



Role of the Rare Earth Elements in Fluid Catalytic Cracking

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Rare earth metals are a key component in fluid cracking catalyst, and are also used in small portions in almost every advanced industrial product. World wide demand for rare earths has increased due to consumer demand for light weight, super-miniaturized electronic components such as cell phones, iPods, and flat panel displays, as well as increased demand for 'green'

technologies such as hybrid cars and wind turbines. So-called "rare earths" are actually more common than more familiar metals, but tend to be concentrated in hard to extract ore deposits. As a result, the world's supply tends to come from only a few sources; China alone accounts for 95% of the world's rare earth output. Recent export quota restrictions on rare earths from

China have caused the price of these critical components to fluid catalytic cracking catalysts to rapidly rise. Because of these new market forces, we present a review here of the role of rare earths in fluid cracking catalysts.

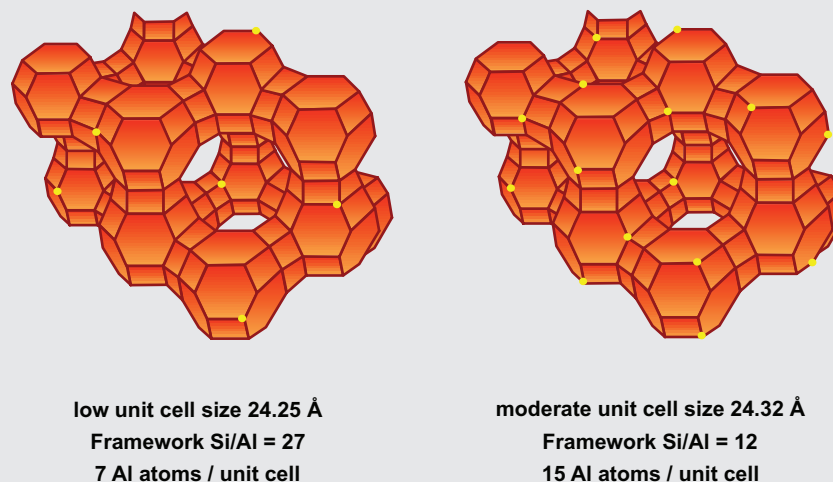
The use of rare earth exchanged zeolites in cracking catalyst was described by Plank and Rosinski¹, both of Socony Mobil Oil, in the

early 1960's. They discovered that rare earth-containing zeolites were about 100 times more active than the traditional silica-alumina amorphous catalysts of the time. This invention was to have a profound effect on petroleum processing. Plank and Rosinski were inducted into the Inventor Hall of Fame in 1979.

Grace Davison fluid cracking catalysts are complicated mixtures of several components that are designed and tailored to meet the requirements of a particular FCC unit and feedstock. The rare earth elements perform two critical roles in the FCC catalyst. First, they control the activity, coke selectivity, and olefin selectivity of the zeolite portion of the catalyst. Second, in units that run high vanadium and consequently suffer from severe deactivation conditions, rare earths are used as vanadium traps, improving the coke selectivity even more and also improving the activity retention of the catalyst.

The zeolite component of the fluid cracking catalyst is responsible for most of the cracking activity. Since rare earths are used to control the activity and selectivity of the zeolite portion of the catalyst, a brief discussion of zeolites is warranted. Grace Davison catalysts use rare earth ultra stable Y type zeolite, or REUSY zeolite which was invented in the late 1960's by McDaniel and Maher², both of W. R. Grace, and as the name implies is a very stable zeolite. A stick figure representation of the framework structure of Y type zeolite is shown in Figure 15. The structure is composed of a framework of tetrahedrally coordinated silicon or aluminum atoms by oxygen atoms that are shared between the tetrahedral

Figure 15
Framework Structure of Y-Zeolite



sites. In Figure 15, the tetrahedral vertices represent silicon or aluminum atoms and the “sticks” connecting them represent oxygen atoms. The active sites of the zeolite are associated with the aluminum atoms, which are represented in Figure 15 by yellow dots, for clarity. As may be evident in Figure 15, zeolites are very high surface area materials, about 900 m²/g. For comparison, one heaping tablespoon of zeolite has the equivalent surface area of an American football field. Another useful visualization is to consider that if a hydrocarbon feed molecule “lays down” on the surface of the zeolite and it encounters an active site (yellow dot in Figure 15), it may undergo a cracking reaction. For the purposes of this discussion, we will use the expression “active site density” to mean “framework aluminum site density” to stress that the sites in the zeolite responsi-

ble for cracking are associated with the framework aluminum sites.

The active site density controls the activity of the zeolite portion of the catalyst. Careful chemical structural research work done in the 1960's determined that the unit cell size (UCS) of the zeolite, as measured by x-ray diffraction, is proportional to aluminum site density, hence, the active site density in the zeolite. The unit cell dimension is an easy and attractive method to gauge the site density in the zeolite in equilibrium catalyst (Ecat). The higher the UCS, the higher the site density. For instance, a zeolite with UCS of 24.40 Å has a high site density of active sites, whereas a UCS of 24.30 Å would be considered moderate, and a UCS of 24.25 Å would correspond to low site density.

The role of zeolitic rare earth is to manipulate the in-use active site density of the zeolite as measured by the UCS. Zeolites used in cracking catalysts undergo reactions in the high temperature steam environment of the regenerator that destroy the active sites. As catalysts age in the FCC regenerator, the UCS is always dropping by a reaction called “dealumination” of the zeolite, where the active sites react with steam and become consumed irreversibly. (Using the visualization analogy from above, the yellow dots in Figure 15 are removed by the “dealumination” reaction.) The rare earth ions in the zeolite retard this deleterious reaction from occurring, and thereby retard the lowering of the UCS with catalyst age. *This active site preservation is critical to the activity in the unit.* Manipulation of the active site density of the catalysts with rare earth, renders a broad spectrum of catalyst activity and/or selectivity profiles available to refiners.

Table V shows that the UCS of a series of lab deactivated catalysts increases uniformly with rare earth content. This means that the zeolite active site density in the catalyst is increasing, and hence, the activity of the catalyst is also expected to increase. Table V also shows the conversion at constant catalyst-to-oil ratio for the same catalysts. Here again, the intrinsic activity of the catalyst increases with UCS, or rare earth content. In this way, the activity of the catalyst is controlled not only by the zeolite content, but also the rare earth level on the zeolite.

Site density not only controls the *intrinsic activity*, but also the *selectivity*, of the zeolite in the catalyst. High site density zeo-

Table V
Properties of Lab Deactivated Catalysts

Catalyst	Wt.% Re ₂ O ₃ on Catalyst	Unit Cell Size, Å	Conversion, wt.% at Constant C/O
A	1.1	24.24	53
B	1.8	24.27	65
C	2.2	24.31	69
D	3.3	24.34	73
E	3.7	24.36	76
F	5.7	24.41	80

Figure 16
Gasoline and Coke Selectivity Differences

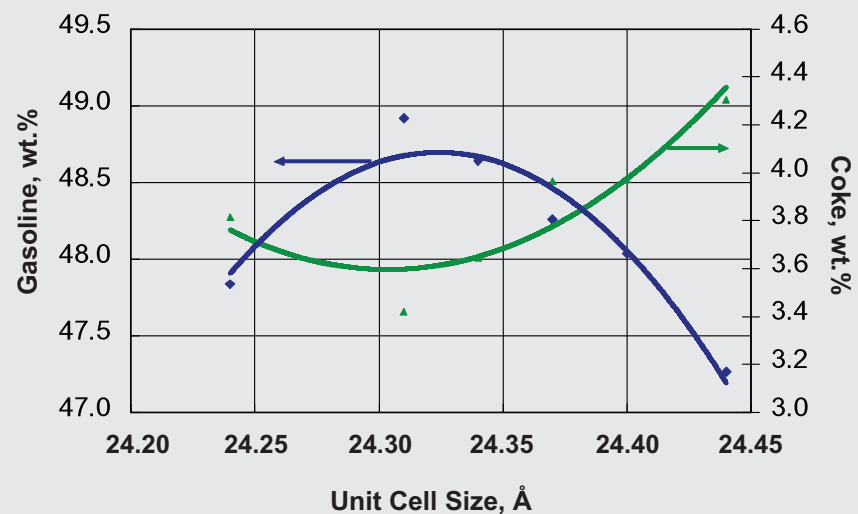


Figure 17
Olefins/RON Decreases with Increasing Unit Cell Size

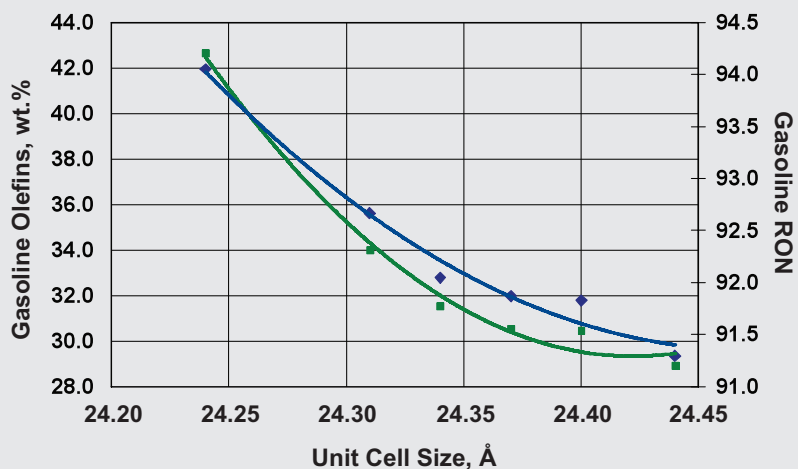
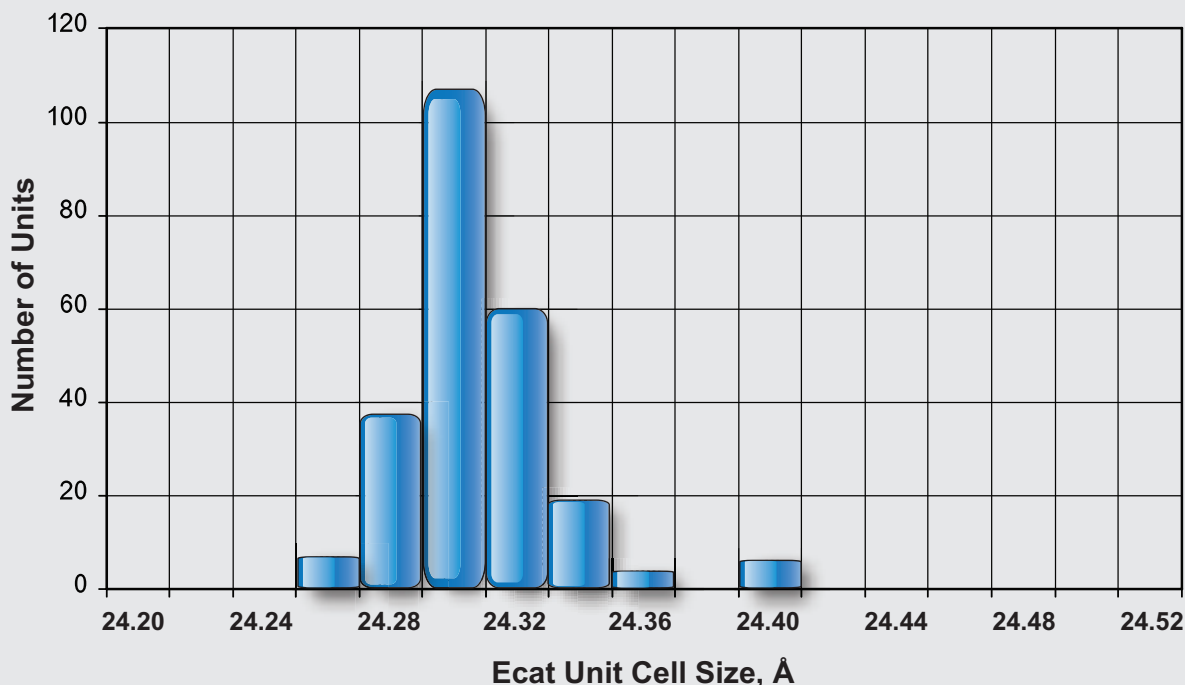


Figure 18
Ecat Data from June to September 2010



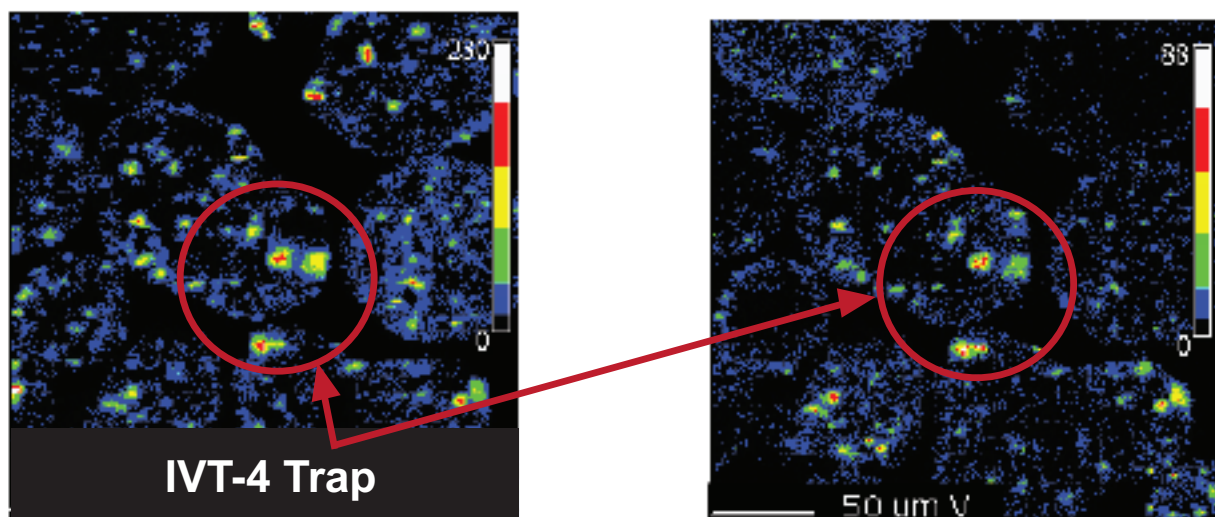
lites have higher intrinsic activity but poorer coke selectivity and lower gasoline olefins (lower research octane number or RON), while lower site density zeolites have lower intrinsic activity with much improved coke selectivity and higher gasoline range olefins (higher RON). Work done by Rajagopalan and Peters³ at Grace Davison showed that zeolites with a site density corresponding to a UCS of about 24.30 Å had a “sweet spot” in the activity/gasoline yield versus coke selectivity trade-off. This is shown in Figures 16 and 17, which show the gasoline yield, coke yield, gasoline range olefins, and RON for a range of catalysts with different unit cell sizes. The catalysts were designed to have approximately the same activity, and the comparisons in Figures 16 and 17 are made at constant conversion, in

order to compare the selectivity differences. As discussed, there is a maximum in gasoline and a minimum in coke selectivity for a UCS of 24.30 Å, while the gasoline olefins and RON decrease with increasing UCS. By operating at or near a UCS of 24.30 Å, a refiner can maximize yields and take advantage of the coke selectivity with maximum feedstock throughput. This discovery of the activity and coke selectivity benefits of REUSY was another transforming event in petroleum cracking, taking place in the mid 1980's, which allowed refiners to dramatically increase FCC capacity and improve the overall production of gasoline. (See “The Quiet Revolution: REUSY”).

By far most refiners target the “sweet spot” of around 24.30 Å, as shown in Figure 18, which is

the distribution of UCS's of samples submitted to Grace Davison for Ecat analysis. No refiners operate below 24.24 Å, because the overall zeolite activity would be too low to maintain MAT activity. There are a few refiners operating with UCS in the 24.34 - 24.40 Å range; generally these refiners have a low olefin requirement on the product gasoline and therefore, must operate at a high UCS to control the olefins in gasoline. The rare earth level on the zeolite is a major control variable available to the refiner. While there are many factors which effect the zeolite UCS in the unit, rare earth on the zeolite is the most important, followed by catalyst addition rate. In the most general sense, increased catalyst additions will increase the UCS (decrease catalyst age), but it is not as strong a variable as rare earth. The regenerator

Figure 19
Electron Microprobe Images of IMPACT® Catalyst Technology Ecat



Microprobe analysis confirms that IVT-4 is actively trapping V, thus preserving zeolite activity and selectivities

conditions, metals levels, catalyst loading limitations, etc. all play a role in controlling unit performance and catalyst additions.

Rare earths are also used in the catalyst as vanadium traps to reduce the deactivation caused by vanadium poisoning. Vanadium destroys the zeolite and increases production of coke and light gas. The precursor for vanadium poisoning is vanadic acid, which is volatile in the regenerator. As a result, vanadium in the regenerator is very mobile, and it quickly re-distributes itself to the youngest catalyst particles. Since vanadic acid is an acid, it promotes undesired side reactions that destroy the zeolite. It is advantageous to trap the vanadium into an inert form so that the deleterious side reactions are abated. The rare earths are “basic” oxides and can react with the vanadic acid trap-

ping it and preventing reaction with the zeolite. Grace Davison’s IMPACT® and Nektor ULCC catalyst technologies employ integral rare earth oxide based vanadium traps. The integral rare earth trap technology (IVT-4) has proven to be the most effective technique for controlling vanadium poisoning. Figure 19 shows electron microprobe images of an Ecat that show a strong correlation of vanadium with rare earth. The resultant rare earth vanadates are very stable and inert under FCC conditions, greatly reducing zeolite deactivation and coke and gas production. The coke selectivity improvement due to the IVT-4 technology in IMPACT® catalyst is dramatic (Figure 20). Optimization of the catalyst UCS in combination with integral vanadium trapping make IMPACT® and Nektor ULCC catalysts the most coke selective catalyst tech-

nologies, especially appropriate for high metals operations.

Despite the tightening of supply, rare earth metals remain key components of the FCC catalyst and certain FCC additives, and there are no easy substitutes. Rare earth metals stabilize the zeolite and provide vanadium trapping functionality to those users processing resid. Rare earths are also used in some key FCC additives for pollution control. The recent price escalation is impacting FCC catalyst suppliers and their customers globally. Fortunately for the refining industry, the lighter rare earths that are expected to be relatively abundant in the future provide the best performance.

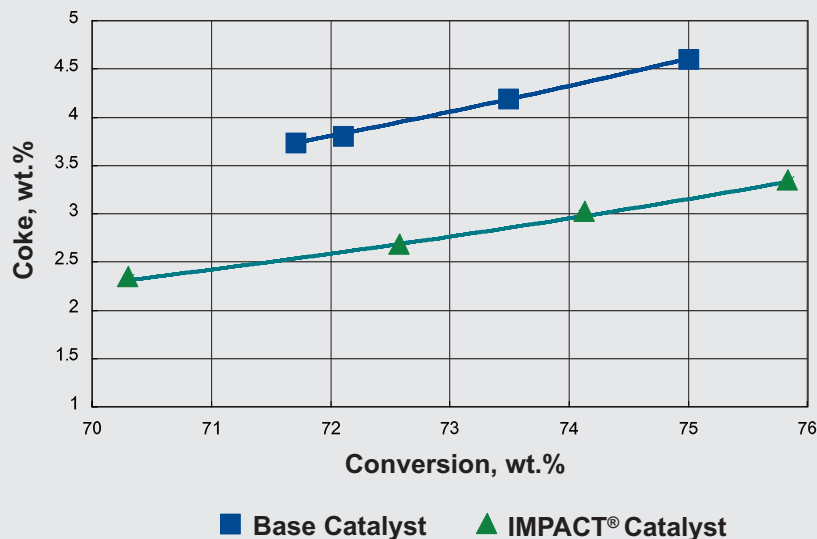
Grace Davison is committed to working with each customer to re-optimize his/her catalyst formulation with the goal of reducing

overall rare earth content of the catalyst while maintaining acceptable performance. Whatever your catalyst requirements, you can feel confident that we at Grace Davison have the capabilities to continue the reputation for quality and service that we have established in our 68 years of serving the world's refineries.

References

1. There are several patents, see for example Plank, C. and E. Rosinski, "Catalytic Hydrocarbon Conversion with a Crystalline Zeolite Catalyst. 1964: US3140253 (A)".
2. There are several patents, see for example Maher, P.K. and V. McDaniel, "Z-14US and Method of Preparation Thereof. 1966 : US3293192".
3. Rajagopalan, K. and A.W. Peters, "Effect of Exchange Cations and Silica to Alumina Ratio of Faujasite on Coke Selectivity During Fluid Catalytic Cracking". *Journal of Catalysis*, 1987. 106: p. 410-416.

Figure 20
Coke Selectivity is Improved with IMPACT® Catalyst Technology



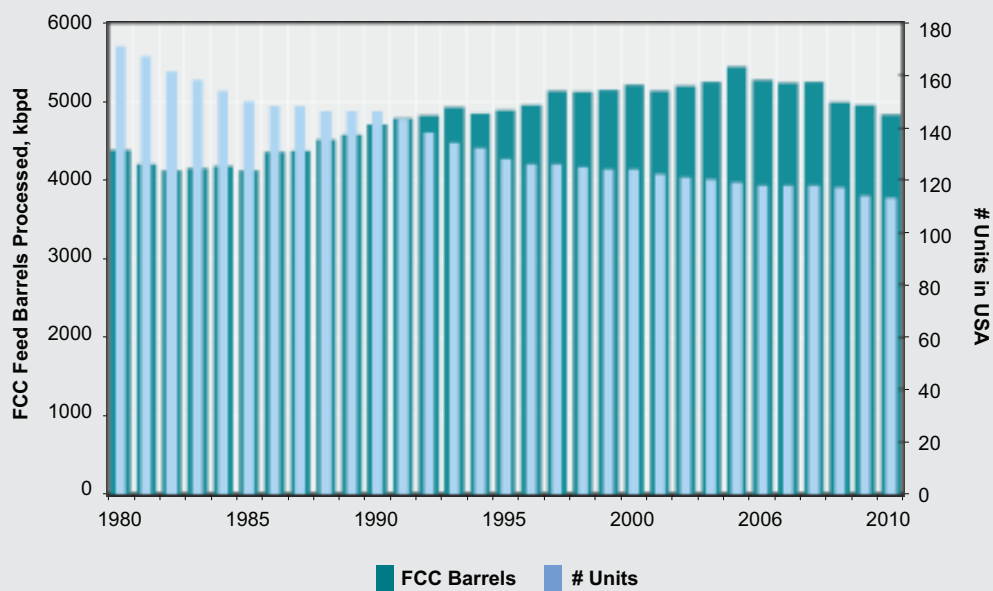
The Quiet Revolution: REUSY

The introduction of rare earth zeolite catalysts over silica alumina based catalysts in the 1960's had a profound effect on the profitability and operation of the FCCU. Venuto and Habib's book "Fluid Catalytic Cracking with Zeolite Catalysts," published in 1979, documents this upheaval. On page one they write, "The importance of catalytic cracking is undisputable...., and the economic impact of zeolite catalysts on catalytic cracking is tremendous." The process of conversion to rare earth zeolite catalysts was swift, taking only seven years

from invention in 1962 to 90% of the US FCC units by 1969. At that time, the "savings to refiners alone" was estimated to be \$250,000,000.

While the game-change caused by the use of zeolite catalysts in the 1960's is undisputed, a second, quieter technological breakthrough occurred in the 1980's. This advance was the introduction of REUSY catalysts by Grace Davison (see adjoining article). Invented in the early 1960's, the full benefits of REUSY were not realized until Rajagopalan and Peters discovered that catalysts equilibrated with a unit

Figure 21
Historical Data - Unit Throughput



cell size of 24.30 Å resulted in optimal gasoline yield at minimum coke. This discovery was to have a profound effect on the FCC in a unique and more subtle way.

Since 1980 the total FCC feed barrels processed per day in the US has grown, while simultaneously there has been a steady drop in the number of units (Figure 21). Essentially, less steel in the ground is processing more feed. A more careful inspection shows that the rate of capacity growth was fastest in the late 1980's and early 1990's, corresponding to the switch to REUSY catalysts. A steady growth in capacity has continued, while the number of FCC units in the US declines.

FCC units operate in heat balance, meaning that all the heat required to vaporize the feed and provide the endothermic heat of reaction is supplied by the burning of coke. An FCC unit will always adjust itself to remain in heat balance by producing enough coke to satisfy the energy requirements. If all the operating conditions remain constant, the effect of a more coke selective catalyst (one that makes less coke per unit conversion) is to circulate more catalyst to satisfy the energy requirements. As circulation rate increases, the consequence of improved coke selectivity is higher conversion for a fixed feed rate without sacrificing conversion.

However, the refiner can capture the value of improved catalyst coke selectivity another way, and that is by increasing the feed rate without sacrificing conversion. More feed can be processed for a given set of conditions because the coke yield per unit feed of the new catalyst is lower. In summary, the benefits of improved coke selectivity are either increased conversion, or increased capacity, or both.

Since the introduction of REUSY catalysts, Grace Davison continues to provide technological advances aimed at improving the overall coke selectivity. Particular emphasis has been in the areas of resid processing and decreased coke produced by contaminant metals. In the early 1990's, Grace Davison introduced matrix technologies for decreasing the coking tendency from nickel. Later in the 1990's Grace commercialized integral rare earth based, vanadium traps, employed in catalysts such as IMPACT® and Nektor ULCC brands. Iron resistant catalyst platforms, such as MIDAS® catalyst, were brought to market in 2003. With an active R&D program focused on innovation, the market can continue to expect further advancements in catalyst coke selectivity from Grace Davison.

Answers to the 2010 NPRA Q&A FCC Questions

85. What is the typical range that you employ for iron content on FCC equilibrium catalyst? What methods are available to determine how iron is accumulated on the catalyst surface? How does the distribution of iron on the catalyst surface impact the FCC operation, yield structure and emissions?

David Hunt

Grace Davison, Houston, TX

Grace receives Ecat samples for most of the FCC units operating worldwide. The figure at right shows the distribution of average equilibrium catalyst Fe levels for 2010 for all FCC units that have provided Ecat samples to Grace. Mean Fe levels are 0.57 wt.% and the highest Fe level in one unit is 1.36 wt.%.

Iron can be detrimental to the unit in many ways including bottoms conversion, catalyst circulation stability and SO_x emissions.

Yaluris¹ showed using an Electron Probe Micro-Analysis (EMPA) technique that iron from organic iron sources is primarily a catalyst surface contaminant. Yaluris also used scanning electron

microscopy and optical microscopy techniques to confirm Fe is a surface contaminant. The figure on page 27 is an EMPA image of an FCC catalyst particle cross section. Warmer colors on the surface of the particle confirm that Fe and CaO are primarily surface contaminants.

Yaluris¹ discussed how Fe contamination can lead to pore closure and nodule formation.

The presence of Na and CaO can act as fluxing agents, aggravating the effect of Fe. The figure on page 27 shows decant oil or main fractionator bottoms yield vs. Ecat Fe plus CaO levels. Decant oil increases at the higher contaminant levels due to the damaged catalyst pore structure.

Question 85
Ecat Fe Distribution, wt.%

