Clariant Catalysts

INDUSTRIAL METHANOL CATALYSTS – TODAY AND TOMORROW

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Public

Uwe Flessner
BU Catalysts
05.10.2015

what is precious to you?

CLARIANT AT A GLANCE

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Clariant at a Glance

6 116
Sales 2014 (CHF m)
from continuing operations

235
Net result 2014 (CHF m)
from continuing operations

4
Business Areas

867
EBITDA 2014 (CHF m)
before exceptionals

14.2 %
EBITDA margin 2014
before exceptionals

110 in **60**
companies countries

17 003
Employees 2014

A globally leading company in specialty chemicals

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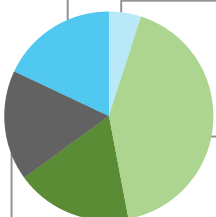
Business Area Catalysis

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.

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Milestones of Clariant's commitment to Sustainability

2009

RESPONSIBLE CARE® GLOBAL CHARTER signed

2010

FIRST SUSTAIN-ABILITY REPORT published

2011

ENVIROMENTAL TARGETS 2020 established

2012

SUSTAINABILITY REPORT rated at GRI A+

2013

UN GLOBAL COMPACT signed

DJSI INDEX EUROPE entered

2014

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

Corporate strategy: The **sustainability strategy pillar** has been added in the second half of 2014, »Add value with sustainability«

Syngas – THE Universal Platform

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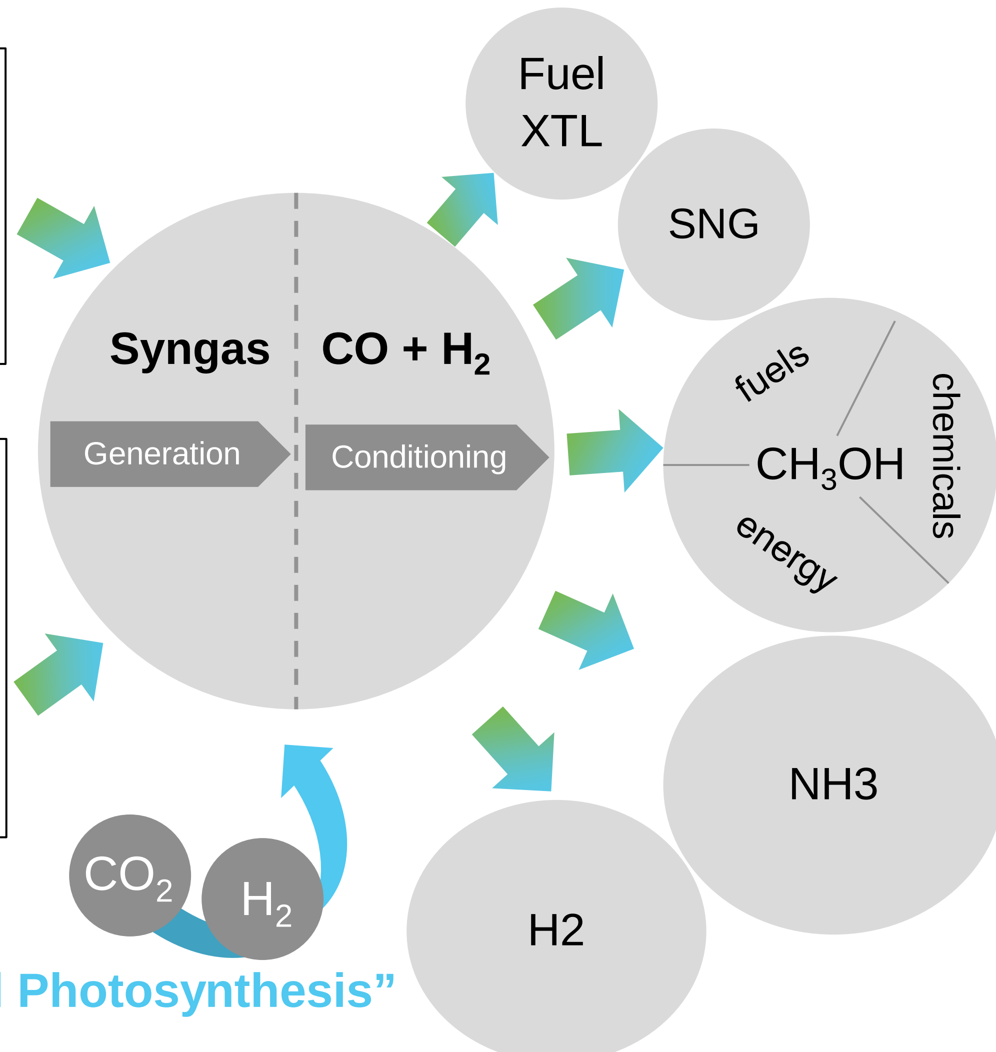
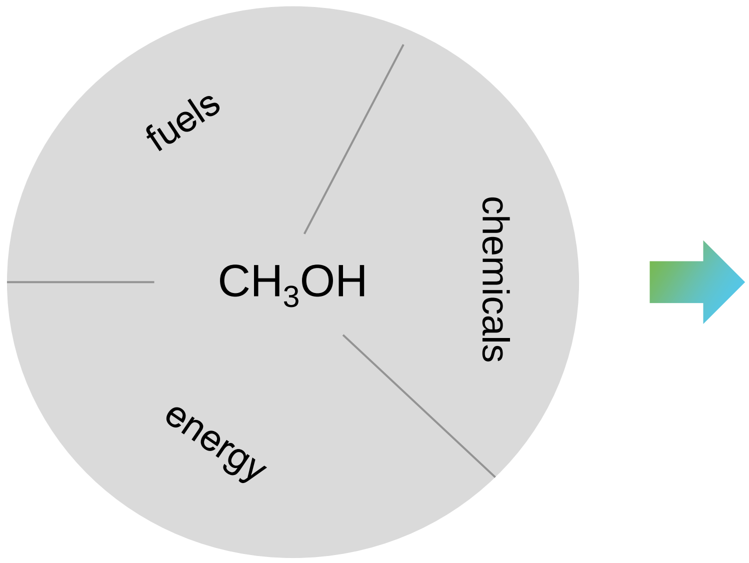
Syngas: Universal Platform for Chemicals and Fuels

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

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



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

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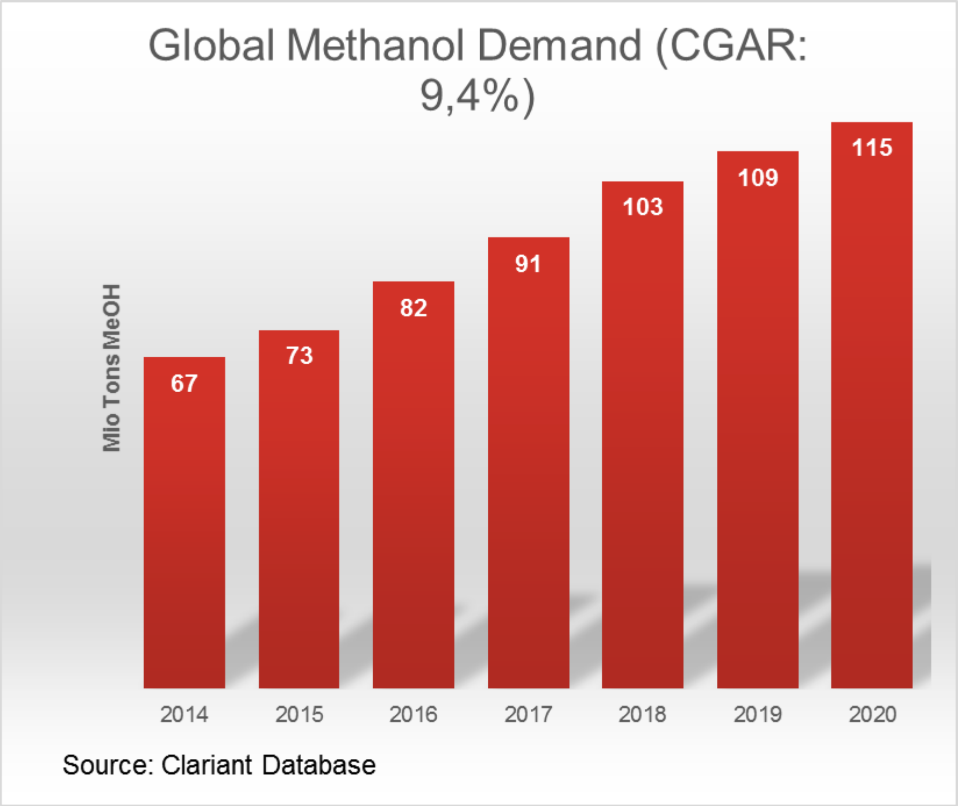
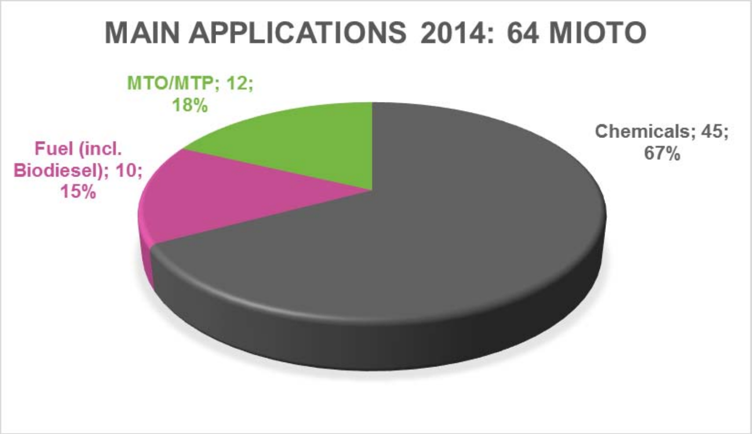
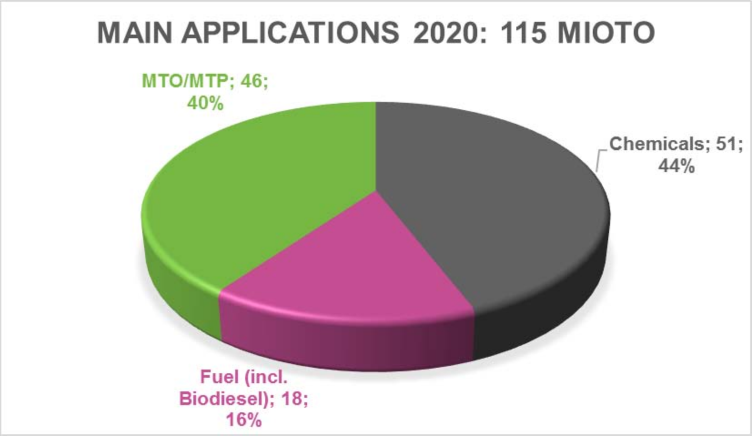
Methanol Global Demand: Strong Growth Ahead







Source: Clariant database

MeOH Technology

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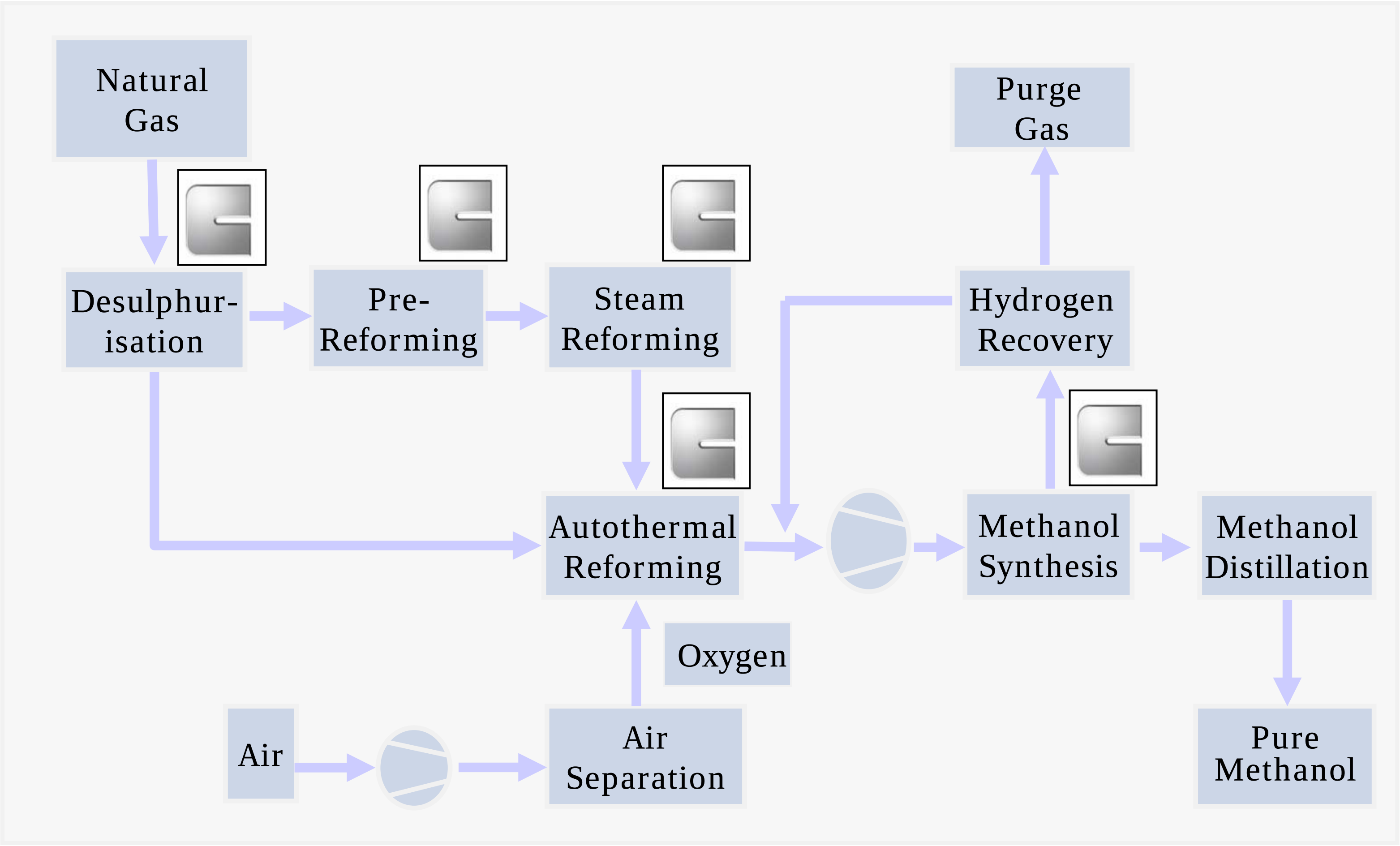
Methanol from Natural Gas: Catalysts are Enabling the Process



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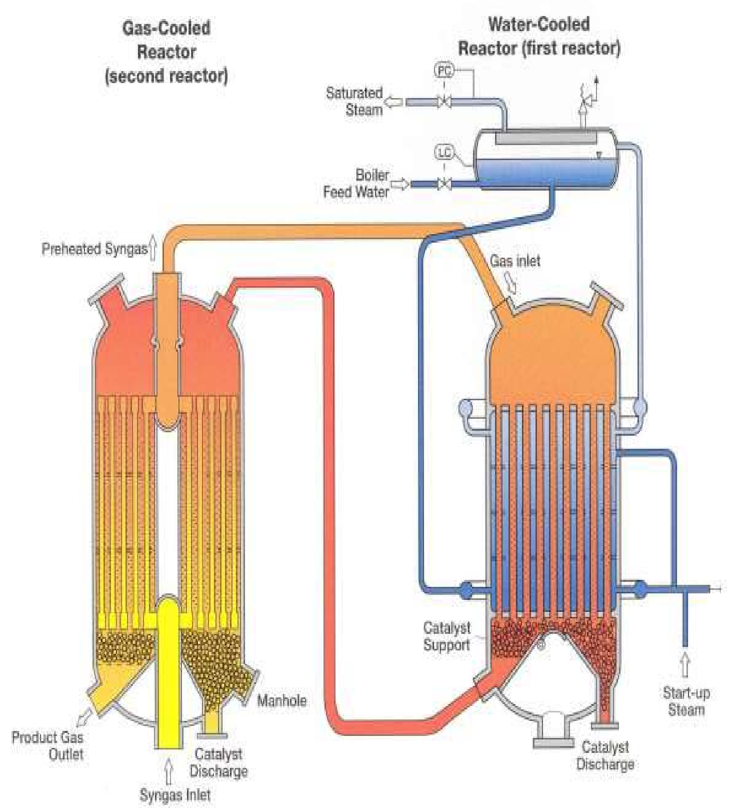
Methanol Process: Technology and Partnership

- 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



AIR LIQUIDE

Lurgi MegaMethanol® process

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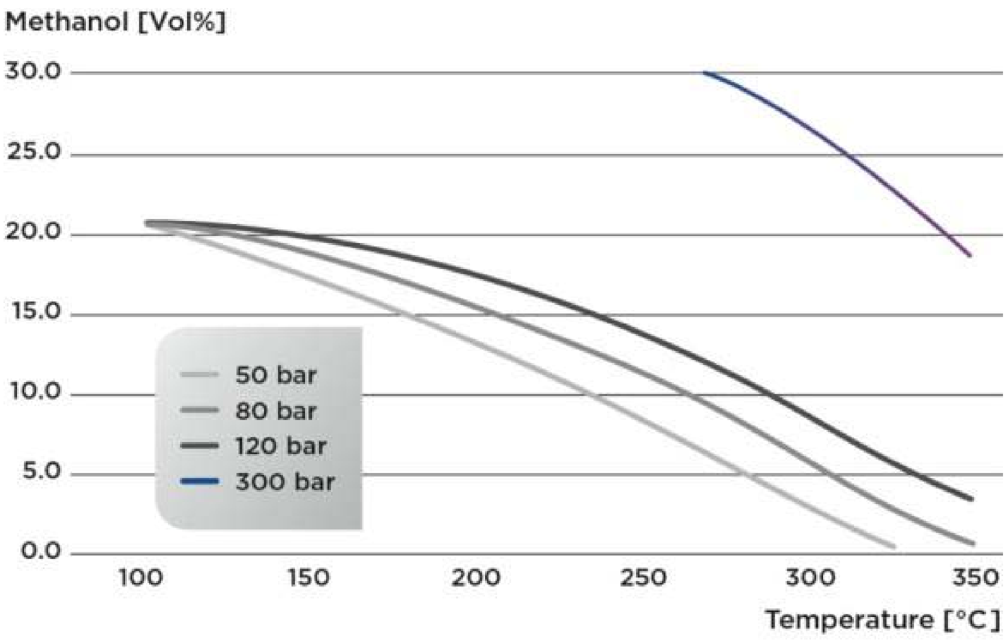
Industrial Methanol Synthesis



- Catalyst type: ternary Cu – ZnO, Al_2O_3 based
- Catalyst shape: 6 x 4 mm tablets MegaMax® 800

Fiedler et.al. **2005** In: *Ullmanns Encycledia*, „Methanol“

Syngas Innovation for Improved Sustainability

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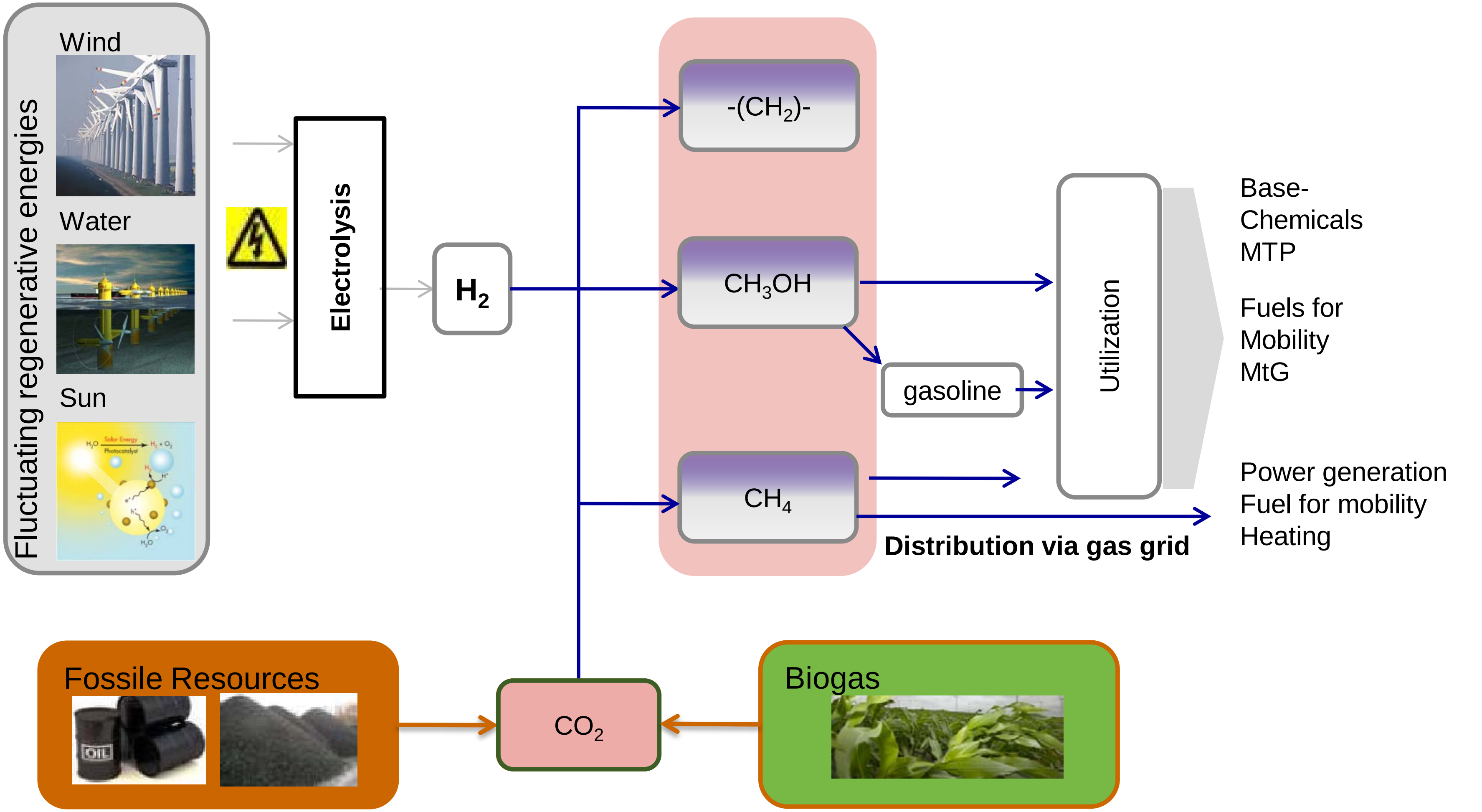
Syngas Innovation for improved Sustainability
CO2 Capture & Conversion / H2 Storage



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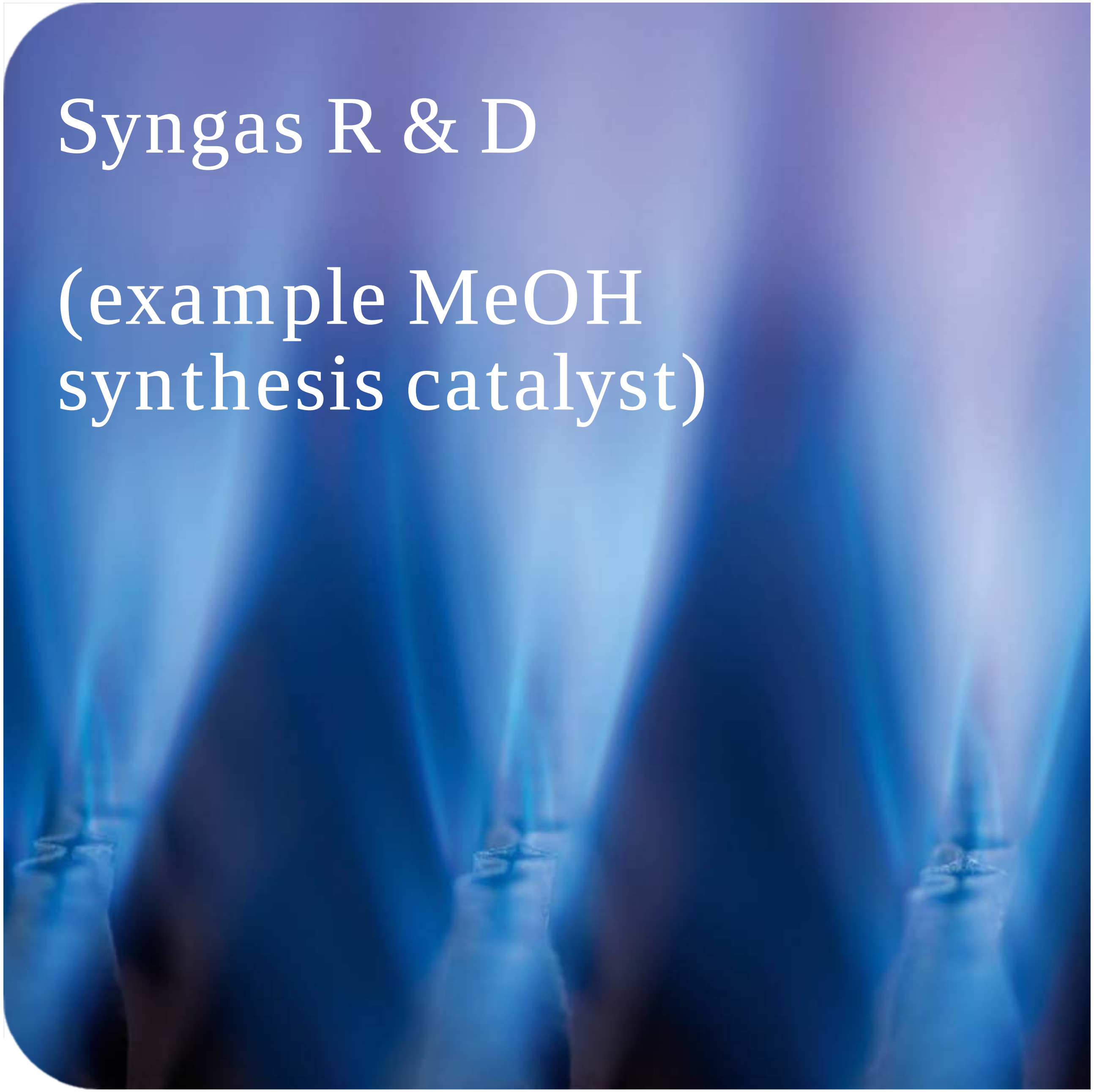
Syngas Innovation for improved Sustainability CO2 Capture & Conversion / H2 Storage

- **Power to Gas**: CO_2 to CH_4
  - SNG (Synthetic Natural Gas) catalysts are already part of Clariant's catalyst portfolio
  - CH_4 can be fed to existing CH4 infrastructure including storage capacities
- **Power to Liquid**: CO_2 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 CO_2 based alternative: Power to Liquid (Liquid Organic Hydrogen Carriers - LOHC)**
  - Storage of H_2 by hydrogenation of aromatic systems
  - Cooperation between Clariant and University of Erlangen

Syngas R & D

(example MeOH synthesis catalyst)



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Operation Conditions (MeOH Synthesis): Significant Differences Depending on Feedstock

Parameter	NG	Coal	Biomass	CO2
CO/CO_2	0.8	3-4	4-8	∞
$\frac{(H_2 - CO_2)}{(CO + CO_2)}$	3.5	4	0.5	2-3
Temperature (°C)	200-300			
Pressure (bar)	75	75	45	30
Production Rate (mt / day)	1.000 - 7.500	5.000	300 -1000	<1000
Operation (h / year)	8.000	8.000	6.000 (cyclical)	8.000

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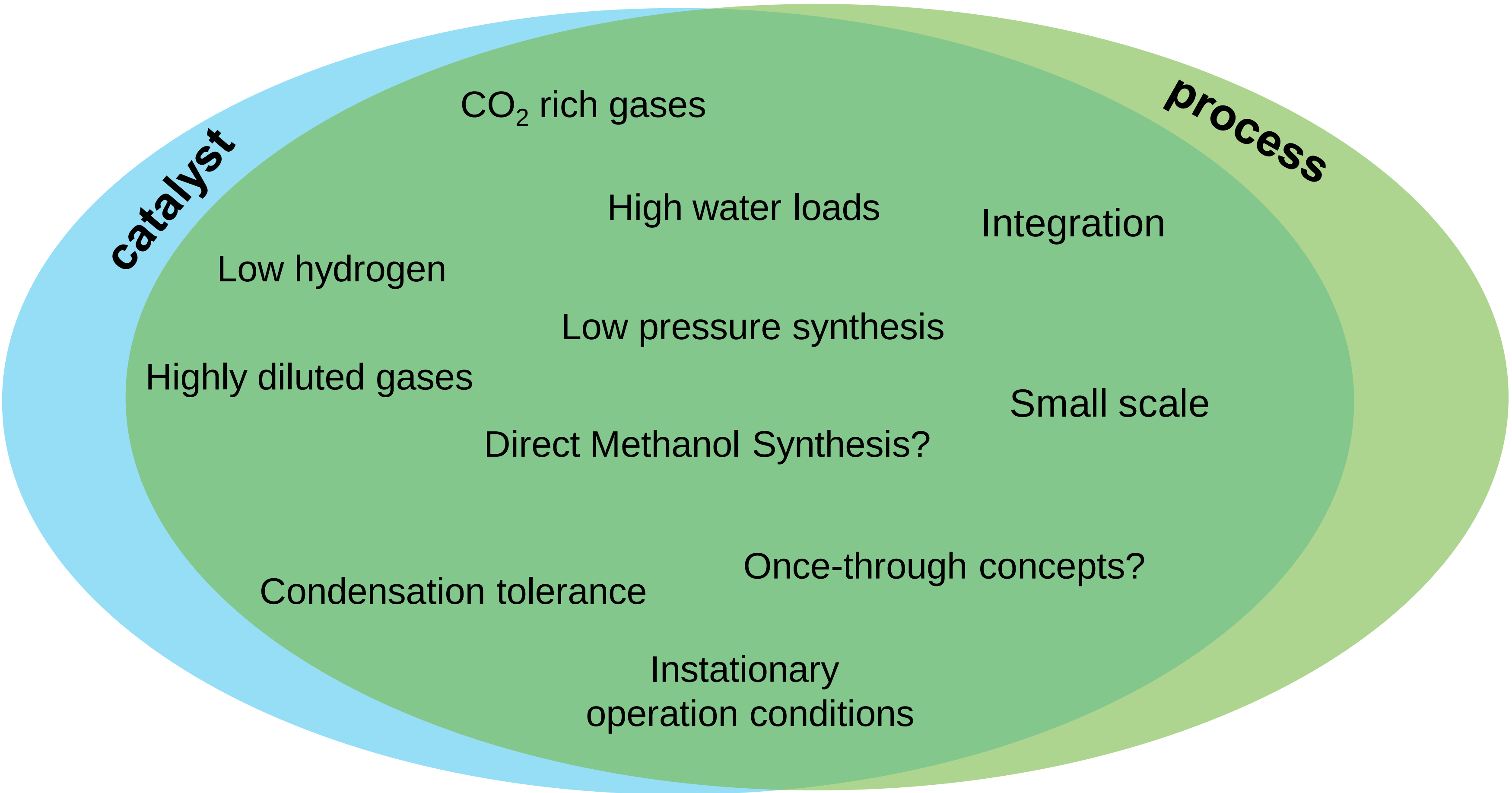
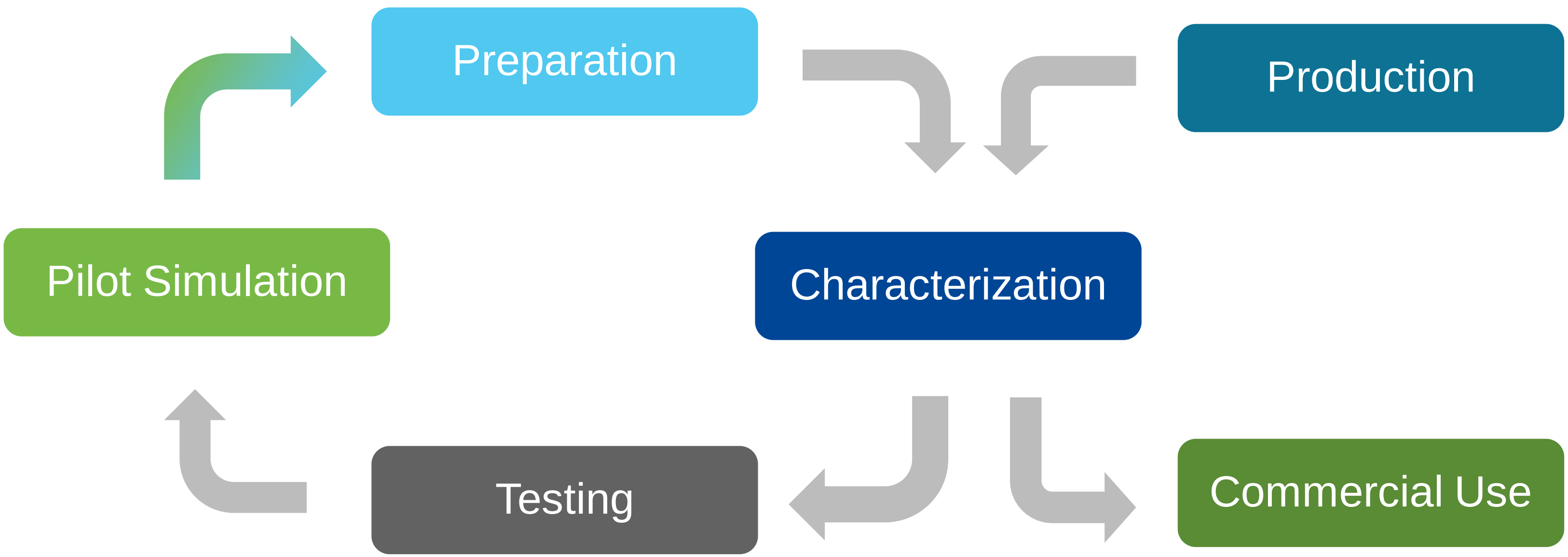
R&D Challenges: Bridge Process and Catalysis Needs



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**

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State of the Art Catalysts: How it's made!

– Based on ICI synthesis in the 1960s

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

Cu, Zn, Al-anion$_{aq.}$

+

Soda$_{aq.}$

Activation

$Cu/ZnO/Al_2O_3$

– Is there any further potential?

– Do we really understand what is happening?

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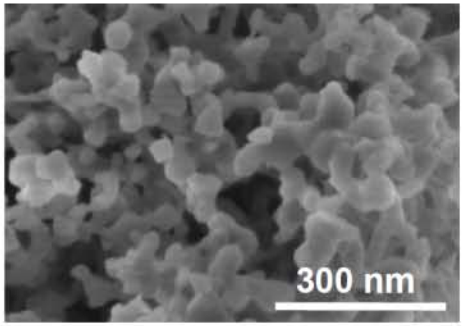
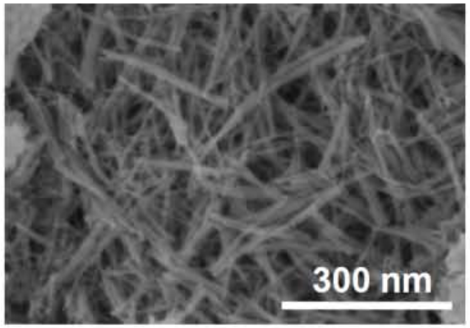
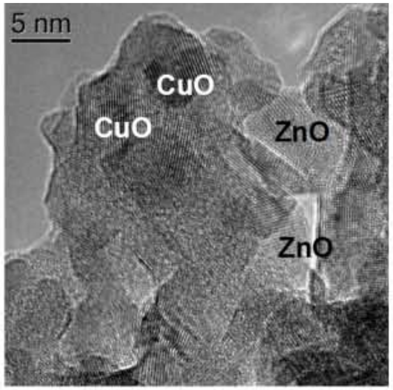
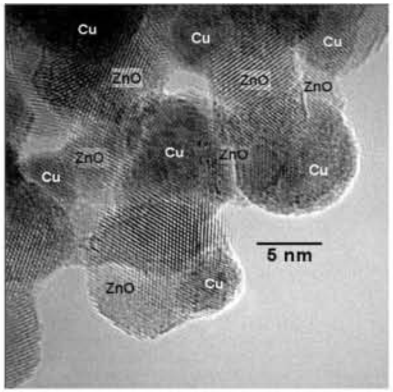
Catalyst Synthesis at Nano-Scale: Phase Transitions

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









Nanostructuring → Mesostructuring → Activation

– Initial texture determines structure and activity of active catalyst

Hartig, Jacobsen, Peukert, *Chem. Eng. Sci.* **2014**,109,158.
Behrens et al., *Science*, **2012**, 18, 893.
Behrens et al., *Chem. Commun.*, **2011**, 47, 1701.

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Reactions in Solution: Precipitation & Ageing

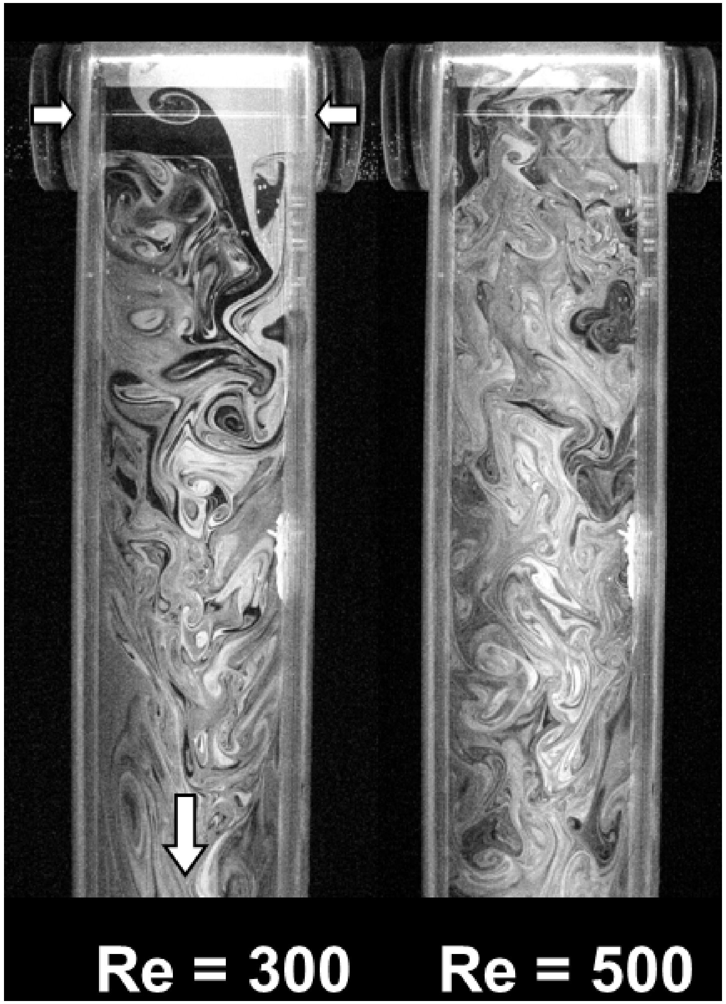
Influence of **preparation parameters…**

- 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



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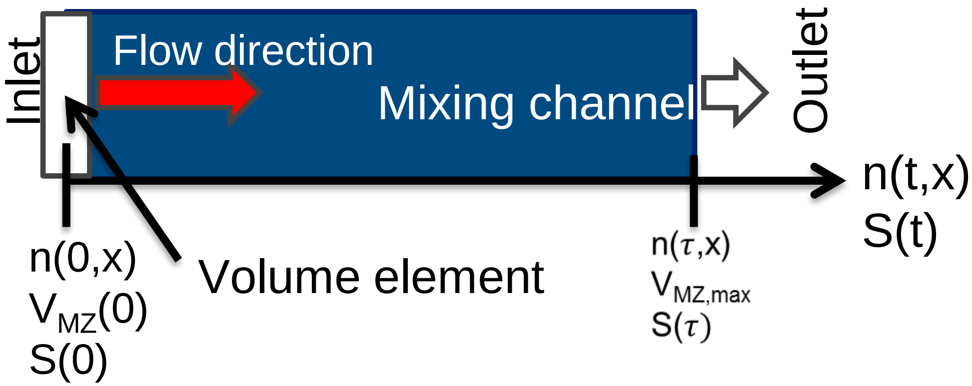
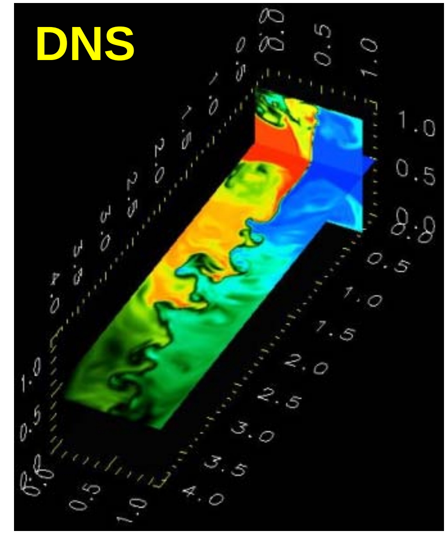
A Model System





Mole and mass balance of aqueous phase

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

Coupling: Mass balance

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

Population balance for disperse phase

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

Principal components

Cu^{2+} / Na^{+} / NO_3^{-} / CO_3^{2-} / H^{+} / H_2O

n(t,x)	Particle size distribution
S(t)	Supersaturation
τ	Residence time

$$S_{Precipitate} = \frac{\left(a_{Cu^{2+}}^{2} a_{OH^{-}}^{2} a_{CO_3^{2-}}\right)^{1/5}}{K_{SP}}$$

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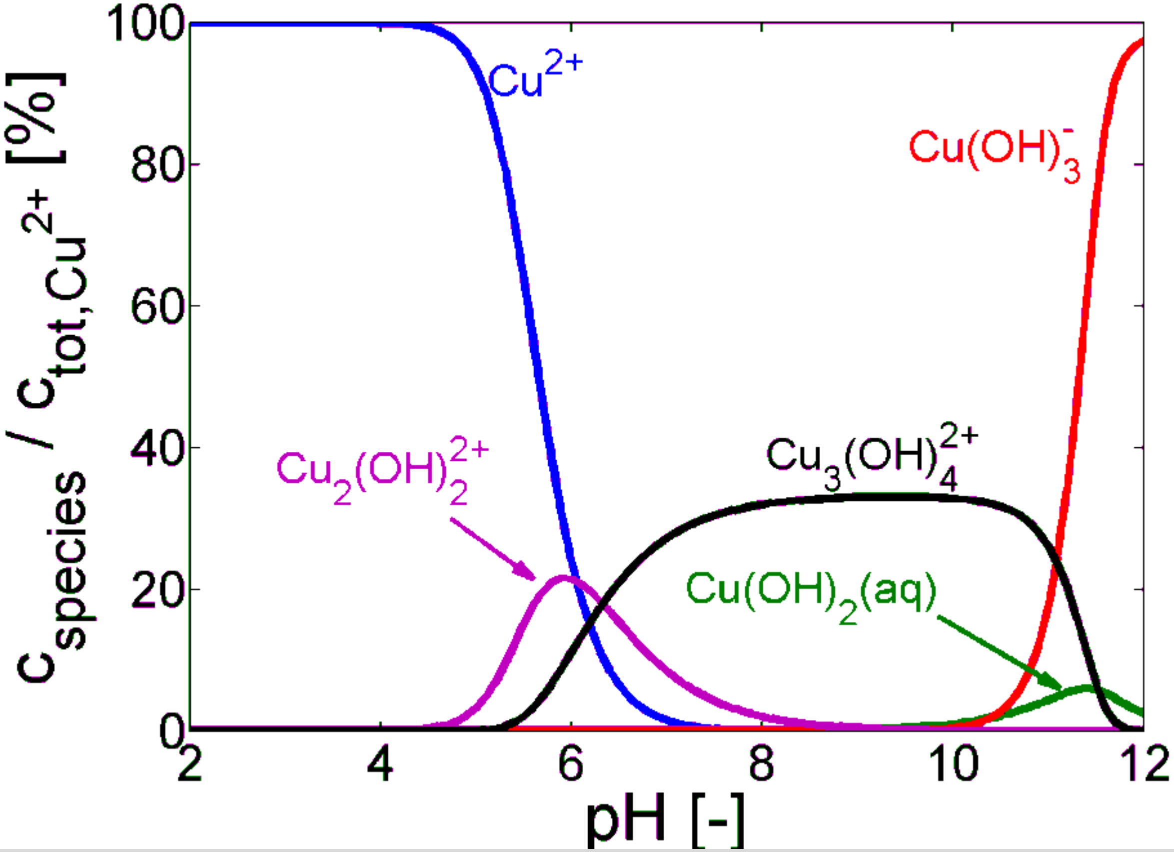
Hydrochemistry: Complex Interaction of Components



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

Hartig, Jacobsen, Peukert, *Chem. Eng. Sci*. **2014**,109,158.

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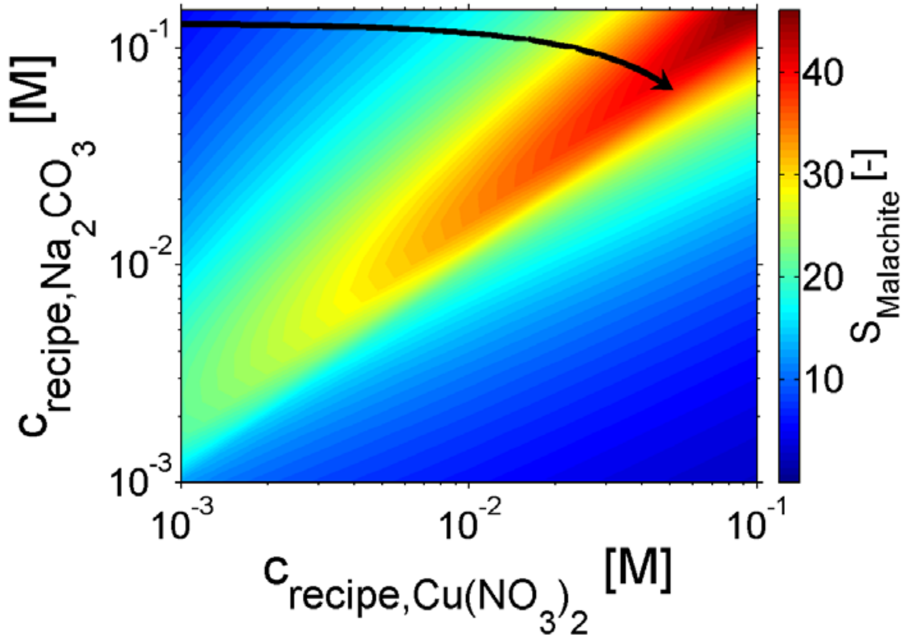
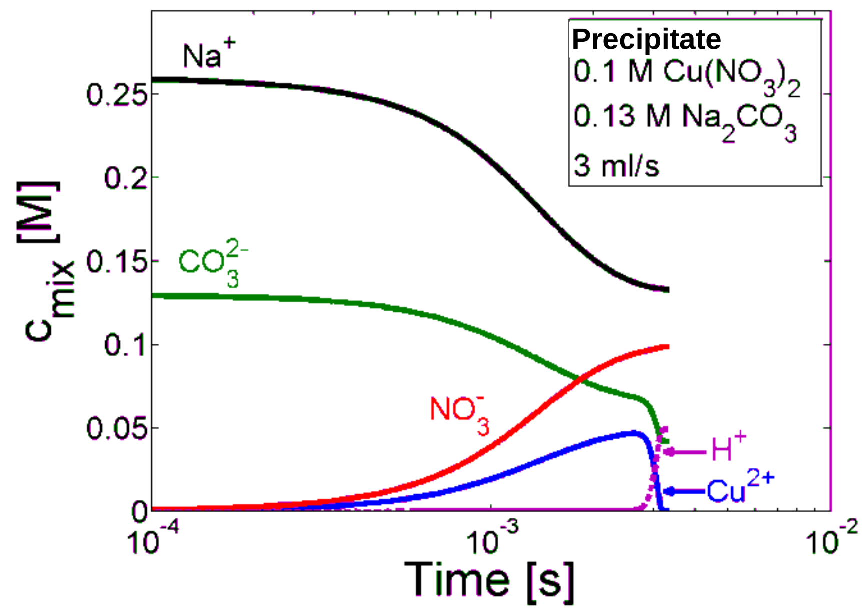
Hydrochemistry Results from Validated Model

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





– Optimize precipitation process

– Tuning material properties

Hartig, Jacobsen, Peukert, *Chem. Eng. Sci*. **2014**,109,158.

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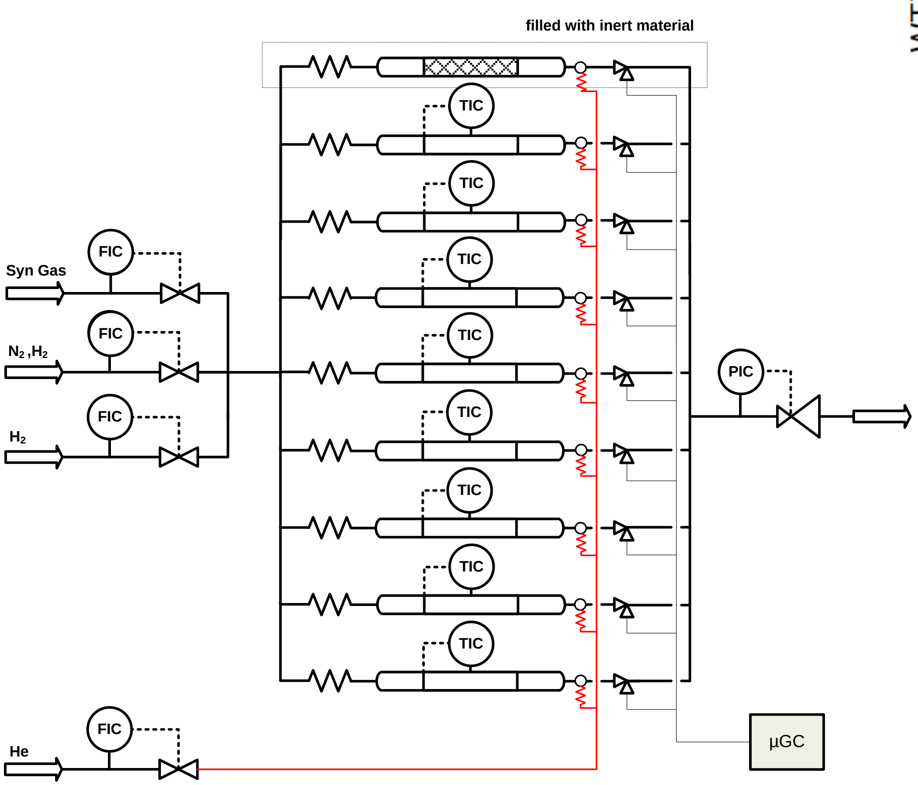
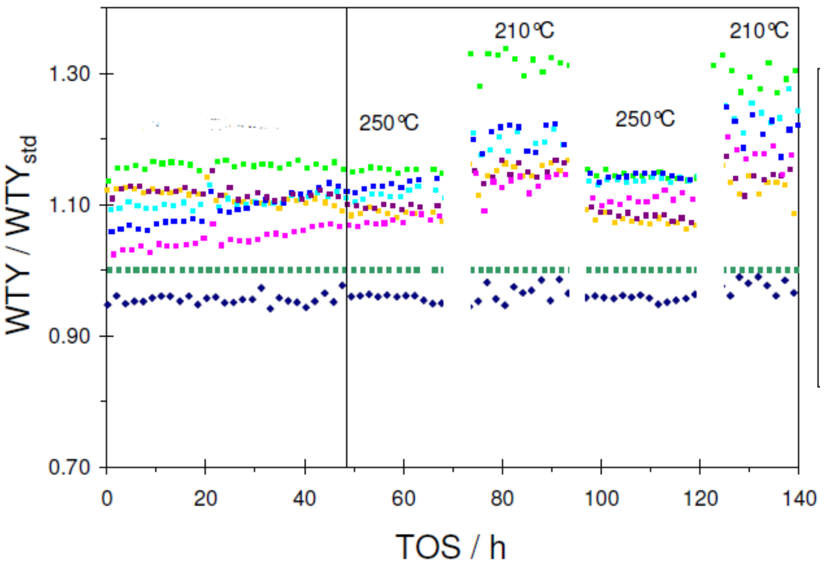
Materials Evaluation & Screening

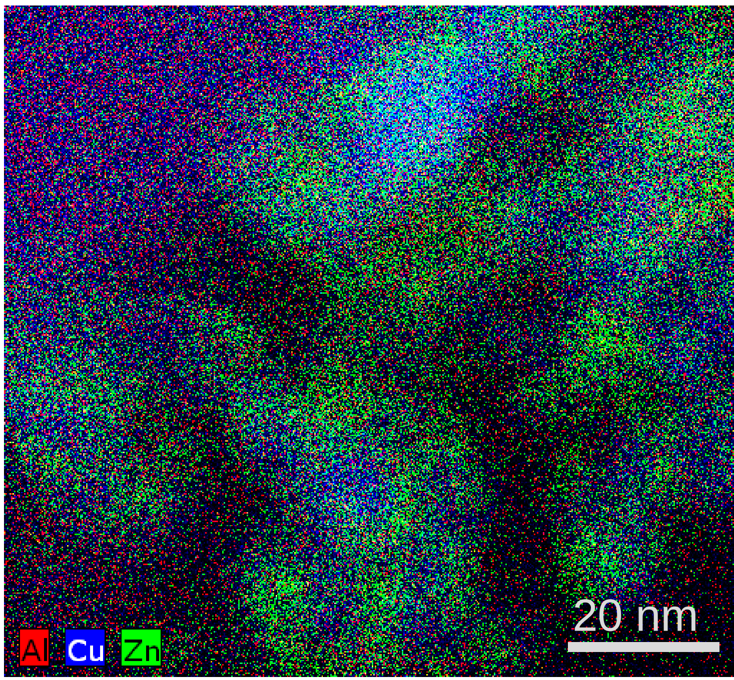
- High-throughput evaluation of powders
- “real-world conditions” in a 2x8 microreactor

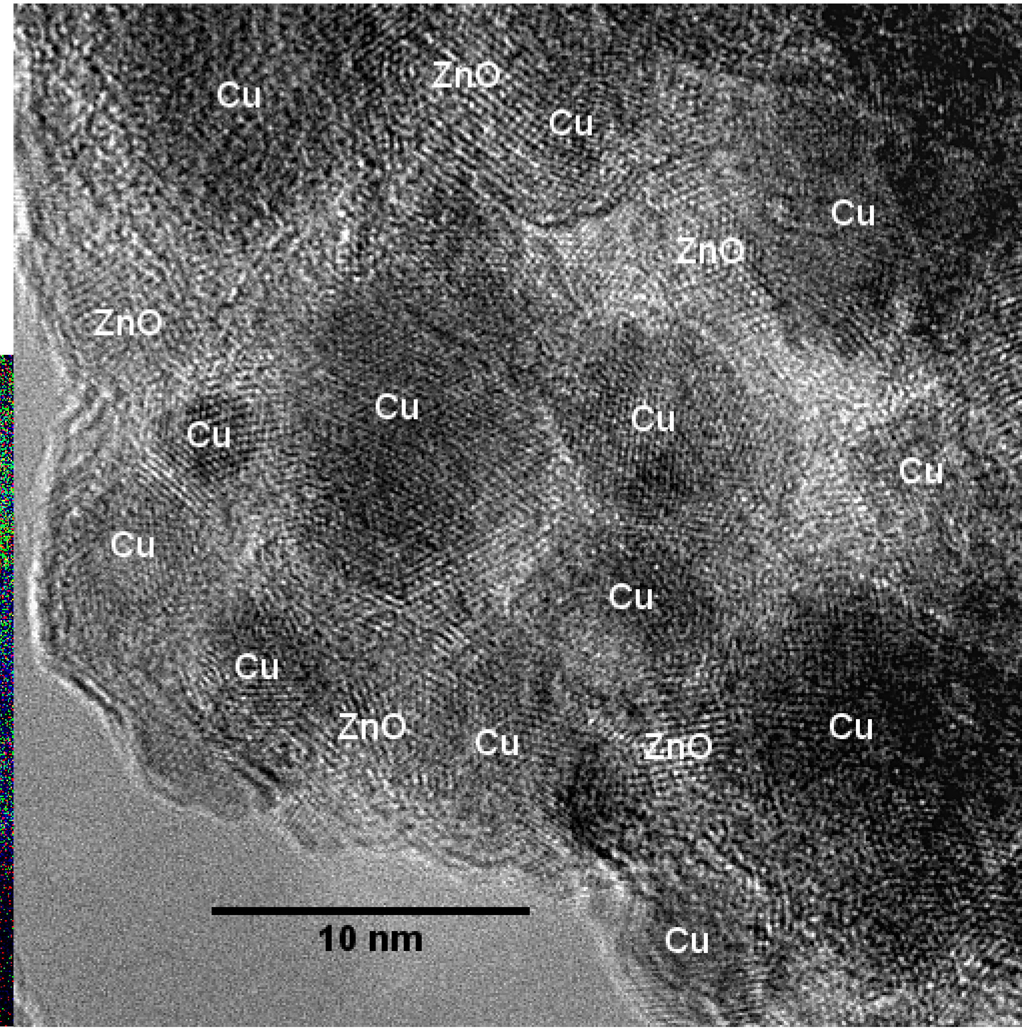




The Active Catalyst on a Molecular View

- HR-TEM in conjunction with EDX or SAED can identify crystallites
- **Task**: relate structure to activity





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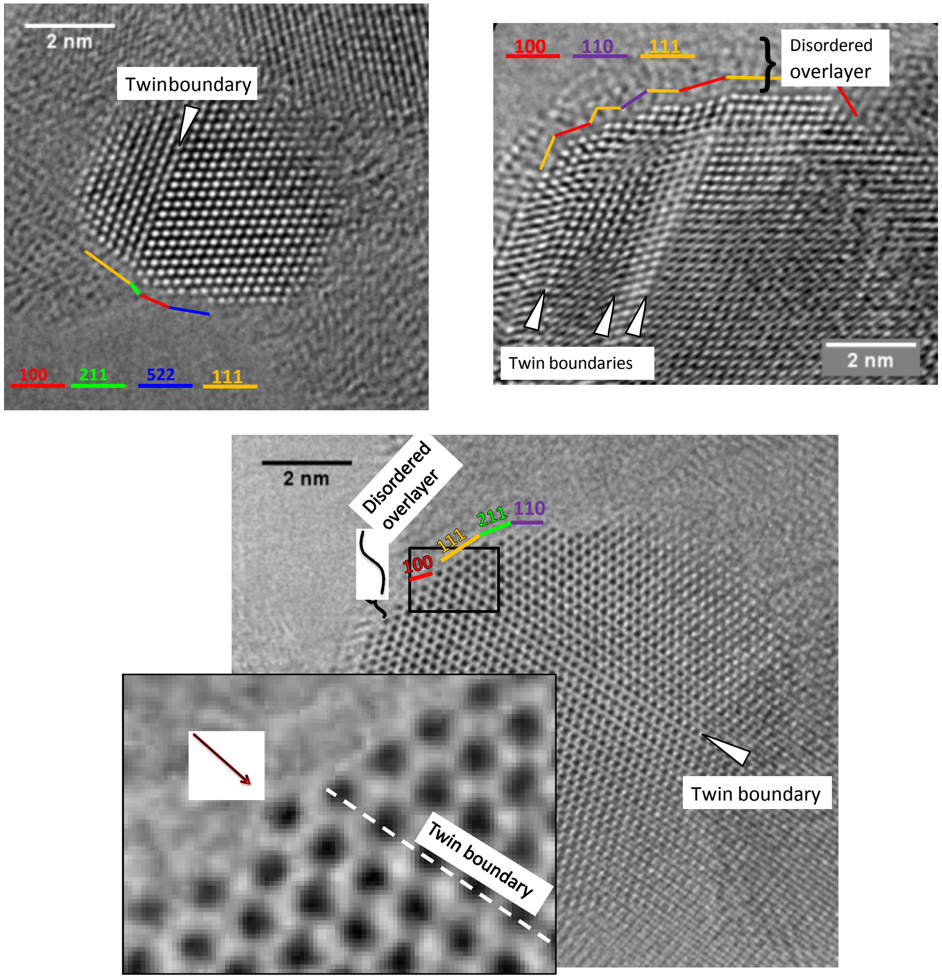
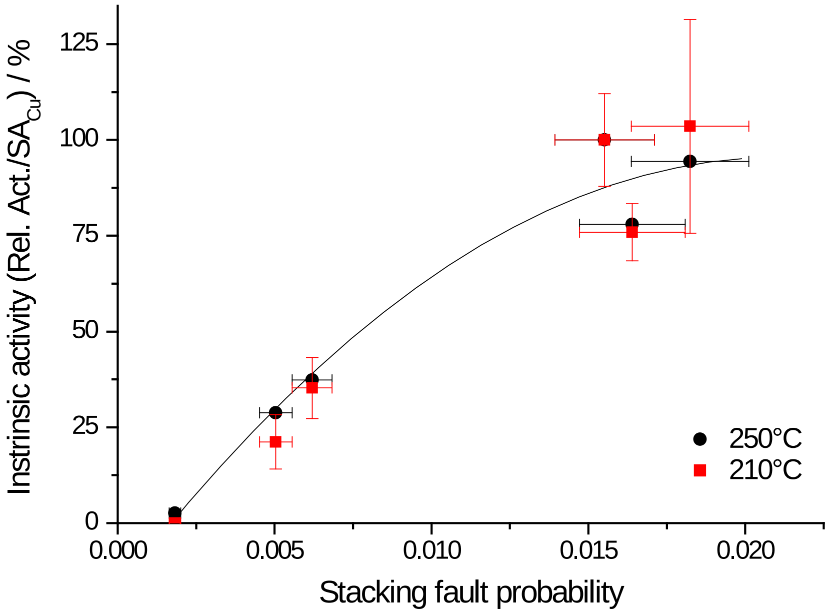
Intrinsic Kinetics / Active Sites on the Nano Scale



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



– Stacking faults are correlated with surface normalized activity

➔ Defect rich materials are desired

Behrens et al., *Science*, **2012**, 18, 893.

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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

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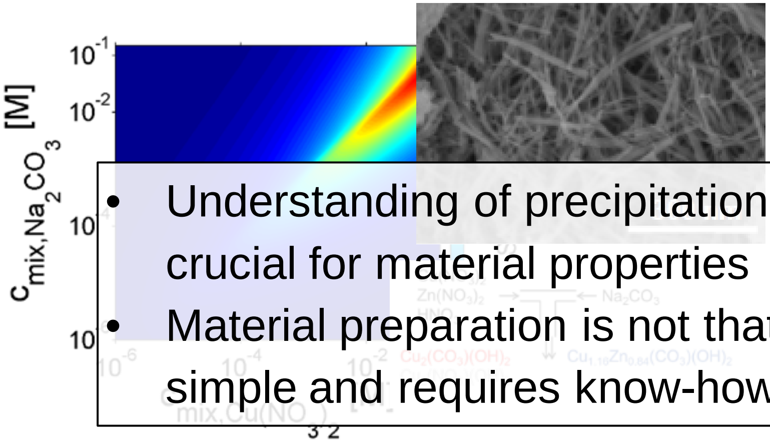
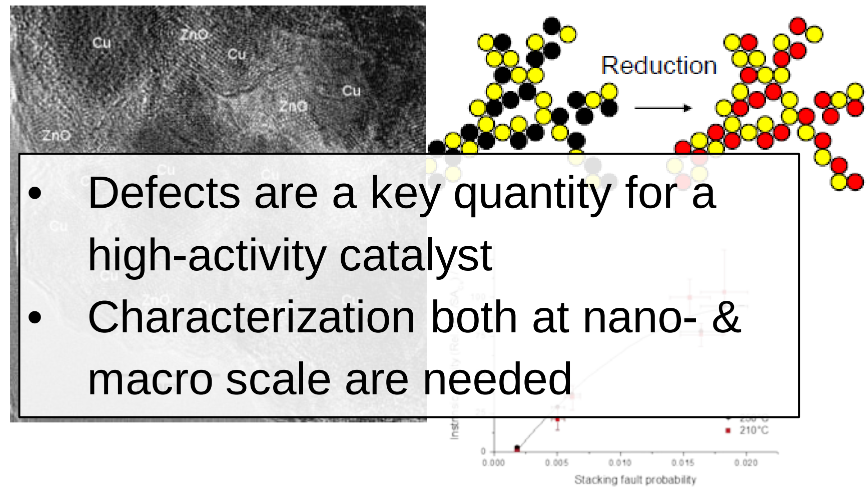
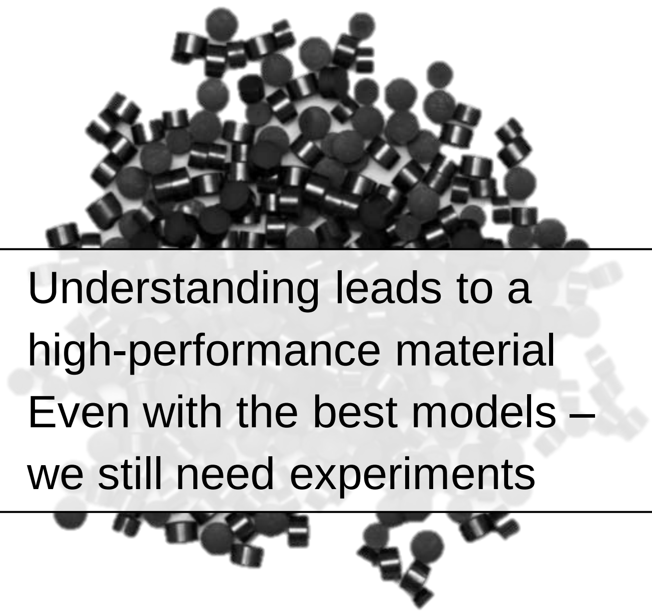
Summary



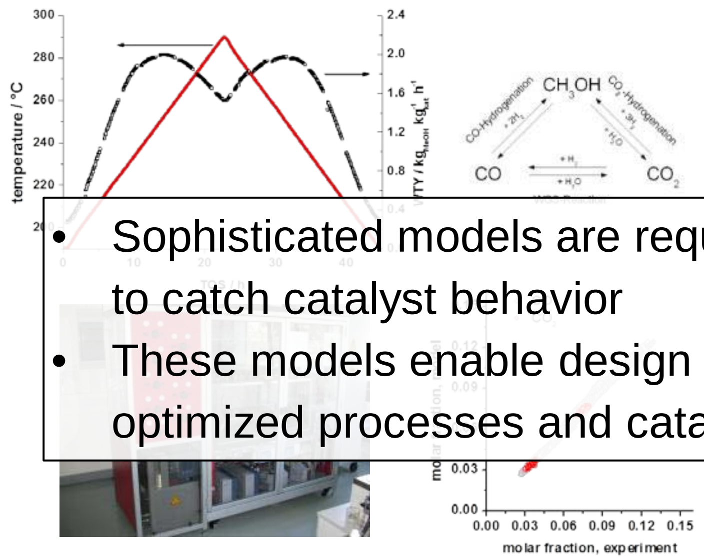
- Understanding of precipitation crucial for material properties
- Material preparation is not that simple and requires know-how



- Defects are a key quantity for a high-activity catalyst
- Characterization both at nano- & macro scale are needed



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



- Sophisticated models are required to catch catalyst behavior
- These models enable design of optimized processes and catalysts

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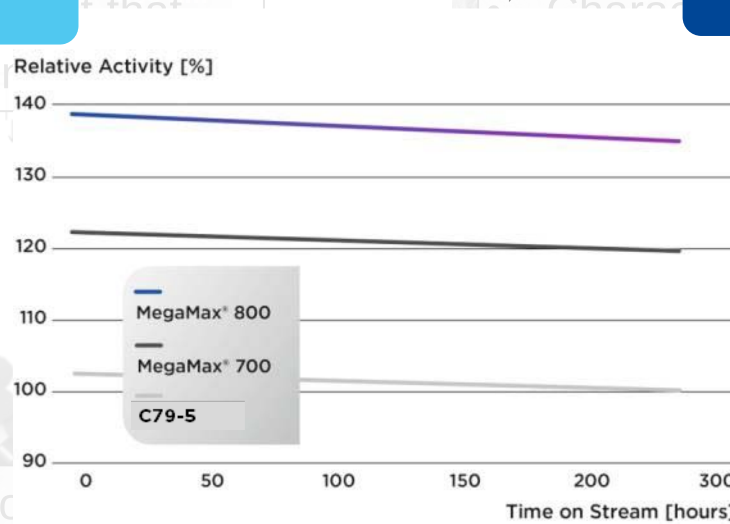
Summary

Preparation → Characterization → Testing → Plant simulation → Preparation



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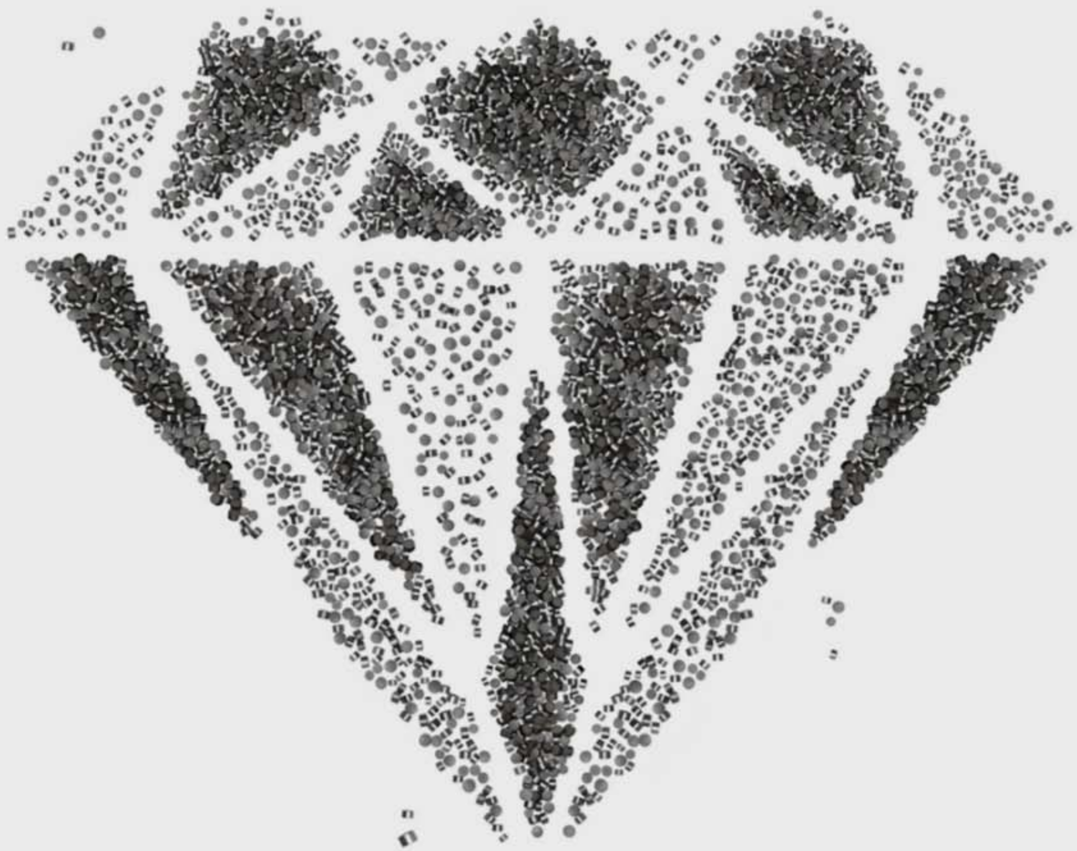

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Selected publications from this collaborative effort

– Hartig, M. A., Peukert, W., Jacobsen, N., & Leuthold, A. (2015). A model-based precipitation study of copper-based catalysts. *AIChE Journal*.

– Hartig, M. A., Jacobsen, N., & Peukert, W. (2014). Multi-component and multi-phase population balance model: The case of Georgeite formation as methanol catalyst precursor phase. *Chemical Engineering Science*, *109*, 158-170.

– Kaluza, S., Behrens, M., Schiefenhövel, N., Kniep, B., Fischer, R., Schlögl, R., & Muhler, M. (2011). A novel synthesis route for Cu/ZnO/Al2O3 catalysts used in methanol synthesis: combining continuous consecutive precipitation with continuous aging of the precipitate. *ChemCatChem*, *3*(1), 189-199.

– Behrens, M., Zander, S., Kurr, P., Jacobsen, N., Senker, J., Koch, G., ... & Schlögl, R. (2013). Performance improvement of nanocatalysts by promoter-induced defects in the support material: methanol synthesis over Cu/ZnO: Al. *Journal of the American Chemical Society*, *135*(16), 6061-6068.

– Behrens, M. (2009). Meso-and nano-structuring of industrial Cu/ZnO/(Al 2 O 3) catalysts. *Journal of Catalysis*, *267*(1), 24-29.

– Behrens, M., Studt, F., Kasatkin, I., Kühl, S., Hävecker, M., Abild-Pedersen, F., ... & Schlögl, R. (2012). The active site of methanol synthesis over Cu/ZnO/Al2O3 industrial catalysts. *Science*, *336*(6083), 893-897.

– Fichtl, M. B., & Hinrichsen, O. (2014). On the Temperature Programmed Desorption of Hydrogen from Polycrystalline Copper. *Catalysis Letters*, *144*(12), 2114-2120.

– Fichtl, M. B., Schumann, J., Kasatkin, I., Jacobsen, N., Behrens, M., Schlögl, R., ... & Hinrichsen, O. (2014). Counting of oxygen defects versus metal surface sites in methanol synthesis catalysts by different probe molecules. *Angewandte Chemie International Edition*, *53*(27), 7043-7047.