Computational Material Science at BASF

BASF
The Chemical Company

Workshop Trieste, August 2013, michael.rieger@basf.com

BASF – The Chemical Company
We create chemistry for a sustainable future

BASF
The Chemical Company

- Sales 2012: 72 129 million €
- EBIT 2012: 6 647 million €
- worldwide 110 782 employees
- 6 verbund sites and approx. 380 production sites worldwide

BASF – The Chemical Company
Organization

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Segments and Divisions as of January 1, 2013

Chemicals	Performance Products	Functional Materials & Solutions	Agricultural Solutions	Oil & Gas
Petrochemicals	Dispersions & Pigments	Catalysts	Crop Protection	Oil & Gas
Monomers	Care Chemicals	Construction Chemicals		
Intermediates	Nutrition & Health	Coatings		
	Paper Chemicals	Performance Materials		
	Performance Chemicals			

Innovation at BASF
R&D 2012 at a Glance

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Research for the future: with our innovative products and processes, we provide sustainable solutions for global challenges.

- Expenditures for R&D circa €1.73 billion, world leader in chemical industry
- Since 2005 increase of R&D expenditures up to 60%
- Around 3,000 projects, 10500 employees
- Strongest innovation power in the chemical industry (No.1 in the Patent Asset Index™)
- Sales target 2020: circa €30 billion from product innovations

1	Chemicals	10 %
2	Performance Products	20 %
3	Functional Materials & Solutions	20 %
4	Agricultural Solutions	25 %
5	Oil & Gas	2 %
6	Corporate Research, others	23 %

We Create Chemistry
From Chemicals to Chemistry

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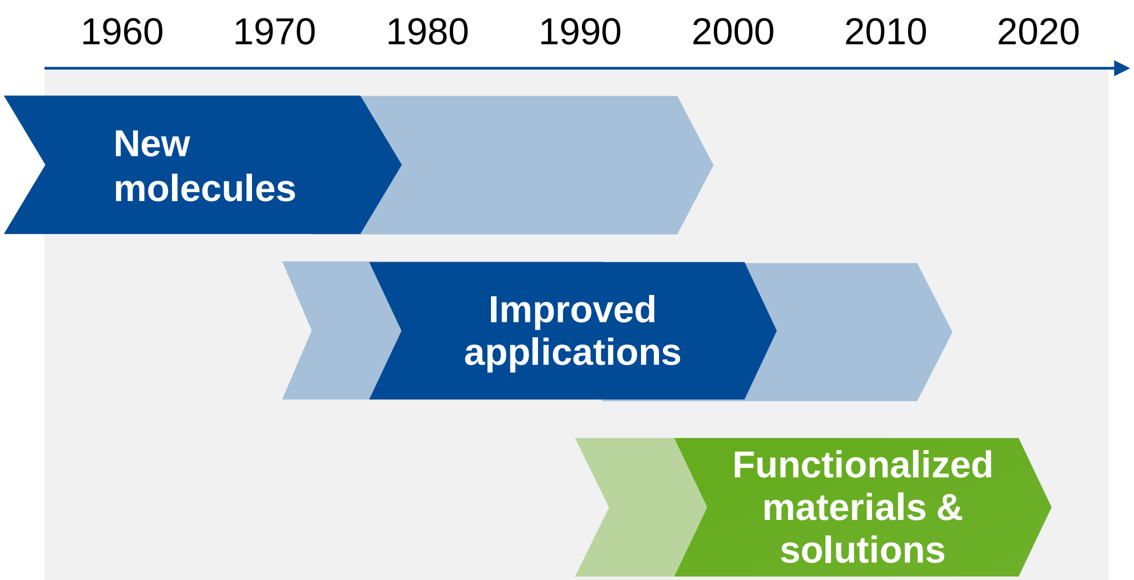

Batteries, membranes ...

From chemicals to chemistry: the innovation focus changed

Tasks

- Chemistry as key enabler for functionalized materials & solutions
- Interdisciplinary approach
- Deep understanding of customer value chains required

The Future of the Chemical Industry
Demographic Challenges Set the Stage

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Nine billion people in 2050 but only one earth


Resources, Environment & Climate


Food & Nutrition


Quality of life

Chemistry as enabler

The Future of the Chemical Industry
Many Growth Opportunities

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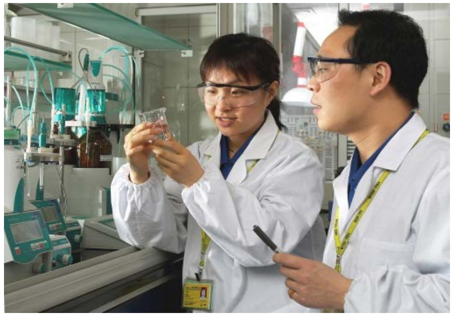
Nine billion people in 2050 but only one Earth

Chemistry as enabler

Sustainability and innovation as main driver

Innovation focus on materials & solutions

Growth of chemical production above GDP



60% of chemical production in emerging countries

Chemistry-Based Innovations
Growth and Technology Fields

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Resources, Environment & Climate	Food & Nutrition	Quality of life

Chemistry as enabler

	Transportation	Construction	Consumer Goods	Health & Nutrition	Electronics	Agriculture	Energy & Resources
Key Customer Sectors							
Growth Fields*	Batteries for Mobility	Heat Management	Enzymes	Medical Solutions	Organic Electronics	Plant Biotechnology	E-Power Management
	Lightweight Composites					Functional Crop Care	Wind Energy
							Water Solutions

Technology Fields

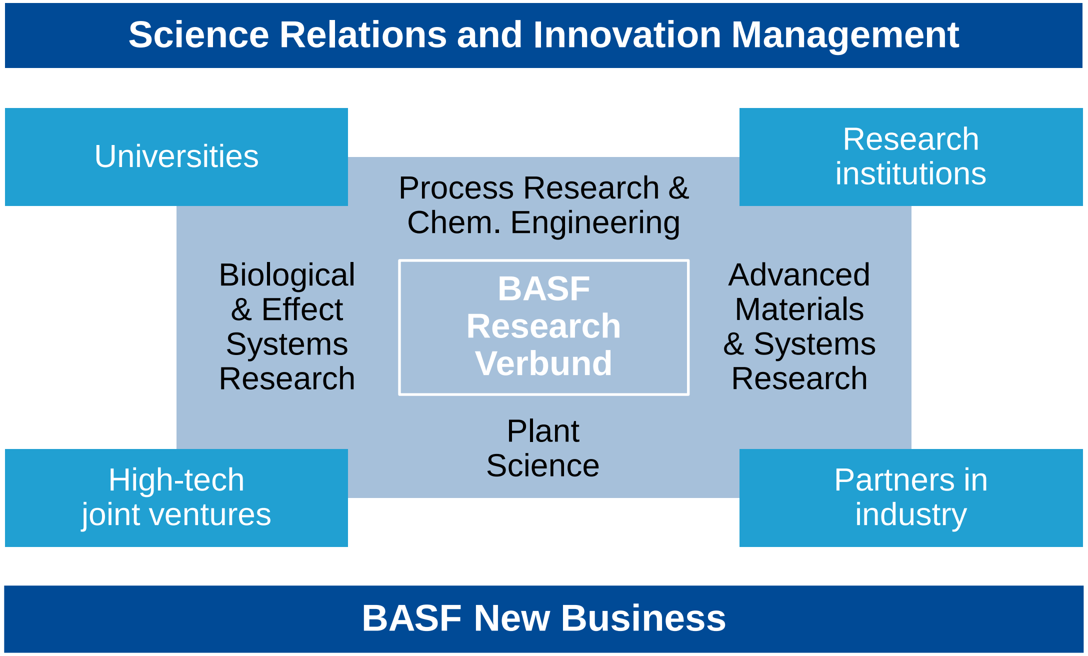
- Materials, Systems & Nanotechnology
- Raw Material Change
- White Biotechnology

* including growth fields still under evaluation

Innovation
Global Know-How Verbund

Thanks to our close cooperation with numerous partners from science and business worldwide, we have created an international and interdisciplinary Know-How Verbund.

- Approx. 10,500 employees in R&D worldwide
- Know-How Verbund with about 600 excellent universities, research institutions and companies



Global Know-How Verbund
Inside BASF and with Partners

Technology Platform
Advanced Materials & Systems Research

We develop functional materials and system solutions for a sustainable future targeting the automotive, construction, home & personal care, packaging, water and wind industry.

Competencies

- Develop new structural and functional materials, additives, dispersions as well as composites and hybrid systems
- Optimize products and processes, develop new smart-scale production concepts
- Provide comprehensive characterization and modeling methods and establish structure-property relationships

Innovation examples

- Advanced composite materials for new lightweight concepts of load-bearing car parts and high-performance wind rotor blades
- System solutions for water purification based on flocculants, anti-fouling additives and polymeric membrane materials

Technology Platform
Biological & Effect Systems Research

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We develop new active substances, methods, processes and systems for a wide range of applications, e.g. in crop protection, pharma, nutrition and energy management.

Competencies

- New chemical and biological crop protection products
- Efficient and energy-conserving production of (bio)chemicals
- Materials and systems for lighting, displays & energy conversion
- Modeling and formulation
- Development of alternative methods in toxicology

Innovation examples

- Development of crop protection blockbusters, e.g. F 500®, Kixor ®, Xemium®
- Biotechnological production of vitamin B_2 and enzymes for animal nutrition, biopolymer Schizophyllan for enhanced oil recovery
- Organic solar cells for the concept-car smart forvision

Technology Platform
Process Research & Chemical Engineering

The Chemical Company

We develop new technologies and processes and optimize existing processes for the manufacture of basic chemicals, intermediates and fine chemicals.

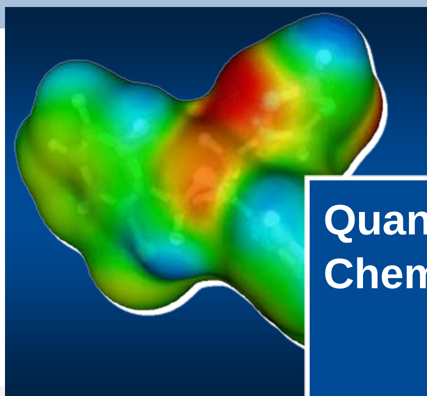
Competencies

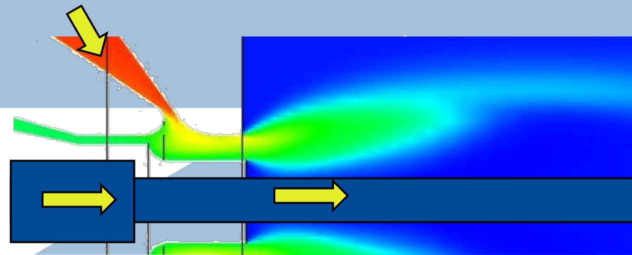
- Synthesizing basic chemicals, intermediates, fine chemicals and new materials
- Chemical, refinery and environmental catalysis
- Battery components and electrochemistry
- Process development and unit operations

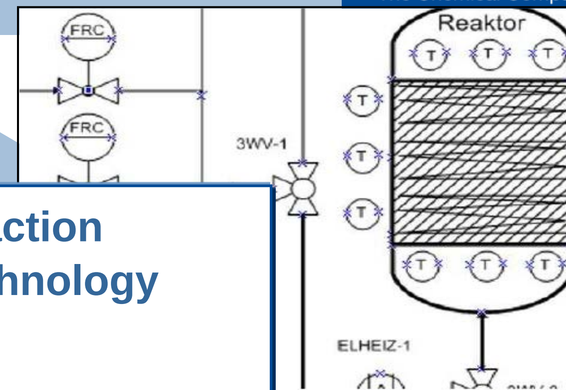
Innovation examples

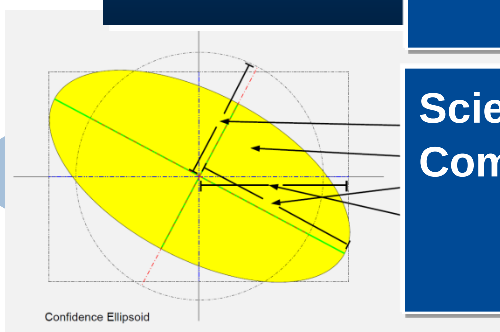
- Resource-efficient process for the synthesis of propylene oxide (HPPO)
- Improved lithium-ion batteries and new battery concepts

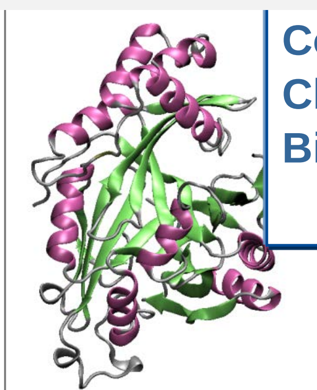
Computational Competence Centers in R&D
Organization

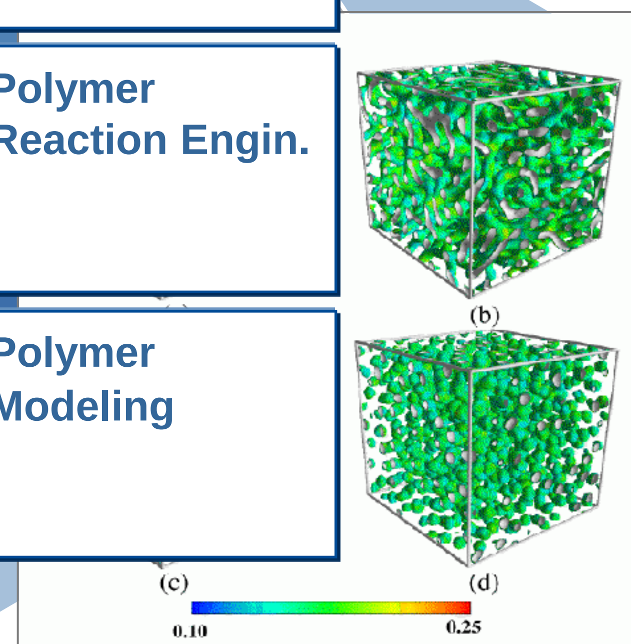












Quantum Chemistry

Fluid Mechanics

Reaction Technology

Scientific Computing

BASF Research Verbund

Polymer Reaction Engin.

Computational Chemistry and Biology

Bioinformatics

Polymer Modeling

Applications of Modeling to Growth Fields
Batteries for Mobility

Battery materials of BASF will enhance battery life-time and reduce cost with no compromises on safety.

Existing activities

- Chemicals and materials for lithium-ion batteries
  (cathode and anode materials, electrolytes, binders, solvents)
- Work on concepts for next generations of batteries
  (lithium-sulfur, lithium-air)
- Establishing the global business unit “Battery Materials”

Targets

- Position BASF as a leading materials and components supplier by utilization of technology and business synergies
- Find innovative solutions for future mobility

Applications of Modeling to Growth Fields
Organic Electronics

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BASF provides material systems solutions for mass applications in organic electronics.

Existing activities

- Material systems for OLEDs (displays and lighting)
- Printable materials for circuit boards and displays
- Contract manufacturing of organic dopants for display applications

Targets

- Position BASF as provider of material solutions for next generation displays and lighting
- Creating system know-how and technology synergies in synthesis, formulation and up-scaling
- Enter new markets based on BASF's core competencies

Applications of Modeling to Technology Fields

Raw Material Change (Catalysis)

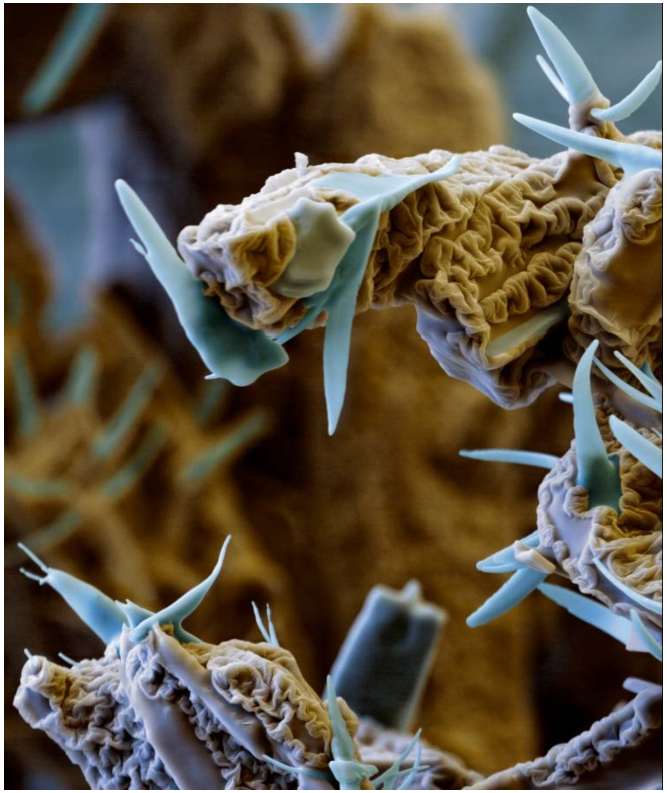
We work on sustainable processes for using alternative raw materials such as natural gas, biomass and CO_2.

Research focus

- Increased use of natural gas, biomass and CO_2 as basis for raw materials
- Integration of competencies: synthesis, catalysis, process development and unit operations, high-throughput methods

Examples of existing activities

- Natural gas:
  Olefins from natural gas by using dehydrogenation technologies
- Carbon dioxide (CO_2):
  Synthesis of formic acid and acrylates
- Biomass:
  Lignocellulose as a raw material



Homogeneous Catalysis - Quantum Chemical Catalyst Screening (work by A. Schäfer)

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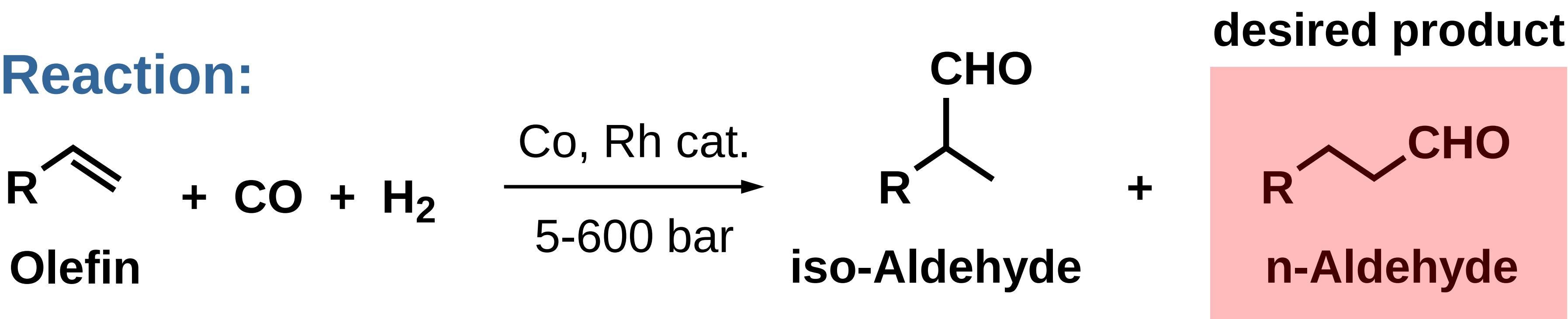
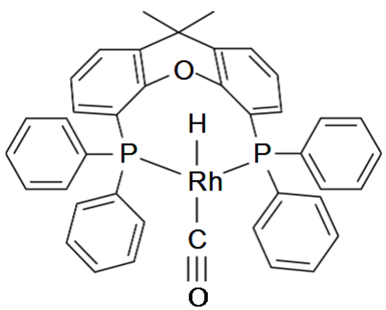
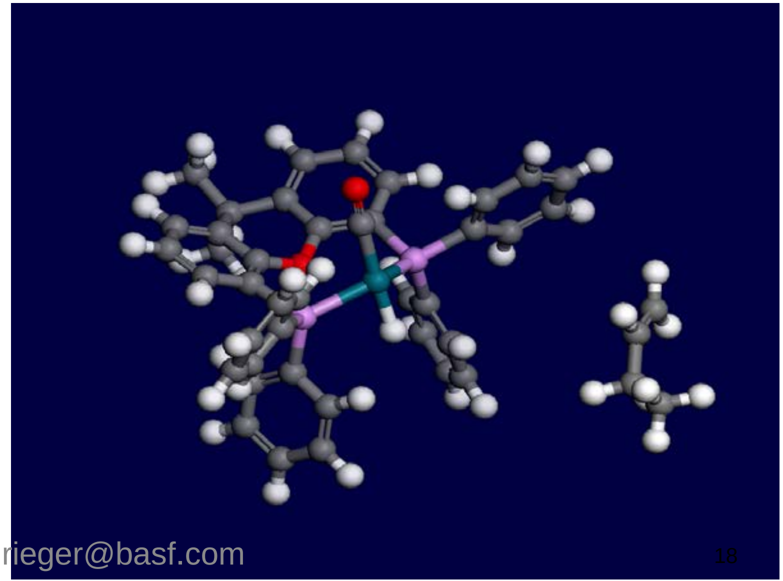
Hydroformylation of Olefins

Reaction:



Catalyst:

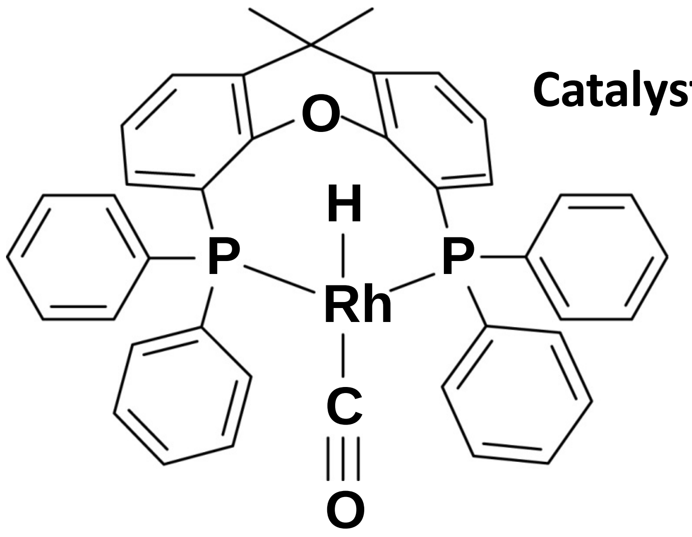




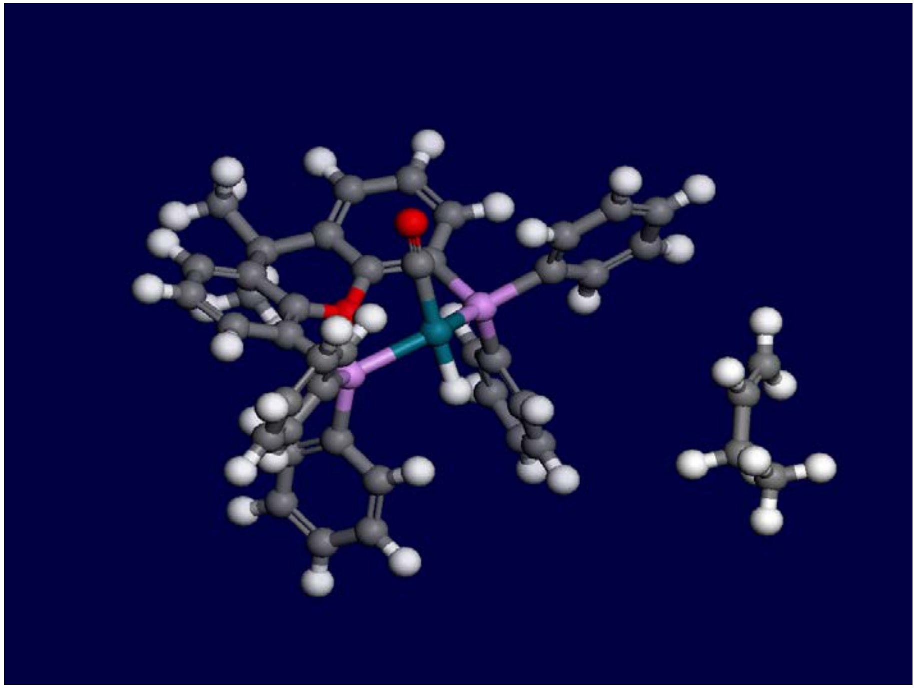
Goal:

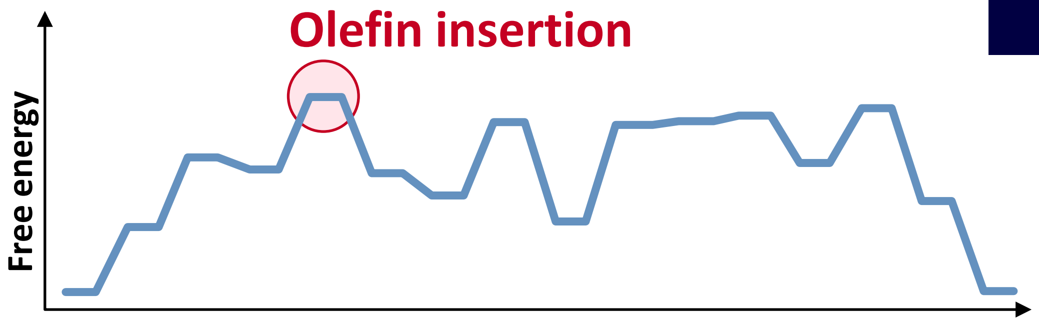
Design catalysts for n-selectivity

The catalyst in action - a molecular production machine



Catalyst





simulated catalytic cycle

Reaction pathway and selectivity

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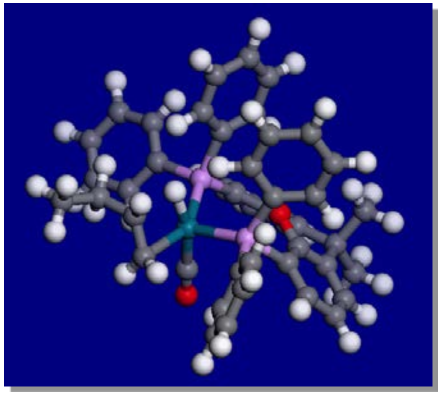
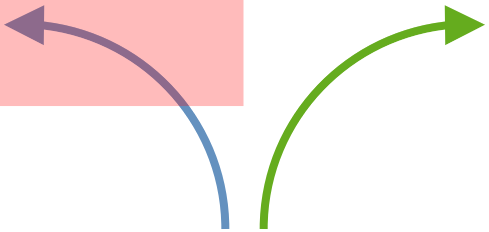
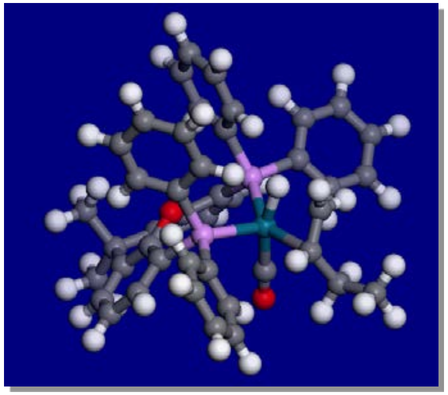


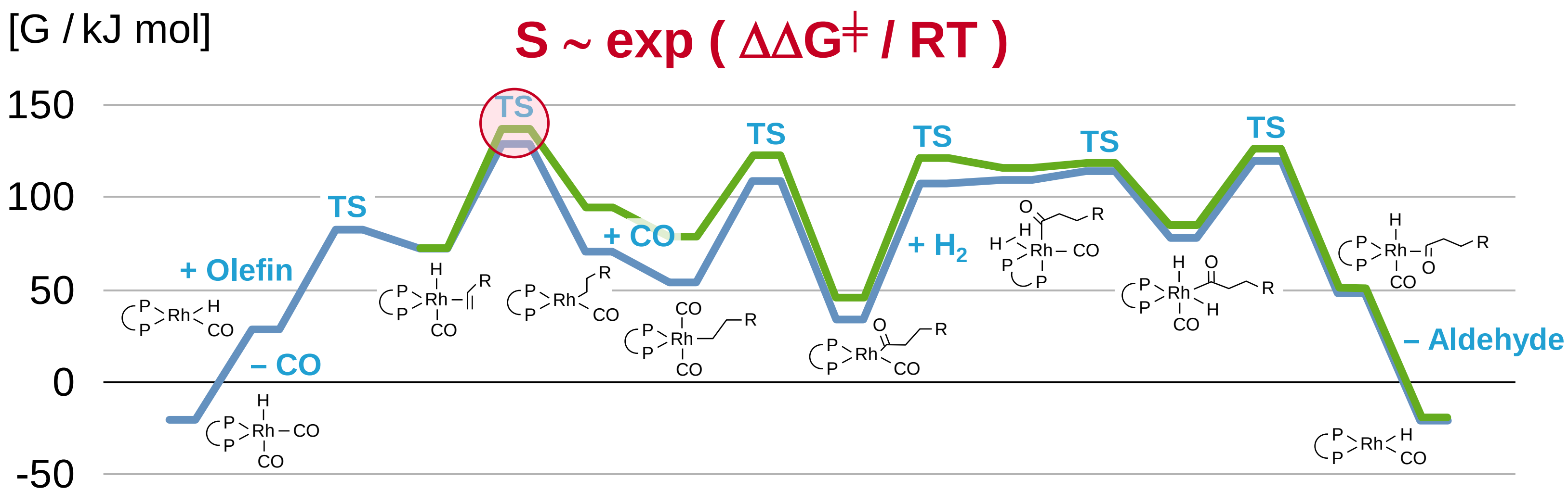
desired product

n-product

i-product

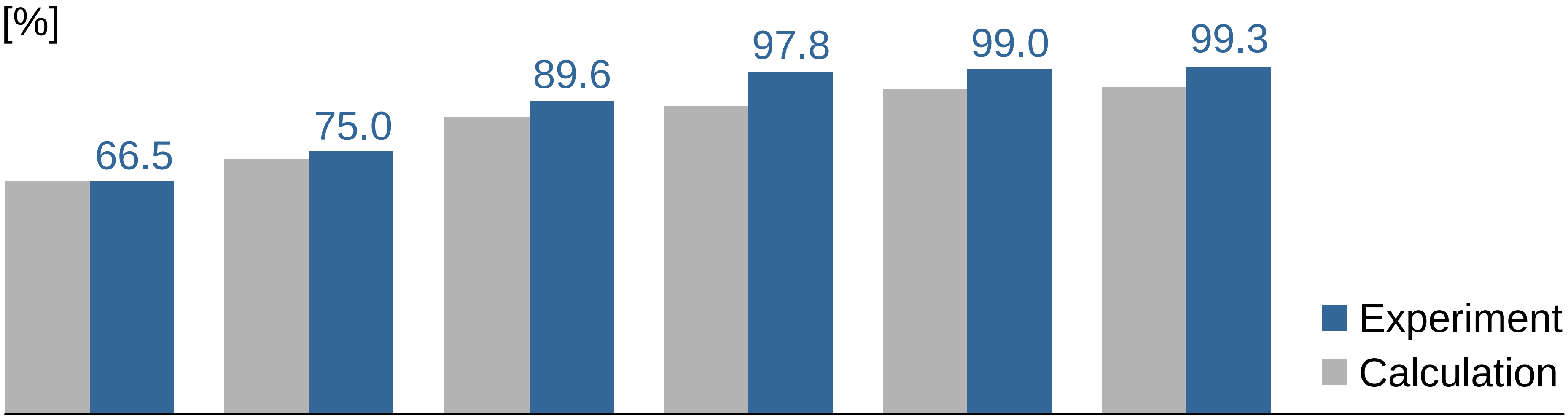


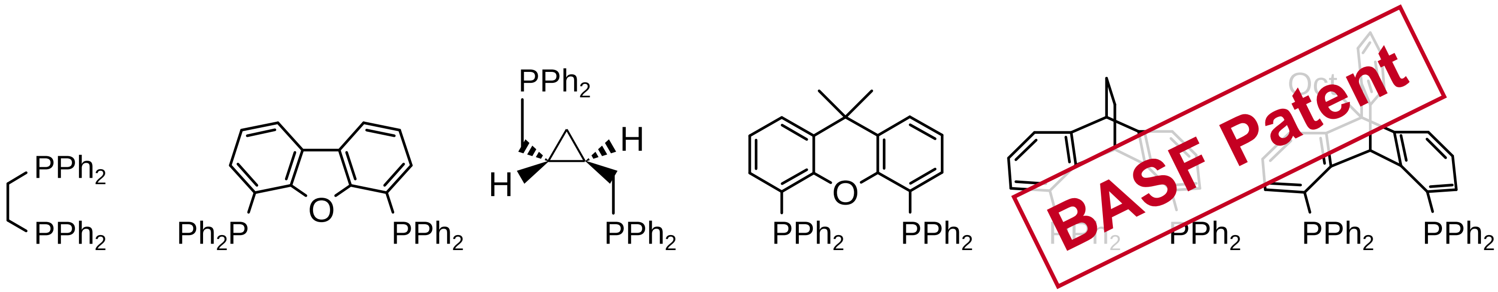




Screening for optimal ligands using the identified descriptor

Comparison of calculated and experimental selectivities





In collaboration with
Prof. Hofmann, Uni Heidelberg

Heterogeneous Catalysis
- Deactivation and particle shapes

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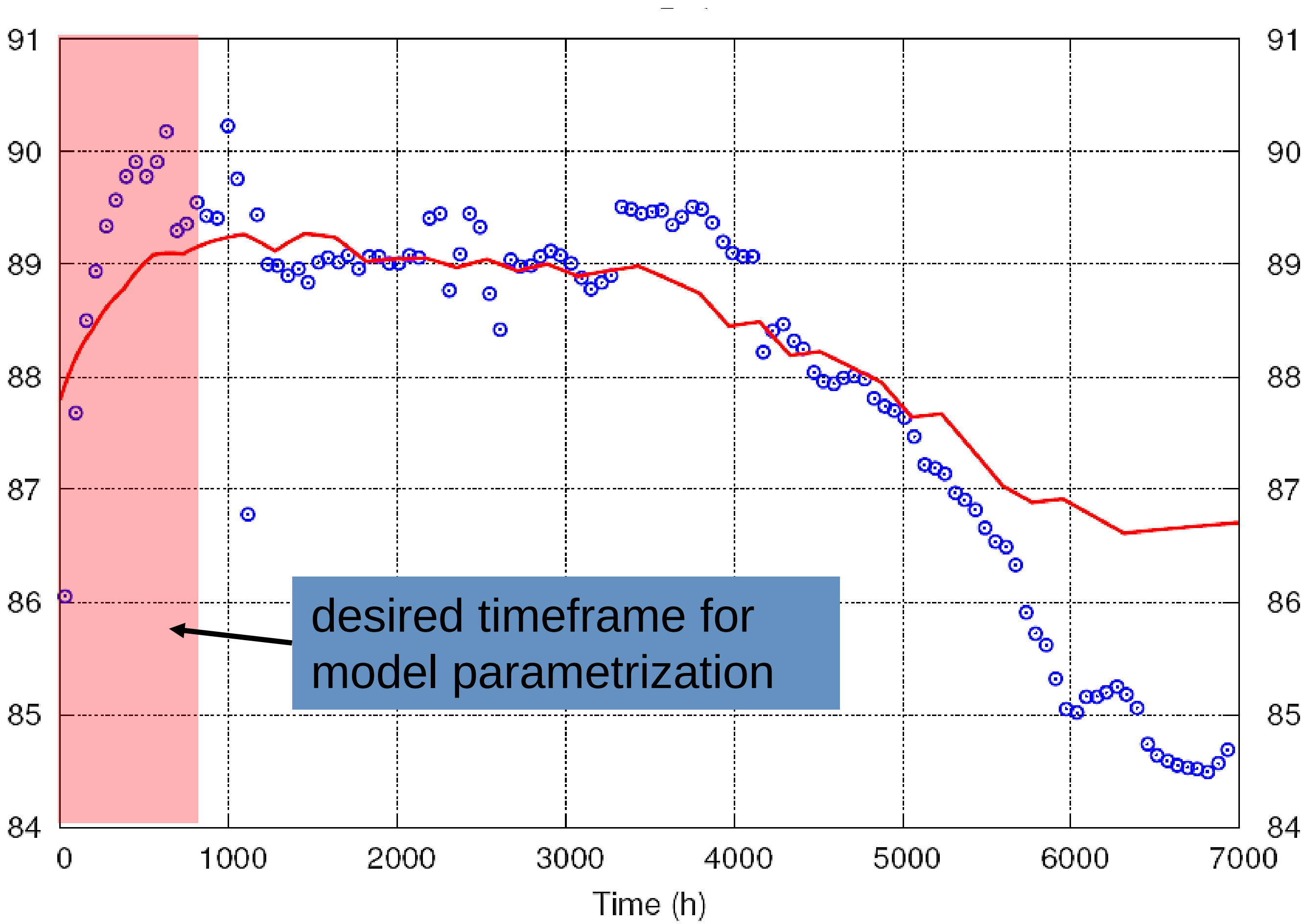
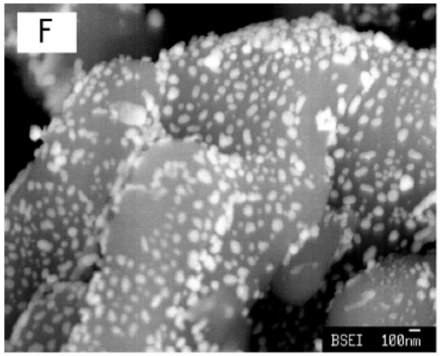


- Application:
  Lifetime prediction using short-time experiments

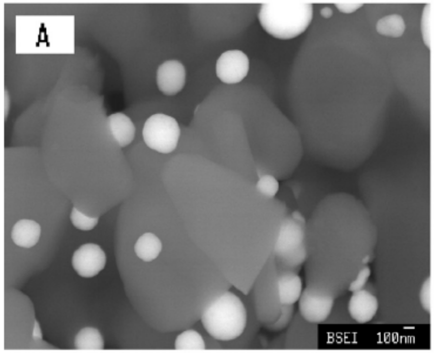
The catalyst particles change shape in the process

fresh catalyst



optimal Ag particle size ~ 100nm

aged catalyst (14 months)



N. Macleod et al. Catal. Letters 86 (2003) 1-3

Caused by a complicated set of microscopic processes

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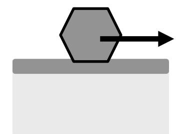
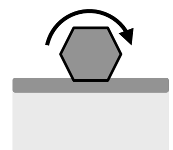
microscopic mechanisms:

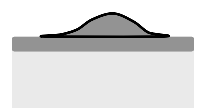
- Particle translation



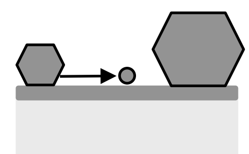
- Particle rolling



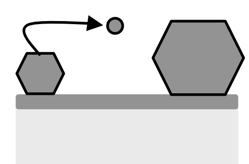
- Particel flow



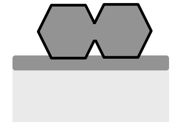
- Atom/cluster migration on surface



- Atom/cluster migration in gas phase

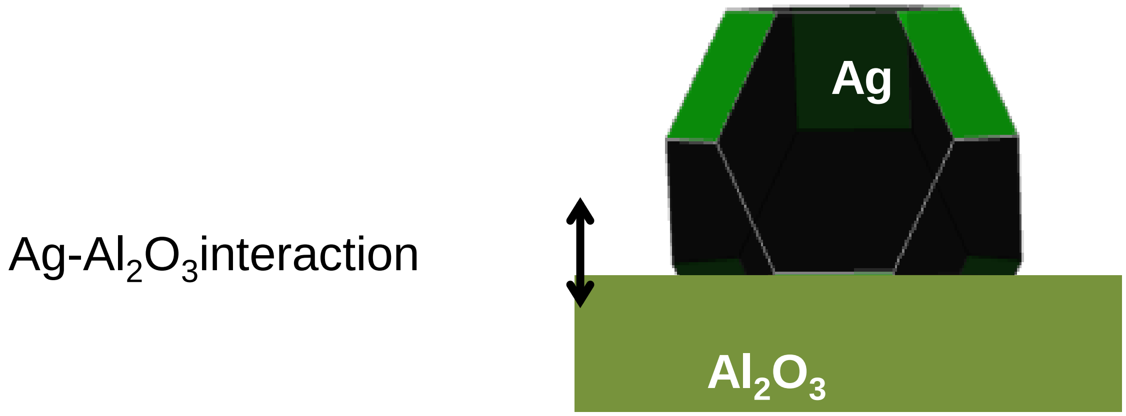


- Particle coalescence



First step – the particle shape
(work done together with Monica Garcia-Mota)

- **Prediction of the equilibrium composition and shape of supported Ag nanoparticles on α-Al_2O_3**



Predictions using a theoretical approach

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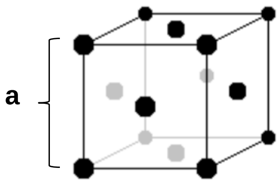
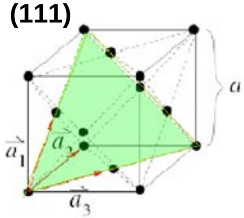
bulk Ag



(111)



Surface free energies

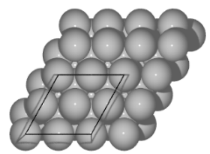
$\gamma^0_{(111)}$ →

$\gamma^0_{(100)}$ →

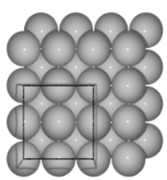
$\gamma^0_{(110)}$ →

DFT calculations surfaces

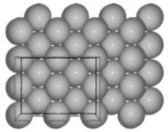
Ag(111)



Ag(100)



Ag(110)



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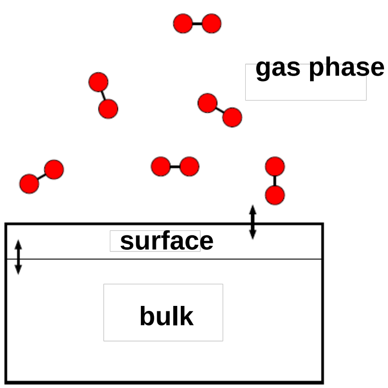
First-principles thermodynamic study

Surface free energy

$\gamma(T, p)$



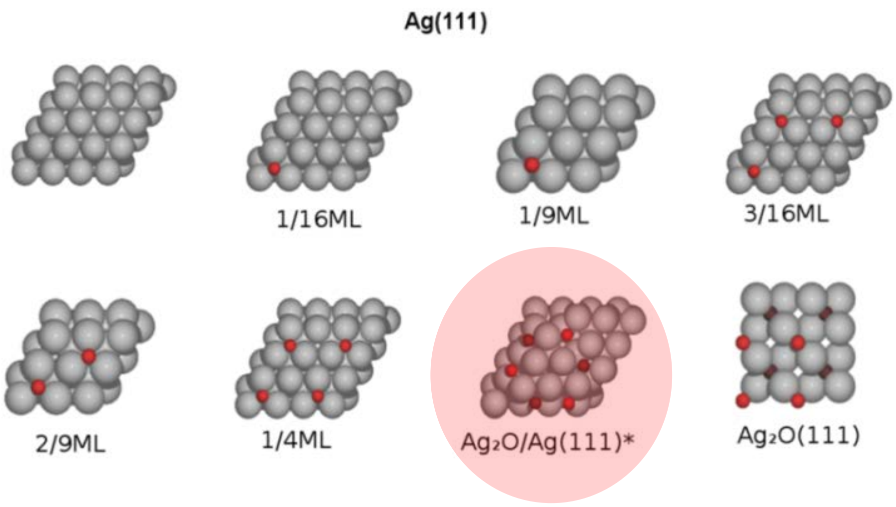
Multi-component system being in equilibrium with atomic reservoirs

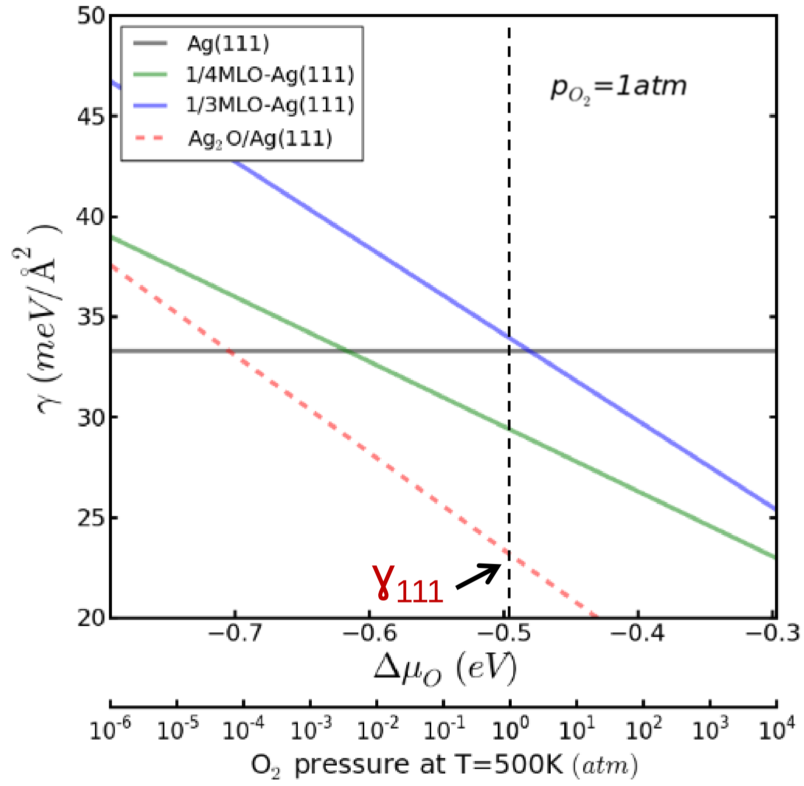
→ **stable surface at (p,T)**

THEORY — *bridging the pressure and temperature gap* → **EXPERIMENTS**

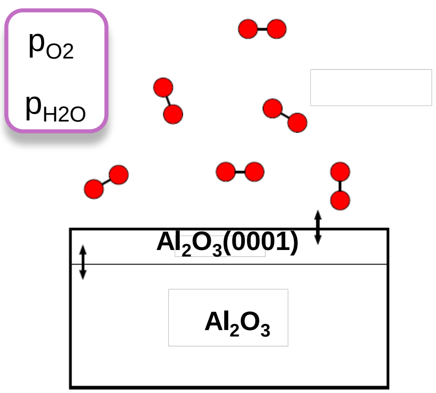
Equilibrium Ag surface

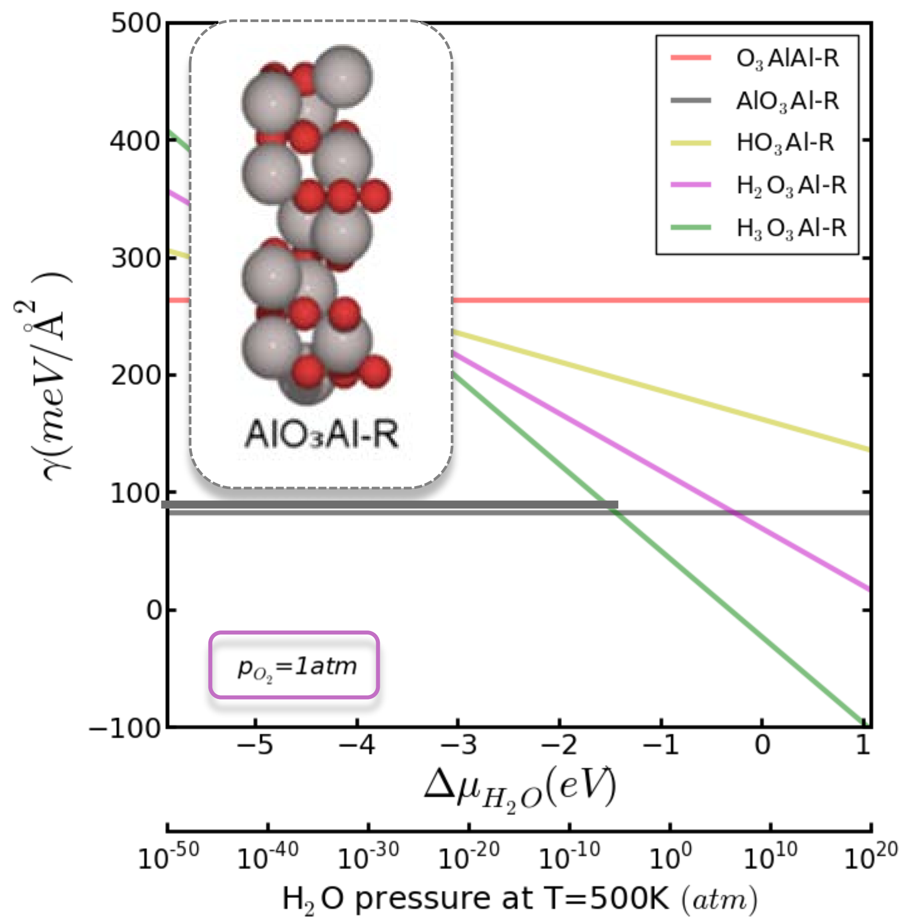
First-principles thermodynamic study



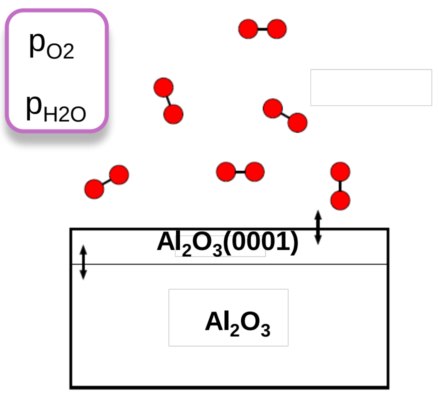


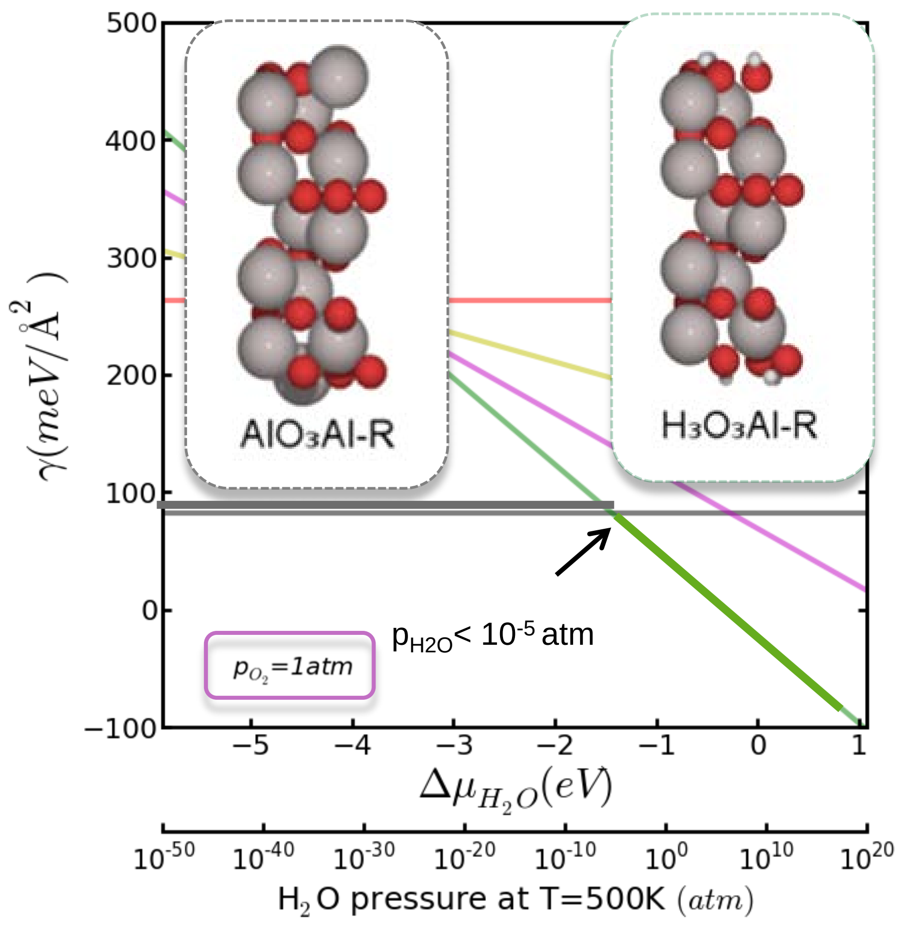
Equilibrium α-Al_2O_3 (0001) surface





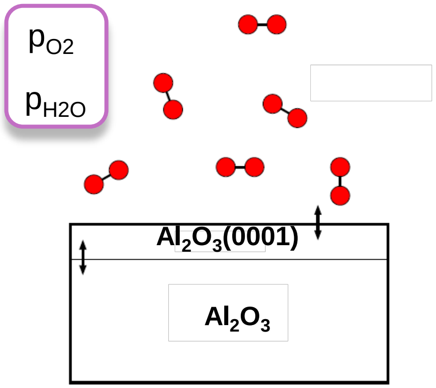
Equilibrium α-Al_2O_3 (0001) surface

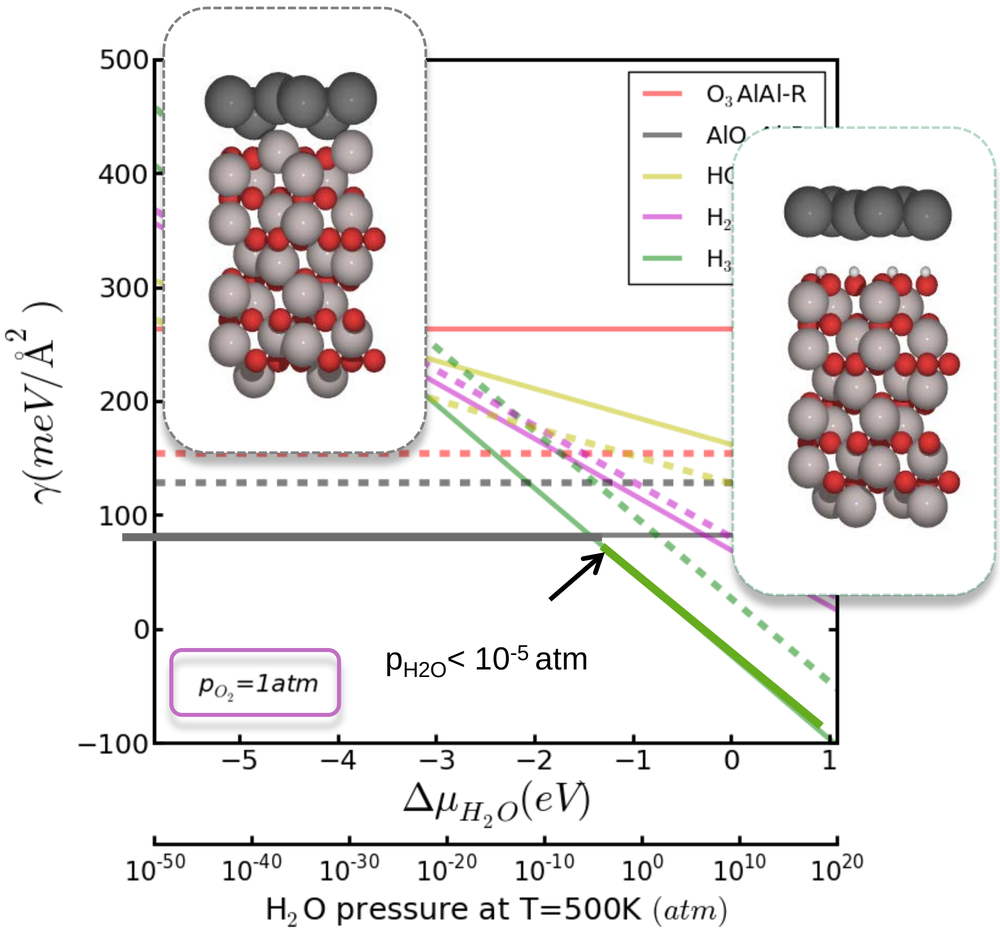




Equilibrium α-Al_2O_3 (0001) surface

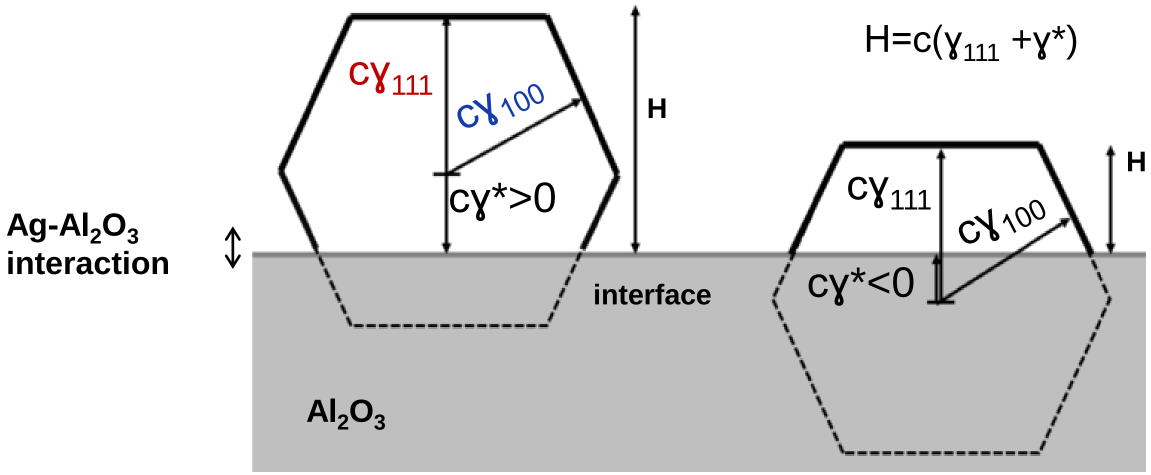
with Ag coverage





Shape of supported Ag nanoparticles on α-Al_2O_3
Wulff-Kaishew construction

- Ag surface free energies



- Effective surface energy

$$\gamma^* = \gamma_{metal} + E_{adh}/A$$

-Equilibrium Al_2O_3 surface

Bringing it all together: Example particle shapes

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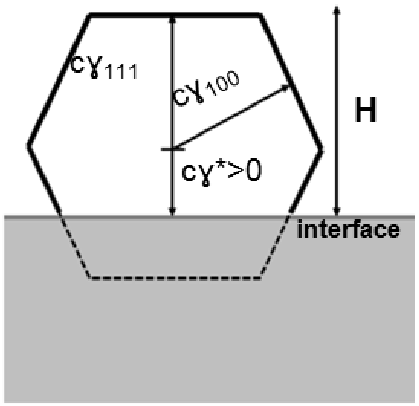
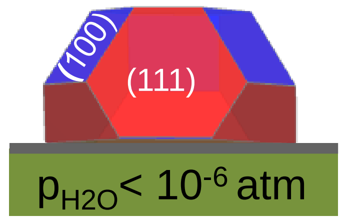


T=500K
p_{O2}=1atm

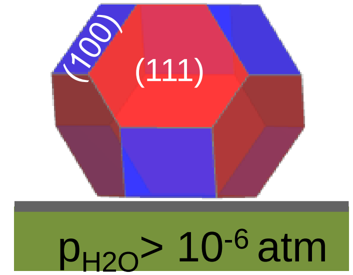
AlO_3Al-R

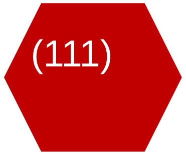
cγ*>0
cγ*< $c\gamma_{111}$

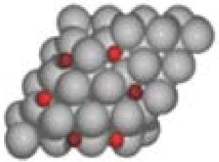


H_3O_3Al-R

cγ*>0
cγ*> $c\gamma_{111}$

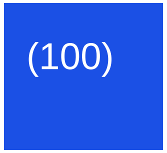


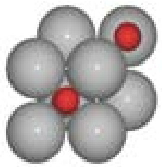




~77 %

~70 %



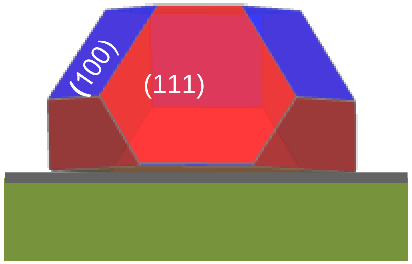


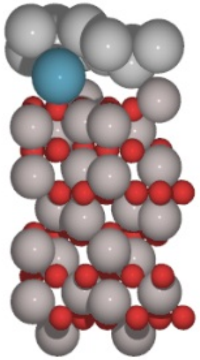
~ 23 %

~ 30 %

Next steps

Study the influence of **promoters**

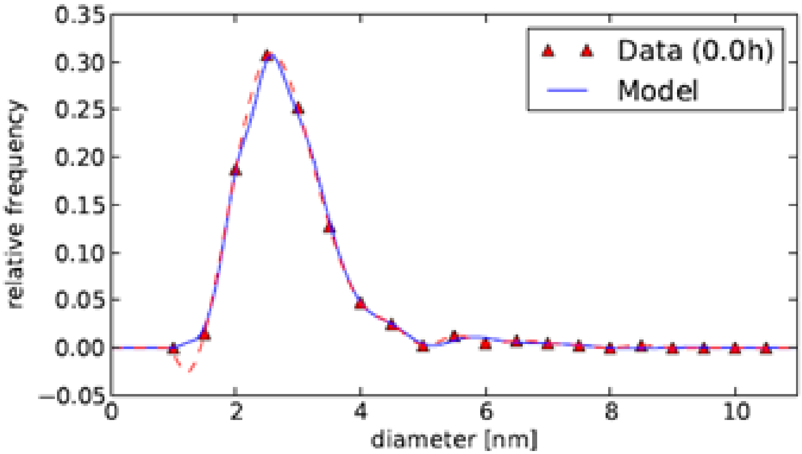




% Ag (100) ⟶ selectivity

binding energies ⟶ sintering

Macroscopic modeling of particel size distributions

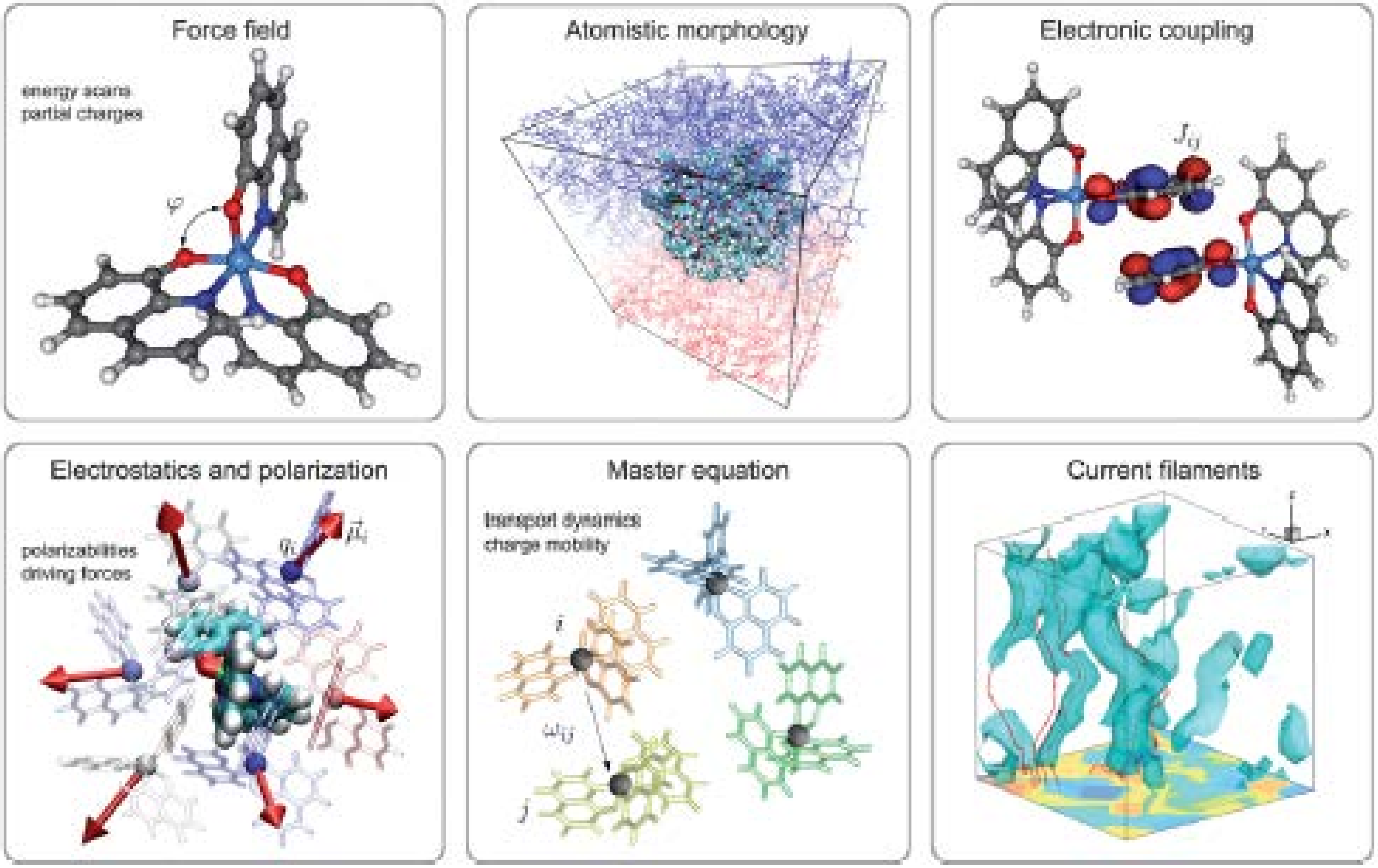


Using a sinterkernel, e.g.

$$\beta(x,y) = \beta_0 \cdot \left(x^{-m} + y^{-m}\right)$$

OLEDs - Multiscale Modeling of Devices

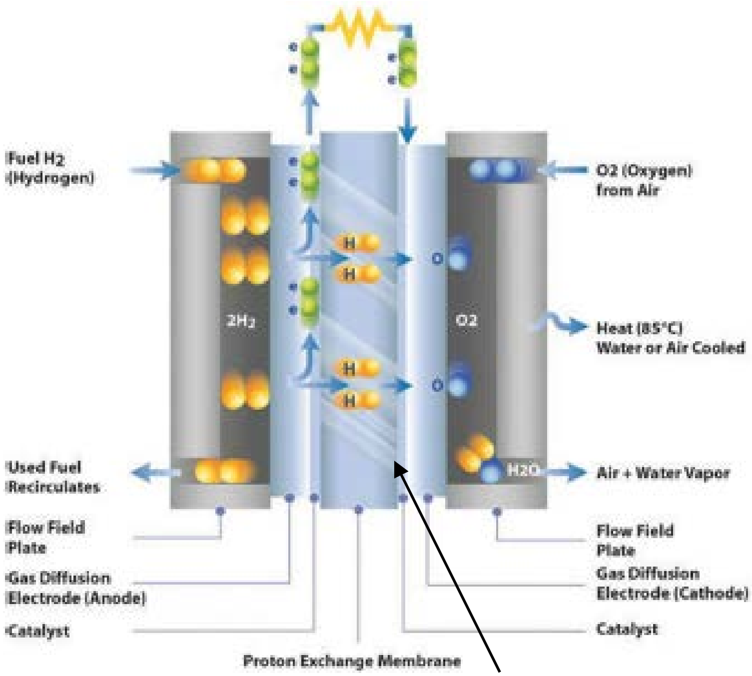
(work by C. Lennartz)



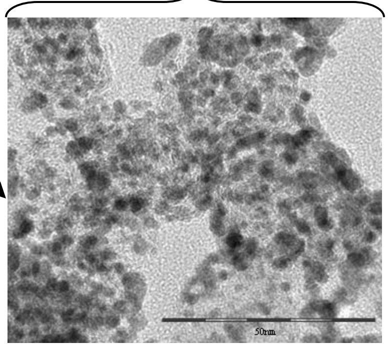
picture taken from J. Mat. Chem. 12, 10971
cooperation BASF (Lennartz) & MPIP (Adrienko)

High Temperature PEM fuel cell degradation (work by A. Badinski)

BASF
The Chemical Company



platinum particle catalyst



hydrogen oxidation reaction

$H_2 \rightarrow 2H^+ + 2e$

oxygen reduction reaction

$0.5\ O_2 + 2e \rightarrow O^{-2}$

Main degradation mechanisms

Ostwald ripening

$\Rightarrow$ effects activity of catalyst

reduction of H_3PO_4 acid

$\Rightarrow$ effects proton transport

The fuel cell model

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Model consists of

2 measurement functions

12 model parameters

2 ordinary differential equations

4 experimental controls:

T, inlet-flow (H_2,O_2,N_2)

$$V_{cell} = E_{Nernst} - \eta_{act} - \eta_{ohmic} - \eta_{mass}$$

$$E_{Nernst} = 1.229 - 0.85 \times 10^{-3}(T - 298.15) + 4.3085\,10^{-5} T \times \ln \frac{x_{H_2} x_{O_2}^{\frac{1}{2}}}{x_{H_2O}}$$

$$\eta_{act} = \frac{RT}{\alpha n F} \ln \frac{j}{2F \frac{k_B T}{h} \frac{A}{A(0)} \frac{k_u c_{acid}}{1+k_u c_{acid}} \frac{k_a x_{O_2}}{1+k_a x_{O_2}} \tilde{k} \exp\left(-\frac{E_a}{RT} + \frac{E_a}{RT_{ref}}\right)}$$

$$\frac{\partial\left(\frac{A}{A_0}\right)}{\partial t} = -k_d \times \exp\left(\frac{\beta_d |V_{cell}|}{RT}\right)\left(\frac{A}{A_0} - \frac{A_\infty}{A_0}\right)$$

$$\eta_{\text{ohmic}} = i \frac{l}{S} \frac{RT}{c_{acid}(zF)^2} \frac{1}{D}$$

$$\frac{dc_{acid}}{dt} = -k_c \exp(-E_c/RT) \frac{c_{acid}}{c_{acid}(0)}$$

$$\eta_{mass} = a_{mass} \frac{RT}{nF} \ln \frac{p_{mass} \frac{A_{act}}{A_{act}(0)} x_{O_2}}{p_{mass} \frac{A_{act}}{A_{act}(0)} x_{O_2} - j}.$$

Goodness-of-fit
Parameter covariance analysis

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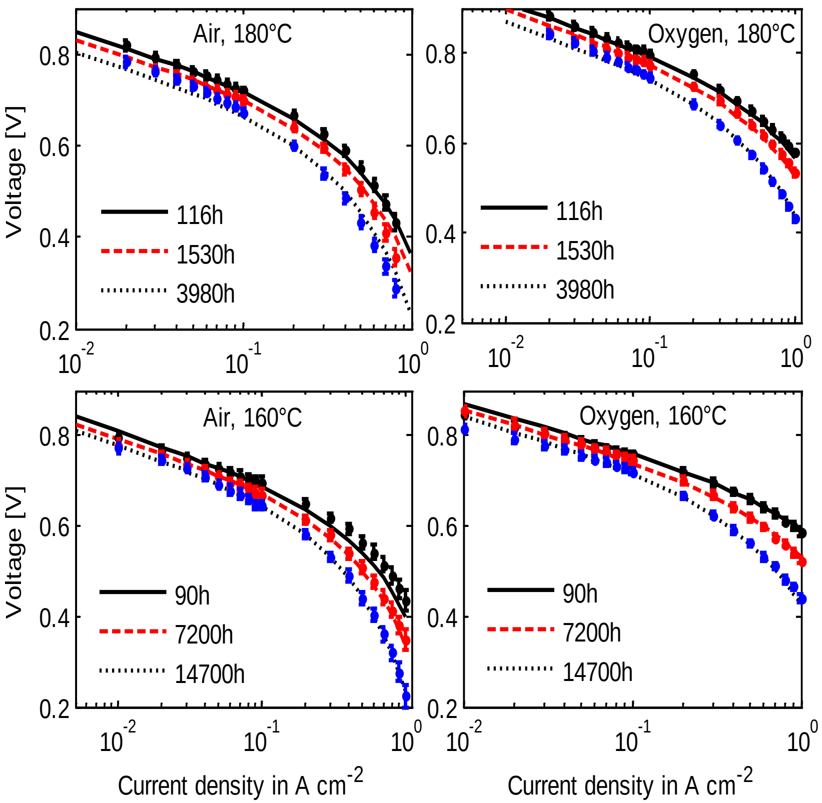
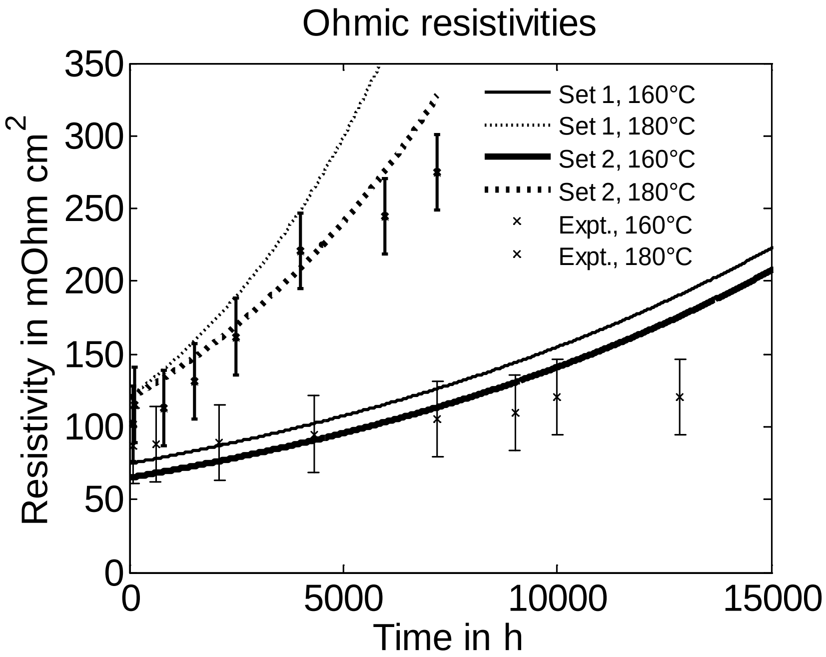


	Value	Error	Units
κ_{acid}	1.44	1.5%	mol/m³h
E_{acid}	74.8	1.7%	kJ/mol
D_0	2.88	2.2%	10^{-10} m²/s
ζ_{mass}	515	11.0%	A/cm²
κ_d	0.44	4.3%	1/h
$\tilde{A}_0$	3.01	6.6%	10^{-21}mol/g
E_a	121	1.9%	kJ/mol
α_c	0.87	0.8%	-
κ_a	2.68	4.2%	-
β_d	118	4.4%	KJ/mol
E_D	35,3	0.79%	KJ/mol
η	5.70	13.5%	-

	Set 1
χ^2	441
Points	559
p	99.96%

Model/data deviation explained by statistical errors with p=99.96%
average parameter uncertainties less then 5%

Model predictions
choose Ohmic resistivity as an example



	Set 0	Set 1	Set 2
χ^2	441	770	527
Points	559	575	575
p	99.96%	1e-6%	85.9%

Model/data deviation explained by statistical errors with p=1e-6% (Set 1)
Model recalibrated with Ohmic resistivity data (Set 2)

Thank you for your attention.

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