Clariant Catalysts

INDUSTRIAL METHANOL CATALYSTS – TODAY AND TOMORROW

what is precious to you?
CLARIANT AT A GLANCE

what is precious to you?
Clariant at a Glance

A globally leading company in specialty chemicals
Business Area Catalysis

**SALES BY REGION**

Total 2014: CHF 729 million

- Europe: CHF 132 m (18%)
- Latin America: CHF 36 m (5%)
- Asia/Pacific: CHF 308 m (42%)
- North America: CHF 132 m (18%)
- Middle East/Africa: CHF 121 m (17%)

**TRENDS & DRIVERS**

- Expansion of a leading market position in all areas of operation
- Well positioned for applications based on shale gas in the US and coal in China
- Continue to foster partnership with leading technology providers
- Concentration on the portfolio and shifting of the resources towards core activities

**KEY FINANCIAL FIGURES 2014**

729
Sales in million CHF

6 – 7%
Growth ambition per annum
Sustainability as a value driver

MANAGING RISKS & CAPITALIZING ON OPPORTUNITIES

The world is changing. Future economic success implies sustainability and social responsibility.

Customers and markets are increasingly aware and sensitive to sustainability.

Governments and Regulators require or rate ESG aspects (Environment Social Governance) of companies.

Understanding where and how sustainability plays a role in our markets is key. Thereby, sustainability is built in Clariant’s value proposition and customer engagement.

Embedding sustainability in Clariant’s processes is happening in many ways. The company has already received Sustainability@Clariant recognition for its efforts.
Milestones of Clariant’s commitment to Sustainability

RESPONSIBLE CARE® GLOBAL CHARTER signed
FIRST SUSTAINABILITY REPORT published
ENVIRONMENTAL TARGETS 2020 established
SUSTAINABILITY REPORT rated at GRI A+
UN GLOBAL COMPACT signed
DJSI INDEX EUROPE entered
DJSI INDEX WORLD AND EUROPE top ranking
SUSTAINABILITY anchored in Corporate Strategy
FIRST RSPO CERTIFICATION received
TOGETHER FOR SUSTAINABILITY (TFS) membership
GRI4 REPORTING STANDARD applied

2009 | 2010 | 2011 | 2012 | 2013 | 2014

Corporate strategy: The **sustainability strategy pillar** has been added in the second half of 2014, »Add value with sustainability«
Syngas – THE Universal Platform
Syngas: Universal Platform for Chemicals and Fuels

Non-conventional Hydrocarbons:
- Shale gas
- Tar sands
- Coal-bed methane
- Flare gas

Raw materials:
- Natural Gas
- Coal
- Heavy Oil
- Oil residues
- Peat
- Wood
- Biomass

“Technical Photosynthesis”
Methanol: Important Base Chemical and Fuel Component

Methanol Chemistry:
- MTP
- MTO
- MTG
- MTA (aromatics)
- Higher Alcohols
- Formaldehyde
- Na-methylate
- Acetic Acid
- Methyl Amines
- Vinyl Acetate
- Methyl formiate
- MMA
- MTBE
- Chloromethanes
- DMT
- Dimethyl carbonate
- Ethanol
- Methyl mercaptane
- DMS
- DMSO
Methanol Global Demand: Strong Growth Ahead

Global Methanol Demand (CGAR: 9.4%)

<table>
<thead>
<tr>
<th>Year</th>
<th>Mio Tons MeOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>2014</td>
<td>67</td>
</tr>
<tr>
<td>2015</td>
<td>73</td>
</tr>
<tr>
<td>2016</td>
<td>82</td>
</tr>
<tr>
<td>2017</td>
<td>91</td>
</tr>
<tr>
<td>2018</td>
<td>103</td>
</tr>
<tr>
<td>2019</td>
<td>109</td>
</tr>
<tr>
<td>2020</td>
<td>115</td>
</tr>
</tbody>
</table>

Source: Clariant Database

MAIN APPLICATIONS 2014: 64 MIOTO
- MTO/MTP: 12; 18%
- Fuel (incl. Biodiesel): 10; 15%
- Chemicals: 45; 67%

MAIN APPLICATIONS 2020: 115 MIOTO
- MTO/MTP: 46; 40%
- Chemicals: 51; 44%
- Fuel (incl. Biodiesel): 18; 16%

Source: Clariant database
MeOH Technology
Methanol from Natural Gas: Catalysts are Enabling the Process

- Natural Gas
- Desulphurisation
- Pre-Reforming
- Steam Reforming
- Autothermal Reforming
- Oxygen
- Air Separation
- Hydrogen Recovery
- Methanol Synthesis
- Methanol Distillation
- Pure Methanol
- Purge Gas

1. Public
Methanol Process: Technology and Partnership

• Successful cooperation with Air Liquide (Lurgi) since the 1980ies

• Advanced catalytic technologies for highest efficiency

• Ongoing R&D and collaboration with Air Liquide: continuous improvements and new products

• Proven success of AirLiquide’s MegaMethanol® and Methanol-to-Propylene (MTP®) technology
Industrial Methanol Synthesis

- Catalyst type: ternary Cu – ZnO, Al₂O₃ based
- Catalyst shape: 6 x 4 mm tablets MegaMax® 800

Fiedler et al. 2005 In: Ullmanns Encyclopedia, „Methanol“
Syngas Innovation for Improved Sustainability
Syngas Innovation for improved Sustainability
CO2 Capture & Conversion / H2 Storage

Electrolysis

Wind
Water
Sun

Fluctuating regenerative energies

-CH2-

H2

CH3OH

CH4

Utilization

Distribution via gas grid

Fossil Resources

CO2

Biogas

Base-Chemicals
MTP

Fuels for Mobility
MtG

Power generation
Fuel for mobility
Heating
Syngas Innovation for improved Sustainability
CO2 Capture & Conversion / H2 Storage

• **Power to Gas**: CO₂ to CH₄
  - SNG (Synthetic Natural Gas) catalysts are already part of Clariant’s catalyst portfolio
  - CH₄ can be fed to existing CH₄ infrastructure including storage capacities

• **Power to Liquid**: CO₂ to MeOH or Fischer Tropsch (F-T) products
  - MeOH and F-T catalysts are already part of Clariant’s catalyst portfolio
  - Final goal of energy change affords chemical storage in all energy sectors (power+mobility+industry), including sustainable liquid fuels (FT, MeOH) or chemicals (via MeOH)

• **Non CO₂ based alternative**: Power to Liquid (Liquid Organic Hydrogen Carriers - LOHC)
  - Storage of H₂ by hydrogenation of aromatic systems
  - Cooperation between Clariant and University of Erlangen
Syngas R & D

(example MeOH synthesis catalyst)
### Operation Conditions (MeOH Synthesis): Significant Differences Depending on Feedstock

<table>
<thead>
<tr>
<th>Parameter</th>
<th>NG</th>
<th>Coal</th>
<th>Biomass</th>
<th>CO2</th>
</tr>
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<tbody>
<tr>
<td>CO/CO₂</td>
<td>0.8</td>
<td>3-4</td>
<td>4-8</td>
<td>∞</td>
</tr>
<tr>
<td>(\frac{(H₂ - CO₂)}{(CO + CO₂)})</td>
<td>3.5</td>
<td>4</td>
<td>0.5</td>
<td>2-3</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>200-300</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pressure (bar)</td>
<td>75</td>
<td>75</td>
<td>45</td>
<td>30</td>
</tr>
<tr>
<td>Production Rate (mt / day)</td>
<td>1.000 - 7.500</td>
<td>5.000</td>
<td>300 -1000</td>
<td>&lt;1000</td>
</tr>
<tr>
<td>Operation (h / year)</td>
<td>8.000</td>
<td>8.000</td>
<td>6.000 (cyclical)</td>
<td>8.000</td>
</tr>
</tbody>
</table>
Different SynGas feedstocks require **different processes** and **tailored catalysts**
The R&D Approach: Interconnected Disciplines

- Understanding the actual **catalytic functions**
- What feature makes it an **active catalyst**
- How to relate **microscopic properties to performance**
- Transferring the principles from **laboratory to production**
- Using **lab kinetic data to improve a large-scale plant**
State of the Art Catalysts: How it’s made!

- Based on ICI synthesis in the 1960s

- Is there any further potential?
- Do we really understand what is happening?

Mixing & Precipitation → Aging → Washing → Drying → Calcination Pelletizing

Cu, Zn, Al-anion_{aq}, + \text{Soda}_{aq} \rightarrow Cu/ZnO/Al_2O_3
Catalyst Synthesis at Nano-Scale: Phase Transitions

Mixing & Precipitation → Aging → Washing → Drying → Calcination

Nanostructuring → Mesostructuring → Activation

Initial texture determines structure and activity of active catalyst

Behrens et al., Chem. Commun., 2011, 47, 1701.
Reactions in Solution: Precipitation & Ageing

Influence of preparation parameters…

- pH, reactant concentrations, temperature
- Mixing

… on disperse properties

- Phase composition
- Particle size distribution & morphology

→ In-depth understanding of complex interactions by simulations & experiments in a T-mixer
A Model System

**Mole and mass balance of aqueous phase**

\[
c_{\text{tot},p} - \sum_{j=1}^{N_j} \alpha_{jp} K_j \prod_{p=1}^{N_p} c_p^{\alpha_{jp}} = 0
\]

**Coupling: Mass balance**

\[
\frac{dc_{\text{tot},p}}{dt} = M - \sum_{i=1}^{N_i} \beta_{i,p} \dot{c}_{\text{solid},i}
\]

**Population balance for disperse phase**

\[
\frac{\partial n_i(x,t)}{\partial t} = -\frac{\partial}{\partial x} \left[ G_i(x)n_i(x) \right] + \sum_{j=1}^{N_i} J_{ij} \cdot n_{\text{nuclei},ij}(x)
\]

**Principal components**

Cu\(^{2+}\) / Na\(^+\) / NO\(_3^-\) / CO\(_3^{2-}\) / H\(^+\) / H\(_2\)O

<table>
<thead>
<tr>
<th>n(t,x)</th>
<th>Particle size distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>S(t)</td>
<td>Supersaturation</td>
</tr>
<tr>
<td>(\tau)</td>
<td>Residence time</td>
</tr>
</tbody>
</table>

\[
S_{\text{Precipitate}} = \left( \frac{a_{\text{Cu}^{2+}}^2 + a_{\text{OH}}^2 - a_{\text{CO}_3^{2-}}}{K_{SP}} \right)^{1/5}
\]
Hydrochemistry: Complex Interaction of Components

- Model solved for given initial conditions is predictive
- Can deliver concentrations as function of pH (for a fixed residence time)

Hydrochemistry Results from Validated Model

- This also offers the possibility to follow a trajectory in the T-mixer

- Optimize precipitation process
- Tuning material properties

Materials Evaluation & Screening

– High-throughput evaluation of powders
– “real-world conditions” in a 2x8 microreactor

![Diagram of experimental setup]

![Graph showing WIT vs TOS]

Filled with inert material

N₂, H₂, Syn Gas

H₂, He
The Active Catalyst on a Molecular View

- HR-TEM in conjunction with EDX or SAED can identify crystallites
- **Task:** relate structure to activity
Intrinsic Kinetics / Active Sites on the Nano Scale

A deeper view of exposed crystal planes: statistical analysis and experiments

Stacking faults are correlated with surface normalized activity

Defect rich materials are desired

From High Throughput to Pilot Scale – Research and Development in One Organization

EXTENSIVE R&D EXPERTISE AND ACCUMULATED KNOWLEDGE ON CATALYST PRODUCTION

From High-Throughput… … to bench scale … to pilot scale

Catalyst synthesis robots Parallel micro test units Bench scale autoclave for precipitation Parallel bench scale test units Pilot stirred autoclaves Pilot scale test reactors with salt bath cooling
Summary

- Understanding of precipitation crucial for material properties
- Material preparation is not that simple and requires know-how
- Understanding leads to a high-performance material
- Even with the best models – we still need experiments

- Defects are a key quantity for a high-activity catalyst
- Characterization both at nano- & macro scale are needed
- Sophisticated models are required to catch catalyst behavior
- These models enable design of optimized processes and catalysts
Summary

• Understanding leads to a high-performance material
• Even with the best models – we still need experiments

Preparation → Characterization

- Understanding of precipitation crucial for material properties
- Material preparation is not simple and requires know-how
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Plant simulation → Testing
Thank you for your attention!

what is precious to you?
Selected publications from this collaborative effort


