2O_5(s) + 3\ H_2O(v) \longrightarrow 2\ H_3VO_4(v)$$

Vanadium mobility varies from unit to unit, depending on, among other things, the level of excess oxygen in the regenerator (10). Catalyst manufacturers have developed more stable zeolites (eg, Z-17, Z-28, Z-30, CSSN, and CSX) and a series of V traps to increase the ability of the zeolite to handle vanadium. These traps are based on Ba, Ti, rare earth, and other elements. Some are more effective than others, but the basic idea is the same, ie, to keep the V away from the zeolite by binding to the surface of an inactive particle (Fig. 3).

Catalyst manufacturers are continuously striving to improve the stability of their catalysts to metals poisoning as resid processing becomes more important in the future. For example, AURORA-LC contains high stability Z-17 zeolite and metals trapping matrix technology that in one commercial example,

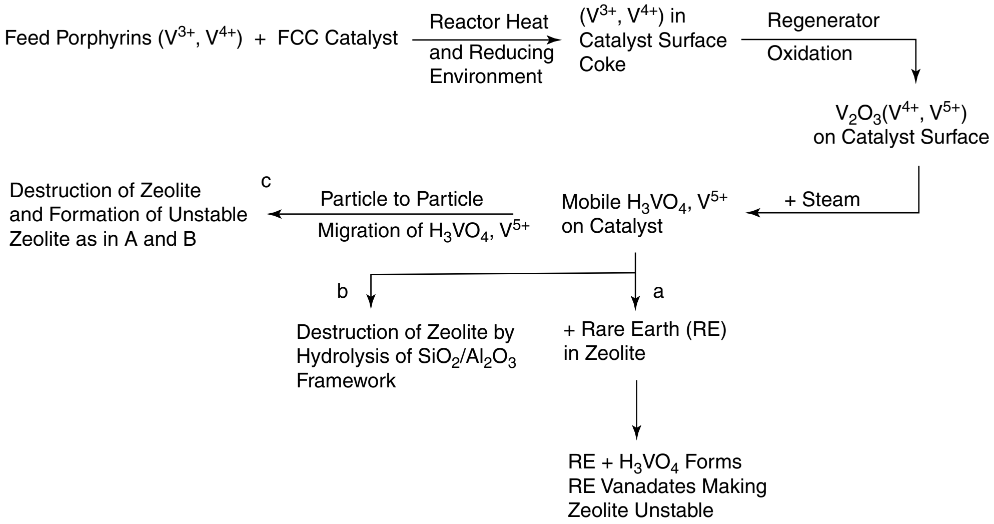


Fig. 3. Vanadium deactivation mechanism.

allowed a refiner to increase profitability by \$4.30/mton of feed in the presence of 18,000 ppm Ni + V (11).

More recently, a breakthrough in resid cracking catalyst technology was made with the introduction of IMPACT (6). Utilizing new high stability Z-28 zeolite technology in combination with a proprietary tunable reactive matrix system that incorporates an integral vanadium trap, IMPACT has demonstrated step-out coke selectivity and bottoms upgrading in the presence of very high levels of contaminant metals (Fig. 4). In one U.S. Gulf Coast application, IMPACT increased profitability by an estimated \$3.10/mton at only 20% concentration in the circulating catalyst inventory (Table 2) (6).

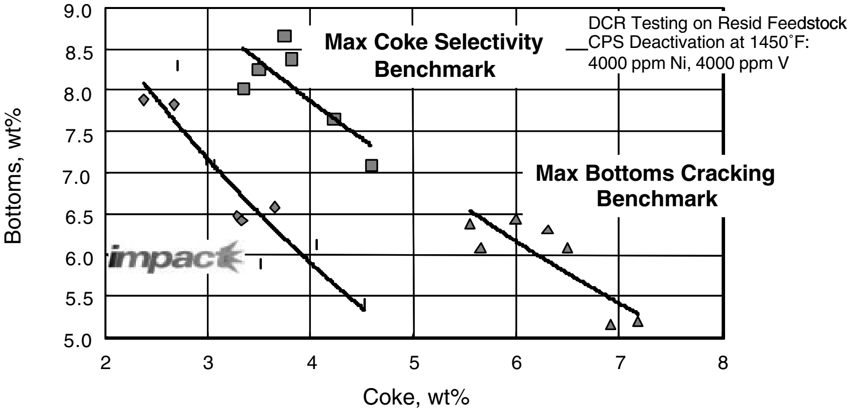


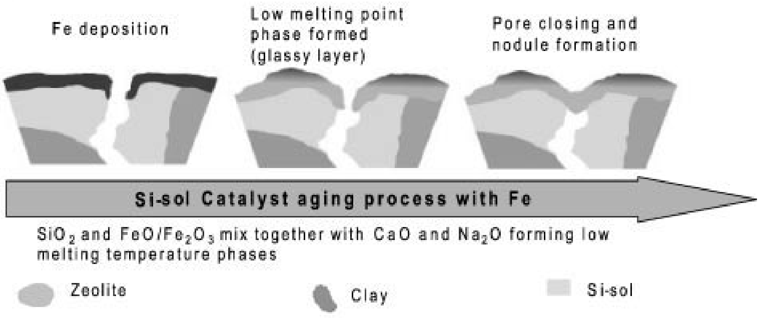
Fig. 4. Recent developments have resulted in the introduction of step-out coke-selective bottoms upgrading FCC catalyst technologies such as IMPACT.

Table 2. **Performance of IMPACT Resid Cracking Catalyst Technology at 20% Turnover**

	Resid catalyst benchmark	20% IMPACT
product yields		
total C_2-, wt%	3.1	3.1
total C_3, vol%	11.5	11.2
total C_4, vol%	18.0	17.4
naphtha, vol%	55.4	58.3
LCO, vol%	16.9	16.1
slurry, vol%	6.0	5.4
coke, wt%	5.6	5.6
conversion, vol%	77.1	78.5
profit margin		
\$/mton of fresh feed		+3.10

Understanding of the effect of Fe contaminants on the FCC catalyst is relatively new and comes from direct observations in the field: dramatic losses in activity sometimes coupled with a loss in bottoms cracking selectivity that appears to correlate with decreased ABD (Average Bulk Density measured in g/cm^3) due to catalyst particles sticking to each other (12). The catalyst sticking

(a) SiO_2 bound FCC Catalysts



SiO_2 and FeO/Fe_2O_3 mix together with CaO and Na_2O forming low melting temperature phases

(b) Al_2O_3 bound FCC Catalysts

Low melting point phases (glassy layer) may form only over high SiO_2 areas of the particle surface. Pores in Al_2O_3 rich areas (Al-sol binder and alumina matrix) remain open.

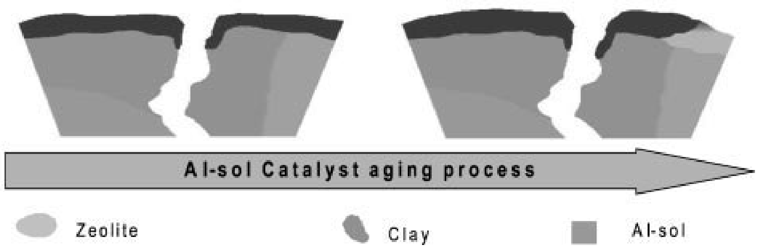


Fig. 5. Mechanism of catalyst deactivation by Fe.

appeared in turn to be correlated with increasing Fe content on the equilibrium catalyst. A detailed account of Fe deactivation is given in Ref. 12. A pictorial representation of the mechanisms leading to catalyst deactivation by Fe for SiO_2 bound and Al_2O_3 bound catalysts is presented in Figure 5.

To minimize catalyst deactivation by contaminant Fe, refiners are recommended to focus on the following where possible:

Feedstocks: Use low Fe, Na, and Ca feeds and reduce its acid content to lower equipment corrosion.

FCC unit: Minimize the regeneration temperature.

FCC catalyst: Use Al_2O_3 bound catalysts instead of SiO_2 bound ones.

4. Short Contact Time (SCT) Cracking

In order to minimize nonselective post-riser cracking, many refiners are revamping their units to operate in the so-called “short contact time” mode. In the FCC operation, catalyst and feed are contacted at the bottom of the riser with cracking reactions proceeding along the length of the riser. Contact time over the length of the riser is $\sim$5–8 s. At the end of the riser, the catalyst and products are separated in the disengager. It is here that product vapor can undergo nonselective (essentially thermal) cracking as hydrocarbon vapors come into contact with hot, coked catalyst.

In the early 1990s, a closed cyclone system was introduced that featured cyclones directly coupled to the end of the riser (13), which allowed rapid separation of the catalyst and products, reducing post riser cracking in the disengager. Today, all major process licensors offer advanced riser termination technologies of one sort or another with one objective in common—reduction of nonselective post-riser cracking.

New processes are emerging where the catalyst/feed contact time is reduced to <2 s. The so-called millisecond catalytic cracking (MSCC) process was introduced in the early 1990s in the United States (14).

4.1. FCC Catalyst Design Considerations for SCT Operations.

Catalysts for SCT operations must be designed taking into account the following considerations (15):

- Catalyst/oil contact time is shorter—leading to lower intrinsic conversion and bottoms cracking.
- Reactor temperature is generally higher—leading to increased conversion and light olefins yields (including increased gasoline olefinicity).
- Catalyst circulation rate is generally increased—leading to an overall increase in selective conversion.
- Regenerator/regenerated catalyst temperatures are generally lower—leading to cooler catalyst/oil mix zone temperature, hence the need for improved feed nozzles to ensure efficient feed vaporisation.

To compensate for the reduced catalyst/feed contact time and consequently loss in conversion, high activity catalysts are needed. The zeolite component within the catalyst has the greatest effect on activity and therefore, proper zeolite selection is very important. In addition, it is very important to choose a matrix with the right level of activity for a particular application to address the reduction in bottoms upgrading that occurs with shorter contact time. Excess matrix activity is undesirable because it leads to poorer coke and gas selectivities. In addition to providing bottoms cracking activity, the matrix should be selected to provide low coke and gas selectivities, particularly in the presence of contaminant metals.

5. Clean Fuels Production

5.1. Gasoline Sulfur Reduction. Gasoline vapors and tailpipe emissions contain NO_x and VOCs, which can react in the atmosphere to produce ozone, a major component of smog. Toxic compounds (eg, benzene, a known carcinogen) are also emitted by vehicles. In the United States, Federal Reformulated Gasoline (RFG) Phase 2 specifications went into effect in 2000, requiring reductions in tailpipe emissions of these pollutants as calculated by the Environmental Protection Agency's (EPA) Complex Model. Gasoline RVP, sulfur, olefins, and aromatics content all play important roles in meeting RFG Phase 2 requirements.

Sulfur recently has come under even further scrutiny. Sulfur in gasoline degrades the performance of catalytic converters by poisoning the active sites (16). In order to improve catalytic converter performance and meet lower tailpipe emissions standards, the EPA has determined that gasoline sulfur levels must be reduced. The EPAs Tier 2 specifications require that gasoline sulfur average 30 ppm at the refinery level by 2006 with a per-gallon cap of 80 ppm. The 30 ppm requirement represents a >90% reduction in gasoline sulfur from baseline levels. The California Air Resources Board (CARB) has gone even further. Current CaRFG-2 specifications already require an average gasoline sulfur level of 30 ppm and proposals for CaRFG-3 would lower average gasoline sulfur to 15 ppm.

The rest of the world is not far behind. European specifications will require 50 ppm sulfur in gasoline and diesel in 2005 with a likely move to 10 ppm by 2008. Many Asian countries including, but not limited to, Japan, Korea, and India have also recently lowered sulfur specifications in transportation fuels.

In order to achieve these low levels, refiners have a number of choices including gas oil hydrotreating, FCC feed hydrotreating, gasoline sulfur adsorption processes, and gasoline hydrofinishing (17). Each of these techniques has debits associated with it. Some, like gasoline hydrofinishing, lead to a reduction in gasoline olefins and thereby reduce gasoline octane. Some, like feed hydrotreating, have a high demand for molecular hydrogen, which is often in short supply in the refinery. Lowering gasoline end point can significantly lower gasoline volume. Furthermore, it may be difficult to find a home for the high sulfur heavy gasoline, without further processing. Thus, there is great incentive for refiners and catalyst manufacturers to find ways to reduce gasoline sulfur directly in the FCC unit.

Gasoline Sulfur Speciation. FCC gasoline contributes to >90% of the total gasoline pool sulfur with the remaining 10% originating from straight

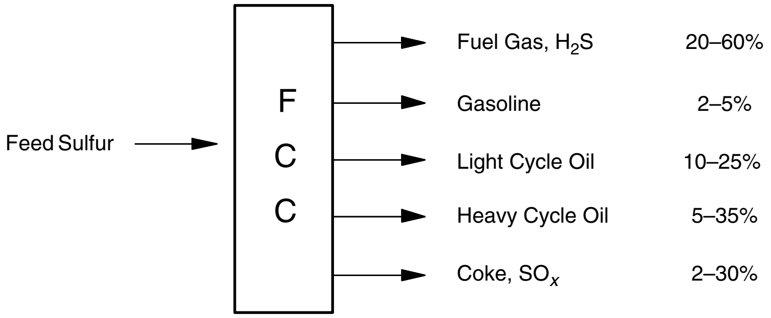


Fig. 6. Sulfur distribution in the FCC products.

run naphtha. The sulfur in the gasoline is concentrated (up to 50%) in the higher boiling region (>193°C). Moreover, only ~2–5% of the sulfur in the FCC feedstock ends up in the gasoline as summarized in Figure 6.

The sulfur compounds in the FCC gasoline typically comprise mercaptans, thiophene, C_{1-4} substituted thiophenes, thiophenol, C_{1-2} substituted thiophenols, tetrahydrothiophene, and benzothiophene (Fig. 7).

Reaction Mechanism. In an FCC unit, typically ~35–45% of the feed sulfur is converted to H_2S, 2–5% is found in coke, 5% in gasoline and the rest ends up in the LCO and bottoms (18,19). The reactivity of feed sulfur compounds and the mechanism by which they end up in gasoline is a subject of ongoing study. Mercaptans and sulfides are converted to H_2S and do not significantly increase the amount of sulfur in gasoline. Hydrogen sulfide production from FCC has been found to correlate well with the amount of non-thiophenic sulfur in the feedstock

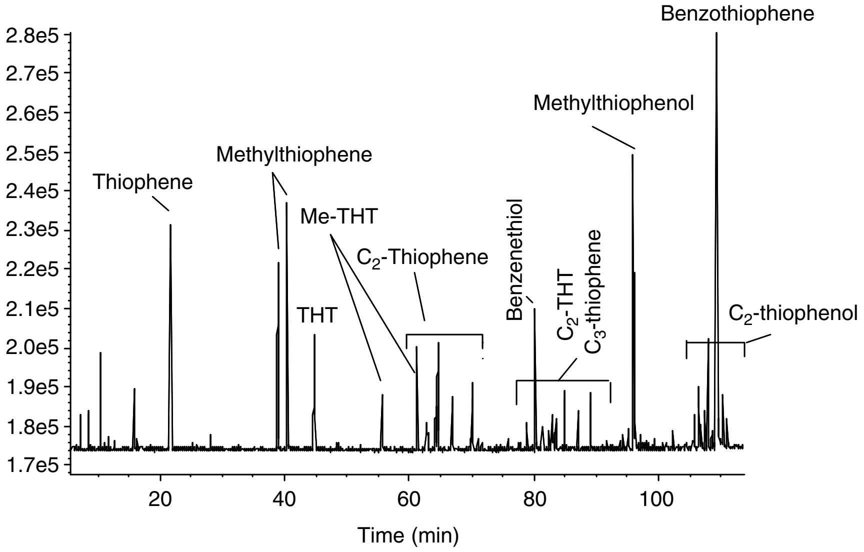


Fig. 7. GC-AED Analysis of a typical FCC gasoline.

(19). Huling and co-workers (20) and Nguyen and Skripek (21) correlated sulfur in FCC gasoline with the sulfur species in FCC feed. Alkylthiophenes and aromatic sulfides are believed to be the key contributors to gasoline range sulfur.

The concentration of sulfur in gasoline is only weakly dependent on conversion as a result of opposing effects (18,21). Mercaptans and alkylthiophenes are unstable with respect to desulfurization. The concentration of these species decrease with increasing contact time or as gasoline overcracking occurs. However, benzothiophene, formed by dealkylation of higher molecular weight sulfur compounds, is relatively stable with respect to desulfurization. In general, the concentration of benzothiophene increases with conversion. At constant conversion, the concentration of sulfur in gasoline increases with riser temperature due to increased dealkylation reactions of aromatic sulfur species. The sulfur content of gasoline increases as gasoline cut point temperature is increased, because of the inclusion of benzothiophenes.

Gasoline Sulfur Reduction Catalyst/Additive Technologies. Approaches for developing GSR catalyst/additive technologies may include: (*1*) direct desulfurization of thiophenes and thiophenols from the product gasoline, (*2*) adsorption of gasoline sulfur precursors; or (*3*) alkylation of gasoline sulfur precursors into a higher boiling range fraction. The best alternatives are obviously (*1*) and (*2*) since they do not transfer the sulfur to the other liquid products. In addition, it is desirable that the additive converts the sulfur compounds into H_2S and hydrocarbon products rather than to coke.

Sulfur reduction additives such as GSR-1, commercialized in 1995, and its successor, D-PriSM, commercialized in 2001, have been shown to be most effective at reducing sulfur species in the light FCC naphtha and have been used in >20 refineries worldwide (17). Based on solid Lewis acid (ZnO-based) technology, D-PriSM has provided up to 35% sulfur reduction on a reduced endpoint FCC gasoline. The availability of D-PriSM as an additive allows the inventory to be base loaded for rapid sulfur reduction response and it can be used in conjunction with any base FCC catalyst.

As an alternative to sulfur reduction additives, catalyst technologies such as SuRCA and SATURN have been successfully commercialized (17). The SuRCA catalysts are designed to completely replace the conventional FCC catalyst in the circulating inventory, while maintaining or even enhancing existing yields and selectivities. In addition to inherent cracking activity and selectivity, SuRCA catalysts contain sulfur reduction functionality, which has provided full-range gasoline sulfur reductions as high as 30% commercially. In contrast to sulfur reduction additives, SuRCA is effective across the entire gasoline boiling range. Additionally, reductions of 10–20% in LCO sulfur have been observed in some applications.

SATURN catalyst technology incorporates a gasoline sulfur reduction functionality that is effective over the entire gasoline boiling range. SATURN has exhibited gasoline sulfur reductions as high as 50% in pilot plant testing. Reductions in LCO sulfur from 10 to 30% have also been observed. As with SuRCA, the SATURN catalyst is custom-formulated with both cracking activity and sulfur reduction functionality so that it can replace the conventional FCC catalyst in the circulating inventory with minimal impact on yields and selectivities. The magnitude of the sulfur reduction observed with this product is such that select refiners may find that use of SATURN would allow them to comply with upcoming clean fuels regulations while avoiding the significant capital expense of an FCC feed or naphtha hydrotreater (17).

5.2. Gasoline Olefins Reduction.

It is well known that the hydrogen-transfer activity of the FCC catalyst can significantly affect gasoline olefins levels. Typically, increasing the rare-earth content of the catalyst increases hydrogen-transfer activity, thereby decreasing gasoline olefins. However, when using conventional FCC catalysts, the decrease in gasoline olefins is often accompanied by large reductions in LPG olefins and gasoline research octane number (RON), and poorer coke selectivity (22). The loss of valuable propylene, butylenes, and octane barrels is often not economical, even for the gasoline olefin-constrained refiner.

RFG catalysts have been introduced as a solution to this problem. While RFG catalysts are specifically designed with maximum hydrogen-transfer activity to reduce FCC gasoline olefins, this is accomplished without the economic penalties mentioned above. Gasoline olefins can be significantly reduced [reductions up to 40% rel. (15% abs.) have been observed commercially] while keeping propylene, butylenes, and gasoline RON constant. Coke selectivity is also maintained, even at very high metals levels (22).

Following the early success in the Murphy-Meraux, LA refinery (23), RFG catalysts are now in use in >10 FCC units around the world and continue to show outstanding activity and stability in addition to olefins reduction in some of the most severe resid applications. Equilibrium catalyst (Ecat) zeolite unit cell sizes of 24.40 Å and higher have been maintained without sacrificing coke selectivity in FCC units with Ecat $Ni + V$ levels of 8,000–12,000 ppm. A recent example of the commercial performance of an RFG catalyst show a reduction in gasoline olefins from 38 to 28 vol%, while maintaining LPG olefins, gasoline RON, and coke selectivity, and increasing conversion all at a higher average metals level (17).

6. Environmental Issues: Controlling Emissions from the FCC Unit

6.1. Reducing Particulate Emissions.

During normal operation, an average FCC unit may replace ~1% of its catalyst inventory to make up for particle attrition. The physical properties of FCC catalysts are designed for optimum fluidization and low attrition. A trade-off exists between the mechanical strength of the catalyst and the desire to limit erosion of FCC hardware (24–26).

The nature of the binder is an important consideration. Commercial experience shows that alumina-sol bound catalysts have outstanding unit retention characteristics compared with other catalyst systems as indicated by the data in Figure 8 (8).

6.2. Reducing SO_x Emissions.

Sulfur oxides (generally referred to as SO_x) have been shown to be a leading cause of environmental damage, especially due to their contribution to the formation of acid rain, and their role in the formation of aerosols. In the United States, the EPA New Source Performance Standards (NSPS) enforcement initiative has led to voluntary agreements between the EPA and refiners to reduce emissions (27). Known as Consent

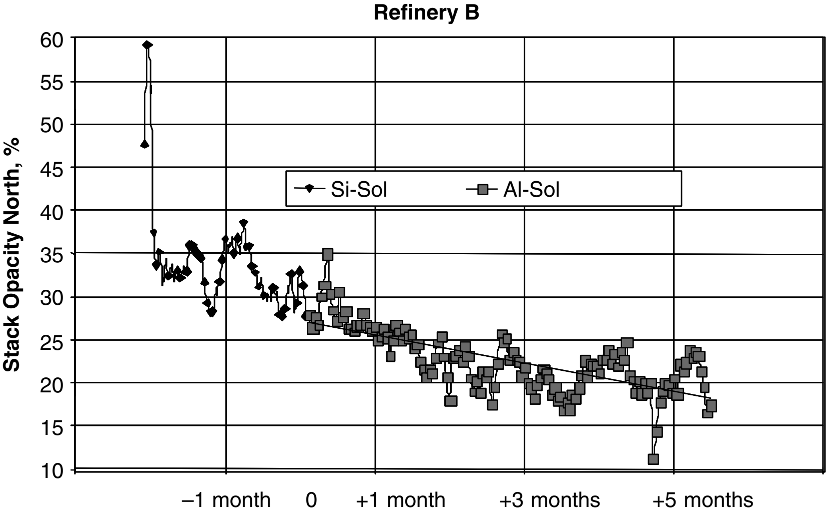


Fig. 8. Al-Sol catalysts show outstanding unit retention in commercial operations (8).

Decrees, these agreements currently cover ~45% of the industry and typically require refiners to reduce FCC unit SO_x emissions to <25 vppm. The SO_x is formed in the FCC regenerator from the combustion of sulfur containing molecules bound in coke. Although only a small percentage of the feed sulfur ends up in coke, typically <10%, all of the sulfur in coke is oxidized to SO_x (18). The concentration of SO_x in the FCC flue gas can vary from <100 ppm to several thousand ppm, depending on feed sulfur levels and speciation. Although hydrotreated feeds typically produce lower SO_x emissions, the percentage of the feed sulfur going to coke is usually higher than for virgin feeds. Up to 30% of feed sulfur has been reported in the coke depending on the nature of the feedstock (28).

FCC unit SO_x control options include (*1*) feed hydrodesulfurization, (*2*) 'end-of-pipe' solutions such as flue gas scrubbing, and (*3*) the use of SO_x-transfer catalysts. Options (*1*) and (*2*) are capital intensive but do provide additional benefits. The SO_x-transfer catalysts or additives require little or no capital and can be implemented quickly.

SO_x Additives. SO_x additives have been commercially available since the early 1980s. These early additives were marginally effective at reducing SO_x. However, this changed with the introduction of DESOX. Its patented spinel structure has proven to be the most effective material available for SO_x reduction. DESOX reduces (or more correctly transfers) SO_x through a three-step mechanism: (*1*) oxidation of SO_2 to SO_3, (*2*) capture of SO_3 by proprietary metal spinel, and (*3*) release of H_2S in the FCC reactor (Fig. 9) (29).

DESOX technology has been used extensively throughout the refining industry (>100 units worldwide) (27). Refiners have achieved SO_x reductions in excess of 90%, which has usually been accomplished at a cost of $500–900/ton of SO_x removed. There is no thermodynamic limit to the amount of SO_x that can be reduced using DESOX. Indeed commercial experience at several locations shows that emissions can be <10 vppm.

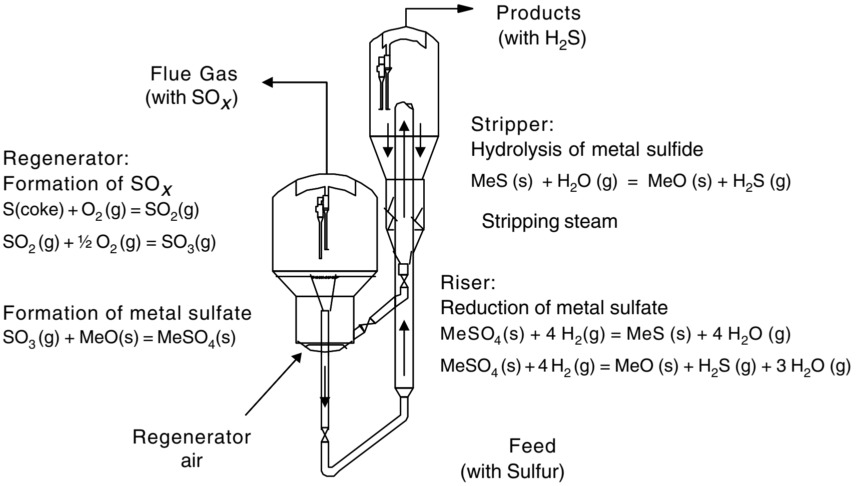


Fig. 9. Catalytic SO_x reduction.

Figure 10 shows the results of a test a refiner conducted to determine if reaching 25 vppm SO_x was feasible using a catalytic additive (30). Since the only goal of the test was to determine if 25 vppm could be reached, the base case was considered relatively unimportant, and was reduced to one day. Upon base loading to 1% of inventory, the refiner saw SO_x emissions drop to the 25 ppm range, and was able to hold emissions at that level for an extended period with DESOX additions of 3 wt% of fresh catalyst additions.

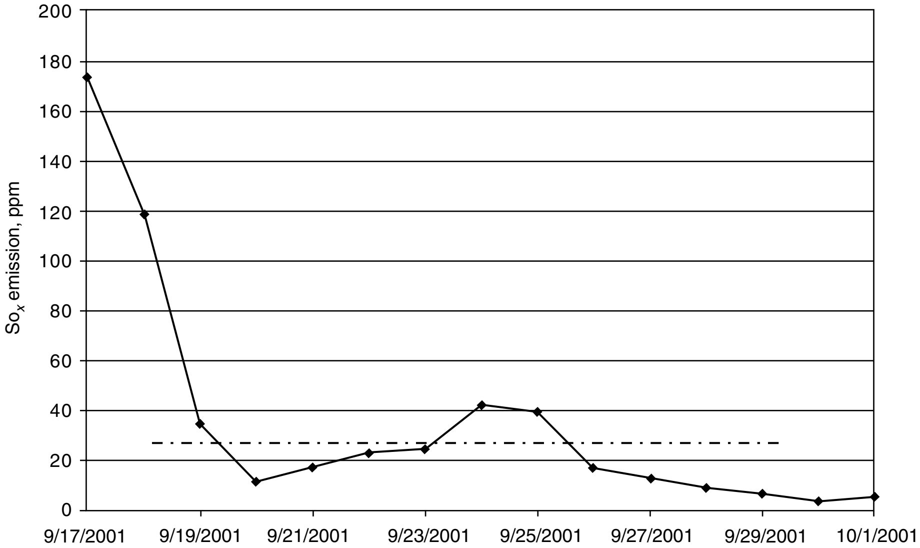


Fig. 10. DESOX is able to sustain SO_x emissions below 25 vppm at refinery A . Average SO_x reduction is 85% with 71% of the SO_x emissions below 25 ppm.

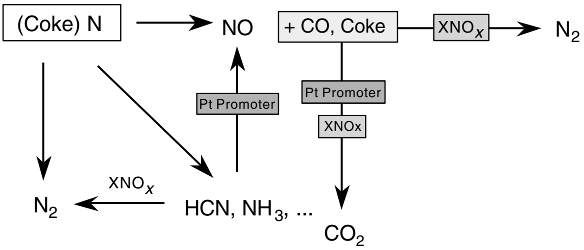


Fig. 11. Mechanism of NO_x formation.

No yield debits have been reported with DESOX (30), even at addition rates >10% of catalyst additions, and DESOX has not had any negative effects on equilibrium catalyst properties (30).

6.3. Reducing NO_x Emissions. Environmental legislation aimed at reducing the formation of ground-level ozone is forcing refiners to reduce their emissions of NO_x, a recognized ozone precursor. The FCCU regenerator is typically the single largest point source of NO_x within a refinery and poses a very challenging environment for controlling NO_x. The NO_x levels in the FCC regenerator flue gas are typically in the range of 100–500 ppm and may need to be reduced to <20 vppm.

A nitrogen balance around an FCC unit shows that ~ 50% of the feed nitrogen ends up in the coke deposited on the catalyst (31). The burning of the nitrogen containing coke during the regeneration, generates primarily N_2, but also NO and occasionally small amounts of NO_2 and N_2O.

The chemistry of NO_x formation has been studied in detail and a proposed mechanism is summarized in Figure 11. According to this scheme, NO can be reduced to N_2 with the help of reductants such as coke, CO, and hydrocarbons. Conventional combustion promoters (Pt/Al_2O_3) used to oxidize CO to CO_2 have been shown to increase NO_x emissions. One likely mechanism is that they also oxidize nitrogen intermediates (eg, NH_3 and HCN). In 1996, a low-NO_x combustion promoter, XNO_x, was introduced and shown to reduce NO emissions by >50%. This NO reduction was achieved while maintaining good CO combustion promotion. The results from the commercial use of a low-NO_x promoter are shown in Figure 12 (30). In this case, replacing conventional CO promoter with XNO_x resulted in a 60–70% NO_x reduction while maintaining afterburn and CO emissions control.

NO_x reduction can also be achieved with NO_x reducing additives that do not have CO oxidation functionality. DENOX, was introduced commercially in 1997 and has been shown to decrease NO_x by >50%.

In the United States, Consent Decree protocols typically call for replacing conventional combustion promoters with low NO_x promoters and conducting optimization of NO_x reducing additives at various levels. Figure 13 summarizes Consent Decree test results with DENOX (30). In these trials, uncontrolled or "Base NO_x" has been estimated using six sigma modeling techniques. Drivers for NO_x formation were found to be unit specific, with models containing between 4 and 17 input variables, including nonlinear and interaction terms. "Reduced NO_x" is the average NO_x measured during the trial. In some instances, XNO_x

- FCC Design: UOP Riser, 565 ton inventory
- 62,000 BBL/D of HDT feed
- Base emissions were 90-120 ppm with conventional Pt-based promoter
- XNO_x use reduced NO_x by over 50% to 30 ppm

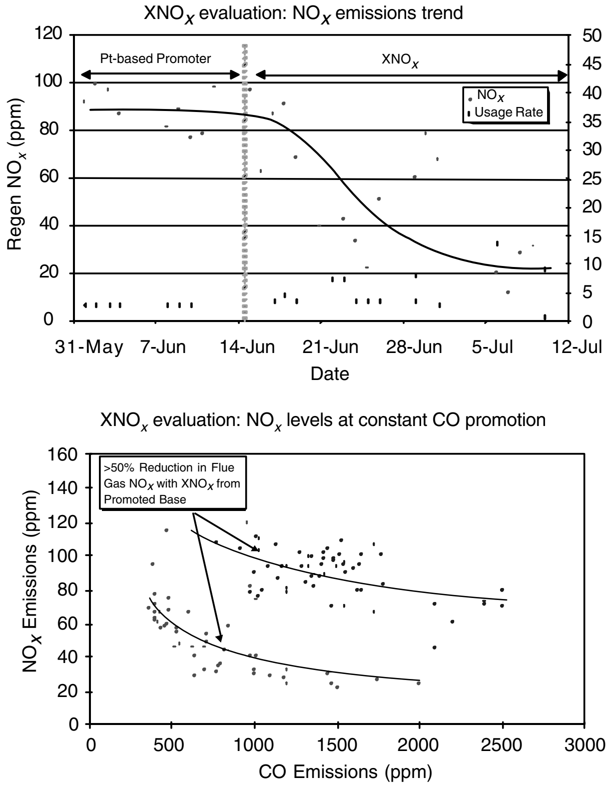


Fig. 12. Commercial performance of XNO_x.

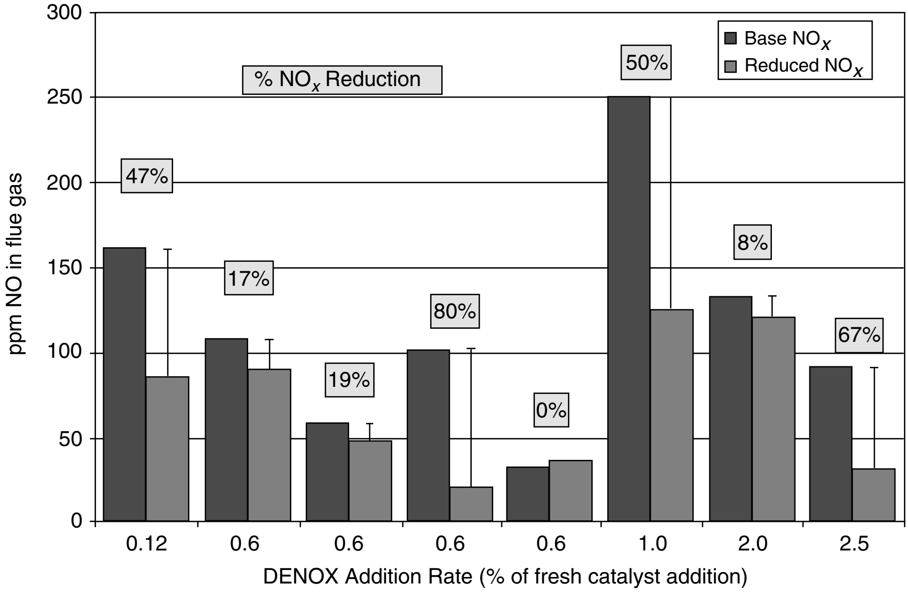


Fig. 13. Summary of consent decree test results with DENOX.

additions started coincidentally with DENOX and it is not possible to separate the relative contribution of each additive.

The amount of additive used in each trial varied greatly, as did the results, with observed NO_x reductions as high as 80%. The effectiveness of an additive for controlling NO_x emissions depends on unit design, mechanical condition, operating parameters, feedstock, etc. The chemistry of NO_x formation and reduction is very complex. As a result the performance of NO_x additives is unit specific.

7. Production of Light Olefins in the FCCU

The next 2–3 years will see a significant growth in the demand for propylene derivatives, particularly polypropylene, that will lead to structural tightness in the global propylene market. Since steam cracker capacity expansion, which is tied to a lower growth rate in the demand for ethylene, is forecast to lag propylene demand and much of the new planned capacity is in the Middle East where light feedstocks will be processed, the petrochemicals industry is looking to operators of FCC processes to fill the propylene supply gap (32).

In the short term, this will lead to opportunities for refiners to further increase margins by using ZSM-5 based additive technologies to produce incremental propylene for sale into the petrochemicals market. In the long term, a number of refiners are considering either revamping their FCC units to operate in "petrochemicals mode" or are considering investing in grass routes "on purpose" propylene production facilities that utilize ZSM-5 based FCC catalyst technologies.

7.1. ZSM-5 Technologies. The addition of ZSM-5 additives is the single most important method to increase the yields of light olefins, particularly propylene, at the expense of gasoline (Fig. 14). Davison Catalysts was the first catalyst manufacturer to supply ZSM-5 based additives for use in FCC units

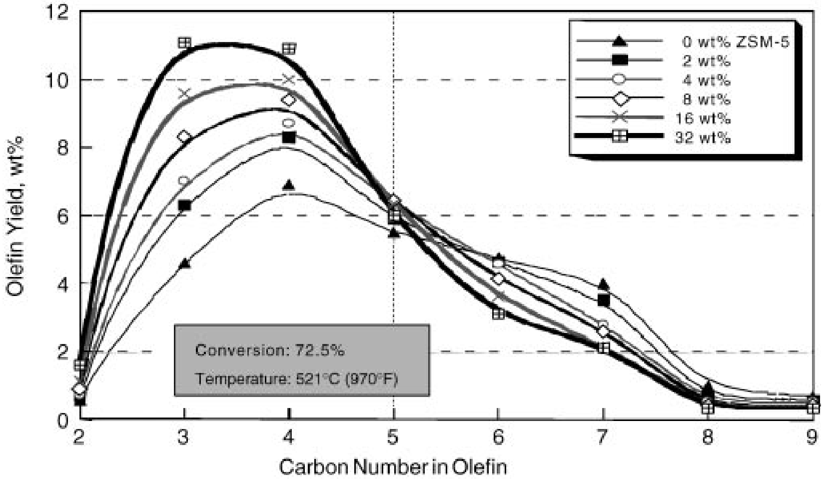


Fig. 14. ZSM-5 converts C6+ olefins to C5− olefins.

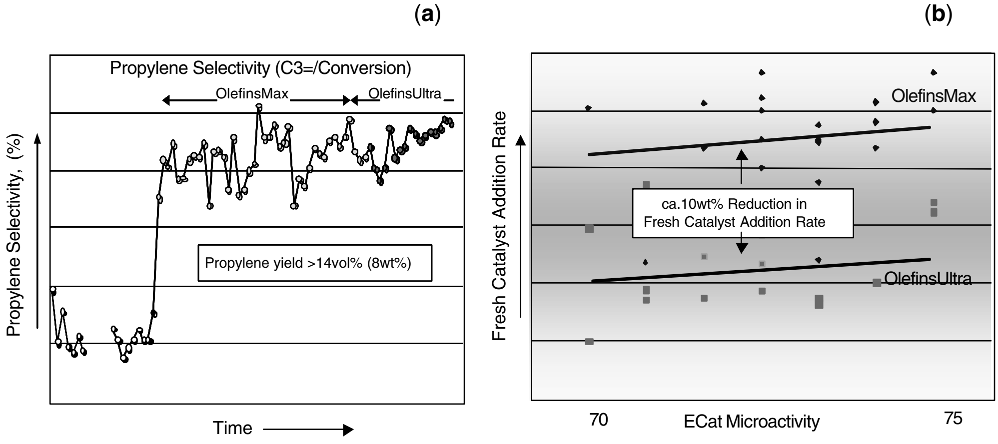


Fig. 15. OlefinsUltra enabled a european refiner to reduce fresh catalyst addition rate while maintaining high propylene yield.

back in 1984, where their primary role was to enhance gasoline octane. Since then, the role of these additives has changed to that of optimizing the yields of high value C3= and C4= olefins, while at the same time capturing the boost in gasoline octane (33).

ZSM-5 additives utilize unique matrix technologies that are designed not only to stabilize the ZSM-5 zeolite and provide the maximum activity per pound of zeolite, but also to minimize unselective cracking that reduce the yield of valuable light olefins. In addition, additives are designed with excellent attrition resistance to minimize losses (33). OlefinsUltra, for example, is formulated with the highest crystal content allowable under a new license agreement. This ultrahigh activity additive enables refiners to achieve high propylene yields that would otherwise require high loadings of less active additives that lead to dilution of the circulating catalyst inventory. In one commercial example, a refiner was able to reduce fresh catalyst additions by ~10% on switching to OlefinsUltra (Fig. 15).

Most recently, Davison Catalysts' APEX project focused on developing catalysts that give yields of propylene in excess of 15 wt% from the FCC unit (33). A new family of Propylene Maximizing Catalysts (PMC) has subsequently been developed based on the IMPACT technology platform that will allow refiners to take propylene production in the FCC unit to a new level. By using proprietary zeolite and matrix technologies, catalysts have been designed that not only produce exceptional yields of propylene (Table 3) but also demonstrate low coke make and good bottoms cracking activity in the presence of contaminant metals.

Propylene yields in excess of 15 wt% are of particular interest to refiners that are considering revamping their FCC units to operate in a "petrochemicals mode". This technology is currently in the commercialization stage, and a first application in an FCC unit is expected to take place later this year.

7.2. Understanding Performance Differences: Phosphorous Stabilization.

One of the important variables that accounts for much of the performance differences observed among ZSM-5 additives manufactured by different

Table 3. **APEX Project: Propylene Maximization Catalyst Technology**

Typical yields (wt%)						
		Conventional FCC	Conventional FCC + ZSM-5 Additive	AP_{PMC}– 140	AP_{PMC}– 150	AP_{PMC}– 200
feed type		Heavy	Heavy	Heavy	Heavy	Light
Ni + V/ppm		5000	5000	5000	5000	<100
reactor temperature	(°C)	535	535	550	565	565
conversion	(wt%)	80	80	80	85	85
propylene	(wt%)	5	9	15	18	22
butylenes	(wt%)	8	10	14	12	17
C5 + gasoline	(wt%)	52	46	36	32	28
LCO + HCO	(wt%)	20	20	20	15	15

suppliers is the stabilization of the zeolite with phosphorus (34). Figure 16 illustrates the effect of phosphorus stabilization for additives formulated with 25 wt% ZSM-5 crystal. The phosphorus-stabilized sample retains much of its initial activity (indicated by comparable delta propylene yield) on steam deactivation compared to the nonstabilized additive. Clearly, this represents the extremes in terms of the effect of phosphorus stabilization on additive activity. The activity level to which the additive equilibrates will depend on how the ZSM-5 zeolite was stabilized during manufacture (34).

Nuclear magnetic resonance (nmr) spectroscopy analysis indicates that phosphorus-stabilized ZSM-5 zeolite is less dealuminated after steam deactivation

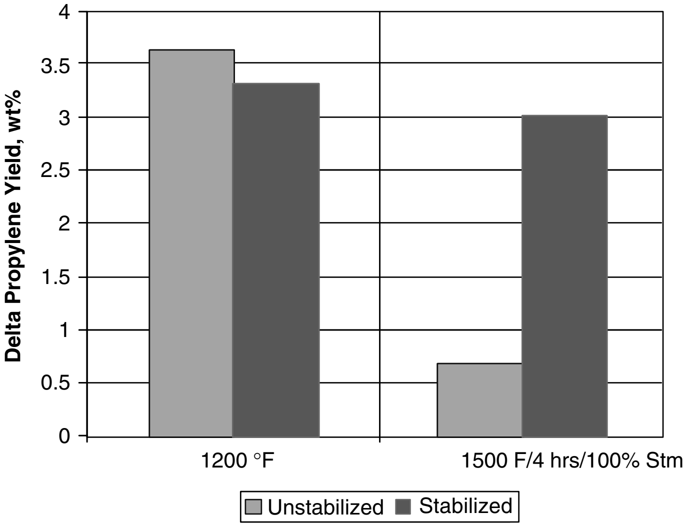
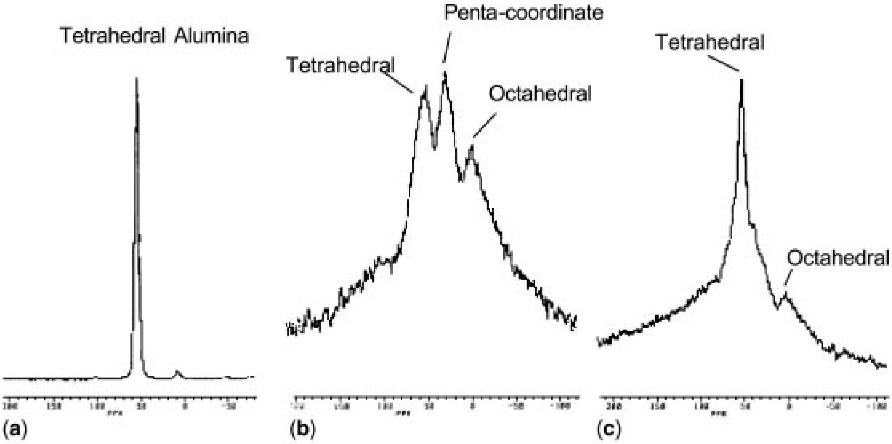


Fig. 16. Activity of stabilized and unstabilized ZSM-5 crystal.



Calcined (fresh) ZSM-5

Steamed Nonstabilized ZSM-5

Steamed P_2O_5-Stabilized ZSM-5

Fig. 17. ^{27}Al nmr spectra of stabilized and unstabilized ZSM-5 crystal.

than standard nonstabilized additives (34). This observation implies that the higher activity/stability of the ZSM-5 in these additives is due to a retardation of the dealumination rate caused by the phosphorus stabilization process. Two independent experimental results substantiate this conclusion. Figure 17 shows the ^{27}Al nmr spectra of (a) a fresh (heat-treated nonstabilized) ZSM-5 and two hydrothermally deactivated ZSM-5 samples; (b) nonstabilized ZSM-5; and (c) P-stabilized. As can be seen, the phosphorus stabilized ZSM-5 retains a significant amount on aluminum in the framework compared to the unstabilized version as evidenced by the large tetrahedral Al peak. Again, the activity retention of the additive in the actual unit will depend on the stabilization process carried out during manufacture.

Differences in phosphorus stabilization of the ZSM-5 zeolite account for much of the performance differences between additives from different suppliers. Surface area and percent ZSM-5 crystal content are not good indicators of catalytic performance especially between additives from different suppliers. ZSM-5 additive performance can vary substantially as a result of differences in ZSM-5 zeolite crystallization and stabilization. This has been seen commercially (34).

8. Conclusions

The FCC unit remains the primary hydrocarbon conversion unit in the modern petroleum refinery. To further improve profitability, refiners are increasing the amount of lower cost, residual feedstocks processed. These feeds are not only heavier, but also contain high levels of contaminant metals compared with conventional vacuum gas oils. Zeolite and matrix technologies in the FCC catalyst have evolved to maximize conversion of these difficult feeds to valuable transportation fuels and light olefins.

Increasingly stringent environmental regulations have also changed the objective function of the modern refinery. Special gasoline sulfur reduction additive and catalyst technologies are now being widely applied in FCC units to help refiners comply with tighter gasoline specifications. Developments in additives technologies have been made in response to environmental regulations on emissions (eg, NO_x, SO_x). In addition, breakthroughs in the stabilization of ZSM-5-based additives and technologies capable of double-digit propylene yields open up opportunities for refiners to increase margins by participating in the petrochemicals market.

Future catalyst developments in the area in FCC are likely to continue to be driven by response to environmental regulation, changes in feed quality, and advances in reactor hardware.

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