Deactivation of Hydrotreating Catalysts in Different Reaction Zones of a VGO FCC-Pretreatment Reactor

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Contents

- FCC-PT process overview
- Reaction zone concept
- Sampling and analysis goals
- Catalyst deactivation by coking and metals deposition
- **FCC Feed Hydrotreater** generates feed to the FCC to improve the quality by removing contaminants and adding H\(_2\)
  - Generates some products directly; e.g., low S diesel
- **Fluid Catalytic Cracker** uses acid-catalyzed cracking to break heavy hydrocarbons down to gasoline and light cycle oils
  - Unit performs better on low contaminants, C/H ratio and N feed
FCC-PT Operates across a Wide Range of Conditions

Feed is heavy with high S, N and C/H (i.e. high aromatic) contents, metal contaminants (Ni, V, As, Si etc.), high ConCarbon (0-4 wt.%) and particulates (FeS, coke fines)

<table>
<thead>
<tr>
<th>Feed</th>
<th>blend of VGO with lube extracts, coker stocks, resid, DAOs</th>
</tr>
</thead>
<tbody>
<tr>
<td>LHSV</td>
<td>hr(^{-1})</td>
</tr>
<tr>
<td>ppH(_2)</td>
<td>bar</td>
</tr>
<tr>
<td>H(_2)/Oil</td>
<td>NI/l</td>
</tr>
<tr>
<td>Temperature</td>
<td>°C</td>
</tr>
<tr>
<td>HDS Target</td>
<td>%</td>
</tr>
<tr>
<td>HDN Target</td>
<td>%</td>
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</tbody>
</table>

\[\text{LHSV} = 0.5-1.2, \quad \text{ppH}_2 = 60-130, \quad \text{H}_2/\text{Oil} = 250-500, \quad \text{Temperature} = 350-420 (EOR), \quad \text{HDS Target} \geq 80, \quad \text{HDN Target} \geq 50\]

Different from ULSD and HC-PT (HDS/HDN conversion > 99%)
FCC-PT Catalyst Performance is Limited by Reaction Conditions

- Even the most active catalysts only reach medium conversion levels
- Very difficult feed treated at relatively low pressure/ppH₂
- In general, temperature is too low to remove all N, which is the main HDS inhibitor, but too high to hydrogenate aromatics to a significant extent.
- Actual conditions (ppH₂, ppH₂S, ppNH₃ and temperature) change throughout the reactor
Reaction Chemistry Changes at Each Point in the Catalyst System

Catalyst System

Sulfur  Nitrogen  H₂S  NH₃  ppH₂  Temperature
A Conceptual Reaction Zone Model: FCC-PT Operates in Zones 1 and 2

<table>
<thead>
<tr>
<th></th>
<th>Zone 1</th>
<th>Zone 2</th>
<th>Zone 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfur content</td>
<td>High</td>
<td>Medium</td>
<td>Low</td>
</tr>
<tr>
<td>Nitrogen content</td>
<td>High</td>
<td>Medium – Low</td>
<td>Very Low</td>
</tr>
<tr>
<td>Polynuclear Aromatics</td>
<td>High</td>
<td>Medium – Low</td>
<td>Zero</td>
</tr>
<tr>
<td>H₂S in Gas</td>
<td>0 – Medium</td>
<td>High</td>
<td>Highest</td>
</tr>
<tr>
<td>NH₃ in Gas</td>
<td>0 – Medium</td>
<td>Medium</td>
<td>High</td>
</tr>
<tr>
<td>H₂ in Gas</td>
<td>High</td>
<td>Medium</td>
<td>Medium – Low</td>
</tr>
<tr>
<td>Main HDS Reaction</td>
<td>Direct</td>
<td>Direct + Hydrog’n Organic Nitrogen</td>
<td>Hydrogenation –</td>
</tr>
<tr>
<td>Main HDS Inhibitor</td>
<td>H₂S</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Main HDN/HDA Reaction</td>
<td>Hydrog’n Org. N, Aroms</td>
<td>Hydrogenation Org. N, Aromatics</td>
<td>Hydrogenation Aromatics</td>
</tr>
<tr>
<td>Main HDN/HDA Inhibitor</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HDS Reaction Rate</td>
<td>Fast</td>
<td>Slow</td>
<td>Fast</td>
</tr>
<tr>
<td>HDN/HDA Reaction Rate</td>
<td>Very Slow</td>
<td>Slow</td>
<td>Slow-Medium</td>
</tr>
</tbody>
</table>

- Reaction zones vary in length and position
- ULSD and Hydrocracking PT operate in all 3 zones
FCC-PT Catalysts

- Optimize performance by sequencing catalysts with functionality selected to match conditions and desired reactions in particular zones of the reactor.

- **Guard Bed**: removes metal poisons (VGO demet), CCR and particulates; volume must be sufficient to protect the main bed catalyst.

- **Main Bed**: depends on unit’s operating strategy / conditions, focuses on HDS, HDN and aromatics saturation to meet unit objectives / constraints.

Feed + H2

Guard Bed

Main Active Catalysts

Products + H2
Sampling of Commercial Reactors

- Reactor fill between 15-800 mt
- Guard bed and main bed may contain multiple catalysts
- Sampling of specific parts of catalyst bed during unloading is difficult (gravity dumping)
- Optimum scenario: 1-5 samples of ca. 1 kg each taken per catalyst layer ~ 0.005% material is sampled
- Chemical and physical analysis:
  - 10-15g sample used ~ 0.000002%
- SEM and TEM:
  - 5-10 extrudates ~ 50-100 mg used ~ 0.00000001%
- Representative sampling essential; confirm any unexpected results
Analysis Goal

- **Guard bed catalysts:**
  - Determine concentration and distribution of metal contaminants
  - Determine coke content

- **Main bed catalysts:**
  - Check for presence of metal contaminants
  - Determine coke content
  - Assess the state of the active phase: MoS$_2$ dispersion

- Challenging because there is so much going on
Analysis of Different Catalyst Layers for Coke and Metallic Contaminants

- Very significant catalyst contamination in commercial operation → deactivation

VGO-demet (160 m²/g):
- 10 wt% MoO₃ → 2.7 at/nm²
- 14 wt% C → 42 at/nm²
- 8 wt% V₂O₅ → 3 at/nm²
- 8 wt% SiO₂ → 5 at/nm²
- Deposited Ni ~ catalyst Ni → 2.3 at/nm² total Ni

- Coke higher at inlet and outlet
  - Higher feed C/H @ inlet
  - Higher Rx Temp @ outlet
Metallic contaminants determine the residual surface area/pore volume in regenerated samples.

Sintering may occur during regeneration.
Apparent Changes in Pore Size Distribution from Deactivation and Regeneration

- Pores “filled” with residual oil, coke and metal deposits in spent catalyst
- Sintering and change of pore size may occur during regeneration
Apparent Changes in Pore Size Distribution from Deactivation and Regeneration

- Pores “filled” with residual oil, coke and metal deposits in spent catalyst
- Sintering and change of pore size may occur on regeneration
- H₂S/H₂ “resulfiding” removes residual oil and soft coke
Typical Contaminants Distribution in a VGO Demet Catalyst: SEM-EDX

- Low activity outer part
- Si near surface
- Ni, V, Fe deposition throughout the particle
Typical Contaminants Distribution in a Main Bed Catalyst: SEM-EDX

- High activity outer part
- All contaminants near surface
Fe Deposits on Main Bed Catalyst Extrudate Surface

- Fe originates mainly from corrosion products (Fe oxide and sulfide) in the field and during transportation / storage
  - Some crudes contain trace amounts of organic Fe compounds
SEM-EDX near Extrudate Surface: Si Deposits Form New Outer Layer on Main Bed Catalyst

- Al defines the original pellet boundary
- Si originates from anti-foam agents used by the refinery
- Fe also in the Si layer
- V on catalyst surface
STEM-EDX Using Extrudate Sections: Main Bed Catalyst Contaminated with As

- Method enables analysis of **specific locations** in the catalyst, as well as **specific crystals** (EDX, morphology)
- Analysis of crystals in spent catalyst location e

- Mismatch of Ni, S and As maps
  - Much broader S distribution
  - More limited As distribution
Ni-S$_x$-As$_y$ Crystals in Close-up: NiS$_x$ Adjacent to NiAs$_y$ and Ni-S$_x$-As$_y$

- You can **zoom in on specific crystals** (maps, concentration profiles) to learn more about their formation

S = red, As = blue, Ni = green
Ni-S$_x$-As$_y$ Crystals in Close-up: NiAs$_y$ between NiS$_x$

S = red, As = blue, Ni = green
Ni-$S_x$-$As_y$ Crystals in Close-up: NiAs$_y$ between NiS$_x$

S = red, As = blue, Ni = green
Ni-S$_x$-As$_y$ Crystals in Close up: Ni-S$_x$-As$_y$ between NiS$_x$

$S = \text{red}, \ As = \text{blue}, \ Ni = \text{green}$
Ni-S$_x$-As$_y$ Crystals in Close-up: Ni-S$_x$-As$_y$ Adjacent to NiS$_x$

**Overall Results**

- Observe mainly separate NiAs$_y$ and NiS$_x$ crystals with variable composition of NiS$_x$
- Only a few mixed Ni-S$_x$-As$_y$ crystals

S = red, As = blue, Ni = green
Example of Ni and V Contaminated Guard Bed
Catalyst: $\text{Ni}_x\text{V}_y\text{S}_z$ Crystals in Close-up

- Analysis of selected crystals in specific locations
- Mismatch of Ni and V maps: $\text{NiS}_x$ vs. $\text{Ni}_x\text{V}_y\text{S}_z$
Ni$_x$V$_y$S$_z$ Crystals in Close-up: Mixed Ni$_x$V$_y$S$_z$ Crystals

- Selective orientations give similar Ni:V ratios of mixed Ni$_x$V$_y$S$_z$ crystals

V = Red, Ni = Green
- Other selective orientations give variable Ni:V ratios of mixed Ni$_x$V$_y$S$_z$ crystals

V = Red, Ni = Green
Ni\textsubscript{x}V\textsubscript{y}S\textsubscript{z} Crystals in Close-up:
Pure NiS\textsubscript{x} next to Ni\textsubscript{x}V\textsubscript{y}S\textsubscript{z}

- Mostly observe NiS\textsubscript{x} and some Ni\textsubscript{x}V\textsubscript{y}S\textsubscript{z} crystals
- No pure VS\textsubscript{x} found: \Rightarrow NiS\textsubscript{x} needed to remove V from oil

V = Red, Ni = Green
Small effect of actual bed T: somewhat larger slabs in reactor bottom

![Graph showing bed temperature vs. reactor holding time]

TEM: State of the Active Phase in Spent Main Bed Catalyst: MoS$_2$ Dispersion Still High
Deactivation of FCC-PT catalysts is mainly due to coke and metal deposits rather than active phase sintering:

- High coke formation in reactor top and bottom
- Large variety of metal deposits in guard bed and also main bed catalyst if not sufficiently protected
- Separate NiAs_y and NiS_x crystals as well as mixed Ni-S_x-As_y and Ni_xV_yS_z crystals
- No pure VS_x found: NiS_x required to remove V
- Variable concentration ratios, no core-shell crystals; crystal formation at random/anything goes
- Small differences in MoS_2 dispersion reactor top versus bottom, outer versus inner part of extrudates \( \Rightarrow \) little active phase sintering
Conclusions

- FCC-PT catalysts perform in a difficult reaction environment
- Analysis of representative spent catalyst samples is essential to understand catalyst performance and deactivation
- Protection of main bed catalyst by effective use of VGO demet catalyst(s) is essential
- Optimize reactor loading scheme (guard bed + sequencing of several main bed catalysts) in terms of activity/selectivity as well as coke resistance and H₂ consumption
- Good understanding of reactor zone chemistry can enhance overall system performance
  - Enables most effective application of existing catalysts
  - Drives development of improved catalysts