Multi-Stage Reaction Catalysts: A Breakthrough in FCC Catalyst Technology

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Multi Stage Reaction Catalysts
An Innovative Manufacturing Technology Platform

- Many commercial processes take advantage of staged reactions with different catalytic attributes
  - Common Refinery example – staged bed hydrotreating reactors

- How can we do this in a circulating system like FCC?

- Through *Innovation* in FCC Manufacturing!

- BASF Multi-Stage Reaction Catalyst (MSRC) combines two or more FCC catalyst functionalities within a single catalyst particle
Flex-Tec®
FCC catalyst for severe resid applications

- Optimized DMS structure
  - Enhanced diffusion of heavy molecules
- Separate particle vanadium trap
- Integrated specialty alumina that passivates nickel thus reducing the metal catalyzed formation of hydrogen and coke
  - This specialty alumina is distributed throughout the catalyst particle but as we will see on the next slide nickel mainly deposits on the outermost portion of the catalyst
ECat (Equilibrium Catalyst) Analysis

**Electron micro-probing**

Vanadium is located throughout the particle.

Nickel is concentrated in the outer-layer of the catalyst (5-10 micron).

**Scanning Electron Microscopy (SEM)**
MSRC Approach

Can we improve upon the DMS based Flex-Tec by distributing the specialty alumina where nickel is predominantly located?

Yes: By using a two stage technology with increased alumina content in outer-stage and none in the inner-stage
Fortress™ is the first product off the new MSRC platform

DMS based product with improved metals tolerance for lowest H2/dry gas generation and lowest coke selectivity

Designed for resid application with high metals
Multi-Stage Reaction Catalysts

Fortress Production Process

**Step 1: Inner stage microsphere**
- Clay slurry → dryer → \( \text{H}_2\text{O} \) → calciner → No Alumina added (~65 µm)

**Step 2: Outer stage microsphere**
- Clay slurry + alumina + Inner stage MS → dryer → \( \text{H}_2\text{O} \) → calciner → Two-Stage (~80 µm)

**Step 3: Zeolite crystallization and after-treatment**
- Microsphere Caustic Silicate → Base Exchange → Rare-earth Exchange → Calciner → Multi-Stage Reaction Catalyst
Technology unique to BASF: first microsphere formed, then zeolite grown across the interface and acts as the binder.

Attrition resistance comparable with current FCC catalyst grades.
Catalyst Development

- The outer-stage is enriched with specialty alumina to make it more effective at nickel passivation over Flex-Tec.

- Outer-stage thickness is consistent for all catalyst diameters (~9 microns).

![Graph showing outer stage thickness (μm)]

![Bar chart showing sieve fraction (μm)]

![Graph showing Al and Ni wt% vs. d (μm)]
Fortress™ Lab Performance

- The properties of Fortress are equivalent to Flex-Tec
- Metals free ACE testing at constant conversion shows similar selectivities indicating no diffusion barrier

### Catalyst Properties

<table>
<thead>
<tr>
<th></th>
<th>Flex-Tec</th>
<th>Fortress</th>
</tr>
</thead>
<tbody>
<tr>
<td>TSA (m²/g)</td>
<td>300</td>
<td>301</td>
</tr>
<tr>
<td>MSA (m²/g)</td>
<td>72</td>
<td>69</td>
</tr>
<tr>
<td>APS (µm)</td>
<td>76</td>
<td>76</td>
</tr>
<tr>
<td>Na₂O (wt%)</td>
<td>0.22</td>
<td>0.20</td>
</tr>
<tr>
<td>Roller (wt% loss/h)</td>
<td>18</td>
<td>16</td>
</tr>
</tbody>
</table>

### Metals Free ACE Testing

<table>
<thead>
<tr>
<th></th>
<th>Flex-Tec</th>
<th>Fortress</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen (wt%)</td>
<td>0.055</td>
<td>0.055</td>
</tr>
<tr>
<td>Total C4- (wt%)</td>
<td>17.14</td>
<td>17.46</td>
</tr>
<tr>
<td>Gasoline (wt%)</td>
<td>50.15</td>
<td>49.95</td>
</tr>
<tr>
<td>LCO (wt%)</td>
<td>15.74</td>
<td>16.1</td>
</tr>
<tr>
<td>Bottoms (wt%)</td>
<td>14.26</td>
<td>13.9</td>
</tr>
<tr>
<td>Coke (wt%)</td>
<td>2.67</td>
<td>2.53</td>
</tr>
</tbody>
</table>
The fresh catalyst was deactivated by Cyclic Metals Deactivation Unit (CMDU).

Testing in an ACE unit using a resid feed showed hydrogen and coke selectivity benefits with Fortress.

### CMDU Deactivated Catalyst

<table>
<thead>
<tr>
<th></th>
<th>Flex-Tec</th>
<th>Fortress</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni (ppm)</td>
<td>2797</td>
<td>2718</td>
</tr>
<tr>
<td>V (ppm)</td>
<td>1133</td>
<td>1050</td>
</tr>
<tr>
<td>Steamed TSA (m²/g)</td>
<td>115</td>
<td>123</td>
</tr>
<tr>
<td>Steamed MSA (m²/g)</td>
<td>36</td>
<td>38</td>
</tr>
<tr>
<td>ZSA/MSA</td>
<td>2.2</td>
<td>2.2</td>
</tr>
</tbody>
</table>

### ACE Testing

<table>
<thead>
<tr>
<th></th>
<th>Flex-Tec</th>
<th>Fortress</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen (wt%)</td>
<td>0.53</td>
<td>0.44</td>
</tr>
<tr>
<td>Total C4- (wt%)</td>
<td>15.32</td>
<td>15.11</td>
</tr>
<tr>
<td>Gasoline (wt%)</td>
<td>49.44</td>
<td>50.41</td>
</tr>
<tr>
<td>LCO (wt%)</td>
<td>20.14</td>
<td>20.15</td>
</tr>
<tr>
<td>Bottoms (wt%)</td>
<td>9.86</td>
<td>9.85</td>
</tr>
<tr>
<td>Coke (wt%)</td>
<td>4.71</td>
<td>4.05</td>
</tr>
</tbody>
</table>
Fortress™ Lab Performance
ACE Testing with CMDU Deactivation

- 20% lower hydrogen yield
- 10% lower coke yield
CPS vs CMDU Testing (5000 ppm Ni, 1000 ppm V)

Bias against FORTRESS with CPS deactivation

- Uniformity of nickel distribution with CPS deactivation creates a clear bias in testing for Fortress.
- Exaggerated H₂ and coke yields with lab dispersed Ni.
- Inner-stage of Fortress does not passivate against contaminate metals because they are not dispersed in the particle interior in commercial operation.
- Ni = 5000 ppm
- V = 1000 ppm
Fortress™ Commercial Trials

- Fortress is being trialed in two locations
- Both locations had been using purchased ECat for metals flushing that was removed prior to the start of the trial for the best comparison
- Data shown covers the most advanced trial

**Commercial Trial 1**

- Resid, short contact time unit located in the US
- Deep partial burn
- Low reactor severity
- Primary constants: wet gas compressor and air blower limited
Fortress™ Commercial Trials

- Typical ECat properties before and after the purchased ECat was removed

<table>
<thead>
<tr>
<th></th>
<th>With Purchased ECat</th>
<th>Without Purchased ECat</th>
</tr>
</thead>
<tbody>
<tr>
<td>FACT</td>
<td>71 wt%</td>
<td>71 wt%</td>
</tr>
<tr>
<td>Nickel</td>
<td>7400 ppm</td>
<td>8900 ppm</td>
</tr>
<tr>
<td>Vanadium</td>
<td>2600 ppm</td>
<td>2700 ppm</td>
</tr>
<tr>
<td>Delta Iron</td>
<td>0.23 wt%</td>
<td>0.30 wt%</td>
</tr>
<tr>
<td>Antimony</td>
<td>2000 ppm</td>
<td>2300 ppm</td>
</tr>
<tr>
<td>Carbon on Catalyst</td>
<td>0.2-0.5 wt%</td>
<td>0.2-0.6 wt%</td>
</tr>
<tr>
<td>Equivalent Nickel</td>
<td>5600 ppm</td>
<td>6800 ppm</td>
</tr>
</tbody>
</table>

Equivalent Nickel is calculated using the equation below

\[ Ni + \frac{V}{4} + \frac{Fe}{10} + 5 \cdot Cu - \frac{4}{3} Sb \]
Commercial ECat Results

Reduced ACE Hydrogen Yield with Fortress

- Removing of the purchased Ecat did not increase hydrogen yield despite the large increase in metals.

- The ACE hydrogen yield has decreased by 12% (0.41 wt% to 0.36 wt%) with the catalyst change from Flex-Tec to Fortress at similar nickel equivalents.
Commercial ECat Results

Improved ACE Coke Selectivity

- As with the hydrogen yield, removal of the Ecat didn’t increase coke yield
- The coke yield for the same conversion decreased by 17% (4.2 wt% to 3.5 wt%) with Fortress
Commercial ECat Results

Higher ACE Gasoline Selectivity with Fortress

- Gasoline yield increased by 0.5 - 1 wt%
- LPG selectivity did not change going to Fortress
- The yield increase comes from the decrease in hydrogen and coke
Commercial ECat Results

Bottoms Selectivity

- No change in bottoms selectivity
Commercial Results

No Increased Attrition

- The ESP fines particle size analysis shows no shift with the changeover to Fortress.
- The cyclone loss peak is greater than the attrition peak, no loss problem with either catalyst.

![Particle Size vs Fractional (%) Graph]

- Day 103
- Day 68
- Day 40
- Day -3
- Day -72
A post-audit ACE study using the refiners feed

The ACE temperature was set to 995°F and variable cat/oil ratio to generate yield response curves

<table>
<thead>
<tr>
<th>Feed Properties</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>API Gravity</td>
<td>23</td>
</tr>
<tr>
<td>Concarbon</td>
<td>3.0 wt%</td>
</tr>
<tr>
<td>Sulfur</td>
<td>0.2 wt%</td>
</tr>
<tr>
<td>K Factor</td>
<td>11.8</td>
</tr>
<tr>
<td>Nickel</td>
<td>8.7 ppm</td>
</tr>
<tr>
<td>Vanadium</td>
<td>2.4 ppm</td>
</tr>
<tr>
<td>Iron</td>
<td>2.4 ppm</td>
</tr>
</tbody>
</table>
The post audit ACE study validates the ECat trend results of the improved metals tolerance of Fortress resulting in lower hydrogen and coke.

![Graphs showing conversion versus hydrogen content and coke content for Flex-Tec and Fortress.](image-url)
The second commercial Trial of Fortress is also a comparison with Flex-Tec with the purchased ECat removed prior to the trial.

The unit is operating well, but it is too early for results.

Due to the lower metals level, the expected benefit is less than at Trial 1.

<table>
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<th>With Purchased ECat</th>
<th>Without Purchased ECat</th>
</tr>
</thead>
<tbody>
<tr>
<td>FACT 71 wt%</td>
<td>FACT 69 wt%</td>
</tr>
<tr>
<td>Copper 70 ppm</td>
<td>Copper 70 ppm</td>
</tr>
<tr>
<td>Nickel 2700 ppm</td>
<td>Nickel 3500 ppm</td>
</tr>
<tr>
<td>Vanadium 2200 ppm</td>
<td>Vanadium 3200 ppm</td>
</tr>
<tr>
<td>Delta Iron 0.9 wt%</td>
<td>Delta Iron 1.1 wt%</td>
</tr>
<tr>
<td>Antimony 600 ppm</td>
<td>Antimony 900 ppm</td>
</tr>
<tr>
<td>Equivalent Nickel 3400 ppm</td>
<td>Equivalent Nickel 4200 ppm</td>
</tr>
</tbody>
</table>
MSRC-CORE

- Second catalyst offering from BASF under the MSRC manufacturing platform
- CORE’s highly stable zeolite outer stage reduces diffusion path length which
  - Improves selectivity
  - Delivers high bottoms conversion with low coke
  - High gasoline and light olefin yields
- CORE is engineered to provide coke selectivity and gasoline yields on par with NaphthaMax® III with lower rare earth
- The inner stage of CORE serves as the anchor for the highly active outer stage
- Currently undergoing manufacturing trials and scheduled to be ready for commercial trials by 4Q 2011
Improving Mass Transfer
Diffusion path length as only viable option

Reduce the Thiele modulus, $\phi_2$
To improve effectiveness of catalyst

$$\phi_2 = \frac{r}{3 \sqrt{\frac{k' \rho_{cat} C_s}{D_e}}}$$

- Increase diffusivity $D_e$ via porosity
  - Already gave us DMS
- Decrease activity ($k'$)
  - Uneconomical
- Decrease diffusion path length ($r$)
  - Diameter fixed by cyclones
- Dual stage approach:
  - Inactive inner stage reduces ($r$)
  - Particle retained in the FCC
  - Less zeolite is offset with improved zeolite stability
A Winning Combination

- Multi-Staged Reaction Catalyst (MSRC) approach
  - An outer stage of highly stable and active zeolite improves mass transfer by reducing the diffusion path length
  - A stable core serves as an anchor for the active outer stage. Attrition properties are comparable to NaphthaMax III products

- Highly stable and active zeolite yields a reduction on RE usage
  - 25% reduction in zeolite leads to 25% reduction on RE

- Result is DMS-like yields with no penalty for lower RE
Yields match NaphthaMax III with 25% lower REO
BASF has introduced an innovative new FCC catalyst manufacturing platform, Multi-Stage Reaction Catalyst (MSRC)

Fortress™, the first MSRC product, has been successful commercialized

Laboratory testing, refinery trial results, and post-audit testing all demonstrate the improved metals passivation benefits of Fortress

CORE™, the second product, is in commercialization and offers potential for REO reduction

BASF will be introducing exciting new technologies from the MSRC platform in the future!
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