3rd Generation Stabilized Front End Selective Hydrogenation Catalysts Enhance Operational Stability and Maximize Ethylene Gain

Dr. Wolf Spaether
Outline

Acetylene Hydrogenation: Process & Catalyst Principles

Selective hydrogenation of Acetylene
Tail-end vs. Front-end configurations
Tail-end vs. Front-end catalysts

Catalysts: Stabilized Selective Hydrogenation Catalysts

Convergence of Tail-end and Front-end catalyst developments
Clariant’s OleMax® catalyst family

Application: Front-end Hydrogenation Catalysts

Operational challenges

3rd Generation Stabilized catalysts to meet industrial demands

Field Reference Data

Value Proposition

Summary
Acetylene Selective Hydrogenation - I

Ethylene is produced by thermal cracking of hydrocarbon feedstocks

*Primary products include: Ethylene and Propylene*

*By-products include: Hydrogen, CO, Methane, **ACETYLENE**, di-olefins, C4+

Acetylene is a troublesome by-product

*Cannot be separated from Ethylene product by distillation/fractionation*

*Considered a poison to typical downstream applications*

Removal via selective hydrogenation (common) or extraction (rare)

*Selective hydrogenation of Acetylene to Ethylene product (desired)*

*Non-selective hydrogenation of Acetylene to Ethane (undesired)*
Acetylene Selective Hydrogenation - II

Selectivity to Ethylene

Relative amount of Acetylene that is converted to Ethylene Product by single hydrogenation

Non Selective Hydrogenation destroys valuable Ethylene product

By degrading it to ethane fuel value

By lowering the single pass Ethylene output of a Steam Cracker

„Value“ of the Acetylene by product

Typical Acetylene content of a Steam cracker effluent: 2% mol relative to ethylene

Basis: 1 MMTPA steam cracker produces 20,000 MT Acetylene PA

20,000 MT of Acetylene converted to Ethylene equal 24 MMUSD Value
# Acetylene Hydrogenation Schemes

Each process scheme has advantages & disadvantages

<table>
<thead>
<tr>
<th></th>
<th>Tail-End Acetylene Hydrogenation</th>
<th>Front-End Acetylene Hydrogenation</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Feed</strong></td>
<td>C$_2$ cut only</td>
<td>C$_2^-$, C$_3^-$, Raw Gas (includes light end)</td>
</tr>
<tr>
<td><strong>Position</strong></td>
<td>After light end removal</td>
<td>Before light end removal</td>
</tr>
<tr>
<td><strong>Hydrogen</strong></td>
<td>Injected in stoichiometric amounts</td>
<td>Excess hydrogen</td>
</tr>
<tr>
<td><strong>CO</strong></td>
<td>Optionally added, trace amounts</td>
<td>High levels, fluctuating</td>
</tr>
</tbody>
</table>
| **Process control Parameter** | Temperature  
Hydrogen injection  
CO injection | Temperature |
| **Regeneration**        | In-situ                          | No regeneration / ex-situ         |
| **Pros**                | No runaway situation  
Catalyst life >10 years | Lower up-front catalyst cost  
Lower CAPEX  
Higher overall selectivity |
Acetylene Selective Hydrogenation Catalysts

Each process requires a specifically tailored catalyst

<table>
<thead>
<tr>
<th>Catalyst Properties</th>
<th>Tail-End Acetylene Hydrogenation</th>
<th>Front-End Acetylene Hydrogenation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shape &amp; Robustness</td>
<td>Easy to load / low attrition for long lifetime &amp; low pressure drop</td>
<td>Easy to load / low pressure drop / potentially ex-situ regeneration</td>
</tr>
<tr>
<td>Activity</td>
<td>Moderate/High throughout cycle</td>
<td>Moderate - dependent on flow scheme</td>
</tr>
<tr>
<td>Selectivity</td>
<td>High retention throughout cycle</td>
<td>High throughout life time</td>
</tr>
<tr>
<td>CO control</td>
<td>Trend towards zero CO addition</td>
<td>Stable towards CO swings</td>
</tr>
<tr>
<td>Green oil formation</td>
<td>As low as possible</td>
<td>Extremely low as catalyst typically is not regenerated</td>
</tr>
<tr>
<td>Regeneration</td>
<td>&gt; 10 times / high activity/selectivity retention is required</td>
<td>No regeneration / ex-situ</td>
</tr>
<tr>
<td>Regen. cycle time/life time</td>
<td>Minimum 6 months cycle time &gt; 10 years lifetime</td>
<td>Life time ≥ 5 years; trend towards 10 years</td>
</tr>
</tbody>
</table>
Evolution of Acetylene Selective Hydrogenation Catalysts

Ever increasing demand from the industry

<table>
<thead>
<tr>
<th>Generation</th>
<th>Tail-End Acetylene Hydrogenation</th>
<th>Front-End Acetylene Hydrogenation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Generation Zero</td>
<td>none</td>
<td>Ni-based (1950’s)</td>
</tr>
<tr>
<td>1st Generation</td>
<td>Pd on carrier; non promoted (1960’s)</td>
<td>Pd on carrier; non promoted (1970’s)</td>
</tr>
<tr>
<td>2nd Generation</td>
<td>Pd on carrier; promoted (typically Ag) (1990’s)</td>
<td>Pd on carrier; promoted (typically Ag) (1990’s)</td>
</tr>
<tr>
<td>4th Generation</td>
<td>Further increased activity/selectivity balance; bigger plant size</td>
<td>Further increased activity/selectivity balance; bigger plant size</td>
</tr>
</tbody>
</table>

- Evolution: Improved activity/selectivity balance; longer cycle & life time; robust in process
- Catalyst developments FE/TE converge as fundamental principles are better understood
Stabilized Acetylene Selective Hydrogenation Catalysts

C2 Tail End

- Activity Retention
- Cycle length
- Rx Inlet Temp.
- Non Stabilized 2nd Gen
- Stabilized 3rd Gen
- Selectivity Retention
- Increased Cycle Time

C2 Front End

- Activity Retention
- Life cycle
- Rx Inlet Temp.
- Increased Life Time
- Selectivity Retention

▲ Stabilization (introduced with catalyst recipe) applicable for Front End & Tail End
# Stabilized Acetylene Selective Hydrogenation Catalysts

## C2 Tail End

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>OleMax® 201</td>
<td>Industry benchmark in C2TE</td>
</tr>
<tr>
<td></td>
<td>Spherical shape/egg-shell Pd</td>
</tr>
<tr>
<td>OleMax® 207</td>
<td>17 references</td>
</tr>
<tr>
<td></td>
<td>Up to 36 months cycle length</td>
</tr>
<tr>
<td></td>
<td>&gt;&gt; 10 years life time expected</td>
</tr>
<tr>
<td>OleMax® 208</td>
<td>3 references</td>
</tr>
<tr>
<td></td>
<td>Higher activity than OM207</td>
</tr>
</tbody>
</table>

Well proven & established catalyst carriers in combination with advanced recipe

## C2 Front End

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>OleMax® 251</td>
<td>Extra durable tablet</td>
</tr>
<tr>
<td></td>
<td>Widely established in market</td>
</tr>
<tr>
<td>OleMax® 252</td>
<td>Spherical, low bulk density</td>
</tr>
<tr>
<td></td>
<td>De-ethanizer &amp; de-propanizer</td>
</tr>
<tr>
<td>OleMax® 253</td>
<td>Tri-hole, ultra low dp</td>
</tr>
<tr>
<td></td>
<td>De-ethanizer &amp; raw gas</td>
</tr>
<tr>
<td>OleMax® 254</td>
<td>Extra durable tablet</td>
</tr>
<tr>
<td></td>
<td>De-ethanizer; De-propanizer</td>
</tr>
<tr>
<td></td>
<td>Raw gas</td>
</tr>
</tbody>
</table>

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OleMax® 252/253/254

Clariant’s 3rd Generation Stabilized Catalysts for Front-End Hydrogenation
Operational challenges in Front End Selective Hydrogenation

Large excess of hydrogen present
  Potential runaway conditions (Flaring incident)

High CO concentrations
  Fluctuating (change of furnace tubes etc.)
  Significant impact on catalyst activity

Narrow operation Window
  From Acetylene cleanup to runaway
  Puts a lot of stress on operators
The Front End market demands:

- Lower acetylene slip specification (down to < 0.3 ppm)
- Higher selectivity to maximize ethylene yield
- Longer catalyst lifetime (exceeding one major plant turn around)
- Low CO operation requires improved catalyst stability (CO levels as low as 120 ppm)
- Higher stability during CO fluctuations to avoid runaways (wider operating window)

Dedicated R&D Program to meet the challenges
OleMax®254 as example of a 3rd Generation Stabilized Front End Catalyst

❖ 100% increase in Operating Window!

OleMax® 254

Temperature difference between Acetylene clean-up and runaway

Stabilized 3rd Gen

OleMax® 251

Promoted 2nd Gen

ΔT
**CO Stress Test**

**Stability Target:** Reduced sensitivity at high and low CO level

Aggressive lab test developed to determine tolerance to CO swings

<table>
<thead>
<tr>
<th>CO 900 ppmv Selectivity [%]</th>
<th>CO 300 ppmv</th>
</tr>
</thead>
<tbody>
<tr>
<td>OleMax® 251</td>
<td>74%</td>
</tr>
<tr>
<td><strong>OleMax® 254</strong></td>
<td>75%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>CO 250 ppmv Selectivity [%]</th>
<th>CO 60 ppmv</th>
</tr>
</thead>
<tbody>
<tr>
<td>OleMax® 251</td>
<td>28%</td>
</tr>
<tr>
<td><strong>OleMax® 254</strong></td>
<td>74%</td>
</tr>
</tbody>
</table>
Selectivity Advantage

Selectivity Improvement >20% relative to benchmark

Extensive Laboratory Evaluation

OleMax® 254

OleMax® 251

C₂H₂ Conversion

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Conclusion

(applies to all Clariant 3rd Generation Stabilized C2FE OleMax® Catalysts)

OleMax® 252/253/254 provide:

- Excellent overall operability
- Low sensitivity to CO swings
- Minimized risk of off-spec product
- Minimized risk of a runaway
- Increase in cycle length/life time
- Ethylene selectivity increase of over 20% relative to our OleMax® 251

Commercialization of 3rd Generation stabilized Catalysts

- In de-propanizer service → Successful start-up 2007
- In de-ethanizer service → Successful start-up 2009
OleMax® 252

Field Reference of a Stabilized 3rd Generation C2 Front End Selective Hydrogenation Catalyst
Field Reference: Plant A

- Isothermal Reactor control
- De-ethanizer configuration
- 600 KMT nameplate
- Acetylene inlet ~ 0.5% mol
- CO swings occur
- Previous incumbent catalyst required significant adjustment of the reactor inlet temperature over the catalyst life cycle
- Client changed to OleMax®252
- OleMax®252 now operating well into the 5th year
Field Reference: Plant A

Temperature, Acetylene and Feed rate

TOS  

GHSV [v/v/hr] / Ac [ppm]

Acetylene Inlet

Feed rate

Constant Rx

Inlet Temp

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Field Reference: Plant A

Selectivity and Feed rate

Selectivity (%)

TOS

GHSV (h⁻¹)

Artifacts from incorrect analyzer calibration

high Selectivity Retention

Field Reference: Plant A

Selectivity and Feed rate

Selectivity (%)

TOS

GHSV (h⁻¹)

Artifacts from incorrect analyzer calibration

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Field Reference: Plant A – Client’s feedback on OleMax®252

- Outstanding stability
- Excellent response in case of CO swings with minor temperatures adjustments.
- Low Green Oil
- Easy and smooth to start up
- Higher selectivity yields more product and significant additional margin
- Confirm the benefits of a 3rd Generation Stabilized catalyst
- End of run not visible yet due to high catalyst stability
Field Reference: Plant B

- Isothermal Reactor control
- De-ethanizer configuration
- 1000 KMT nameplate
- Acetylene inlet 0.7 – 0.8 % mol
- CO swings occur (700 – 900 ppm)
- Previous 2\textsuperscript{nd} Generation incumbent catalyst required Reactor temperature adjustment of + 20°C over life cycle
- Client changed to 3\textsuperscript{rd} Generation OleMax®253
- OleMax®253 now operating since more than 18 months without reactor inlet temperature adjustment
Field Reference Plant B: Feed Rate & Reactor Inlet Temperature

Feed Rate could be increased

No Rx inlet temperature adjustment since startup

Feed Flow rate (t/h)

Reactor Inlet Temperature (°C)

B inlet Temp. ▲ B feed rate

TOS (day)

Feed Rate

No Rx inlet temperature adjustment since startup

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Field Reference Plant B: Selectivity

High Selectivity Retention since startup

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Field Reference: Plant B
Client’s feedback on OleMax®253

- Significantly improved Stability compared to previous run
- „much easier to operate for our Operators“
- No or only very marginal temperature adjustment needed during CO swings
- Approx. 20% higher selectivity compared to previous run
Economic Value of 3rd Generation Stabilized Catalysts

Basis: 1 MMTPA Steam Cracker

Stability

- Avoidance of 1 flaring incident (24 hrs) per year
- Saving on Ethylene product loss (only) equals > 3 MMUSD

Selectivity

- 20% higher selectivity compared to 2nd generation of catalyst
- Generates additional Ethylene Product: 4,000 MT
- Value differential: Ethylene 1,200 $/MT
  Ethane 210 $/MT
- Value gain: 3.9 MMUSD

Total benefit: 7.0 MMUSD/annum

Payback (on Ethylene gain only) < 1 year
Summary

Meeting the Industry demands
- Improved Activity/Selectivity Balance
- Operational Stability & Increased Life/Cycle times
- Create significant additional value

C2 Selective Hydro catalyst: convergence of developments
- C2FE / C2TE – same fundamental principles apply
- Tailored Catalysts required for different process schemes

3rd Generation Stabilized Catalysts: OleMax® Series
- Developed for full range of C2FE & C2TE Applications
- Feedback from Field References confirm benefits of Stabilization Concept

Ongoing developments
- To further improve Activity/Selectivity balance
- To meet the growing nameplate capacities of new projects
Shukran

Thank You