Sulfur Recovery Catalysts

Driving Sulfur Recovery towards Excellence

Dr. Fabien Porcheron
Agenda

- Introduction
- Sulfur Recovery Unit Catalysts
- Hydrogenation Based Tail Gas Treating Unit Catalysts
- Conclusions
Global Refining Scheme

Axens’ Iran Seminar – 19-20 July 2016 – Paving the Way to a Highly Competitive Refining Industry
Claus Process

Acid gas

Furnace

Air

T ~ 1200°C

Condenser

Reheater

First converter

T ~ 300°C

Condenser

Reheater

Second converter

T ~ 230°C

Condenser

Incinerator

3rd converter

TGTU

Sulfur pit

1/3 \((H_2S + 3/2 O_2 \rightarrow SO_2 + H_2O)\)

2/3 unconverted \(H_2S\)

\(2 H_2S + SO_2 \leftrightarrow 3/x S_x + H_2O\)

Claus Reaction
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## Claus Catalysts Portfolio

<table>
<thead>
<tr>
<th>Type</th>
<th>Name</th>
<th>Shape</th>
<th>Notes</th>
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</thead>
</table>
| **Alumina (Al$_2$O$_3$)** | **CR 3-7** | Standard Claus catalyst 300+ references | Used for very high sulfur recovery  
Recommended for high COS & CS$_2$ hydrolysis yield 300+ references |
| **CR-3S**             |            |       | Optimized Claus catalyst 300+ references                             |
| **Titania (TiO$_2$)** | **CRS 31** |       | Used for very high sulfur recovery  
Recommended for high COS & CS$_2$ hydrolysis yield 300+ references   |
Thermodynamics of the Claus Reaction

The colder the better
(but Sulfur dewpoint limitations)

\[ \text{Catalytic stage} \]

\[ \text{Thermal Stage limited conversion} \]

\[ 2 \text{H}_2\text{S} + \text{SO}_2 \Leftrightarrow \frac{3}{x} \text{S}_x + 2 \text{H}_2\text{O} \]

Claus catalysts shall be designed to prevent condensation of sulfur
Macroporosity is the key factor.
Claus Alumina CR 3-7

- $\text{Al}_2\text{O}_3$ is a well-known Claus active component
- CR 3-7
  - Standard Alumina Catalyst
  - Beads shape
  - Macroporosity (>750 Å) of CR 3-7 is one of the highest on the market
  - Suited for basic priorities: simple conversion & low pressure drop requirements are imposed
  - This low-cost catalyst is attractive when there are no specific processing constraints

Can we further optimize the catalyst structural & chemical properties to reach higher yields?
Of the Importance of Macroporosity

- Large \( S_8 \) molecules have to get out of the catalyst porosity

- Micropores (<30 Å) quickly plugged by liquid sulfur - inactive -

- Mesopores (30-100 Å) difficult diffusion

- Macropores (>750 Å) easy diffusion

- Ultra-macropores (>10 000 Å) even better

Macroporosity has to be tuned in order to minimize the diffusion constraints
The pores of CR-3S are the largest on the market.
Claus Process

\[ \text{CO}_2, \text{HC} + \text{S} \rightarrow \text{COS}, \text{CS}_2 \]

\[ \text{COS} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2\text{S} \]

\[ \text{CS}_2 + 2 \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + 2 \text{H}_2\text{S} \text{  Most difficult reaction} \]
Na$_2$O content has to be in between 1500 and 2500 ppm

Competition products contain 3500 ppm Na2O

Additional step required to manufacture CR-3S
Claus TiO$_2$ Catalyst

- **TiO$_2$ is the ultimate Claus active component**
  - Reaches Claus reaction thermodynamics equilibrium
  - Total COS and CS$_2$ hydrolysis
  - Allows debottlenecking
  - Very long life time & resistant to sulfation

- **CRS 31**
  - Titanium dioxide based Catalyst
  - Cylindrical extrudates shape in 3.5 mm
Best Strategy for TiO$_2$ – Option 1

- **CRS 31 layer in R$_1$**
  - Full COS-CS$_2$ hydrolysis
  - Higher overall recovery
  - Similar life time than alumina loading
Best Strategy for TiO\(_2\) – Option 2

- **Full CRS 31 loading**
  - Outstanding sulfur recovery (thermodynamic limitation)
  - Extended life time (> 10 years)
  - Possible throughput increase

![Diagram showing the process flow with TiO\(_2\) and CS\(_2\) conversion](image)

- Contact time
- CS\(_2\) conversion
- CRS 31
- CR-3S
- CR 3-7
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Hydrogenation Based Tail Gas Treating Units

- **Principle = A small HDT unit**
  - Transformation of Sulfur species into H$_2$S
  - Recycling of H$_2$S to the Claus furnace

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**Diagram:**
- Air, fuel gas, Claus Tail Gas, TGT Catalysts, Quench column, Absorber, Regenerator, Recycle to Claus furnace, to incinerator, to SWS, Reactor Section, Amine Section, water, steam.
### Hydrogenation Catalysts Portfolio

#### CoMo catalysts

<table>
<thead>
<tr>
<th>Shape</th>
<th>Beads 2-4 mm</th>
<th>Trilobes 2.5mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional Temperature</td>
<td><strong>TG 103</strong>&lt;br&gt;- High density, high activity</td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>TG 203</strong>&lt;br&gt;low density, low cost</td>
<td><strong>Released in 2015</strong></td>
</tr>
<tr>
<td>Low Temperature</td>
<td><strong>TG 107</strong>&lt;br&gt;- High density, high activity, the original LT catalyst</td>
<td><strong>TG 136</strong>&lt;br&gt;- Lower density, lower deltaP</td>
</tr>
</tbody>
</table>
Conventional Temperature Catalysts

- Reactor Section
  - Claus Tail Gas
  - TG 103/203
  - Quench column
  - Amine Section
  - Absorber
  - Regenerator
  - Recycle to Claus furnace

- Process Streams:
  - Air
  - Fuel gas
  - Steam
  - Water

- Temperature Range: 260-300°C

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Low Temperature Catalysts

200-240°C

Claus Tail Gas

TG 107/136

Reactor Section

Amine Section

to SWS

to incinerator

Recycle to Claus furnace

Air

Fuel gas

Steam

Water

Claus Tail Gas

Quench column

Absorber

Regenerator

VCMStudy.ir
A Revolution for Existing / New Units

Operation at low temperature
- 40 % savings on energy
- Catalyst payback < 1 year
- Lower CO₂ emissions
- Tripled temp. safety margin

From direct to indirect reheater
- Less risk of misoperations (soot or excess air)
- Longer catalyst lifetime
- Equipment downsized 10%
- Capex reduction 10-15%
- OpEx reduction 20%

Ref.: Marco van Son, Sept. 15th 2005 Brimstone, Vail (CO)
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Driving Sulfur Recovery Towards Excellence

Axens pioneered every evolution in sulfur recovery catalysis over the past 50 years:

- $\text{Al}_2\text{O}_3/\text{TiO}_2$ hybrid: CRS 21 (1972)
- Fe Oxygen scavenger: AM (1976) & AMS
- Pure $\text{TiO}_2$: CRS 31 (1984)
- Optimized Alumina: CR-3S (1994)
- BTX management: CSM 31 (2007)
- Low turndown catalyst: CR-3S LG (2014)

Focusing on the benefits of our customers made us Sulfur recovery catalyst World leader
Axens Complete Portfolio for SRU

**Claus Catalysts**
- CR: Claus alumina
- **CR-3S**: Improved Claus alumina
- DR Series: Active bed supports
- **CRS 31**: Titanium dioxide catalyst
- AM & AMS: Oxygen scavengers
- CSM 31: BTX management

**Tail Gas Treatment Catalysts**
- TG 103: TG hydrogenation catalyst, spherical
- TG 203: TG hydrogenation catalyst, spherical
- TG 107: Low temperature TG hydrogenation catalyst, spherical
- TG 136: Low temperature TG hydrogenation catalyst, extrudate
Thank you! And see you on Axens’ Blog
axens.net/blog