Enhanced Bottoms Cracking and Process Flexibility with MIDAS® FCC Catalyst

This premium bottoms cracking FCC catalyst family is formulated with advanced zeolite stabilization technology plus matrix metals passivation technology and has been successfully applied to a wide range of feed and feed contaminants.

Yee-Young Cher  
Technical Service Representative

Rosann Schiller  
Senior Marketing Manager

Grace Catalysts Technologies  
Columbia, Maryland, USA

Jeff Koebel  
National Technical Sales Leader

Grace Catalysts Technologies  
Chicago, Illinois, USA

Middle distillates, including on-road and off-road diesel, marine fuels and No. 2 heating oil, represent the largest and a growing market share of refined petroleum products. However, the renaissance of North America crude production will have a profound effect on refinery yield slate. Many of the new crudes are lighter and will increase refinery light ends yield. Growing volumes of domestic crude are being processed outside of PADD’s II and III despite pipeline congestion. Several refiners have announced projects to source light oil via rail, barge or truck to plants along the US East and West coasts. Longer term, surpluses are expected in the lighter products (LPG and naphtha) and deficits forecasted for gasoil and diesel.

Overall, the trade balance for distillate streams is tight globally. The closures of large refining complexes in the Atlantic basin, changing fuel specifications, and growing demand for gasoil and distillate in the emerging regions and Europe add to the expected supply imbalance. Amid declining gasoline demand in North America, refiners require an FCC catalyst that enhances distillate production yet selectively minimizes light product yield. In a world where fuel demand is satisfied through a careful balance of free trade, a single storm or refinery upset often triggers price volatility in product markets. The ability to respond quickly to capture short-term market opportunities is critical. Grace’s premium bottoms cracking family, the MIDAS® catalyst series, can be used to enhance your FCC process flexibility and capture incremental profit as opportunity arises. MIDAS® cracks deep into the bottom of the barrel, enhancing total distillate and liquid yield, and has been proven in over 100 refineries that vary broadly in feed composition and operating modes. The flexibility that MIDAS® brings to your refinery, used neat or as a component in a GENESIS® catalyst system, can enhance the yield value by $0.40-1.00/bbl of FCC feed.

MIDAS® is a moderate zeolite to matrix ratio FCC catalyst that has been successfully applied in half of all the North America FCCU capacity. Its success is driven by the fact that MIDAS® effectively cracks all feed types: heavy resids, severely hydrotreated light feeds, and shale oil-derived feed streams, via the three-step
The relatively large molecules at the bottom of the barrel that need to be converted must first be cracked by the catalysts’ matrix acidity. With molecular sizes of 10-30 Å, the hydrocarbons are too large to fit into the zeolite pores, which are typically below 7.5 Å. It is important that the catalyst have the proper pore size distribution to enable large feed molecules to enter, crack into lighter products, and diffuse out before being over-cracked to coke and gas. For free diffusion of resid molecules (>1000°F) to occur, the catalyst pore diameter needs to be 10-20x the size of the molecule, or 100-600 Å. The desired pore volume should be in the large mesopore region 100-600 Å. The benefit of mesoporosity for bottoms cracking is well understood. However, not all the measured pore volume is created equal. Catalysts with similar total pore volume measurements can vary widely in pore size distribution. MIDAS® is designed to have high mesoporosity in the 100-600 Å range, typically twice as high as competitive offerings (Table 1). Optimal porosity is required for effective kinetic conversion of bottoms. Midas catalysts crack deeper into the bottoms than competitive technologies in the market today.

Commercial examples of high MIDAS® mesoporosity, as measured by Hg porosimetry of Ecats, are shown in Figure 1. Note that Hg intrusion measures the porosity greater than 36 Å, therefore the result specifies the porosity associated with the catalyst matrix only; N2 adsorption or desorption must be used to capture zeolite porosity.

Grace’s in-house manufacturing and quality monitoring of the specialty alumina used in MIDAS® provides control over the resulting porosity. It is generally accepted that micropores (<100 Å diameter), though effective for cracking, lead to poor coke and gas selectivity as a result of poor diffusivity and over-cracking. Some competitive benchmarks with high surface area and activity are also high in matrix microporosity, resulting in wet gas compressor limitations that suppress feed rate and ultimately profitability. In contrast, MIDAS® catalyst has the lowest amount of small pores and the highest amount of large mesopores. Optimal porosity guarantees best-in-industry gas selectivity and coke-selective bottoms conversion. High pore volume also serves to enhance the fluidization characteristics.

### TABLE 1: Mesoporosity Comparison with Competitors

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Total</th>
<th>Micropores</th>
<th>Mesopores</th>
<th>Macropores</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>36-100Å</td>
<td>100-600Å</td>
<td>600+Å</td>
</tr>
<tr>
<td>MIDAS®</td>
<td>0.389</td>
<td>0.092</td>
<td>0.206</td>
<td>0.091</td>
</tr>
<tr>
<td>MIDAS®</td>
<td>0.412</td>
<td>0.107</td>
<td>0.232</td>
<td>0.071</td>
</tr>
<tr>
<td>Cat 1</td>
<td>0.388</td>
<td>0.116</td>
<td>0.102</td>
<td>0.168</td>
</tr>
<tr>
<td>Cat 2</td>
<td>0.413</td>
<td>0.082</td>
<td>0.089</td>
<td>0.232</td>
</tr>
</tbody>
</table>

**FIGURE 1: Pore Volume Comparison of Commercial Ecats**

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The bottoms cracking mechanism discovered by Zhao. The catalyst design minimizes the thermal and catalytic factors that result in coke formation. The result is deep bottoms conversion, regardless of the starting feedstock.

Resid streams present the greatest challenge in terms of deep bottoms conversion. The dynamic molecular dimensions of paraffins and aromatic species vary based on carbon number and molecular configuration. Paraffins species present in the 700-1000°F boiling point fraction of FCC feed are typically in the C14 to C34 range for normal paraffins. The dynamic molecular size of these compounds is 12-20 angstroms (Å). The heavy resid fraction also contains an abundance of aromatic molecules (C14 to C60) in the 700-1000°F boiling range. The range of molecular size for aromatics is 12-25 Å. Even aromatic carbon molecules up to 60 carbon number are still less than 30 Å in molecular size.

Porphyrins are organic, cyclic macromolecules that consist of a ring of nine or more atoms. Porphyrins are aromatic species often present in resid fractions and characterized by a central gap that can bond to a metal atom, such as nickel, vanadium, or iron. If a porphyrin is complexed with vanadium, it is termed a vanadyl porphyrin. The size of these metallic complexes also varies with carbon number, but is in the same dimensional range as typical resid hydrocarbons: 10-30 Å.
Several units have observed substantial improvement in the Ecatalyst fluidization factor following a reformulation to MIDAS® or GENESIS®3. Later in this paper, the selectivity advantages of MIDAS® will be highlighted with commercial examples of catalytic performance.

The proprietary matrix in MIDAS® can withstand the most severe applications, particularly those challenged by high levels of contaminant iron and calcium. High alumina content in FCC catalyst is known to reduce the degradation of the catalyst surface due to Fe and/or Ca poisoning7. Optimum distribution of mesoporosity also plays a role in maintaining performance, because diffusion to the active sites remains unhindered despite the high contaminant metals. MIDAS® has been successful in maintaining bottoms conversion in units with some of the highest levels of contaminant Fe on Ecatalyst in the industry.

A good bottoms cracking catalyst requires high matrix surface area (MSA). However the activity of a high matrix catalyst needs to be balanced with an appropriate level of zeolite without compromising attrition characteristics. Additionally, an appropriate rare-earth exchange level on the zeolite is critical to ensure optimal coke selectivity. An optimum exists in the relationship between zeolite unit cell size (UCS) and coke selectivity8. Too often, high matrix catalysts also have a high UCS, meaning they are over-exchanged with rare earth. Low zeolite input formulations with high rare-earth exchange (albeit low total rare earth on catalyst!) will retain a higher percentage of the fresh zeolite surface area in a severe regenerator, but the penalty for this over-exchanged zeolite is poor coke selectivity. The rare-earth exchange in MIDAS® catalysts is optimized to result in a formulation that lies in the so-called ‘sweet’ spot for best coke selectivity. Table 2 shows the average Ecatalyst properties of MIDAS® relative to competitive high MSA catalysts. The right distribution of mesoporosity coupled with optimal activity and UCS gives MIDAS® the coke selectivity edge in commercial cracking.

Commercial Experience

MIDAS® design features have led to superior performance in many commercial examples. The first example comes from Refinery A that has an FCCU processing a mix of VGO and light resid. The feed is moderately high in metals with good cracking characteristics. The base catalyst was a competitive high MSA catalyst with high rare-earth exchange. The unit suffered from a dry gas constraint, especially in the summer. When the refiner switched to MIDAS®, a 5-10% drop in total dry gas yield at equivalent riser temperature and metals loadings was observed (Figure 2A); this allowed the refiner to maintain maximum feed rate throughout summer. The better coke selectivity of MIDAS® also manifested itself in better coke to bottoms. The charts shown in Figures 2A-C contain actual unit operating data, normalized and presented on a relative basis, demonstrating the superior selectivity of MIDAS®.

<table>
<thead>
<tr>
<th>Z/M</th>
<th>MIDAS®</th>
<th>Competitor A</th>
<th>Competitor B</th>
</tr>
</thead>
</table>

TABLE 2: MIDAS® has an Optimal UCS to Minimize Coke

![FIGURE 2A: MIDAS® Delivers Improved Gas Selectivity at Refinery A](image)

![FIGURE 2B: MIDAS® Reduced Bottoms Yield Despite Higher Rates of Resid at Refinery A](image)

![FIGURE 2C: MIDAS® Improved Bottoms Cracking and Coke Selectivity at Refinery A](image)
At Refinery B, the FCCU was also processing light resid using a high matrix, high UCS competitive catalyst. While rare-earth levels on the zeolite were high, the catalyst itself had low total rare earth because zeolite input was very low. In spite of the high rare-earth exchange and resulting UCS, the unit was constrained on total wet gas and bottoms yield. There wasn’t enough zeolite present to complete the second stage of the bottoms cracking mechanism. Zeolite is critical to reduce the size of the hydrocarbon via dealkylation. Insufficient zeolites cause coke precursors to condense on the catalyst surface and become coke before they can be converted into transportation fuels. Poor coke selectivity translates into subpar bottoms conversion.

Introduction of MIDAS® provided a reduction in bottoms make on the order of 8% for Refinery B. Higher zeolite and optimal UCS improved coke selectivity, and the refinery increased not only the fresh feed rate but also the amount of resid in the feedstock by almost 10%. Higher zeolite also increased the circulating activity, enabling a reduction in catalyst additions on a lb/bbl basis. Incremental resid at lower cat additions caused Ecatalyst metals to increase by 1,000 ppm, which drove a corresponding increase in dry gas. However, the balanced zeolite and matrix surface areas of MIDAS® meant that more feed was converted into valuable gasoline and distillate, rather than LPG and coke (Figure 3).

At Refinery C, the FCCU was processing resid feedstock high in iron (Fe) and calcium (Ca). Over time, the unit suffered from classic symptoms of iron poisoning. As iron nodules built on the surface, Ecatalyst activity, unit conversion and bottoms cracking all began to suffer. A switch to MIDAS® provided higher activity and improved coke selectivity (Figure 4). The coke selectivity advantage drove deeper bottoms conversion. Eventually the feed became heavier and more contaminated. Midas never lost its selectivity edge over the competitive high MSA formulation, despite subsequent increases in Fe + Ca. The high mesoporosity is particularly effective in preventing a loss in cracking activity often seen during periods of high metals loadings. Fe + Ca can form eutectics that serve to essentially melt over the catalyst surface, blocking pores and suppressing conversion. The high mesoporosity of MIDAS® ensures that high diffusivity is maintained. MIDAS® is the preferred FCC catalyst technology for FCCUs processing high Fe feedstocks.

Refinery D routinely processes heavy resid in the FCCU. Similar to the other examples, the objectives were to reduce dry gas and improve the yields of liquid fuels (Gasoline + Distillate), without compromising feedrate. A switch to MIDAS® catalyst met the objectives despite deteriorating feed quality coming to the FCC. Over time, the feedstock became heavier, contained more Concarbon, and had higher metals loadings. Lower dense bed temperatures minimize thermal cracking, reducing dry gas yield. Slurry yield was held constant (Figure 5).
The primary operating objective of the FCCU at refinery E is to maximize LCO yield. Reformulating to a high matrix catalyst from the starting low matrix catalyst presented a challenge for this refinery. A wholesale change in the catalyst formulation was deemed to be risky. Grace introduced MIDAS® to the FCCU in a step-wise fashion. Initially, MIDAS® was blended with their base high zeolite catalyst (also a Grace catalyst) in a 50/50 ratio. The FCCU realized a reduction in slurry yield of 12% (Figure 6). Refinery E later increased the amount of MIDAS® to 100% of the fresh catalyst requirement. Again, a step-change improvement in slurry was observed, and the incremental conversion was maintained as distillate as desired. Higher distillate yield (+15%) was observed over a wide range of conversion levels with MIDAS® over the original base catalyst.

FIGURE 4: Despite Higher Contaminant Metals, MIDAS® Improved Bottoms Cracking and Coke Selectivity at Refiner C

FIGURE 5: At Refinery D, MIDAS® Increased G+D Yield and Reduced Dry Gas at Similar Feed Rate
**Performance Summary**

MIDAS® is Grace’s premium high matrix bottoms cracking catalyst family. MIDAS® is designed to possess the key characteristics necessary for selective conversion of heavy FCC feed molecules. These characteristics are controlled during proprietary manufacturing processes of Grace specialty aluminas, zeolites and ultimately the whole catalyst itself. The net result is a product with:

- Maximum matrix mesoporosity to minimize coke and gas formation and maximize bottoms upgrading
- Ideal pore size diameters to preserve free diffusion in and out of the catalyst, even in the face of metals contamination
- Optimized rare-earth exchange to deliver best-in-industry coke selectivity
- Balanced zeolite-to-matrix activity to maximize product value from the FCC.

MIDAS® contains the highest mesoporosity in the desired range of 100-600 Å and the most optimal UCS in the market, providing a clear selectivity advantage over competitive catalysts. Several distinct grades are available, suitable for a wide range of feed and operating objectives. The catalyst’s excellent in-unit fluidization properties are an ideal solution for FCCs with fluidization or circulation difficulties. Applied neat or in a GENESIS® catalyst system, MIDAS® provides refiners the option of running difficult or opportunity feedstocks to the FCC without suffering from poor coke and gas selectivity. Finally, MIDAS® provides the flexibility to fine-tune the yield of the individual product streams to exploit short or long term economic opportunities.

In summary, MIDAS® FCC catalyst should be considered by any refiner who desires:

- Deeper bottoms cracking
- Enhanced bottoms conversion against an air blower constraint
- Ability to process high Fe and Ca feedstocks, such as Bakken or Eagle Ford
- Incremental fuels yield, i.e. LCO or G +D maximization
- Relief against a wet gas compressor constraint when cracking resid
- Capability to process opportunity crudes
- Improved catalyst fluidization characteristics
- Flexibility to capture the value of opportunity crudes
- Ability to shift between gasoline and distillate modes of operation
- Rapid catalytic response to capture short-term economic opportunities

![Figure 6: Refiner E Observed Higher Distillate Yield Over a Range of Conversion Levels with MIDAS®](image_url)
People on the Move

In our continuing effort to support the growth and productivity activities in Grace Catalysts Technologies, the following changes have been made in the Refining Technologies organization:

Hongbo Ma recently transferred to FCC Technical Sales Representative, reporting to Jeff Koebel. Since joining Grace in 2007, Hongbo was a Senior R&D Engineer for Technical Support in RT. He holds a Ph.D. in Chemical Engineering from the University of Wisconsin.

Jeff Koebel has been promoted to the position of National Technical Sales Leader, reporting directly to Bob Gatte. Jeff joined Grace in 2004 and has been serving as Technical Sales Representative within the RT North America business. Before joining Grace, Jeff spent 14 years at UOP, serving as a Design Engineer, before being promoted to a Senior FCC Technology Specialist. Jeff has a B.S.In Mechanical Engineering from the University of Illinois.

Kristen Wagner recently transferred to FCC Technical Sales Representative reporting to Jeff Koebel. Kristen, who was previously Clean Fuels Product Manager in RT Marketing, joined Grace in 1997 as a Process Supervisor at our Curtis Bay Works. She has held various positions in Manufacturing, Quality Assurance and Marketing at Grace. Kristen received her B.S.Ch.E from the University of Maryland.

Steve Gremillion recently joined Grace as an FCC Technical Sales Representative reporting to Shahab Parva. Prior to joining Grace, he held process engineering positions at CITGO Petroleum, JAB Energy Solutions and Polaris Solutions. A registered Professional Engineer, Steve holds a B.S.Ch.E. from McNeese State University.

References


