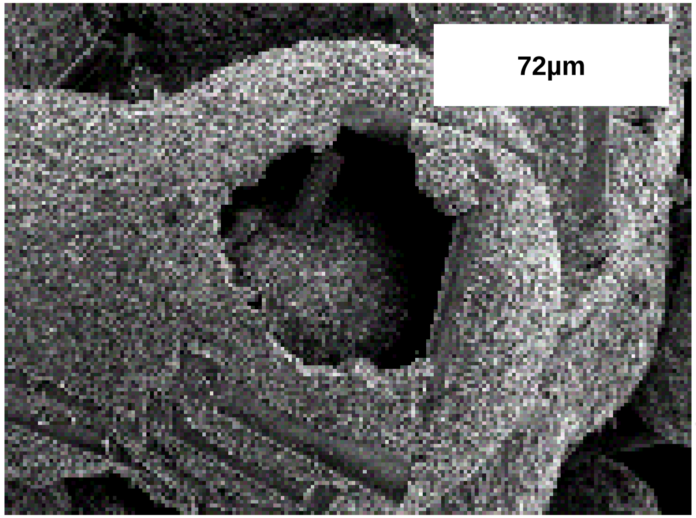
Robert Schlögl

NANOSTRUCTURE AND CATALYSIS:



Cu AS CASE STUDY

THIS AN ADVANCED MATERIAL?)

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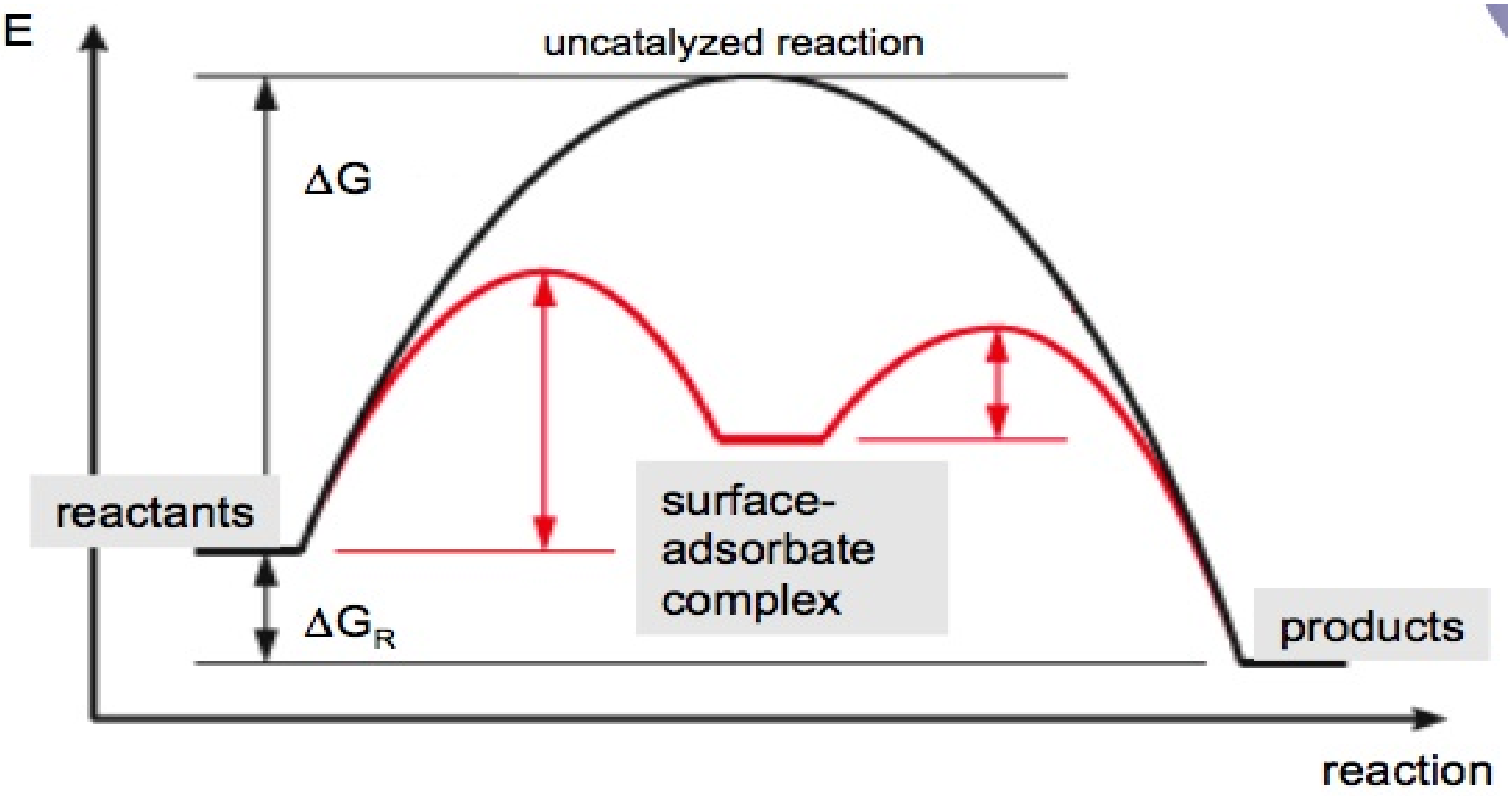
Function of a catalyst: Static SM



Adsorbate structures dynamical (chemical waves)

Bulk is “irrelevant”, no chemical transformations sub-surface

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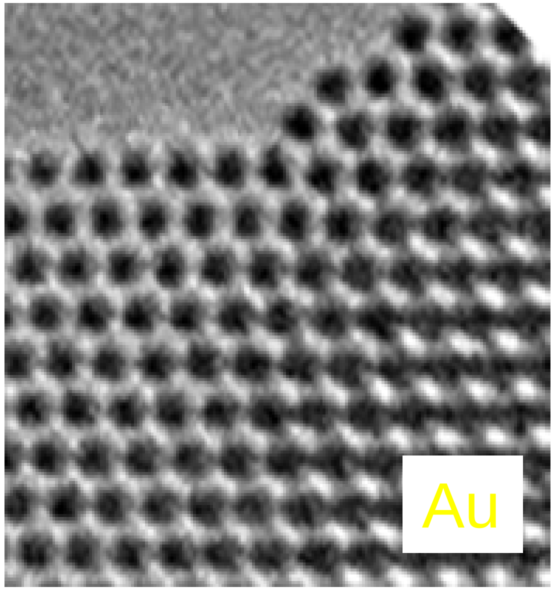
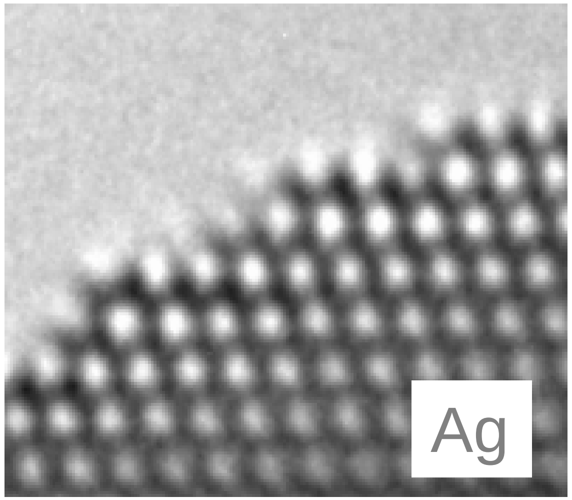
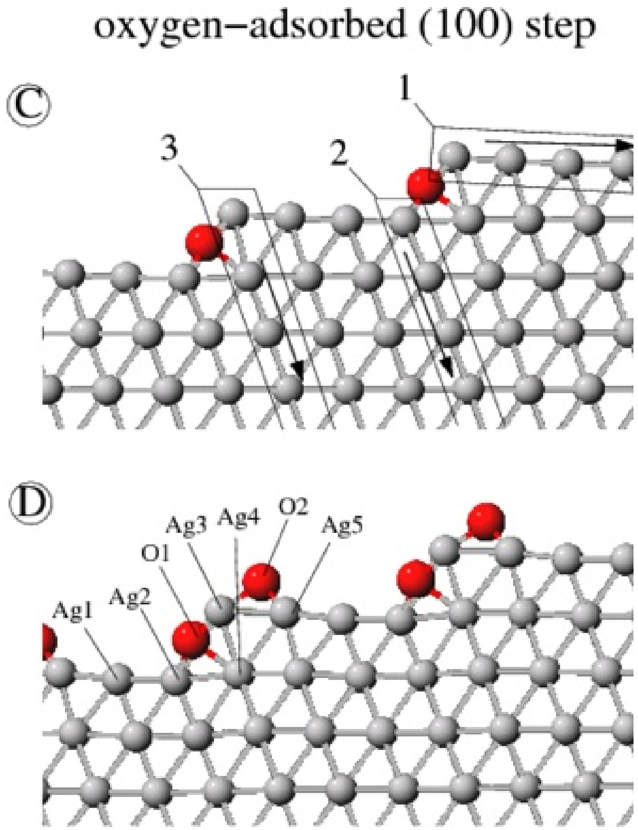
Defects: Oxo-philicity







T. Jakob
M. Scheffler

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Beyond the SM: dynamics

- Static model good at best for 1-step processes controlled by adsorption.
- Most reactions exhibit several pathways; multi-step process with selectivity.
- Catalysts are functional materials expressing isolated active sites through contact with their reagent.
- Catalyst-reactant interaction kinetics (gas-solid diffusion) is critical.

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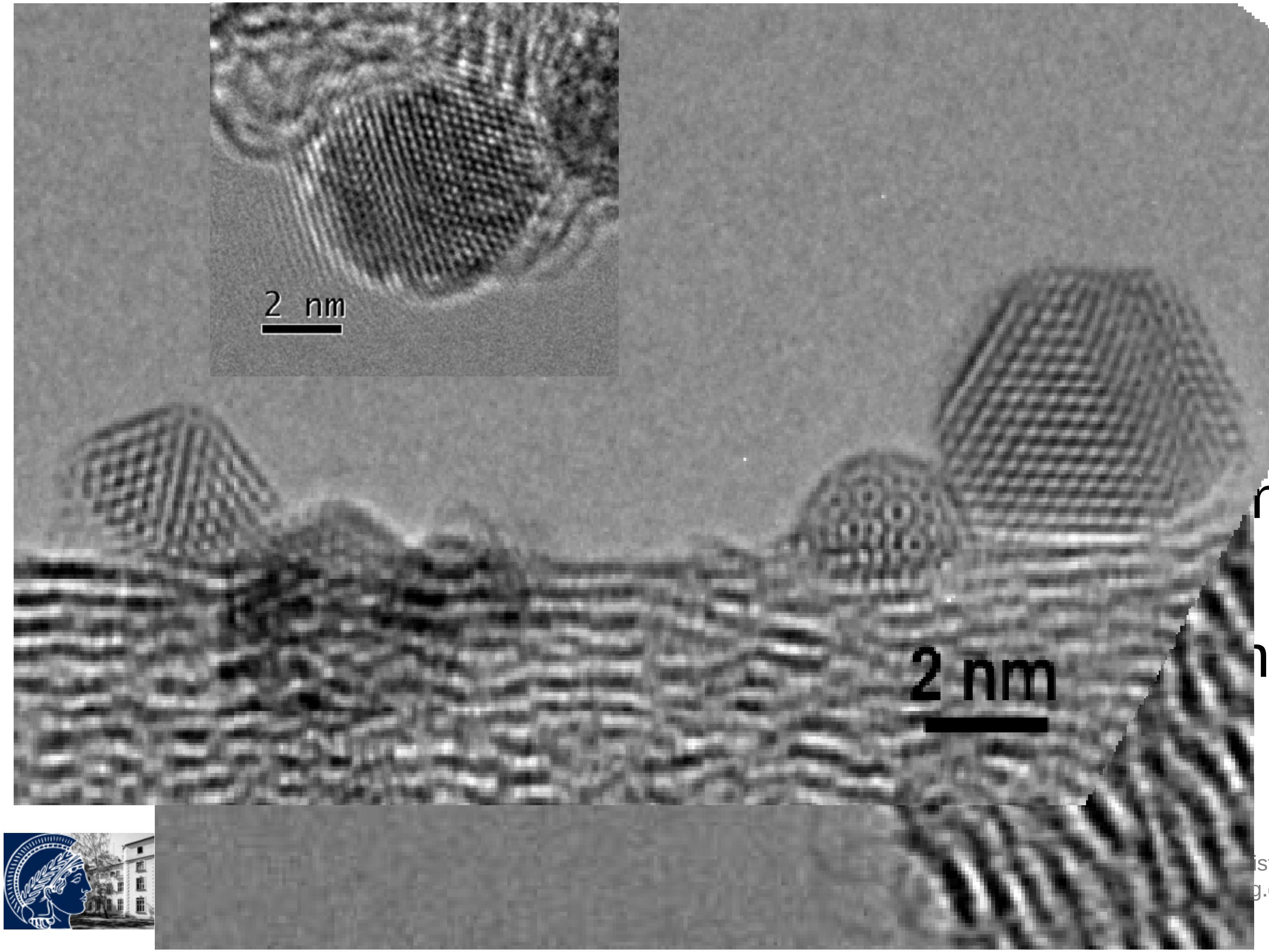
Nanostructuring in Catalysis



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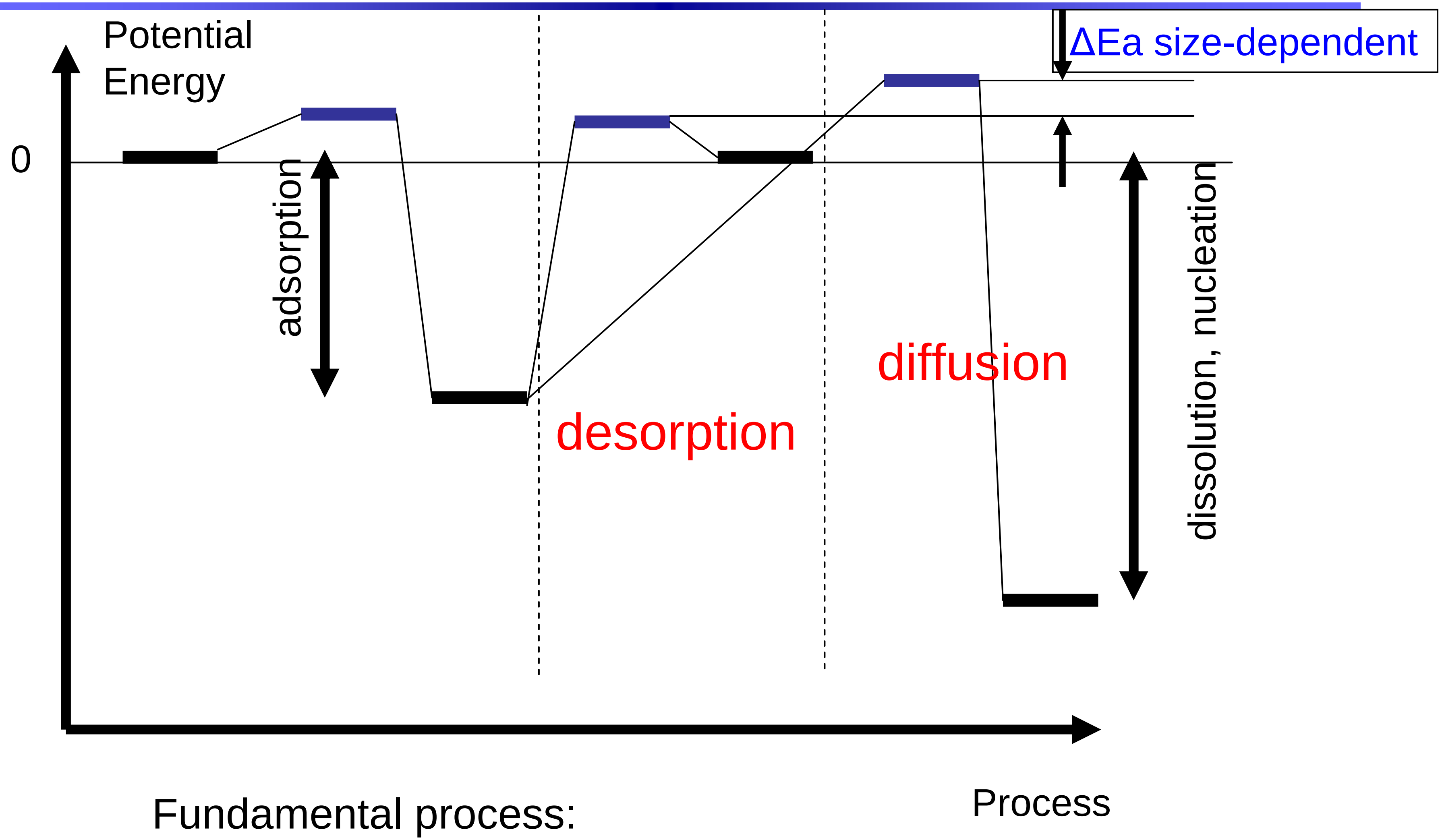
Dynamics: excluded for large objects



Fundamental process:
Desorption-dissolution (phase formation)

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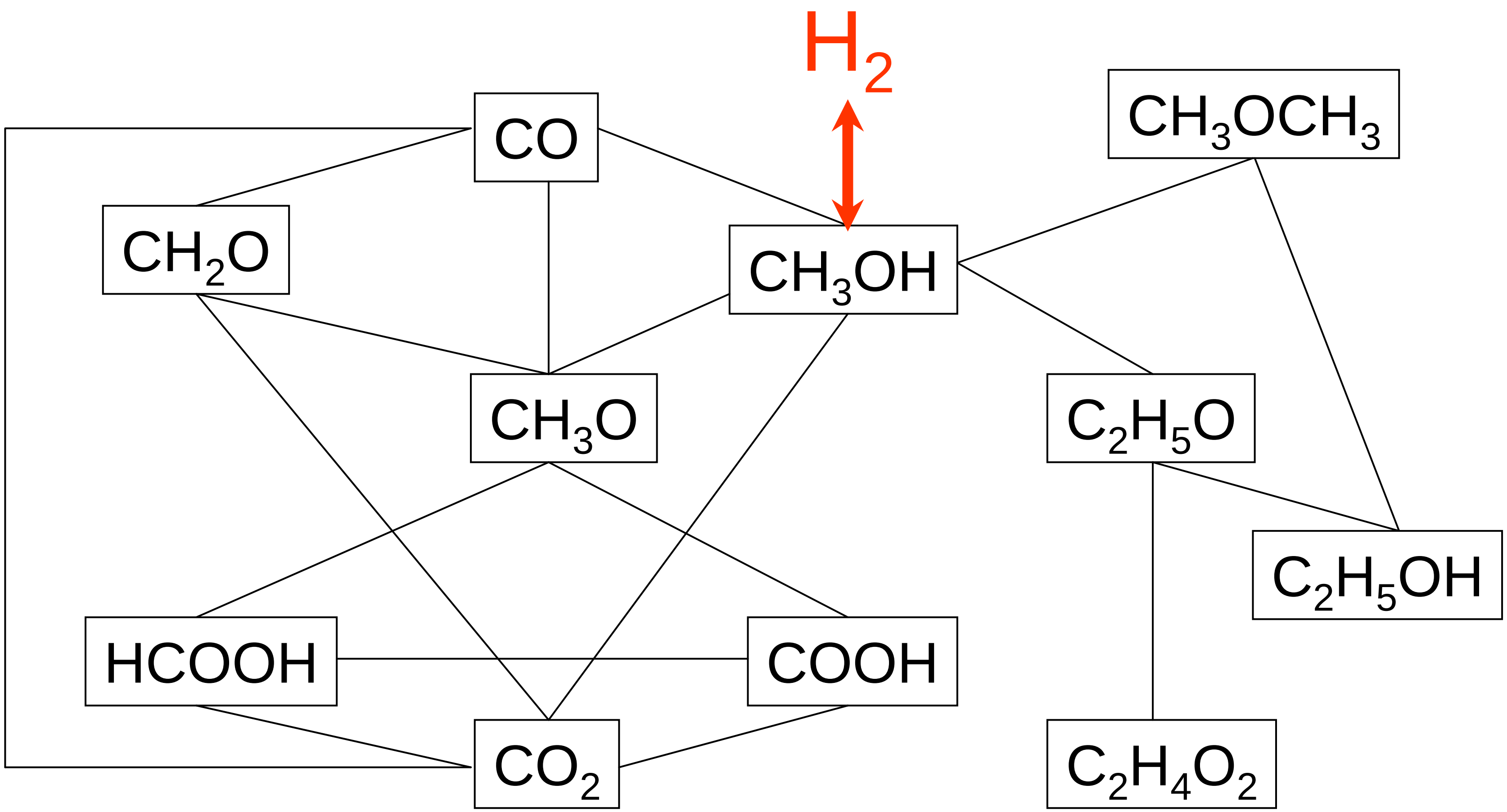
Selectivity in C1: Cu does it all



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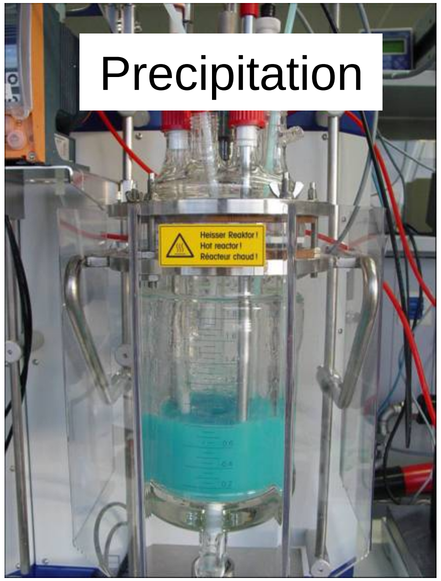
Catalytic Cu: not just Cu?



Ageing

Washing / drying

Calcination

Reduction

$Cu/ZnO/Al_2O_3$

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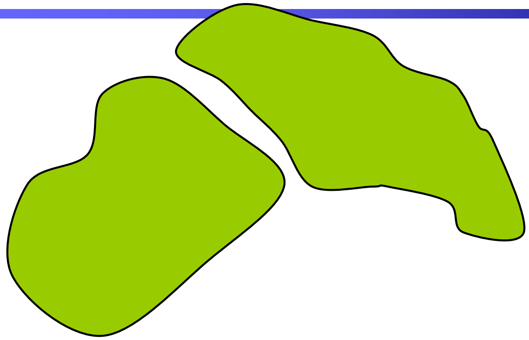
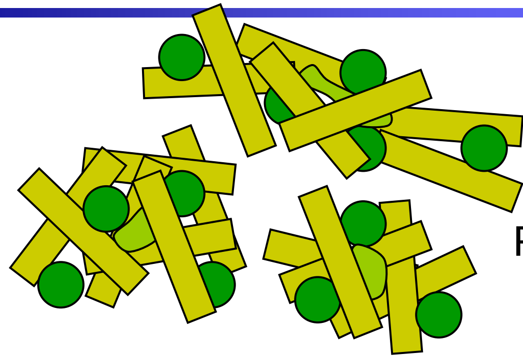
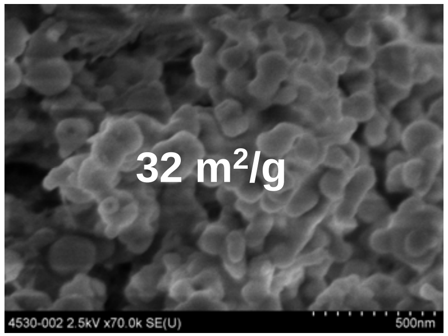
Chemical memory

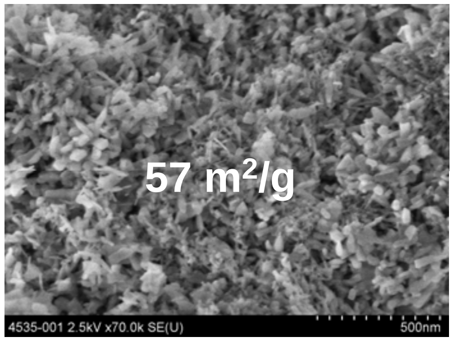


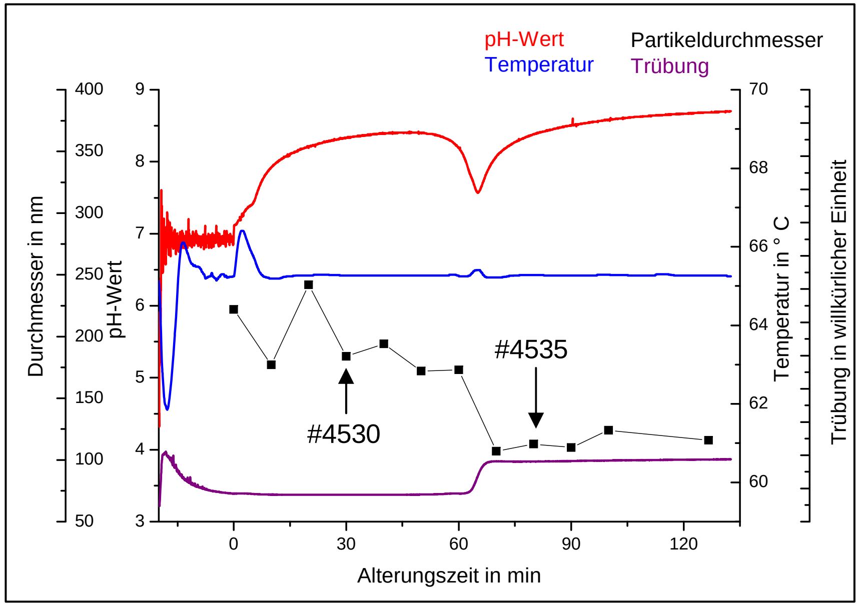
Ageing →



Colour change: Restructuring of Cu-O into chains







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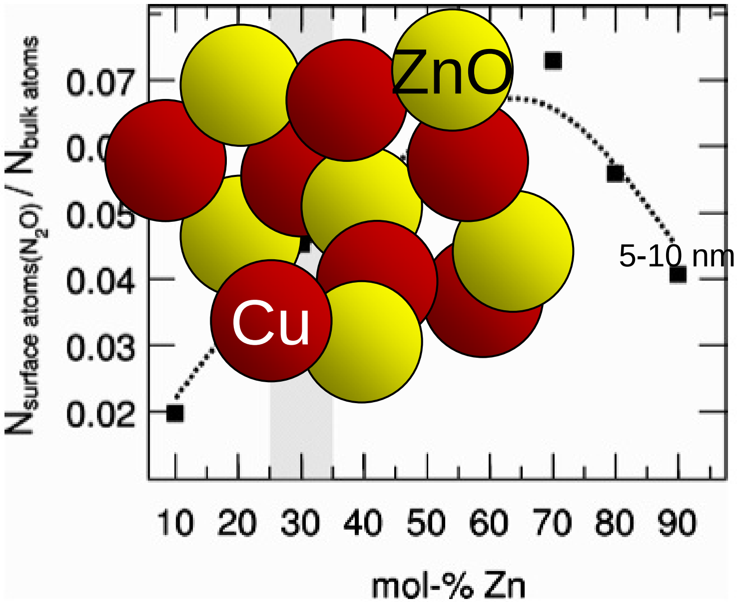
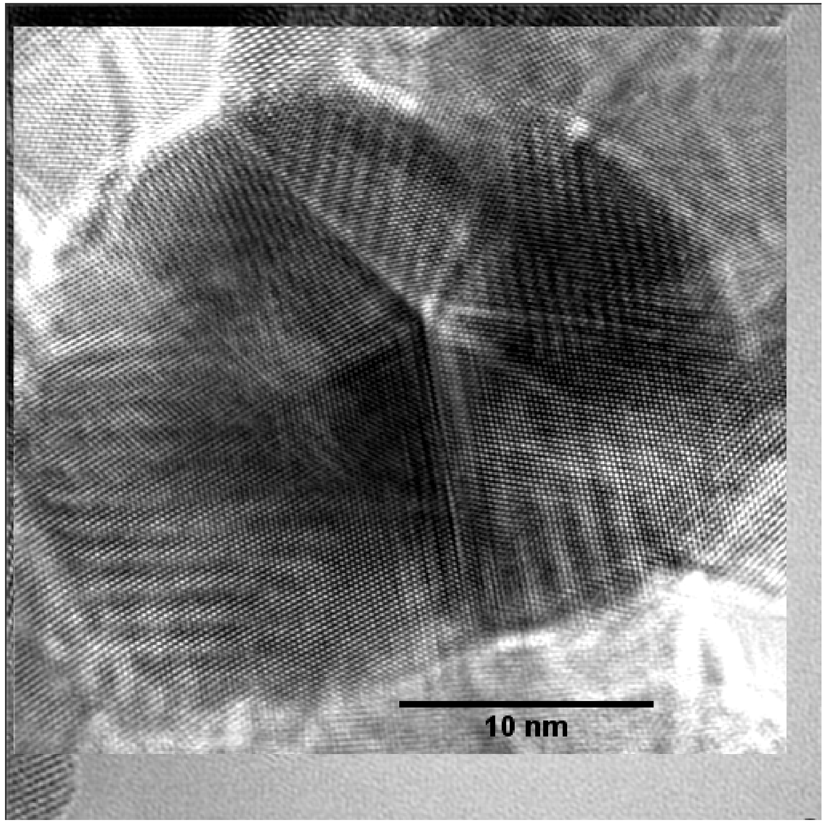
Supported vs diluted Cu





Supported and diluted (technical) systems are quite different in structural hierarchy

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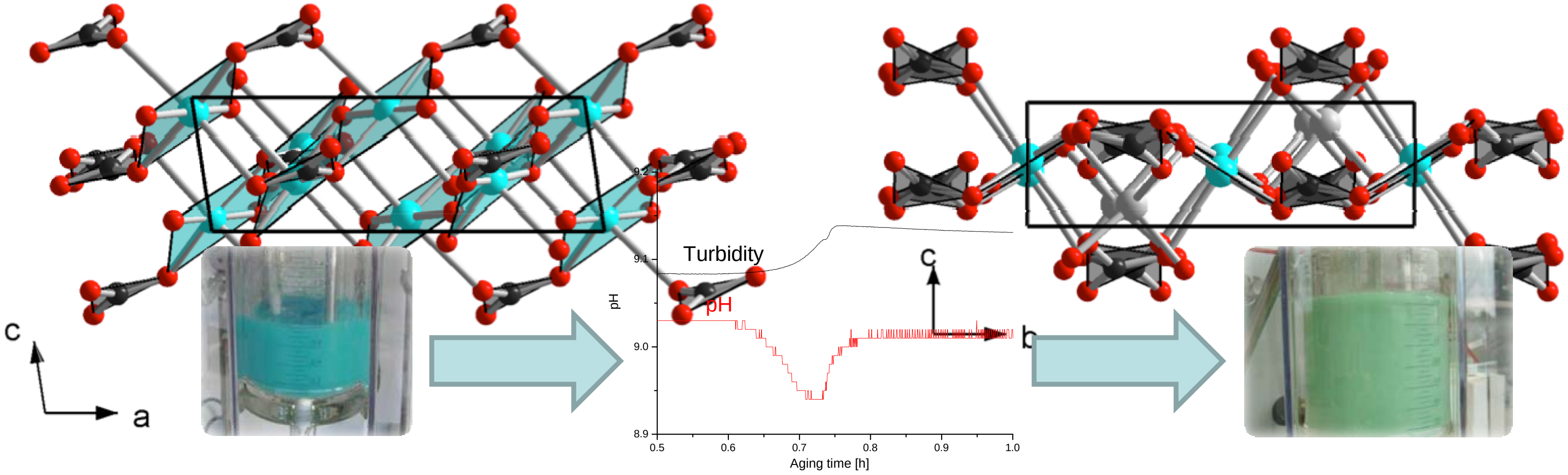
The right phase: composition



X-ray amorphous / malachite — pH drop — rosasite / crystalline

Al-content →

Zn-content ↓

0 % — Malachite $Cu_2(CO_3)(OH)_2$

< 28 % — Zincian Malchite $(Cu,Zn)_2(CO_3)(OH)_2$

> 28 % — Zincian Malachite + Aurichalcite $(Cu,Zn)_5(CO_3)_2(OH)_6$

Zincian Malachite (Al-incorporated) + Hydrotalcite-like by-phase $(Cu,Zn)_{1-x}Al_x(OH)_2(CO_3)_{x/2}$ * m H_2O

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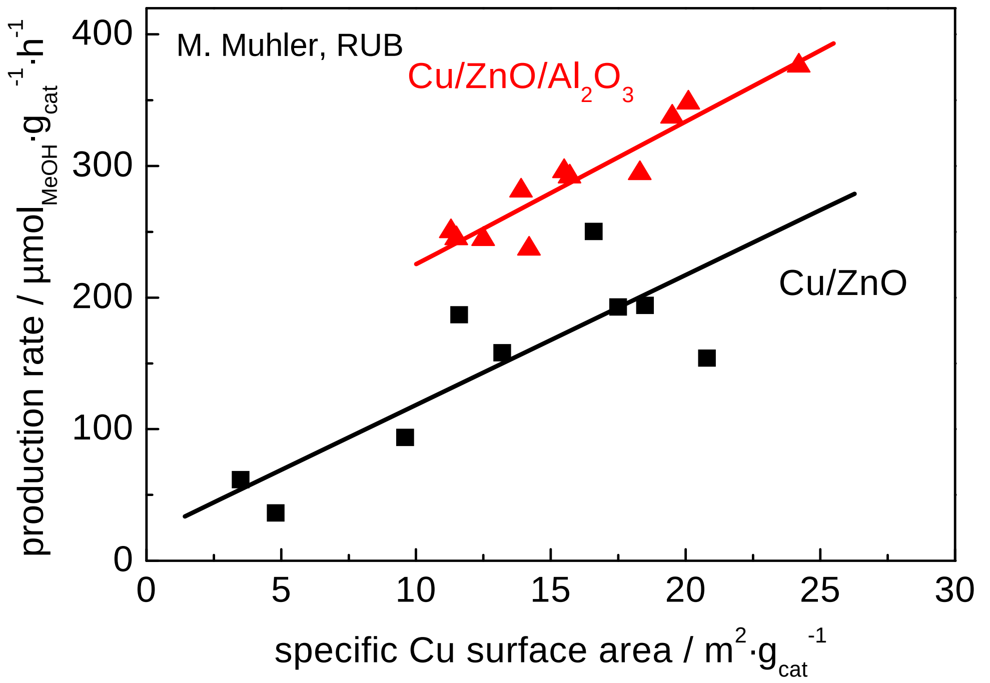
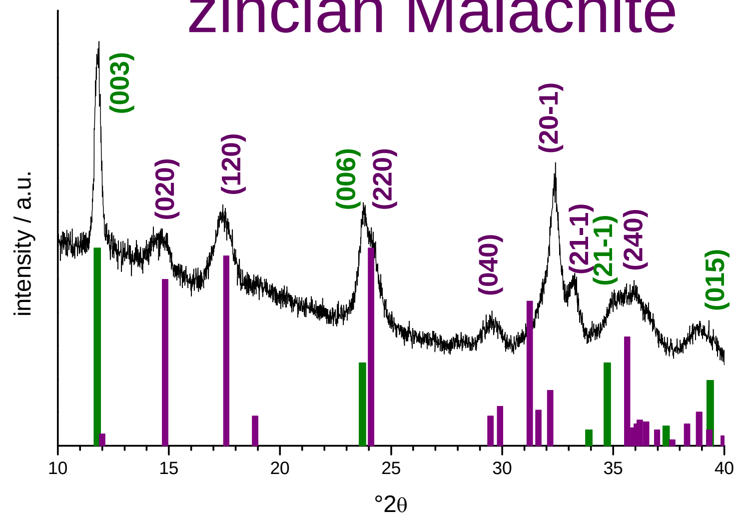
Ternary catalyst: Role of Al



Hydrotalcite, zincian Malachite



Cu:Zn:Al = 60:25:15

Cu SA clearly not the sole parameter controlling productivity

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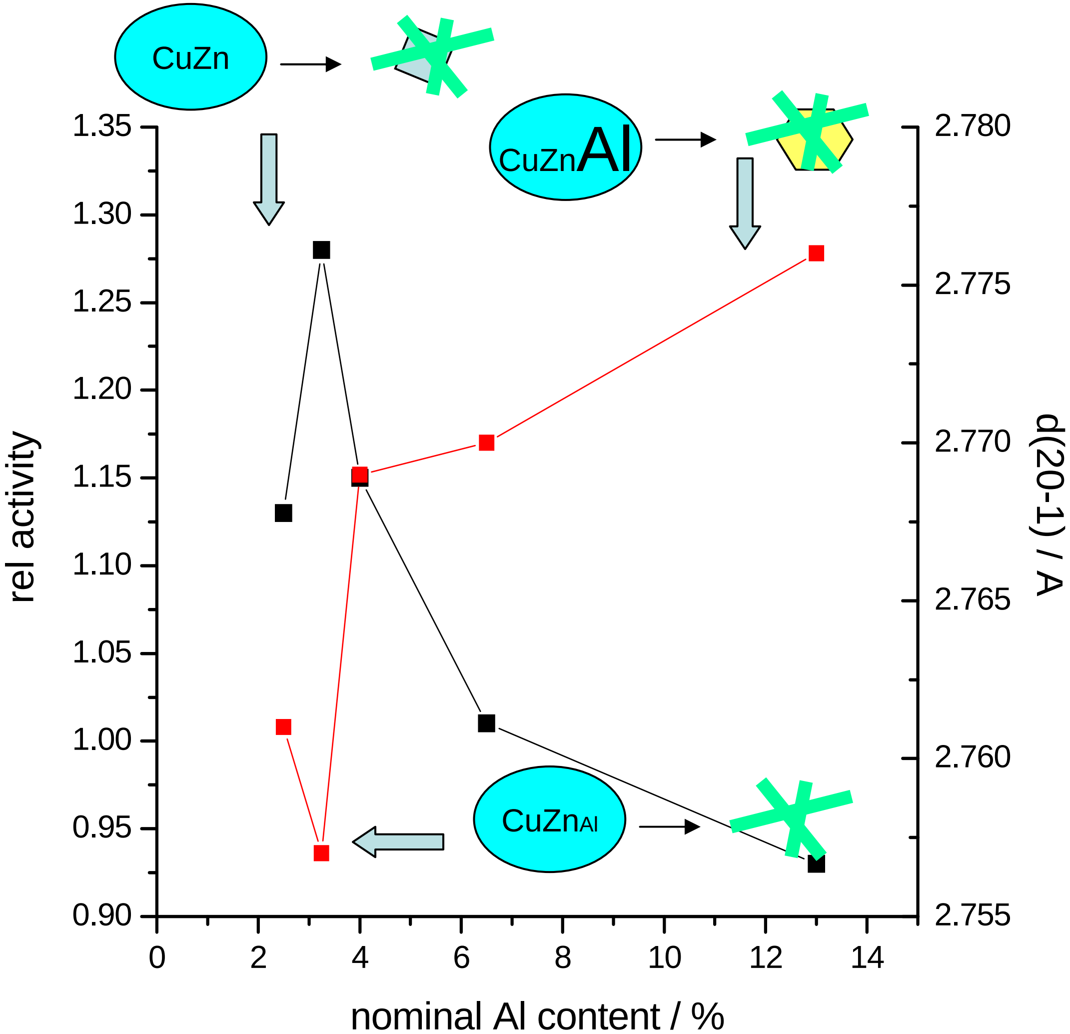
Structure-activity correlation

at 60 bar and 613 K



If the concentration (chemical potential) of Al^{3+} is high, Al-rich side-phases are formed (Hydrotalcite)

Activity test: 600 h tos

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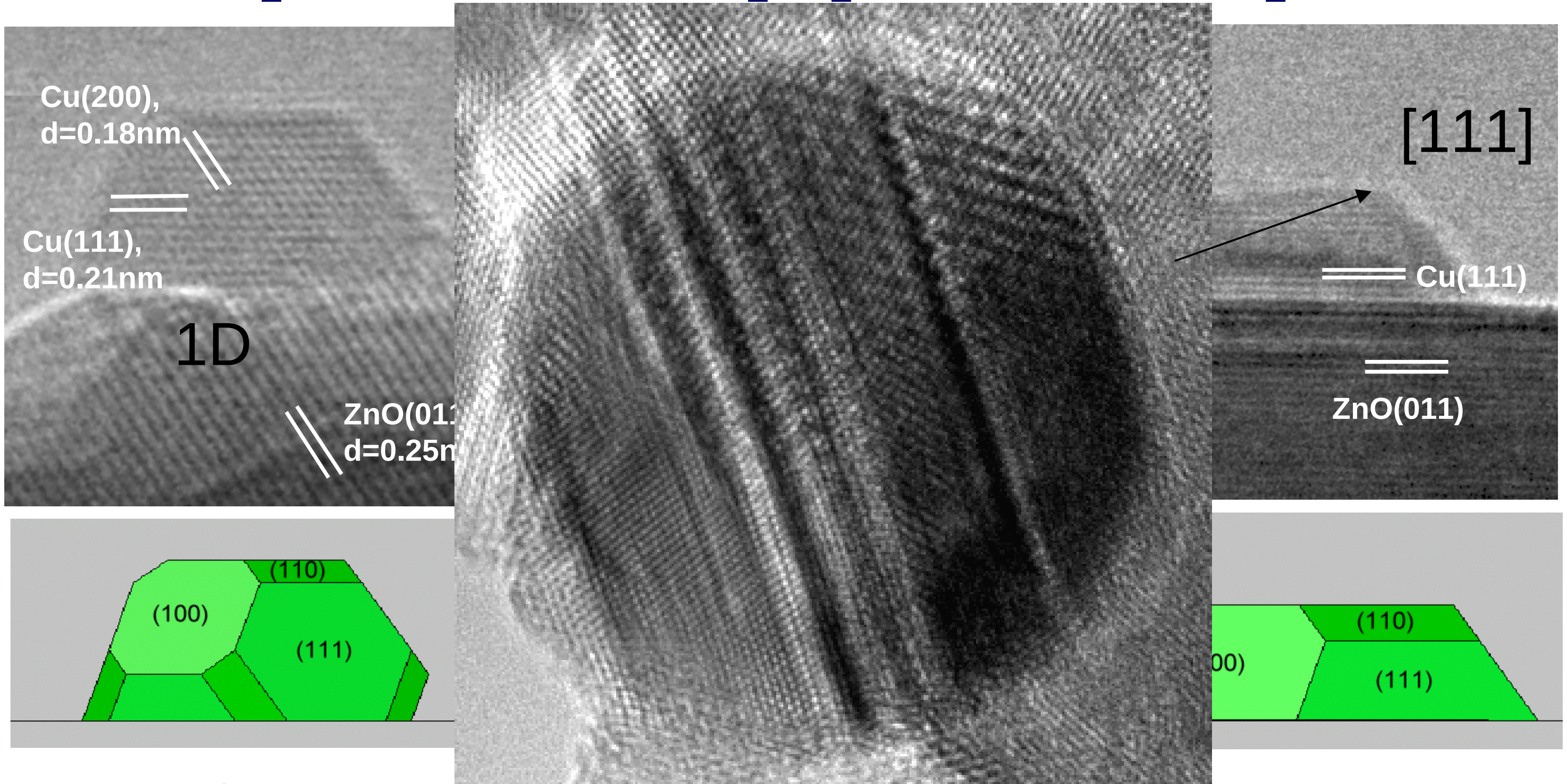
Active “nano-copper”

H_2	H_2/H_2O	H_2/CO



1.5mbar, 220°C	**1.5mbar, H_2/H_2O=3/1, 220°C**	**1.5mbar, H_2/CO=95/5, 220°C**

Hansen, Wagner et al., Science 295 (2002), 2053

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Search for active sites

- Typical catalyst: 10 m^2/g Cu SA
  - 10^{20} Cu atoms
  - 30 mMol/gh MeOH = 10^{22} molecules/h
- Every Cu atom: 100 molecules /h
  - tof 0.03 for 100% active sites
  - tof 1 for 0.3% active sites
- Only a marginal fraction of Cu atoms is sufficient for activity: high energy sites become critical: defects are candidates for active sites

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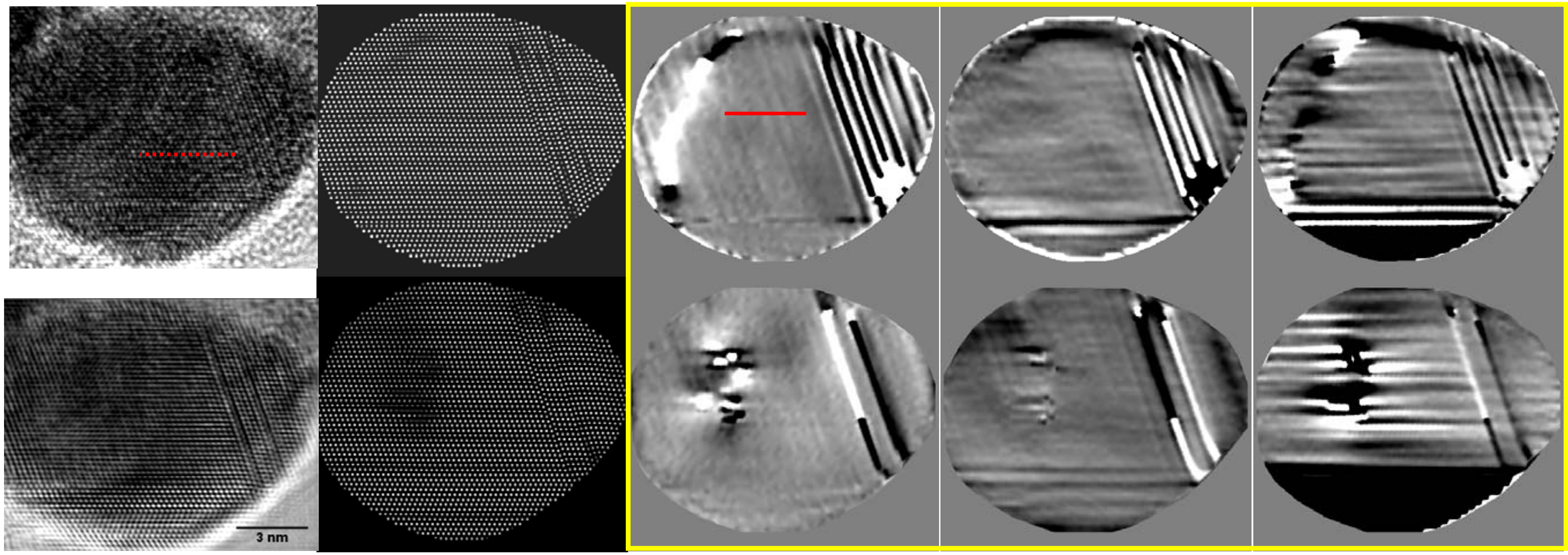
Nano-catalysis: detection of HE sites

Lattice strain from impurities and translational defects creates high-energy sites in a distribution of energy spread.



raw FFT e_{xx} e_{yy} e_{zz}

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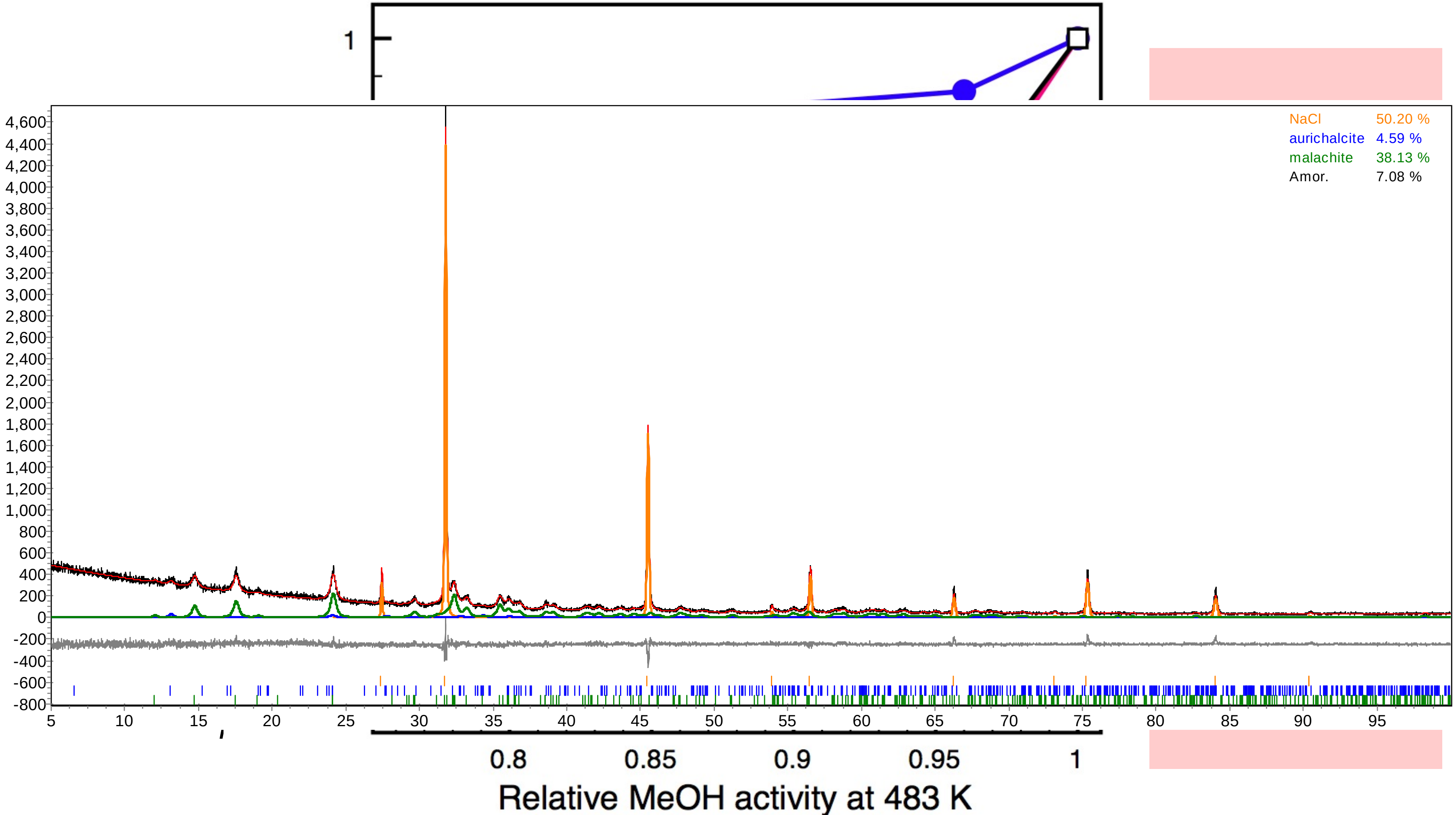
Nanostructure and statistics



In-situ XRD

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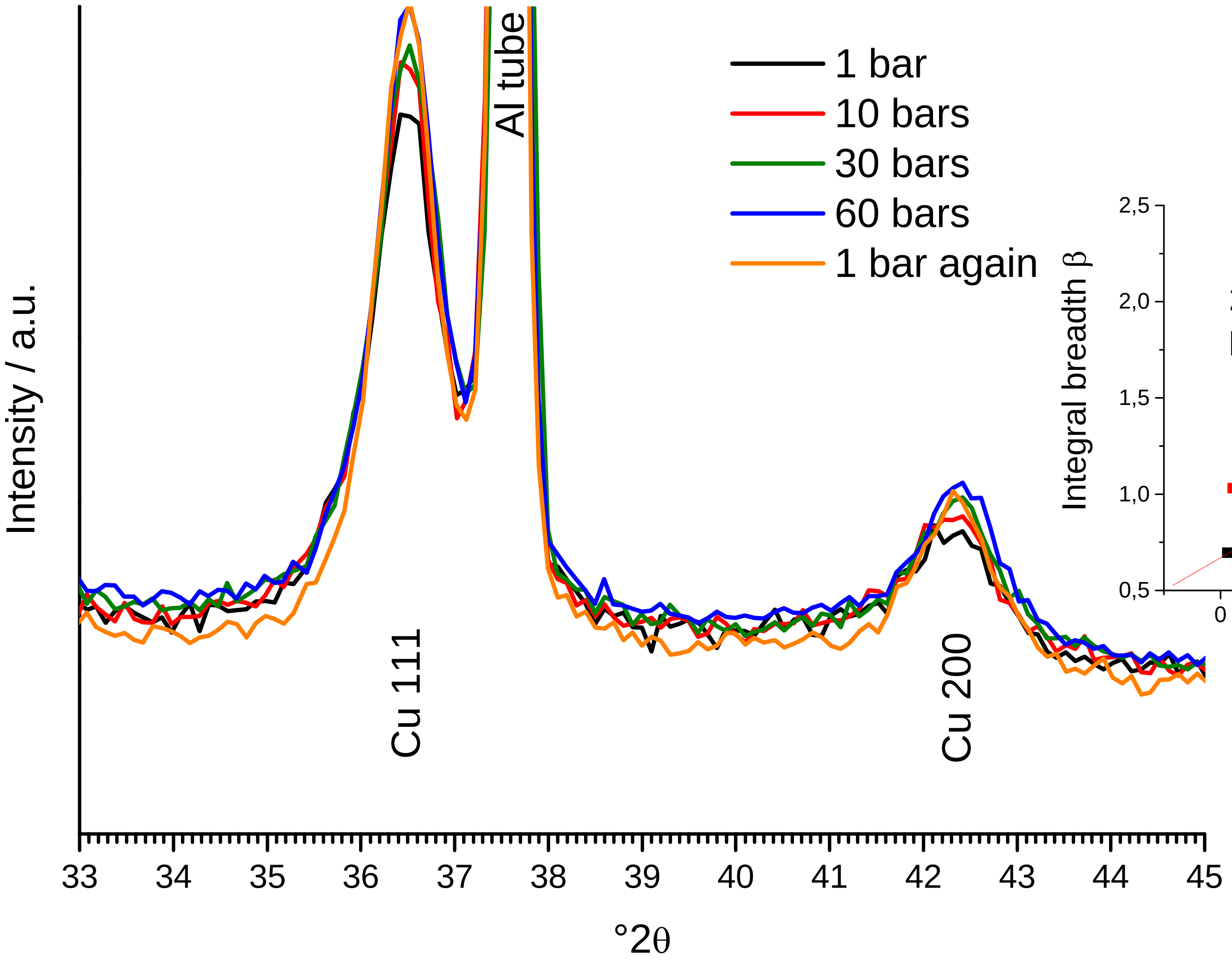
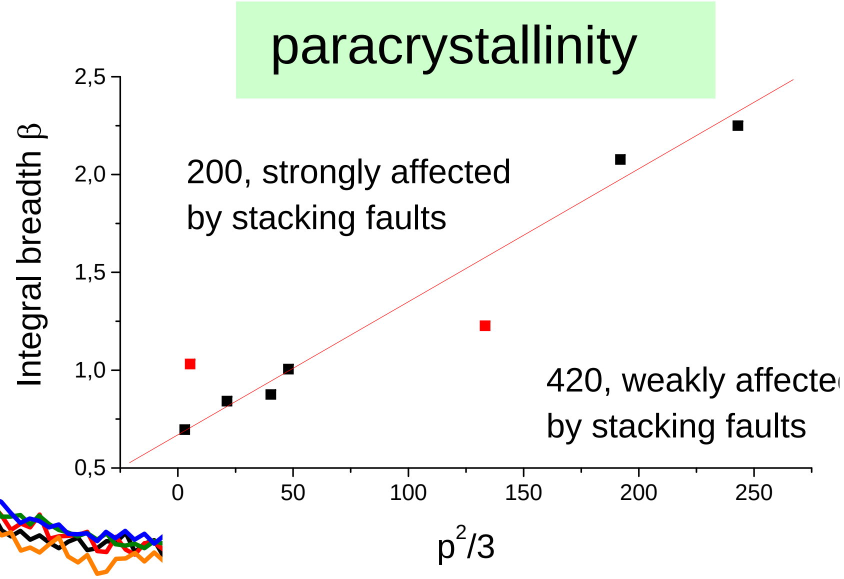
Defected Cu: the active phase





In situ high pressure neutron diffraction

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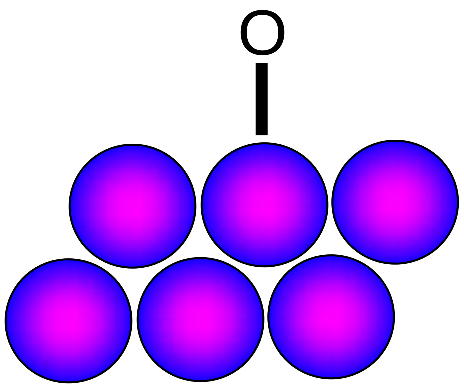
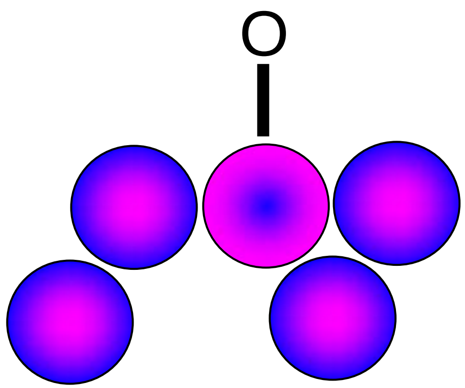
The critical step: role of defects

In the catalytic chemistry of C1 the rds is the hydrogenolysis (dehydrogenation) of adsorbed CH_2O_2 Norskov et al. J. Cat, 1995

An metal-oxygen group is the controlling entity: its detection is controversial between CO in-situ titration (not found) and post reaction frontal chromatography (detected) Waugh, Muhler, Campbell



electrophilic, reacts with CO



nucleophilic, reacts with H (H_2O)

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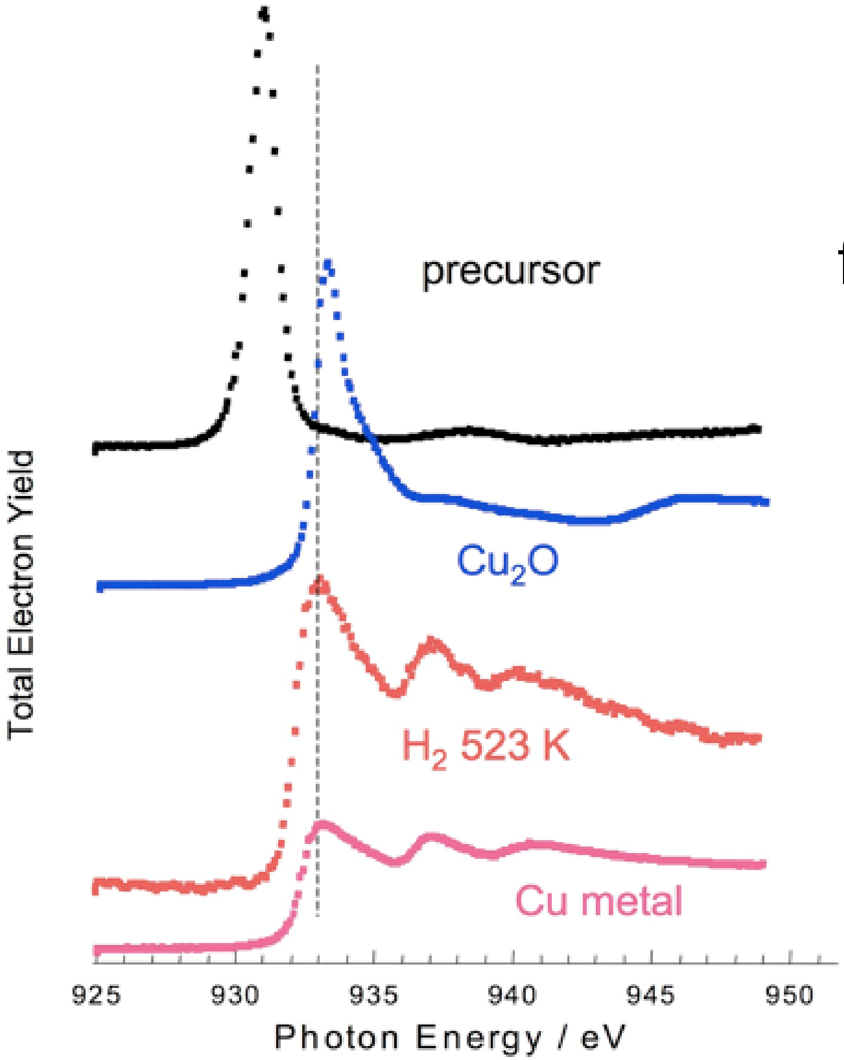
How exactly metallic is active Cu?

By XRD, XPS, TPR, EXAFS active Cu is metallic



In-situ XAS measures the extent of d-band filling at the surface of activated Cu: Much more accurate than XPS chemical shift (agrees exactly with Cu metal value)

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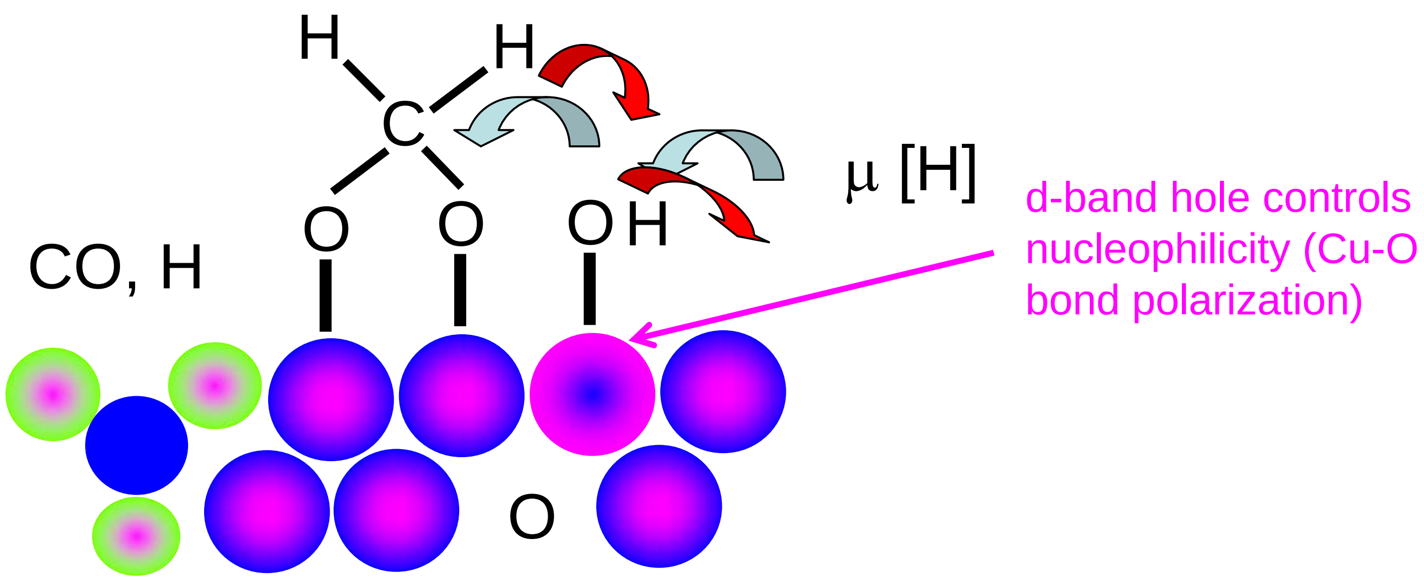
Active site

The minimum requirement is the co-existence of Cu atoms with and without d-band holes (many realizations)



Plausible realization: metal defects for O_{nucleo} , strain-stabilized metastable (110) metal facets and ZnO_{1-x} overlayer (brass from over-reduction)

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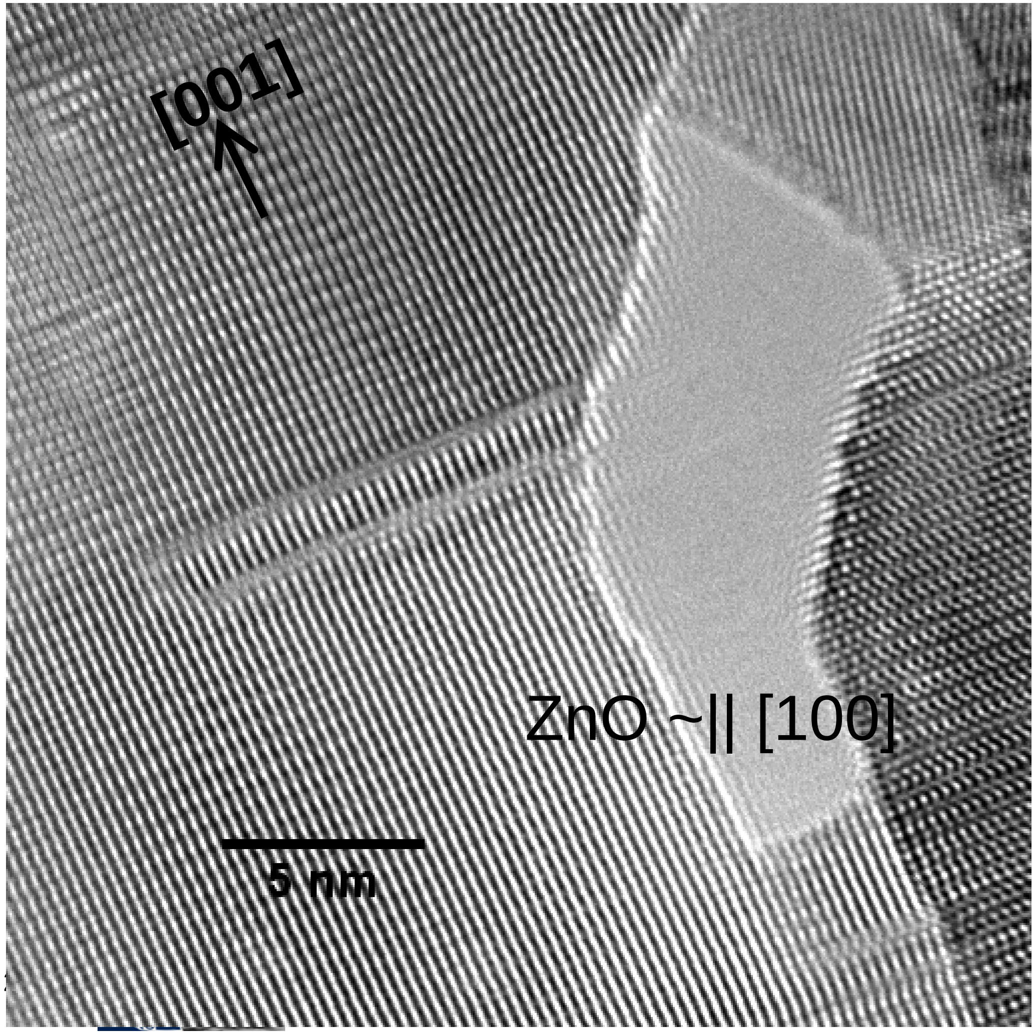
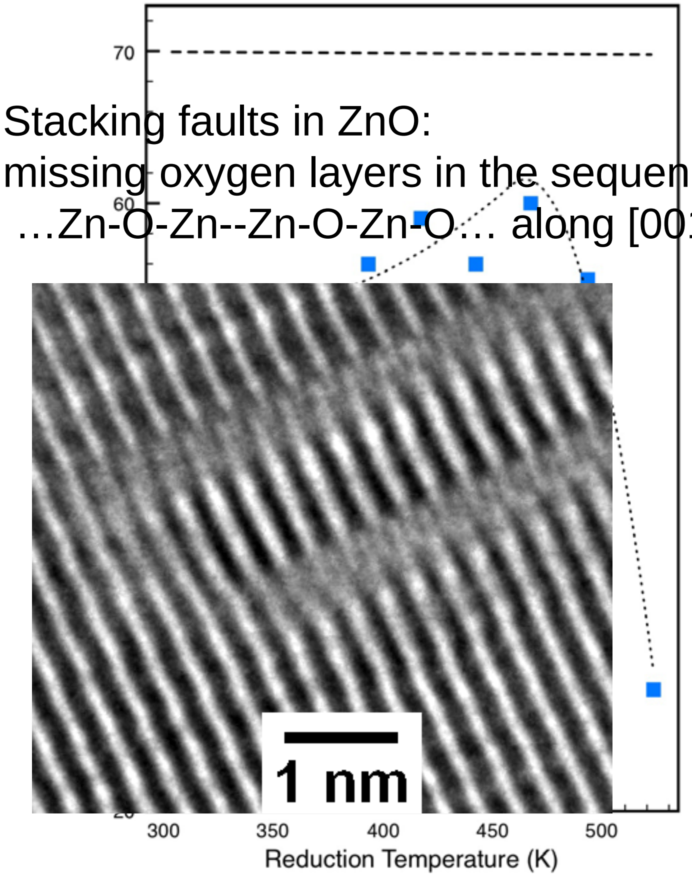
Synergy: nanostructure of ZnO

ZnO undergoes Al-mediated metal-support interaction



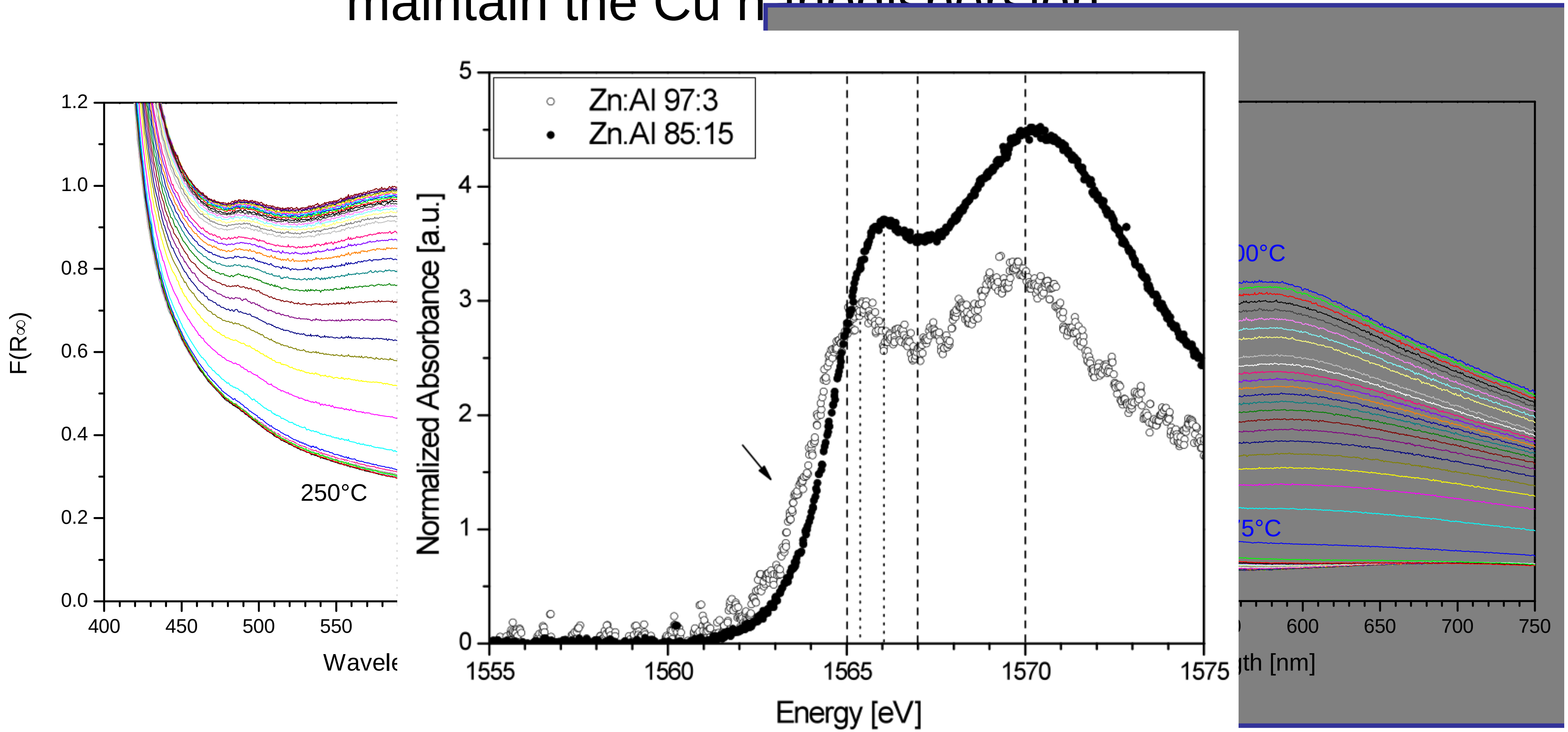


Stacking faults in ZnO:
missing oxygen layers in the sequence
…Zn-O-Zn--Zn-O-Zn-O… along [001]

Cu-Zn neighbouring sites likely to exist

ZnO stability

The necessary reduction of ZnO must be minimized to maintain the Cu nanodispersion



In-situ Cu plasmon resonance

In-situ Al NEXAFS

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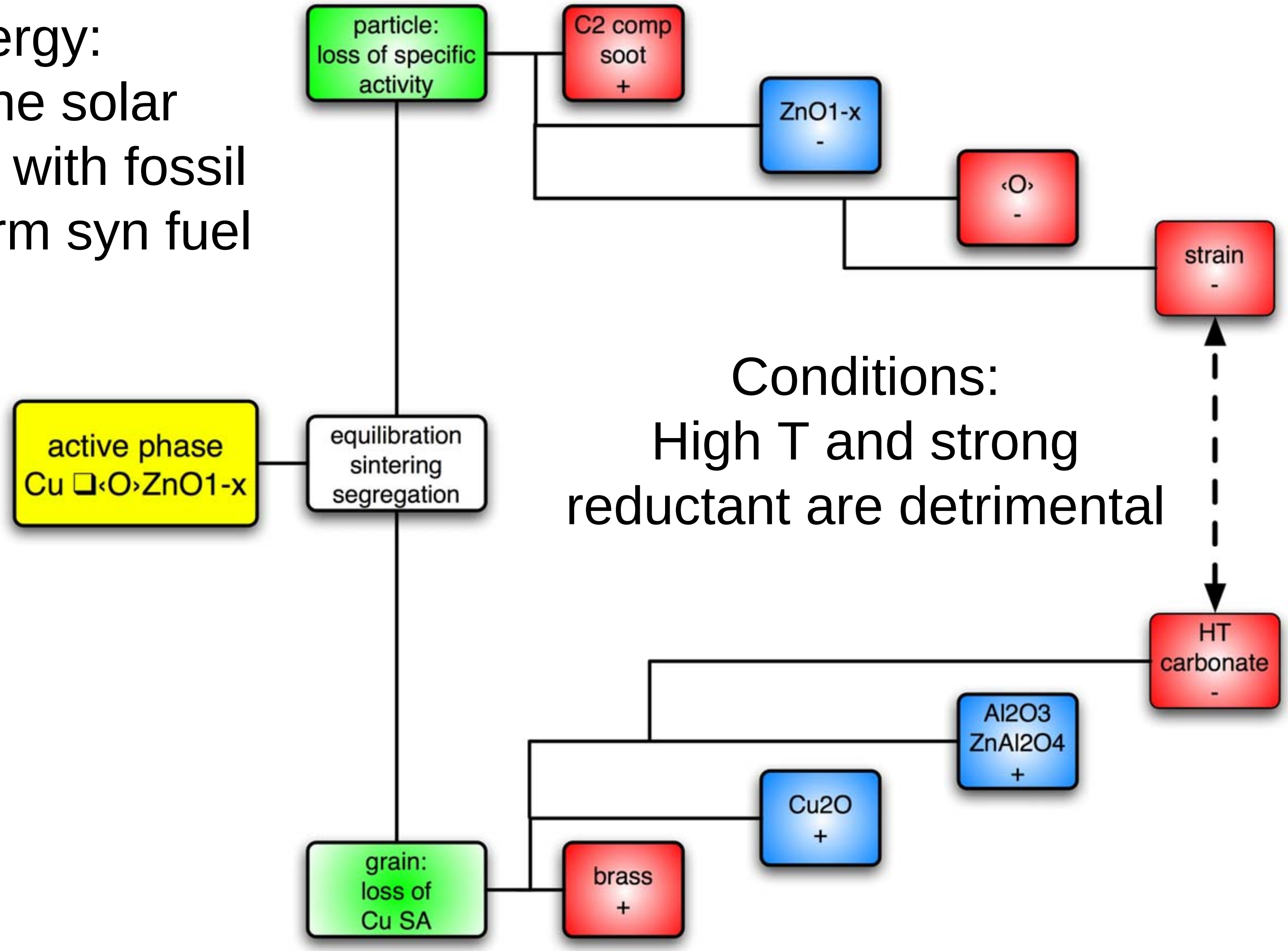
Functional stability: a system

Energy: combine solar hydrogen with fossil CO_2 to form syn fuel



What we achieved

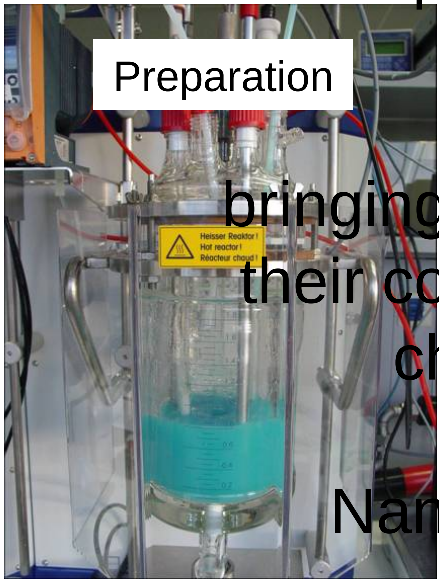
Phenomenologically:

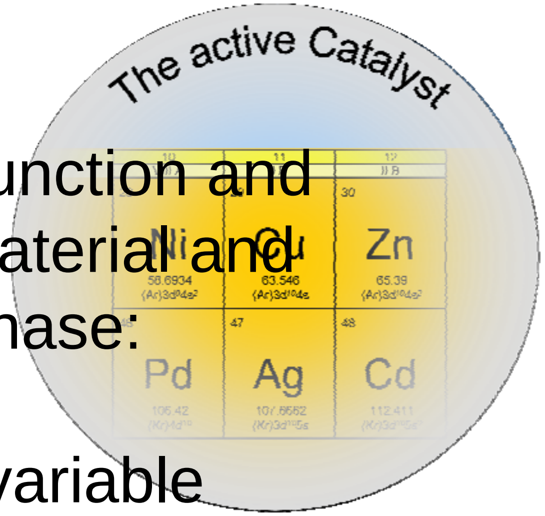
A quantitatve correlation

synthesis parameters with **material's properties** and with **catalytic properties**

Scientifically:

A deep understanding of the critical function of catalyst dynamics mediated by “defects” bringing about the desired complex function and their control by feedback between material and chemical potential of the gas phase:





Nanostructuring as the enabling variable

As the basis for further rational optimization of the system under different operation conditions

Controlled synthesis of phase and morphology of the catalyst precursor as the overarching critical step

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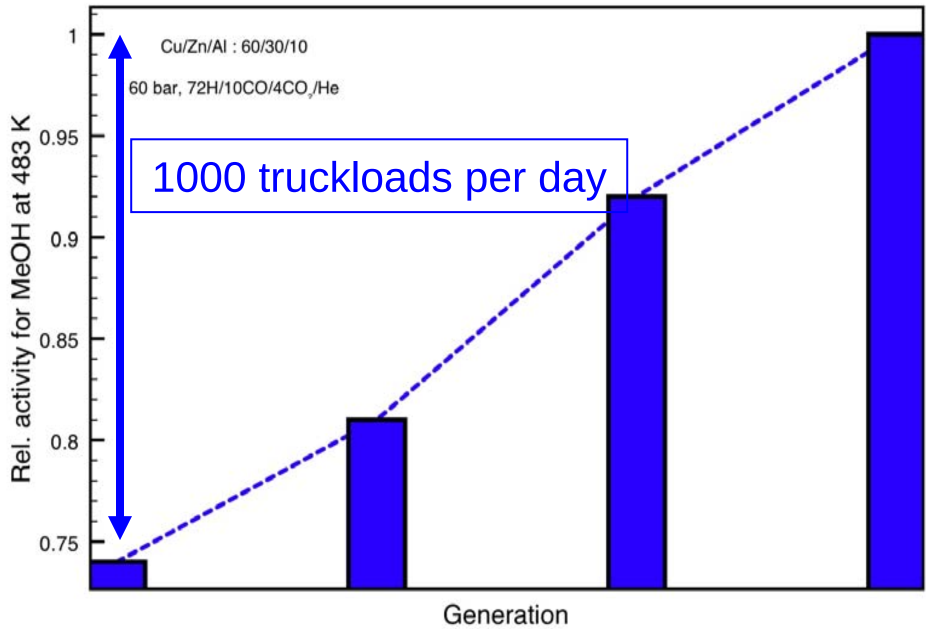
From science to technology

35 Mtons/a for chemicals plus minimum same amount for synfuel



Catalyst improvement without change in composition nor improvement in “dispersion”: control of nanostructure

MeOH an intermediate for polymers and syn fuels

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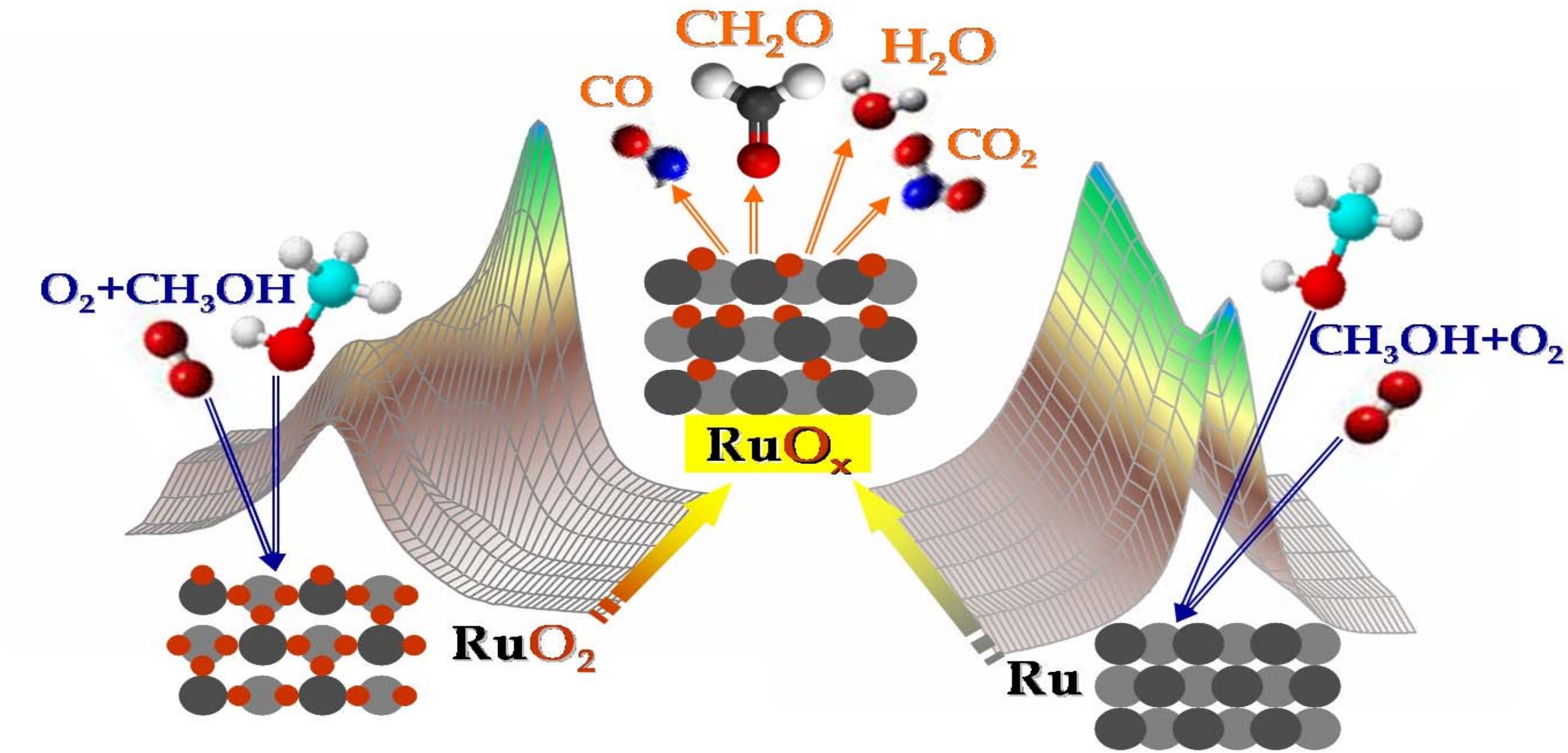
Heterogeneous catalysis has a bright future as we have with nanoscience a means to keep up with its complexity
Thank You

[redacted]

MeOH oxidation: material dynamics



Ru3d: metallic "TSO" for both pre-catalysts at reaction conditions:
Selectivity controlled by electrophilicity of O ad

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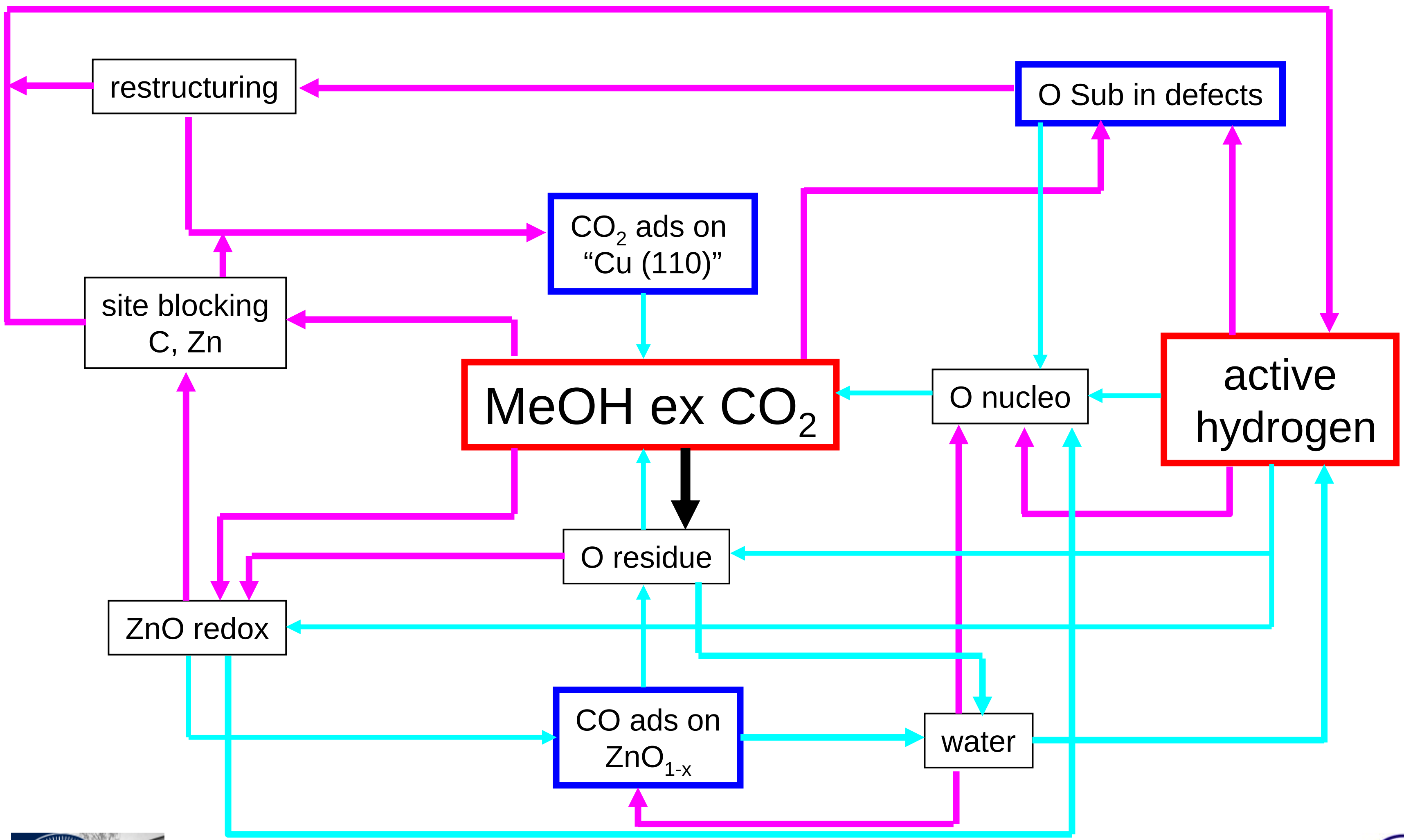
Dynamics and complexity



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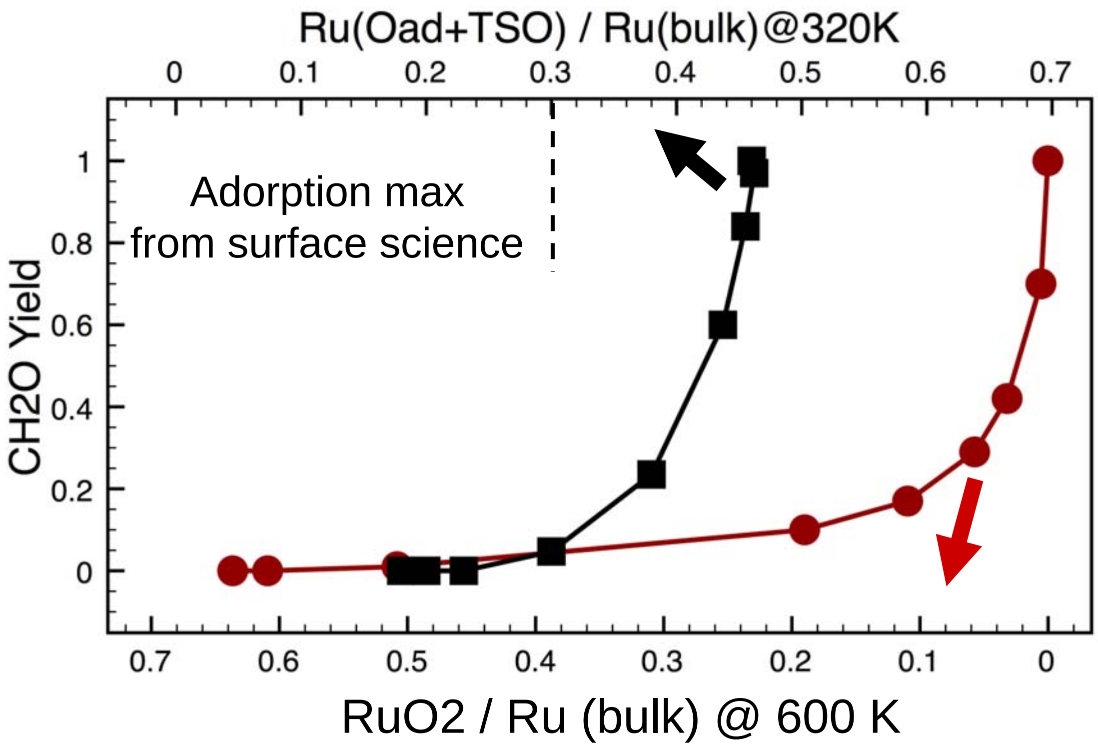
Structure-function relation with Ru: MeOH oxidation

Accumulation of Ru(TSO)

metallic pre-catalyst
p_{CH3OH} / p_{O2}=1.5



Reduction of oxide phase

Correlation between the formation of RuO_x transient surface oxide (TSO) and CH_2O production

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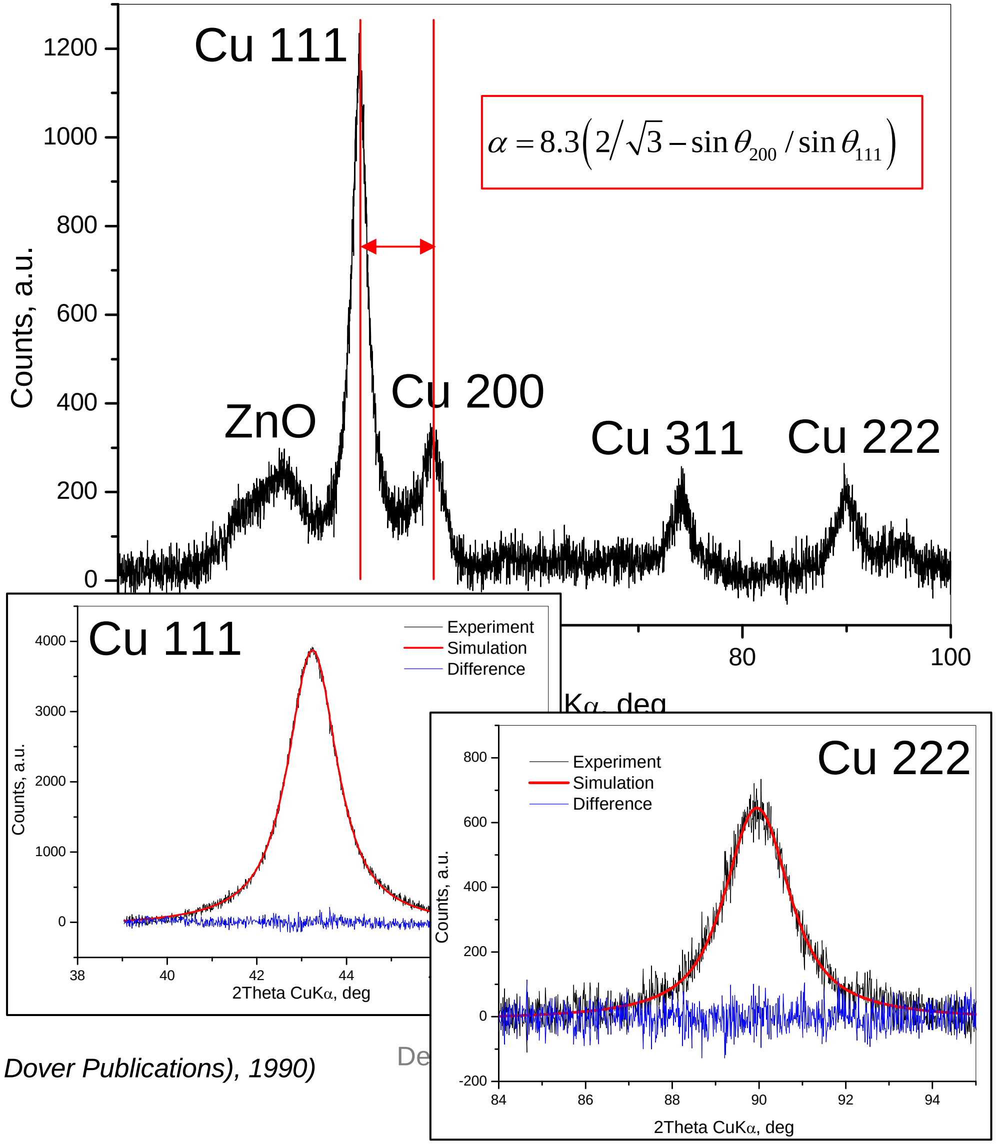
Information available from XRD

- Crystalline phases:
  fcc-Cu, (ZnO)
- Cu lattice constant

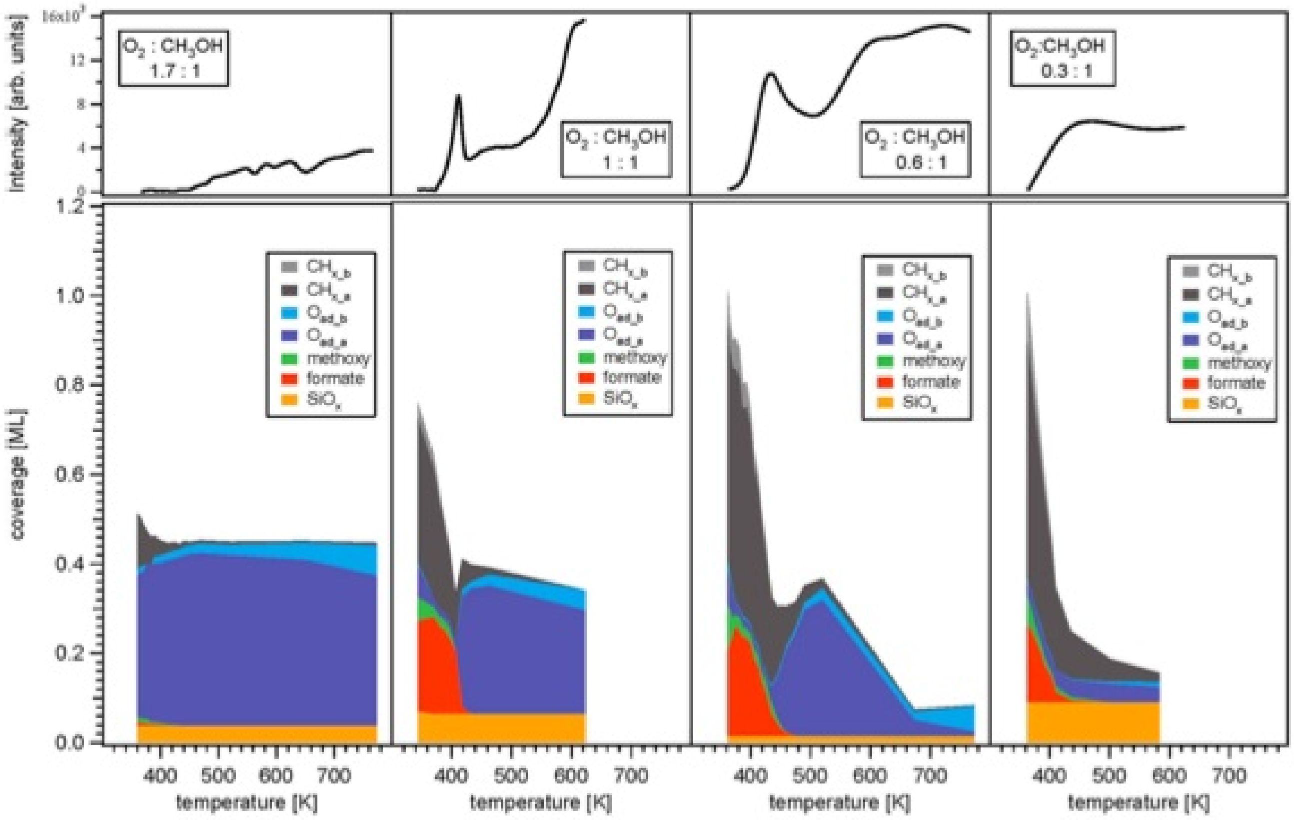
  1% above bulk value of 3.615 Å
- Line profile analysis of XRD patterns
  - determination of XRD domain size D
  - determination of Cu lattice strain (±10%)
  - determination of stacking fault density α

$$1.5\alpha + \beta = \frac{a\left(1/D_{200} - 1/D_{111}\right)}{1 - \sqrt{3}/2}$$



(Warren, B.E., X-ray Diffraction (New York: Dover Publications), 1990)

Nucleophilic oxygen on Cu (110)



S. Günther et al, J.Phys. Chem. 2006

Oxide and nucleophilic oxygen can co-exist even in large excess of MeOH in amounts of below 0.1 ML (10^{-5} mbar oxygen)

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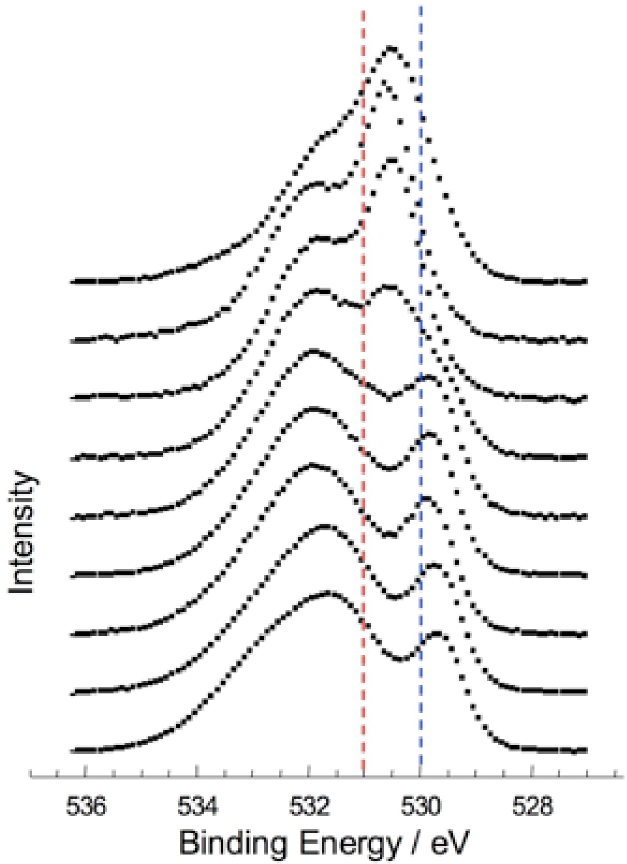
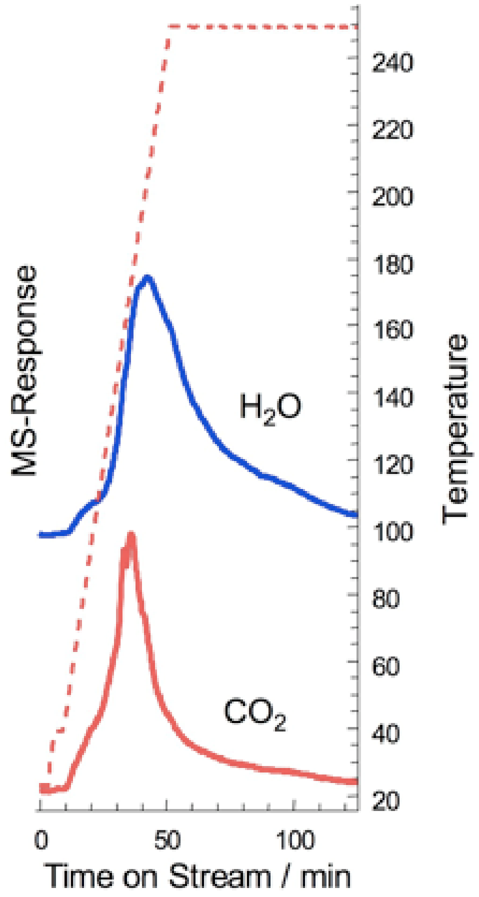
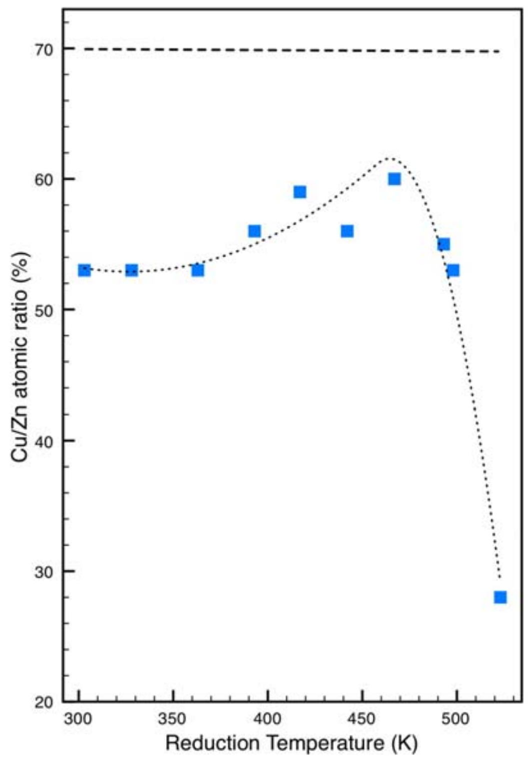
Cu-ZnO dynamics







Cu-Zn neighbouring sites likely to exist

Disperse ZnO_{1-x} on Cu metal

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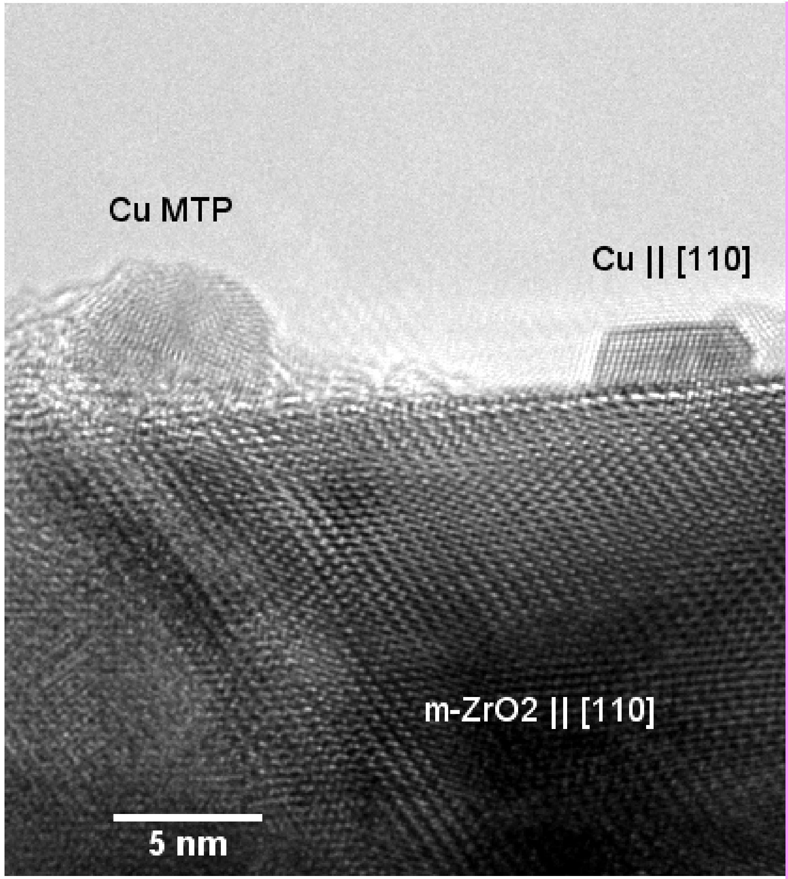
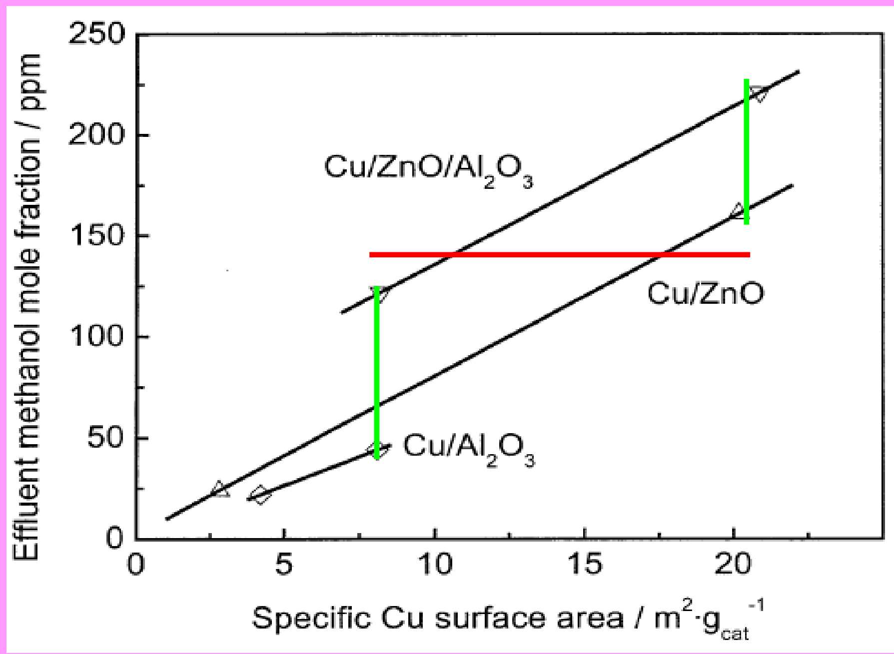
The active particle

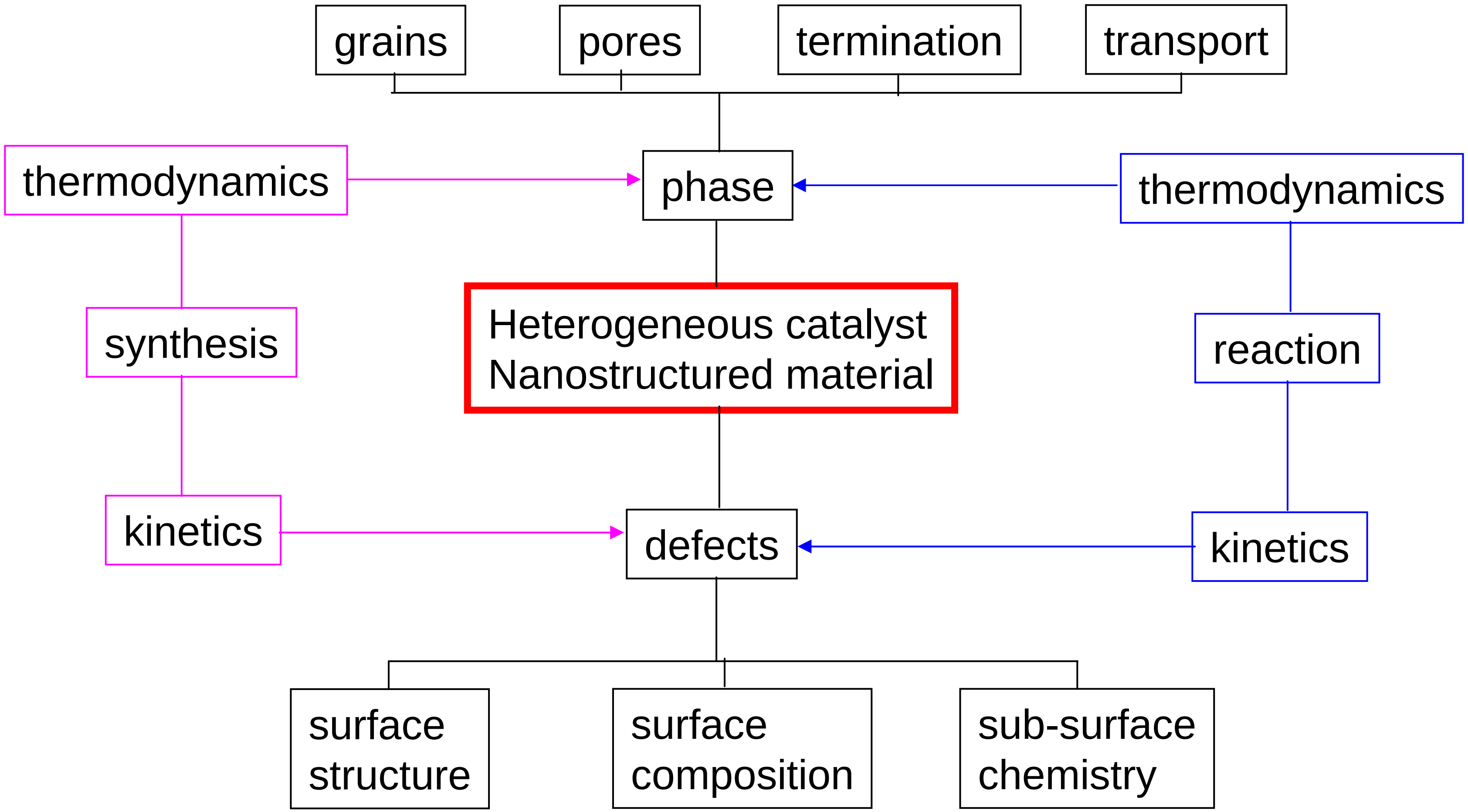




Hinrichsen, et al., Catal.Lett., 86 (2003) 77
Waugh, Catal.Lett. 58 (1999) 163.

On supports: two types of “regular” particles and MTP: beam damage is detectable

In situ functional analysis



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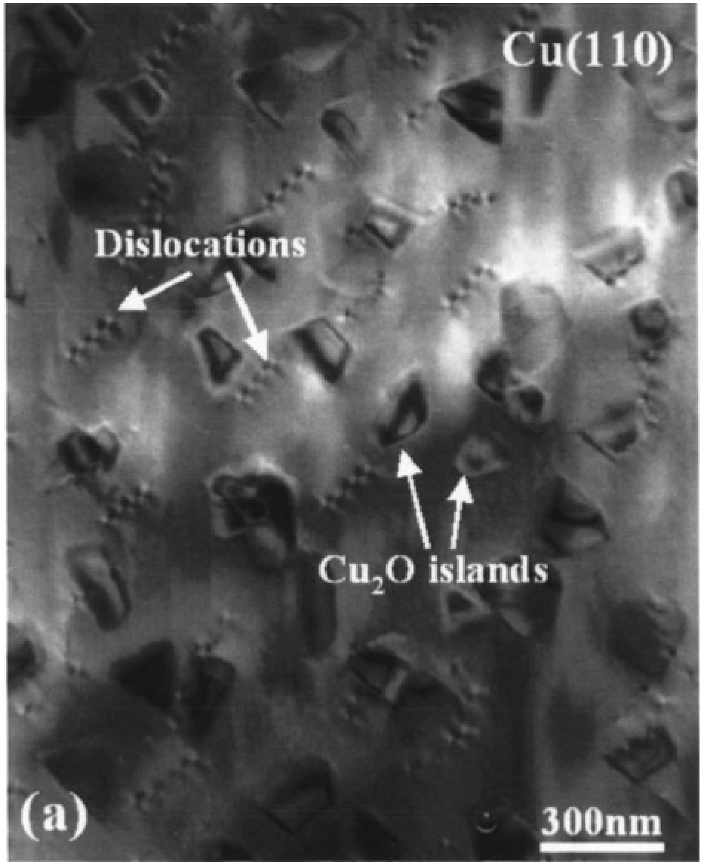
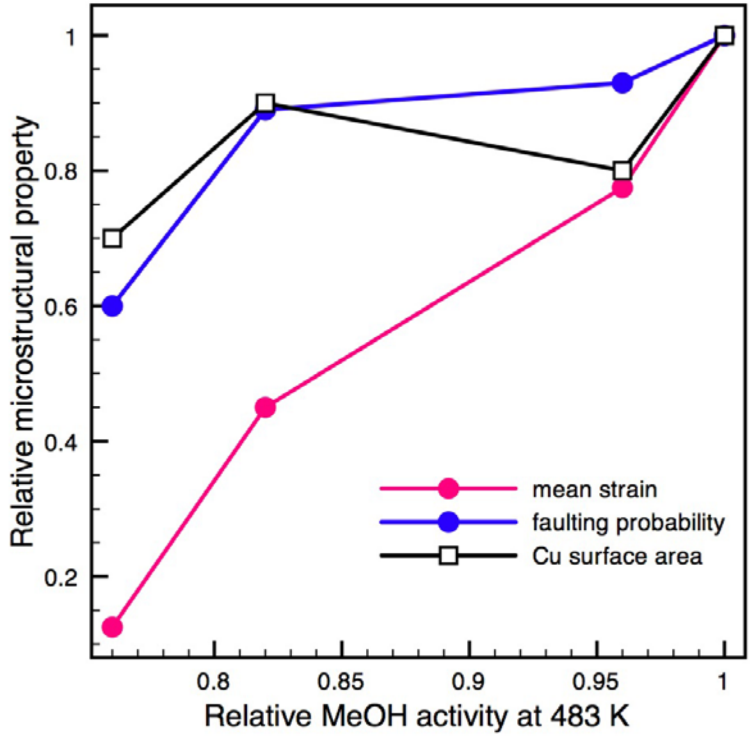
Microstructure of Cu



Active oxygen located at strained sites

Zhuo et al, J. Appl. Phys, 2006



Specific Cu area is only a weak proxy for active sites: XRD-derived parameters are closer: defects are relevant

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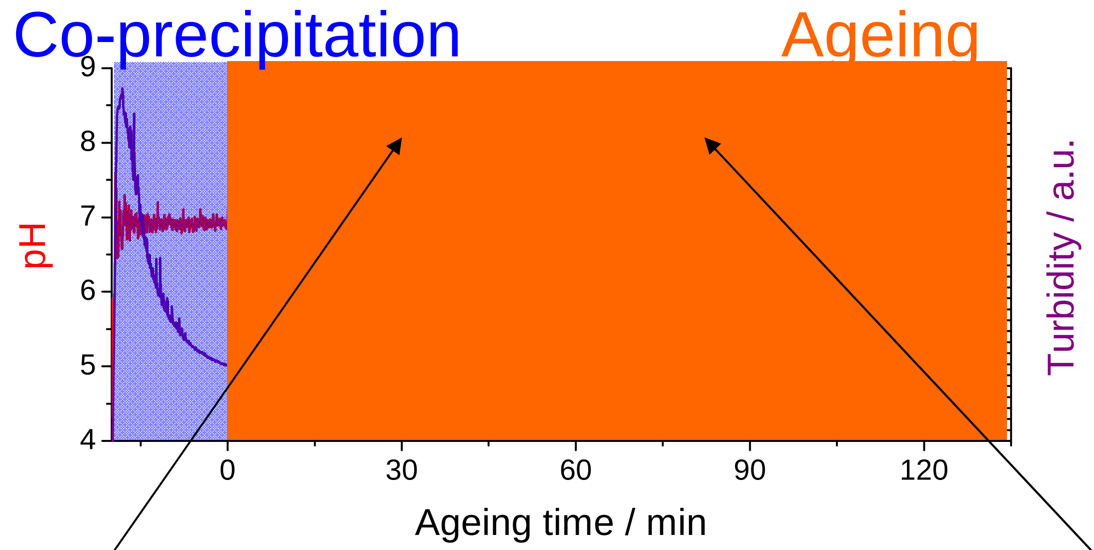
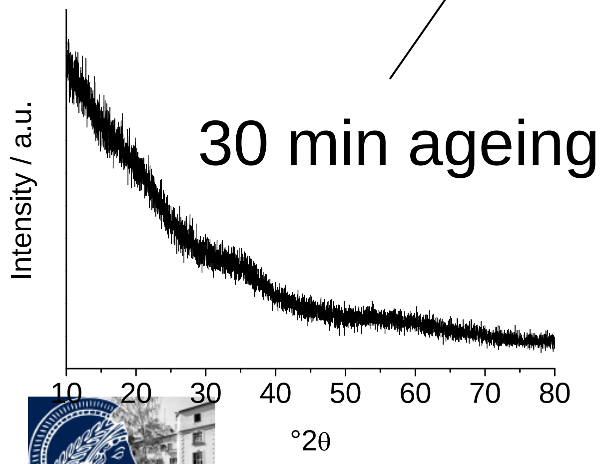
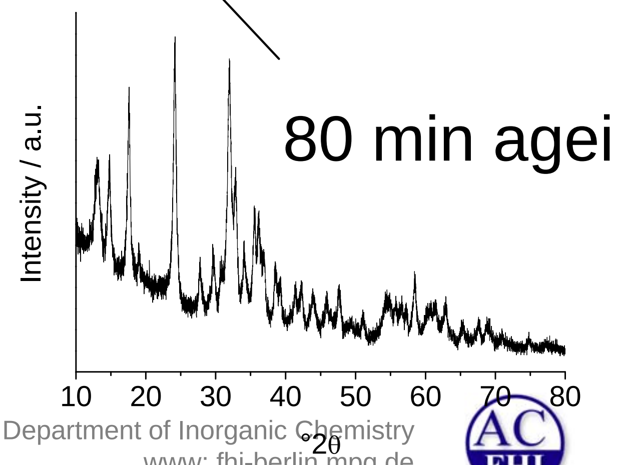
Phase formation during ageing







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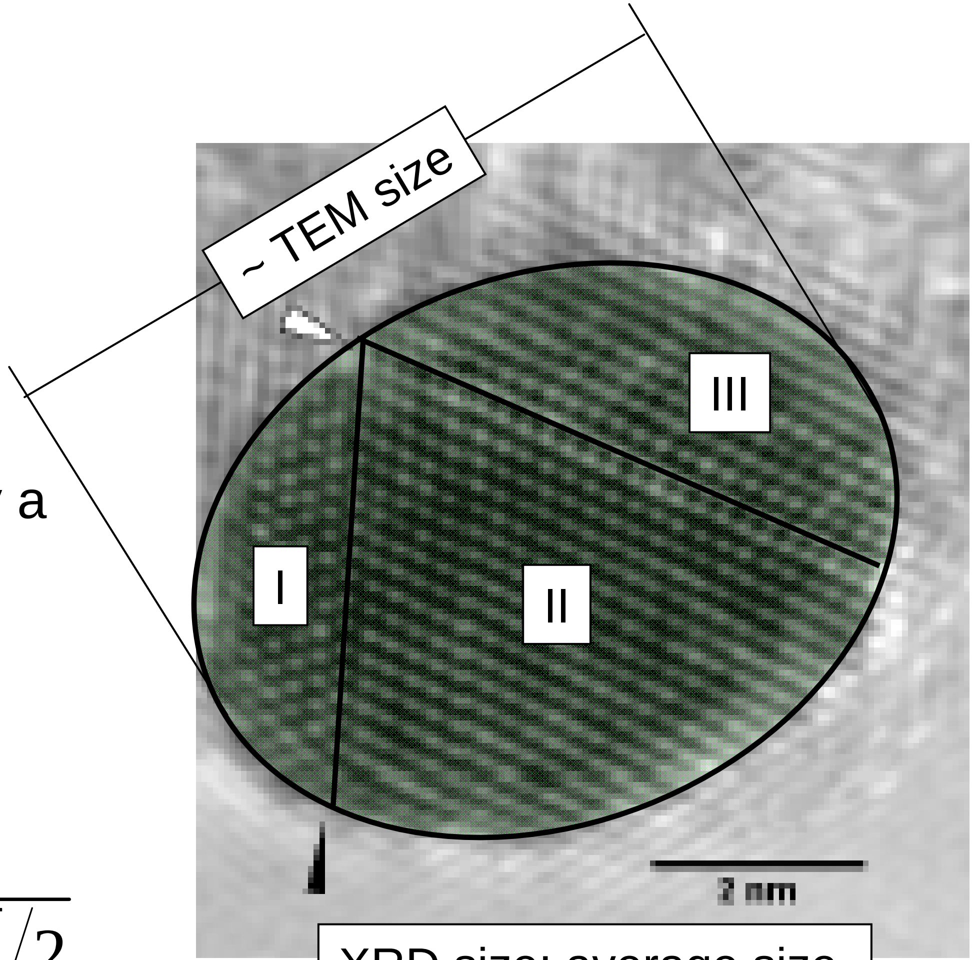
Merging XRD and TEM data

- Assumptions
  - spherical particles
  - XRD domain size < TEM particle size due to planar defects
- Determination of overall faulting probability $1.5\alpha+\beta$ by a combined XRD / TEM approach

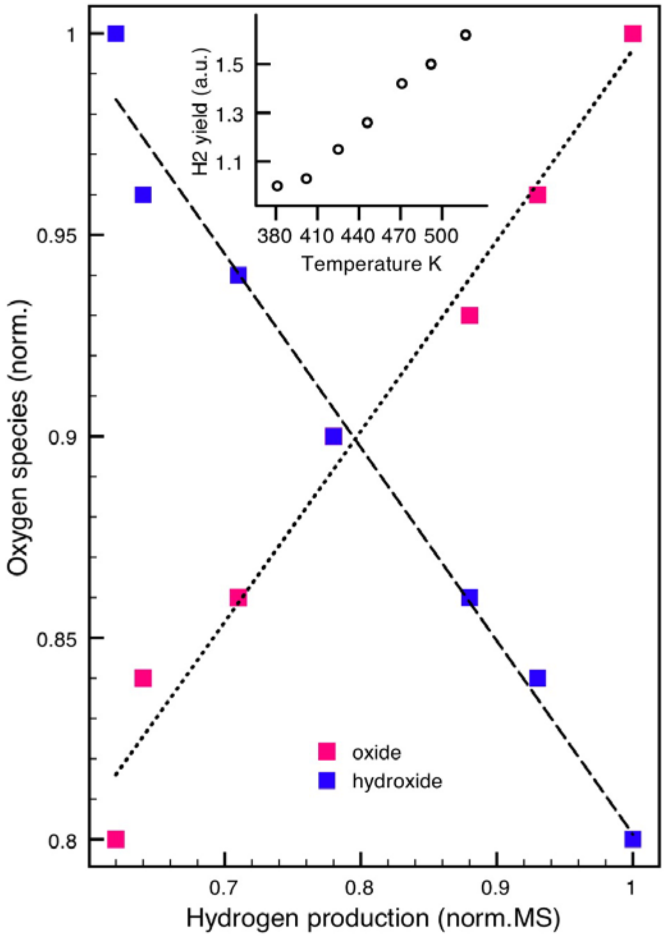


XRD size: average size of volumes I, II & III

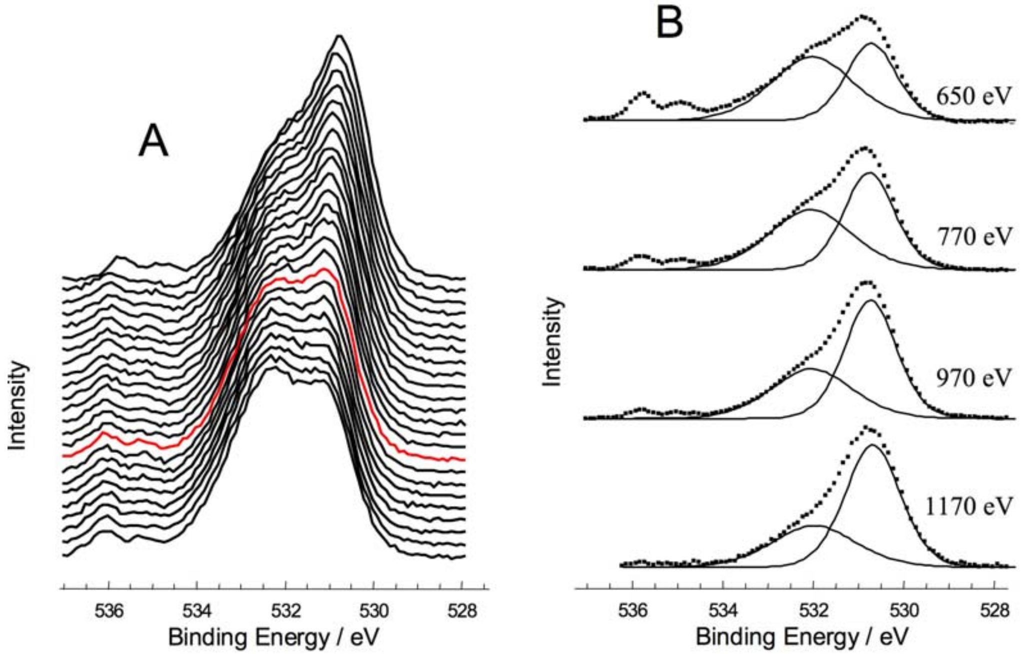
$$D = \frac{a \cdot D_{111}}{a - (1.5\alpha + \beta) D_{111} \sqrt{3}/2}$$

(Kasatkin, I., et al. Angew. Chem. 119, 2007, 7465)

MSR: in situ observation



Despite the presence of water in the feed, any stationary coverage of its chemisorbed state is detrimental for the activity



Nucleophilic oxygen is quite consitent with the BE of the surface - located high energy shoulder

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