Süd-Chemie Catalyst Seminar 2016

Enhanced portfolio of Purification Catalysts

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30th Sept 2016
Overview
- Feed Purification Catalyst Portfolio

Improvements & best practices
- Hydrodesulphurisation Catalyst (HDS): **HDMax series**
- Chloride Guard: **ActiSorb Cl2**
- Sulfur Guard: **ActiSorb S2**
- Dual function HDS cum Sulfur Guard: **ActiSorb G-1**

New Developments
- ActiSorb G1M
- ActiSorb G1ML
- ActiSorb GP 105

Case Study: Kanpur Fertilizers & Cement Ltd (KFCL)
Feed Purification Catalysts

Hydrodesulphurisation (HDS)
(CoMo / NiMo)

Chloride Guard
(Na promoted Alumina)

Sulfur Guard
(Zinc Oxide)
Is it important to have good Purification Catalysts?
Goals for Purification Catalysts

– Avoid unplanned shutdowns due to catalyst poisoning
– Protect & Improve life of downstream catalysts
– Extend life of Primary Reformer Tubes
Catalyst Poisons

1. Sulfur
2. Chlorides
3. Olefins

All 3 components should strictly be part of standard specifications from your NG / Naphtha supplier.
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Hydrodesulphurisation (HDS)

- **Key functions**
  - Converts organic Sulfur to $\text{H}_2\text{S}$
  - Converts organic chlorides to $\text{HCl}$
  - Saturates olefins (with sufficient recycle $\text{H}_2$)
  - Traps metallic impurities

- **Sulfiding**
  - NG with 2-10 ppmv of sulfur, no pre-sulfiding required
  - Olefins in the feed – pre-sulfiding is recommended
  - Naphtha feeds – pre-sulphiding is recommended
HDS: Goals for new catalyst

HDMax 200 / 250 (CoMo)  HDMax 300 /350 (NiMo)

Goals for new HDS catalyst development:

- Significantly lower pressure drop
- Same or higher activity
- Robust with high Crushing Strength & Attrition resistance
HDS: New Development
HDMax 200 HR: 5 x 2.5 Rings

Key advantages (compared to extrusions)

👍 > 50% reduction in pressure drop

👍👍 > 10% higher activity – needs lesser catalyst quantity

👍👍 Crushing Strength & Attrition resistance similar or higher
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Chloride Guard– ActiSorb® Cl2

Why is this important?

- HCl reacts with downstream ZnO catalyst & forms ZnCl2 which sublimes at > 260 deg C
- Causes issues with Reforming catalyst & extreme level of poisoning to Low Temperature Shift catalysts.
- Ammonia industry has experienced severe chloride poisoning in the past
- As a best practice, we recommend using Chloride Guard as overlay on top of ZnO Sulfur Guard
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Sulfur Guard: ActiSorb® S2

\[ \text{H}_2\text{S}_{(g)} + \text{ZnO}_{(s)} \rightleftharpoons \text{ZnS}_{(s)} + \text{H}_2\text{O}_{(v)} \]

- An ABSORBENT, not a catalyst
- ZnO is consumed by \( \text{H}_2\text{S} \) containing gas
- Typical outlet sulfur 0.05 - 0.1 ppm
- Peak performance (pick-up capacity) at > 340 deg C

Key aspects in selection of ZnO sulfur Guard:

- High purity virgin ZnO raw material is required – otherwise leads slow but permanent poisoning of Pre-/ Primary Reformer catalyst
- Myth: Higher ZnO content – doesn’t always mean it is a better adsorbent
- High Surface Area for better kinetics of sulfur absorption
High Vs. Low Surface Area
ActiSorb® S2

Advantages of ActiSorb S2:

• Latest generation with High Surface Area ➔ Higher pick-up capacity
• Super high purity ZnO raw material is used
• Available in various ZnO concentrations & Bulk Densities
Options for optimization of Desulphurization Section

Option-1: Optimised Flowsheet (NG feeds)

Diagram showing the flowsheet with NG feeds, HDS, ZnO, ZnO.
Options for optimization of Desulphurization Section

Option-1: Optimised Flowsheet (NG feeds)
Options for optimization of Desulphurization Section

Option-2: Optimised Flowsheet (NG feeds)

Saves pressure drop of separate HDS converter, but HDS may not be optimally utilized

If there is no lead lag arrangement, 2nd reactor doesn’t need HDS
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Introduction to ActiSorb G-1

ActiSorb G1 is a brilliant dual function catalyst:

**Function-1:** Hydrogenation of organic sulfur in the presence of H2
(similar to CoMo / NiMo HDS catalysts)

**Function-2:** Absorption of H2S & COS

All this in a single bed!

Catalyst Properties:

- CuO: 1.5%
- MoO3: 3.5%
- ZnO: Balance
- Bulk Density: 1.2 - 1.3 kg/l

These unique characteristics unlocks possibilities for several new process flow schemes for purification section.
Unique attributes of G1

- Ideal for Natural Gas with low Sulfur: < 20 ppm
- Sulfur pick-up as high as with Zinc Oxide
- Maintains Hydrogenation activity even without Sulfur
- No pre-sulphiding required & can startup without H$_2$
- Highly recommended for fine polishing with COS in feed
- Drop-in replacement in ZnO beds, absolutely no other changes required
Eliminates need for separate HDS

- By-pass HDS: Save pressure drop of 0.2 – 0.3 kg/cm²
- Differential cost between ActiSorb G-1 & ZnO is paid-off in < 1 year
Eliminates need for separate HDS

Low cost alternative for low H2S containing feeds (< 5 ppm)
Deep Desulphurisation

ActiSorb S6

Heavy duty fine polishing Sulfur Adsorbent

Highly recommended upstream of Pre-reformer catalyst

- ActiSorb S6 brings ‘S’ < 10 ppb
- Very high concentration of Cu
- Removes COS, H2S and light organic sulfur
- Needs reduction before use
- Improves Pre-Reformer & LTS life
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Issues with Lean & Rich NG

Do you have performance issues when feed is switched between lean NG to rich NG? Do you analyse Sulfur on regular basis?

ActiSorb G1 ML:

- Recommended when there is fluctuating / undetected levels of Organic Sulphur along with H2S
- Rich /Lean NG feeds
- Does not need in-situ reduction
- Enhances life of LTS catalyst
- Drop in replacement for ZnO

Rich / Lean NG

HDS

G1 ML

G1 ML

Mild Copper based
ActiSorb G-1 ML
Issues with Lean & Rich NG

High performance grade for plants using multiple feeds

ActiSorb G1M:

- High copper version of G1 ML
- For fine polishing of H2S & Organic Sulfur heavier feeds
- Does not need in-situ reduction
- Enhances life of LTS catalyst
- Drop in replacement for ZnO
Breakthrough Innovation in Sulfur Absorbents

ActiSorb GP105

ActiSorb S2
Breakthrough Innovation in Sulfur Removal: ActiSorb GP105

Completely new approach for Desulphurisation @ ambient temperature

ActiSorb GP105:
- Ambient temperature operation
- Extremely high pick-up capacity
- Sulfur slips of < 0.05 ppm
- Non-regenerable, but very long life
- Saves energy / Plot Size & Capex for new projects
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Case Background

• Operating on Naphtha feed
• HDS (CoMo) + ZnO design basis
Revamp to NG feed

- Operating on NG
- HDS (CoMo) emptied & ZnO replaced with G-1
### Performance Comparison

<table>
<thead>
<tr>
<th>INITIAL CONFIGURATION (Before Revamp)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>S in Feed</td>
<td>100 ppmv</td>
</tr>
<tr>
<td>HDS Status</td>
<td>Inline</td>
</tr>
<tr>
<td><strong>Pressure drop of system</strong></td>
<td>0.5 kg/cm²</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>FINAL CONFIGURATION (After Revamp)</th>
<th></th>
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<tbody>
<tr>
<td>S in Feed</td>
<td>10 ppmv</td>
</tr>
<tr>
<td>HDS Status</td>
<td>reactor empty</td>
</tr>
<tr>
<td><strong>Pressure drop of system</strong></td>
<td>0.2 kg/cm²</td>
</tr>
<tr>
<td>Expected life of ActiSorb G1</td>
<td>&gt;3 years</td>
</tr>
<tr>
<td>Life achieved till date</td>
<td>3.5 years</td>
</tr>
</tbody>
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ActiSorb G-1 is installed in all 3 lines of Ammonia plant
Summary

- Predominantly most Ammonia are operating on NG, needs fresh approach for Purification flowsheet
- HDS New Development: HDMax® 200 HR – Low pressure drop & High Activity
- Various option for Sulfur Removal:

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Application</th>
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<tbody>
<tr>
<td>ActiSorb S2</td>
<td>Workhorse ZnO based H2S Adsorbent</td>
</tr>
<tr>
<td>ActiSorb G-1</td>
<td>Dual function HDS Cum Sulfur Guard</td>
</tr>
<tr>
<td>ActiSorb S6</td>
<td>Deep Desulphurisation - Recommended upstream of pre-reformers</td>
</tr>
<tr>
<td>ActiSorb G-1ML</td>
<td>Operation with Rich &amp; Lean NG feeds</td>
</tr>
<tr>
<td>ActiSorb G-1M</td>
<td>Plants using multiple feeds (Incl. Naphtha) &amp; history of sulfur issues</td>
</tr>
<tr>
<td>ActiSorb GP105</td>
<td>Breakthrough Innovation: Ambient temperature Sulfur Removal</td>
</tr>
</tbody>
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Ammonia Synthesis
Reforming
High Shift
Low Shift
Methanation
Feed Purification

LIFELINE

thank you all