Wie kontrollieren die Volumeneigenschaften eines Festkörpers seine Oberflächenreaktionen?

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Acknowledgements

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unicat Unifying Concepts in Catalysis

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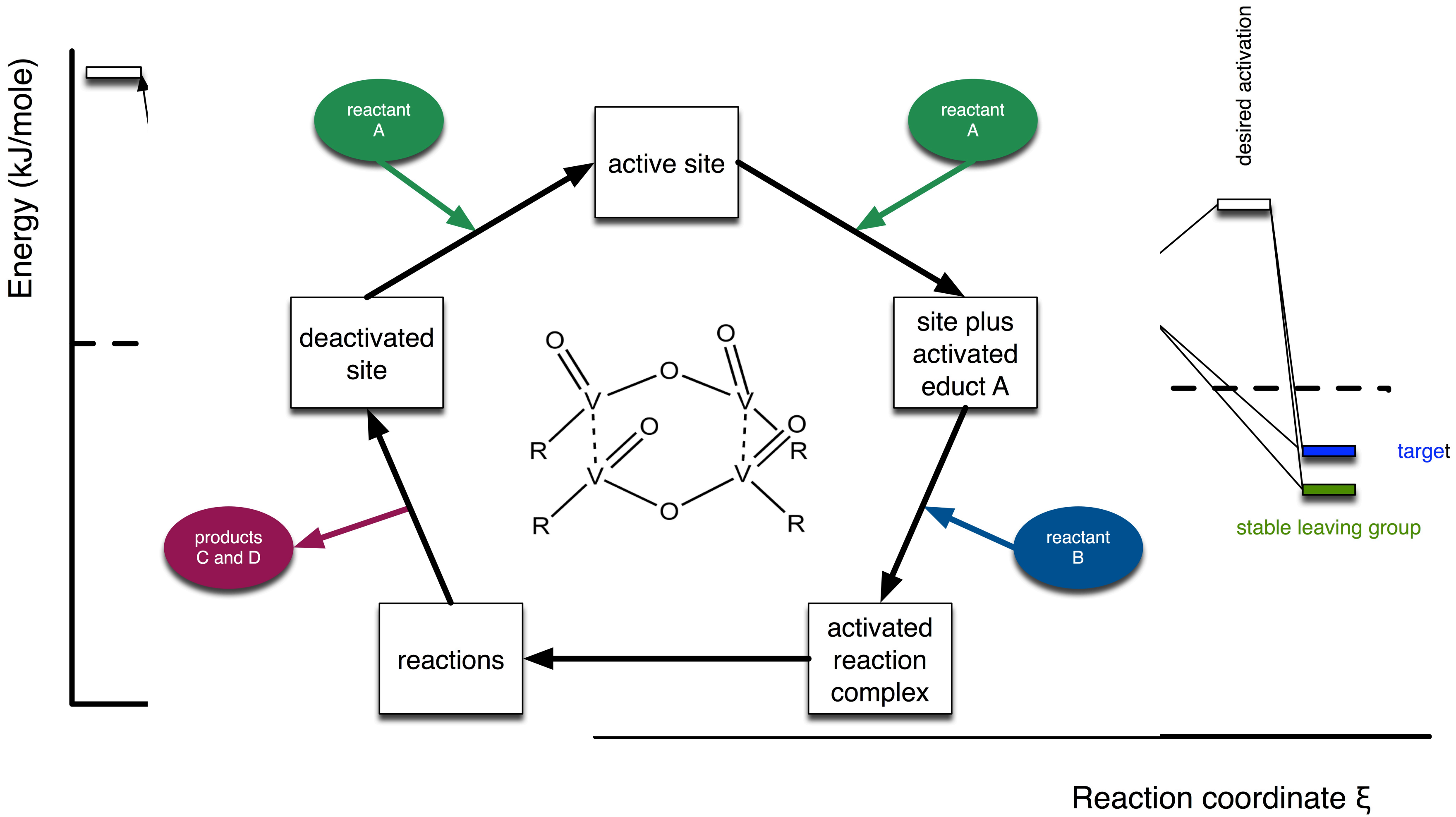
Fundamentals



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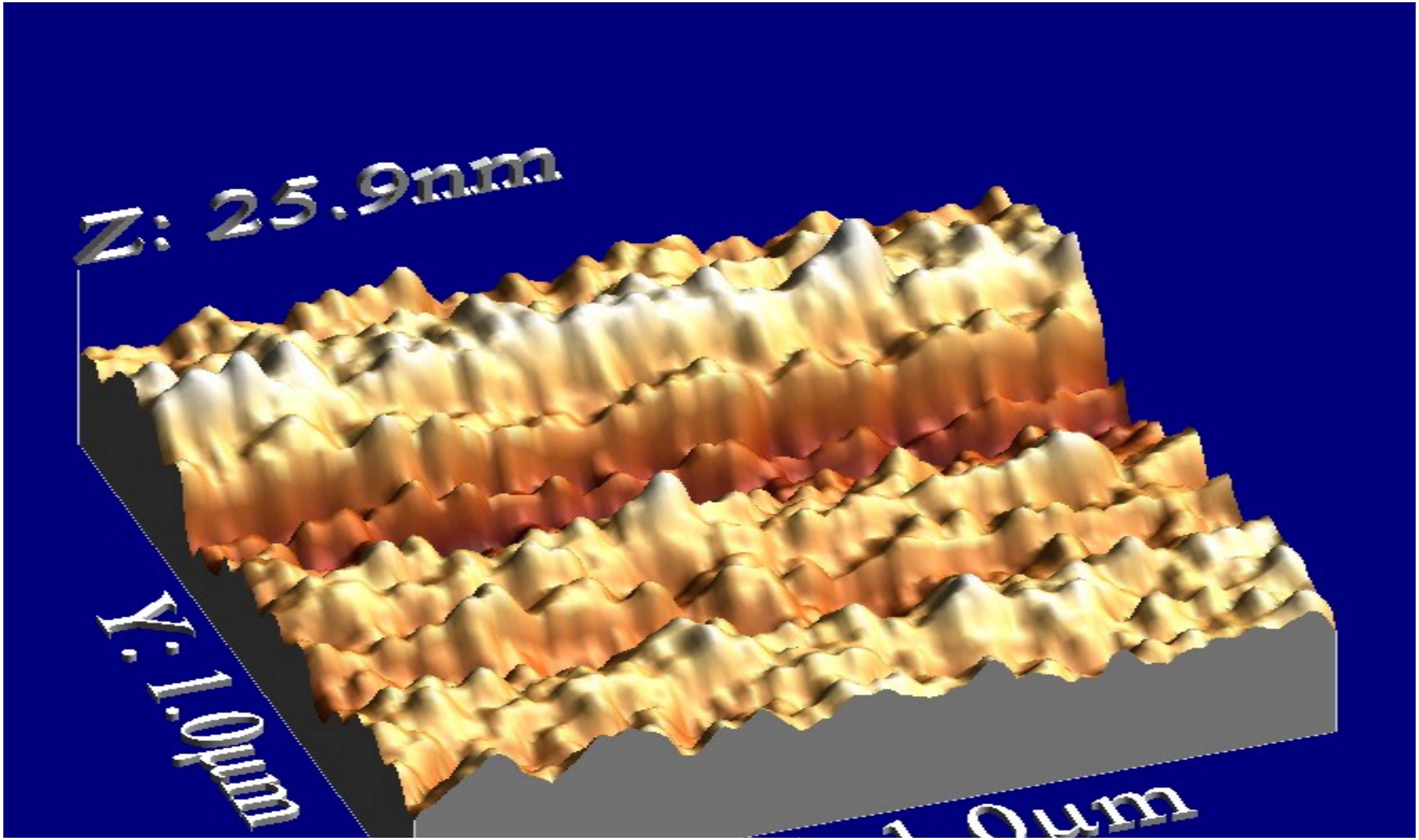
The standard model of heterogeneous catalysis deep understanding, limited function



What has the bulk of a catalyst to do with active sites?: Structure!

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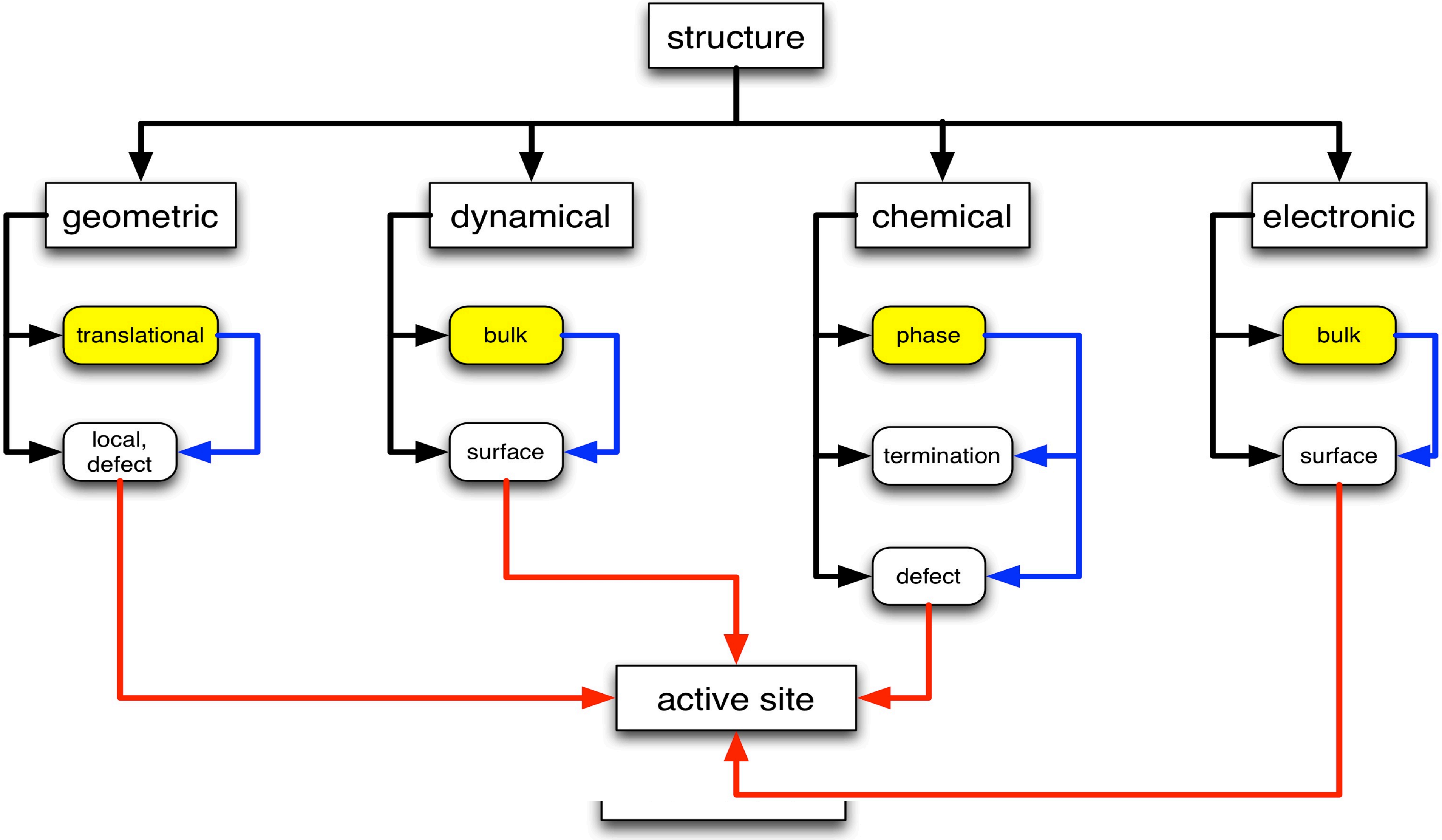
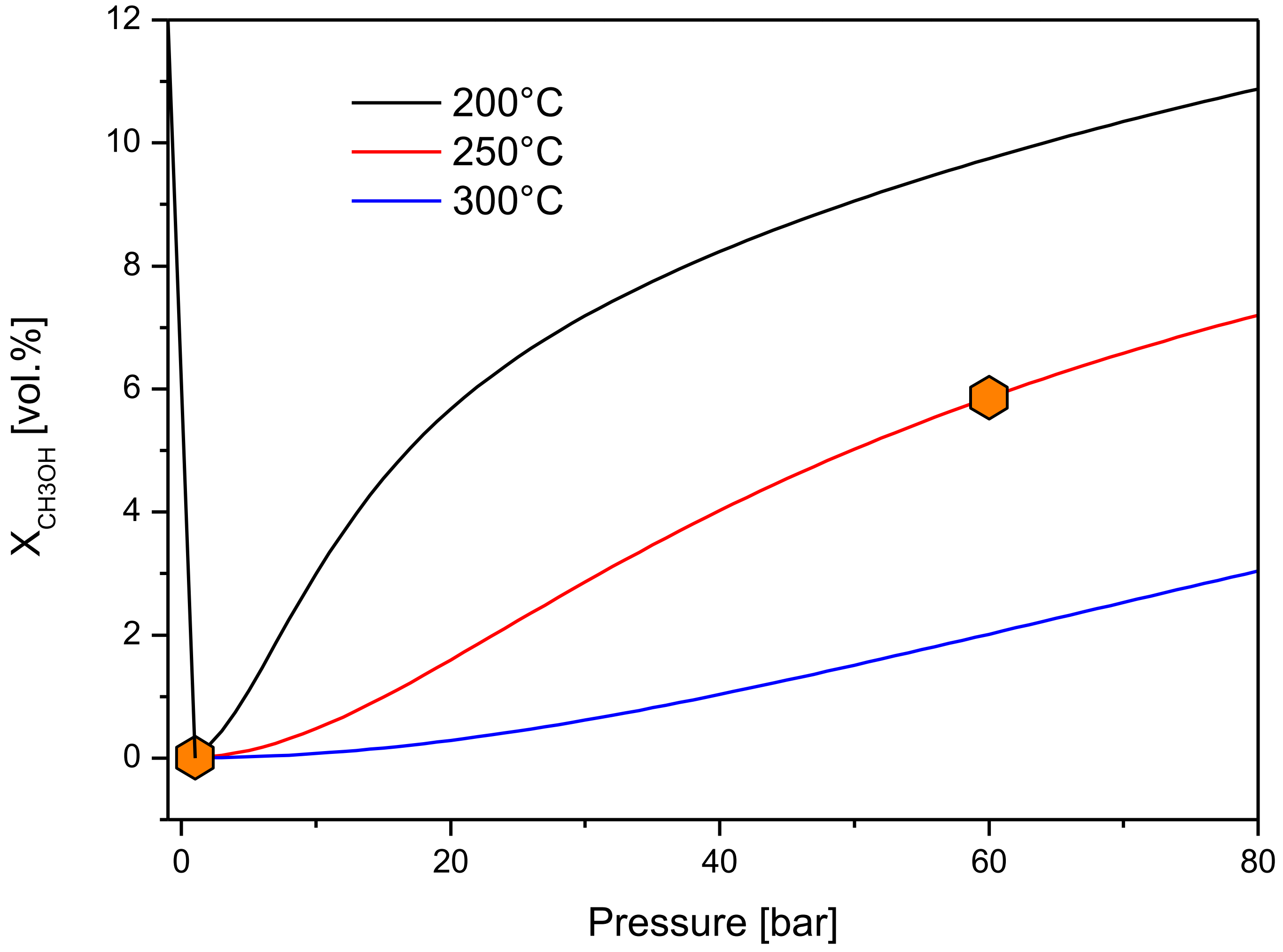
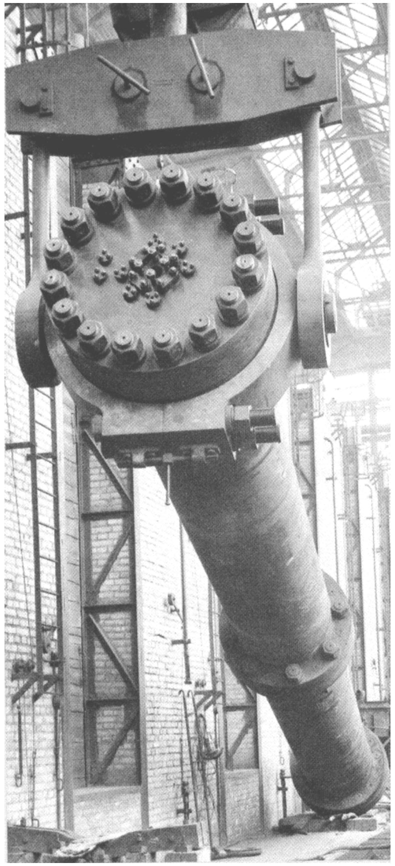


The easy solution: models ?





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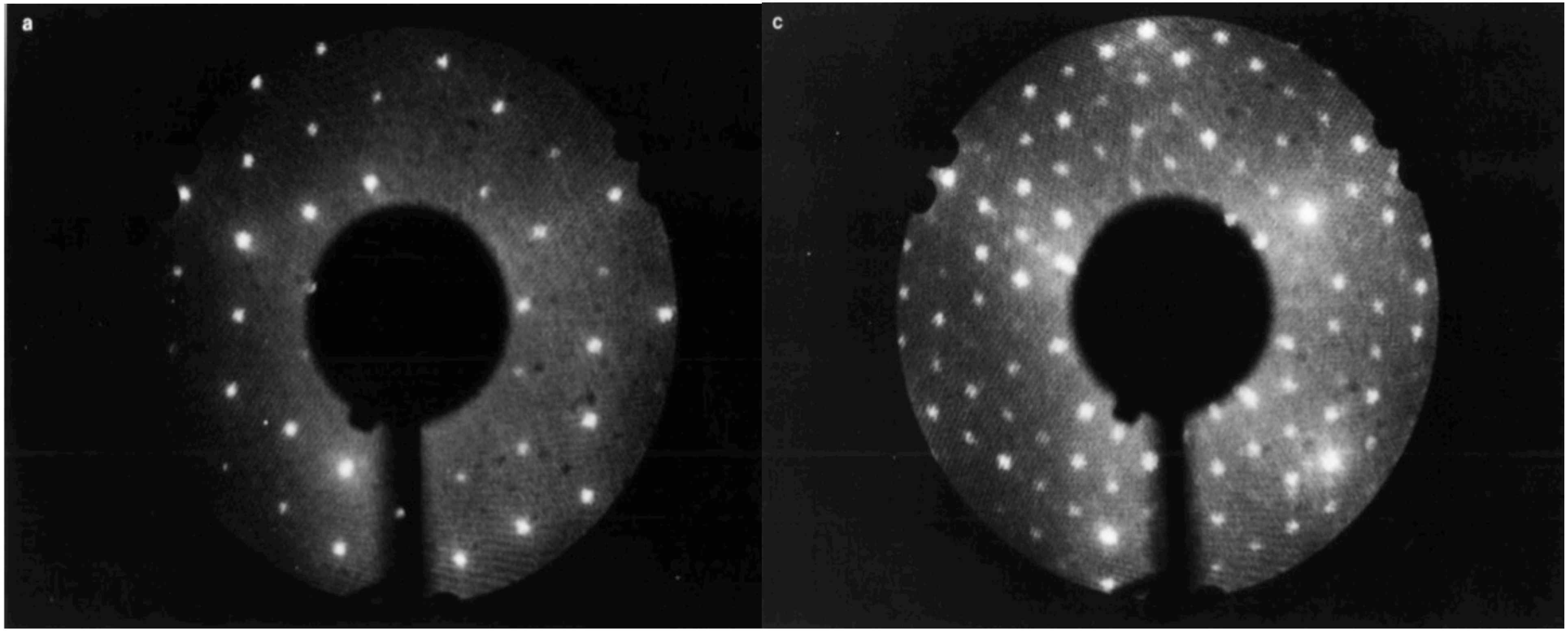
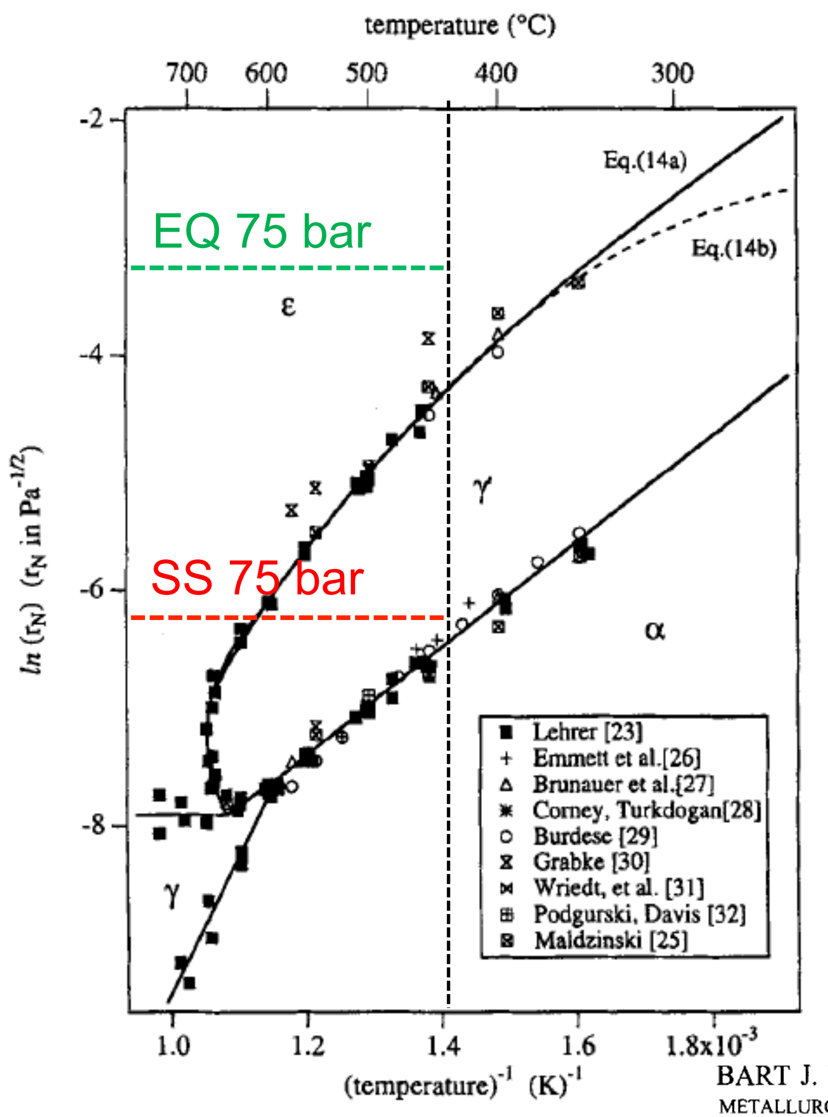
Ammonia synthesis

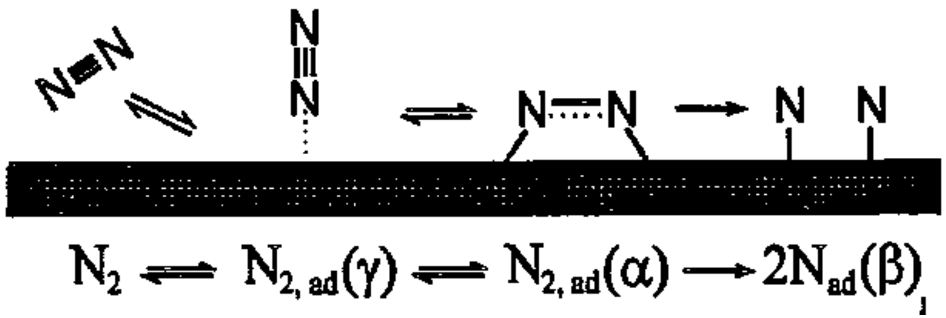


Ib Chorkkendorf et al. (Surf. Sci. 2004) Fe (111) at low and high nitrogen pressure: strong reconstruction at 50 mbar: structure at real pressure still unknown: nitrogen surface chemisorption not strongly affected thus data of Ertl et al. grossly correct: kinetics strongly different.

Nitrides:
origin of active sites (steps)?



BART J. KOOI
METALLURGICAL AND MATERIALS TRANSACTIONS A

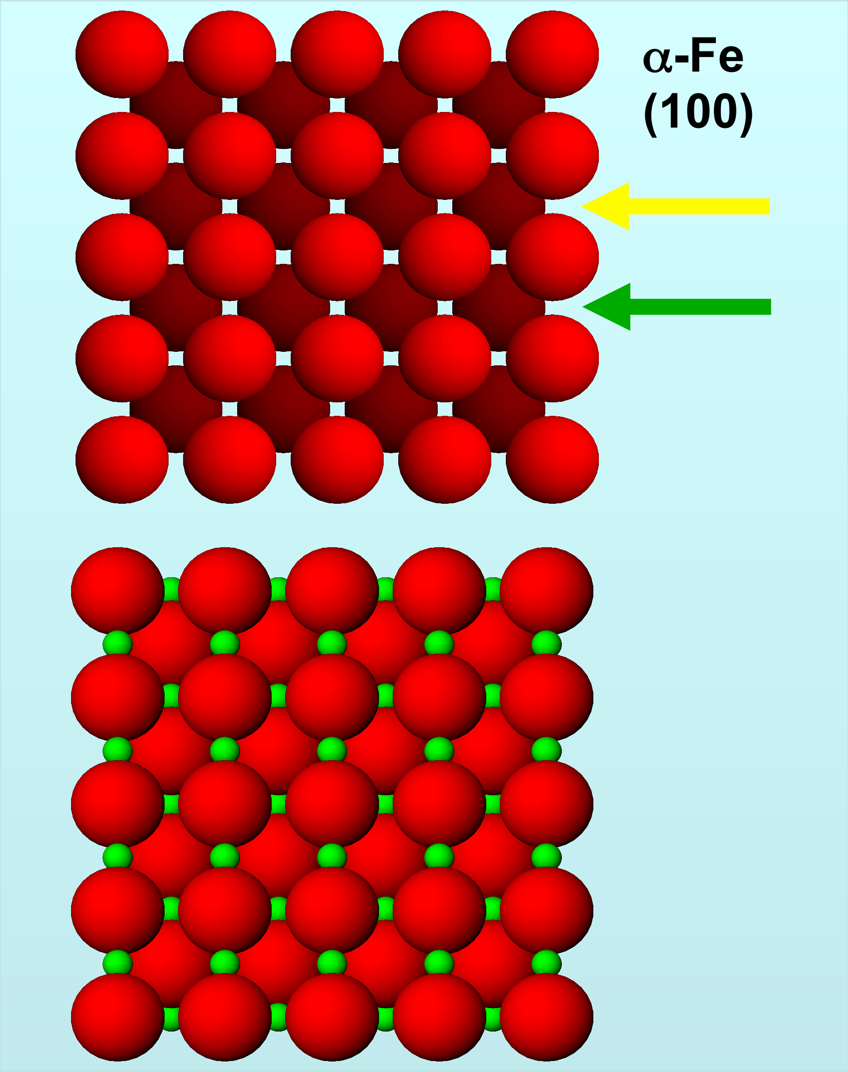


Ever since the ammonia synthesis was discovered it was postulated and rejected that nitrides should play a role:

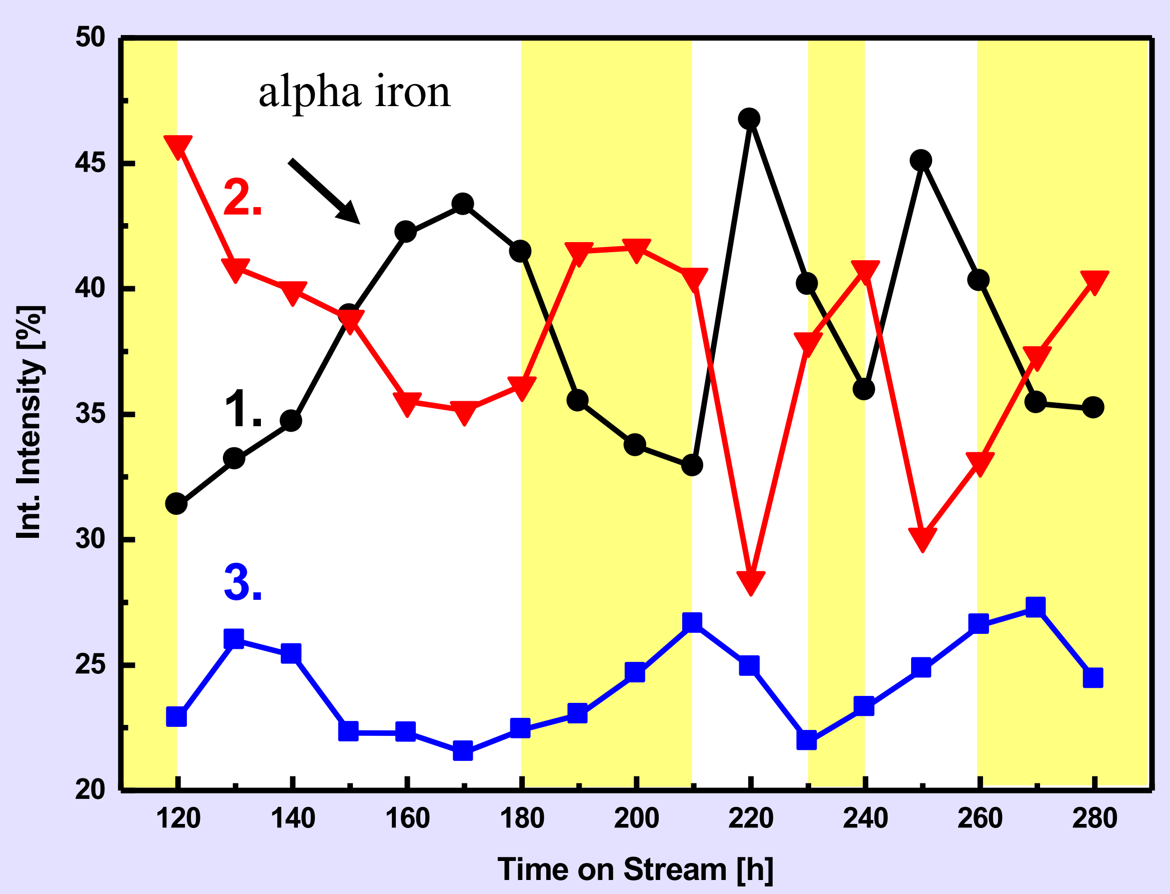
Iron hardening by nitridation is a well-known fact:

At what chemical potential (virtual pressure)?

A veritable phase problem.


α-Fe
(100)

Early observations:
XRD is only poorly suited

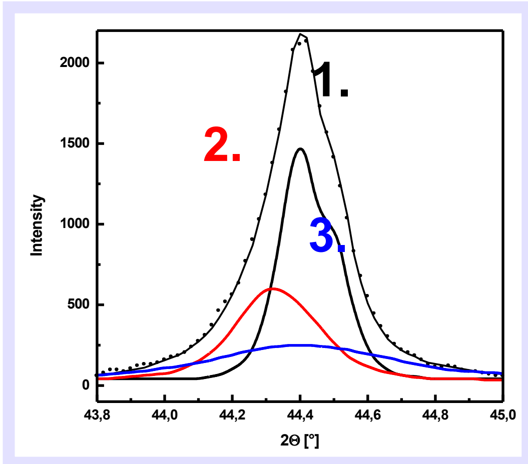


yellow: synth. mix

white: He

650 K, 1 bar pressure

in-situ XRD, integrated intensity of Fe (110)



Fe_{500} N by lattice parameter analysis

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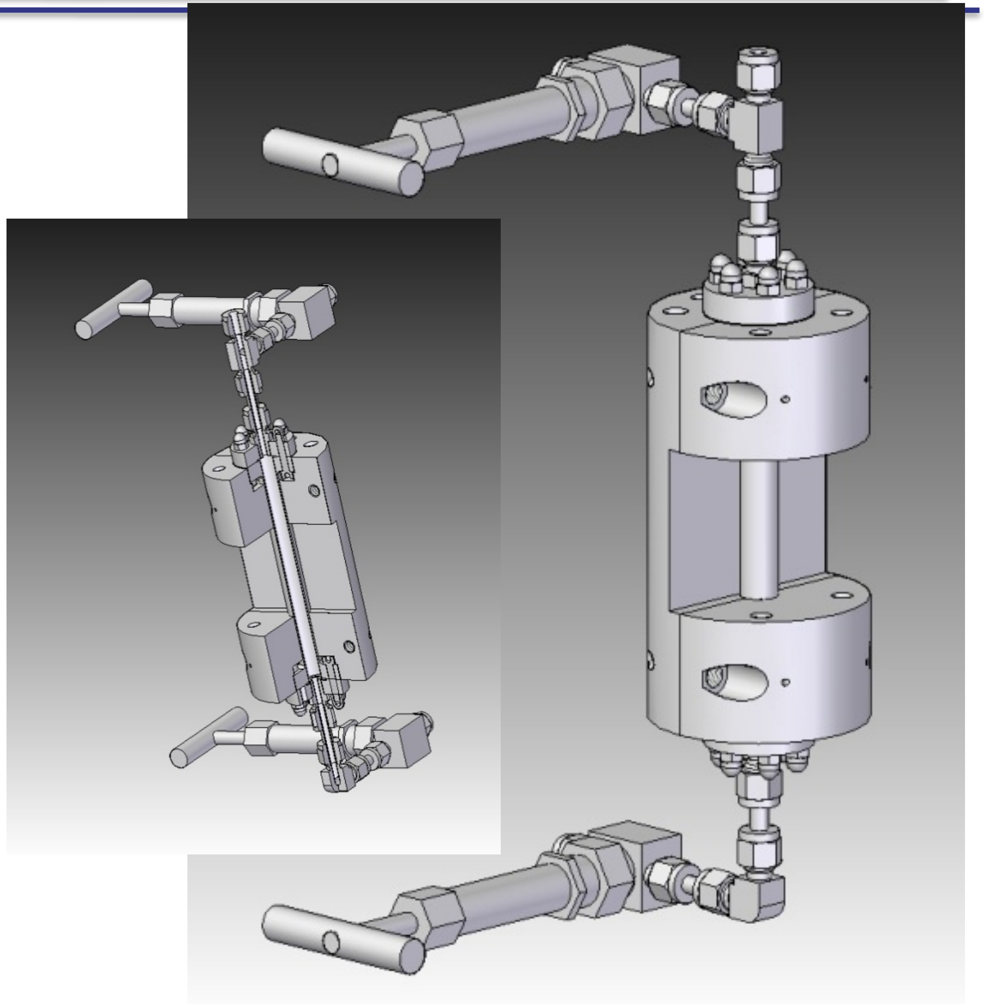
A suitable reactor: neutron diffraction in D_2 at 75 bar

- Finding an alloy which is suitable for reaction conditions, having zero-activity and neutron transmissivity
- Prior to that, Al had overlap with Fe, Swagelok leaks → Ni-based alloy, high strength, tight (also post reaction)



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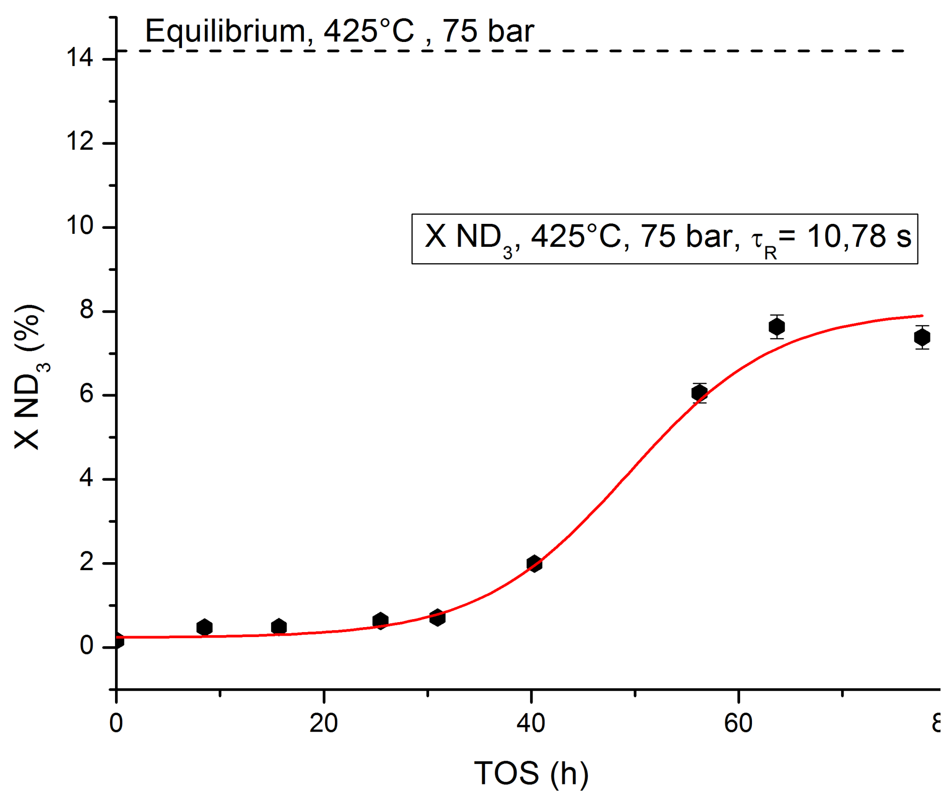
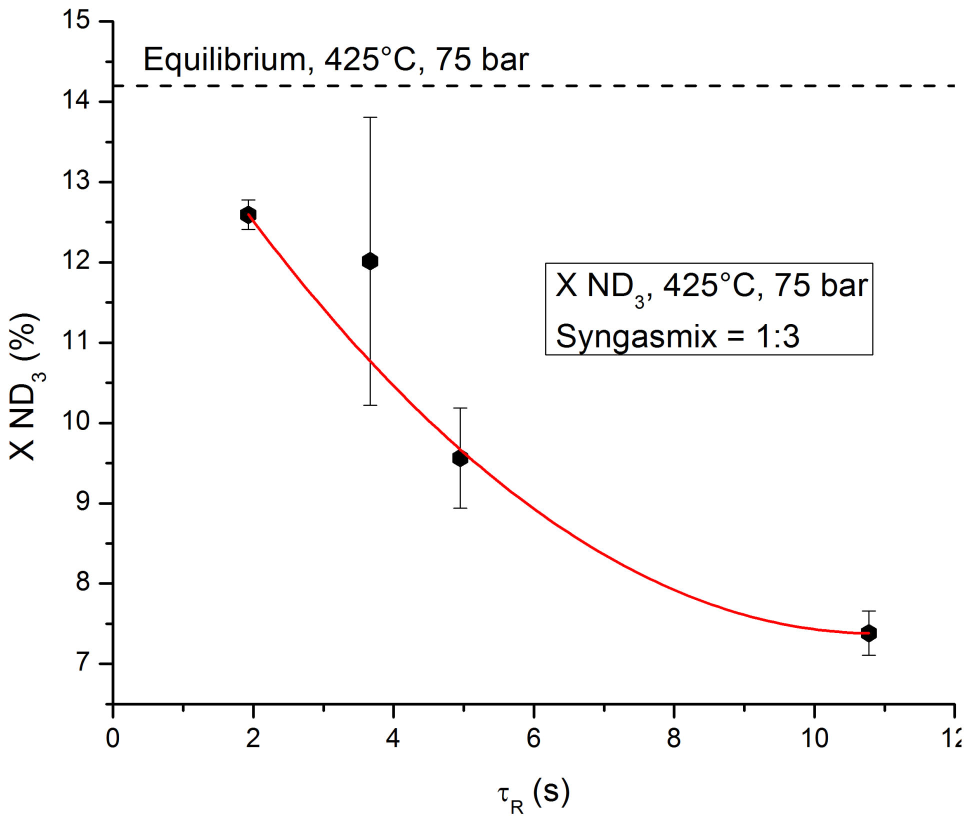
Catalytic performance in-situ

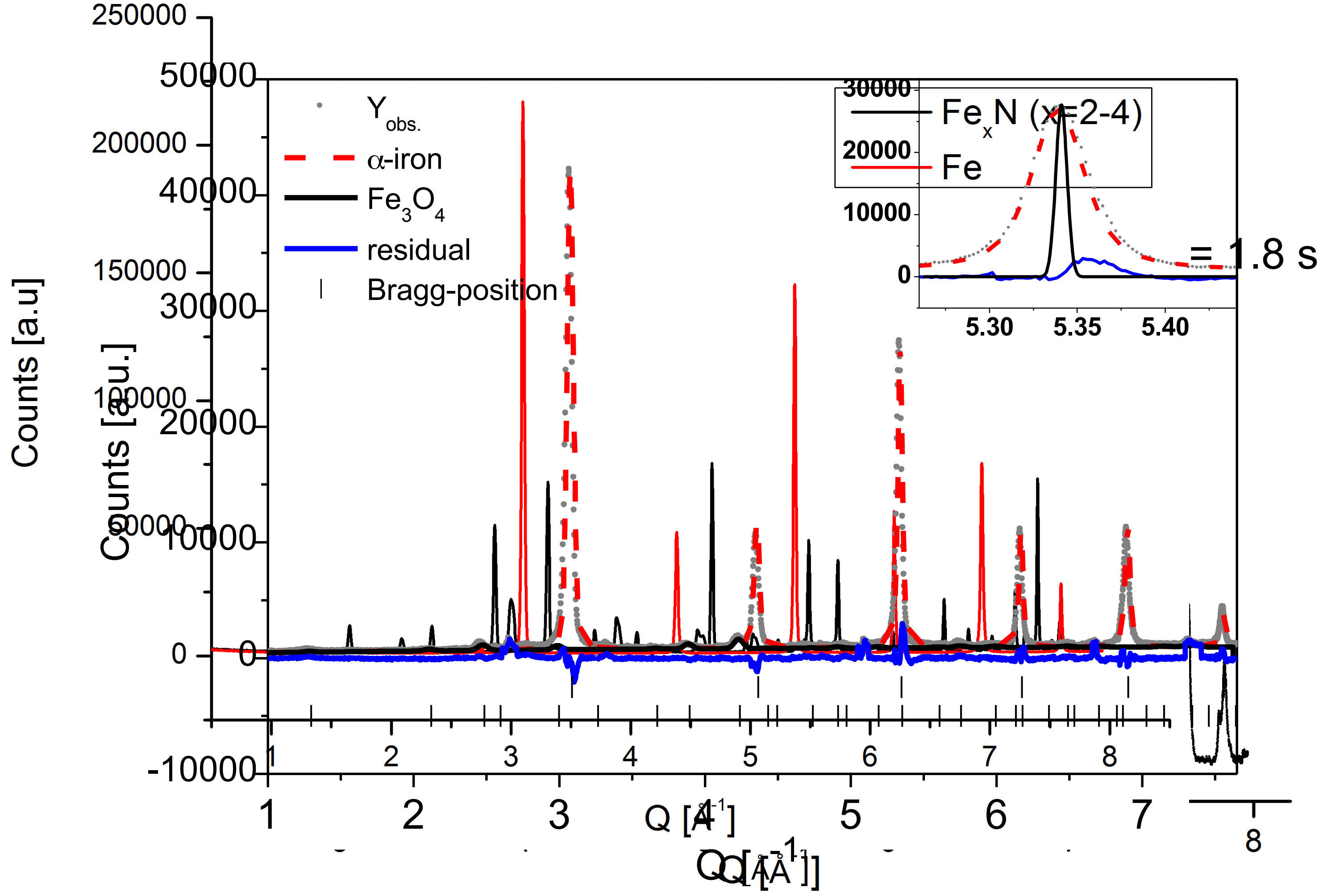
- Carefully reduced catalyst was „dried“ at 160°C and activated in D_2 Syngas from 160°C to 425°C with 0,5 Kpm

While approached steady state, increasing yield by varying flow rate from 8,5 l/h to 38 l/h





Phase analysis in situ: neither pure iron nor a nitride



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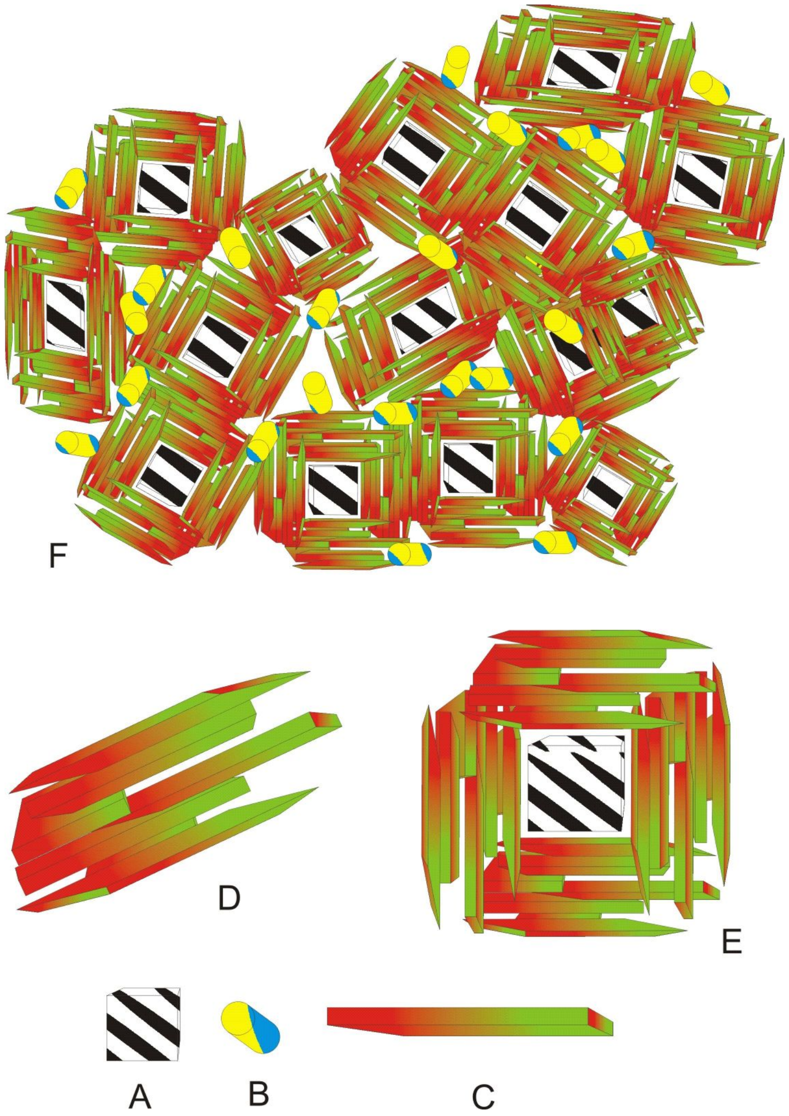
A model
awaiting quantitative confirmation



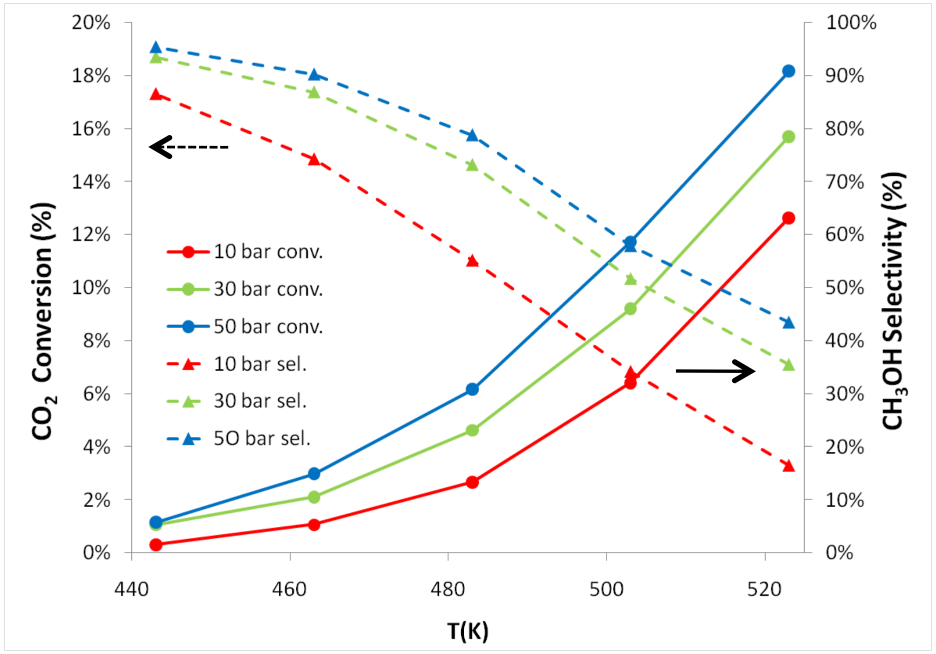
Several geometric arrangements of three “sub-phases” of alpha iron in a polycrystalline sample

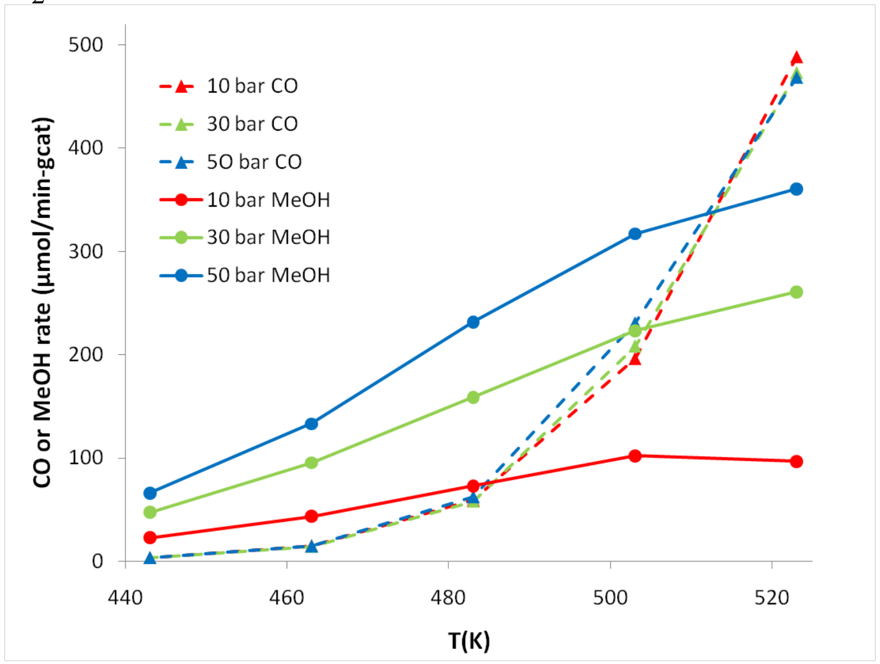
(paracrystal?)

Methanol synthesis: Kinetic observations

$$CO_2 + 3H_2 \longrightarrow CH_3OH + H_2O$$

$$CO_2 + H_2 \longrightarrow CO + H_2O$$





Pressure and Temperature Studies with 200 mg NGM std. Catalyst 20 µm powder
(a representative malachite-derived catalyst) 100 ml/min $CO_2/H_2/Ar$ (3:9:1) in 10 mm OD reactor

The CO shift chemistry is faster than the MeOH synthesis

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Catalyst synthesis

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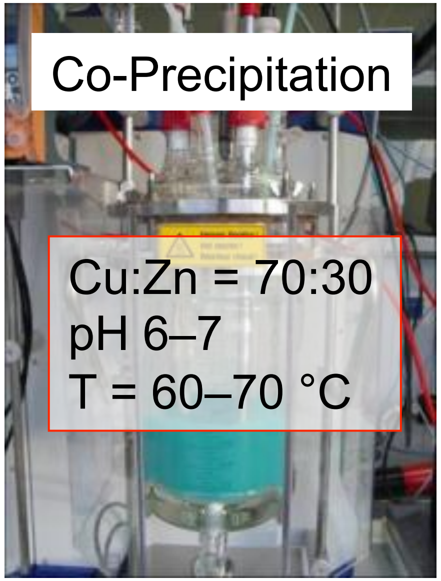
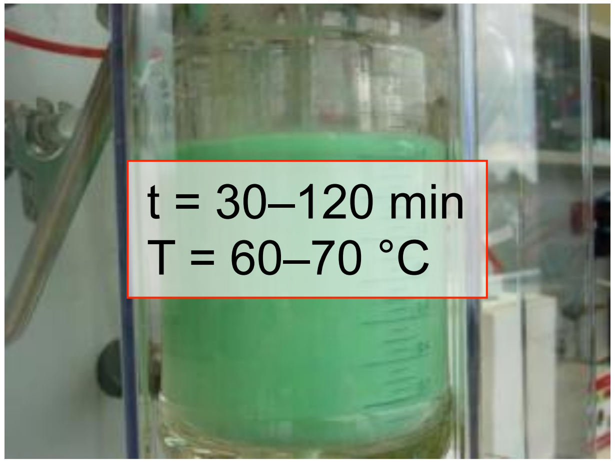
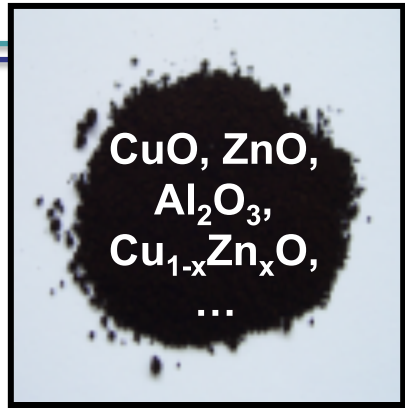


Ageing

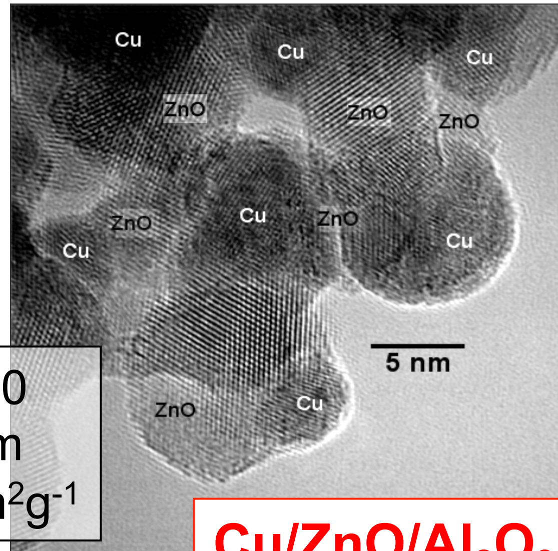


Washing
Drying

Calcination



Reduction

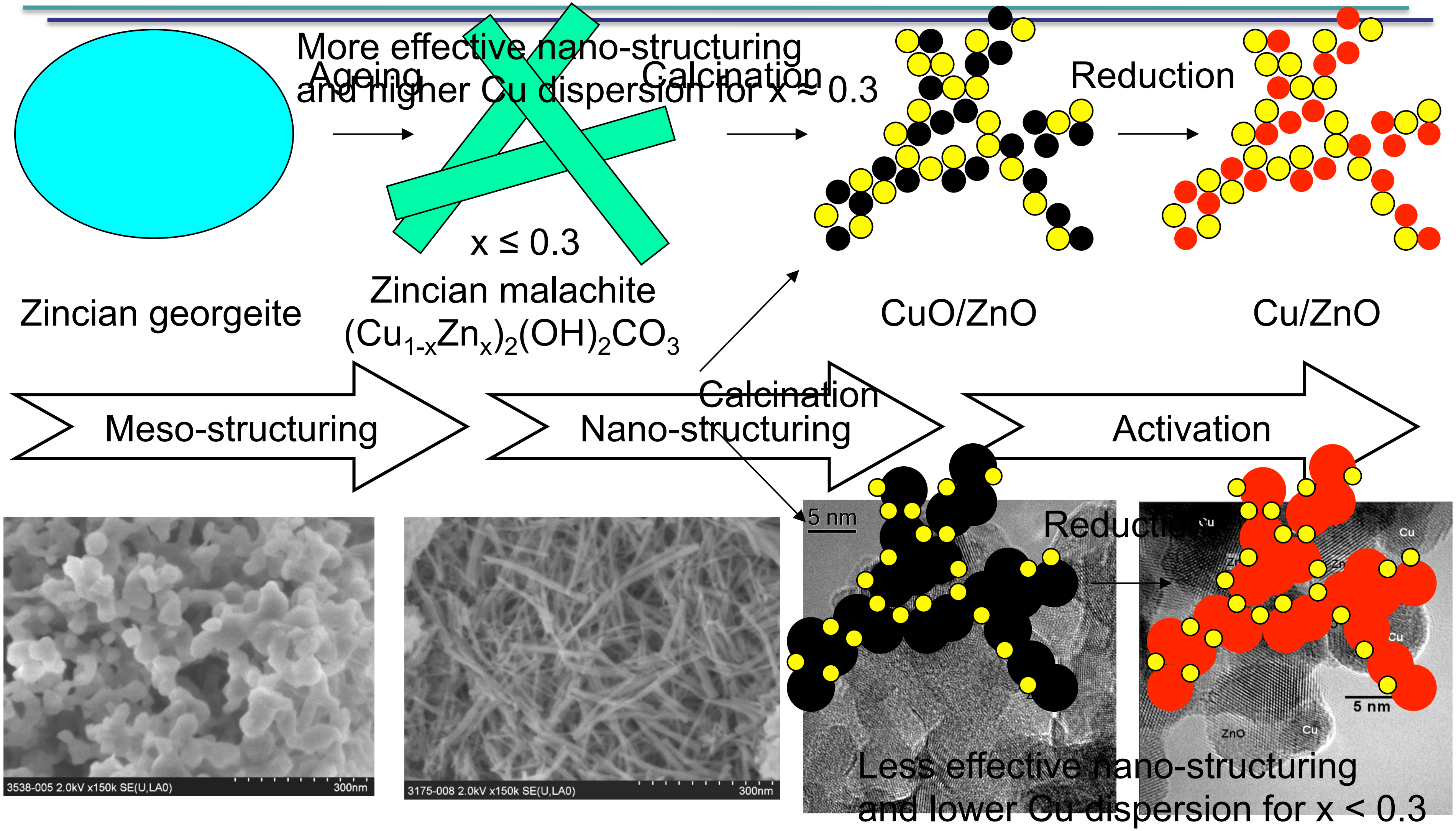


Cu:Zn ca. 70:30
d_{Cu} ca. 7-10 nm
SA_{Cu} ca. 30-40 m^2g^{-1}

$Cu/ZnO/Al_2O_3$

Synthesis developed at ICI (1960s)

Self-organized nanostructuring



Undefinied compact shape
size ca. 100 nm

Thin needles
size ca. 20 × 200 nm

Spherical shaped particles
size ca. 10 nm

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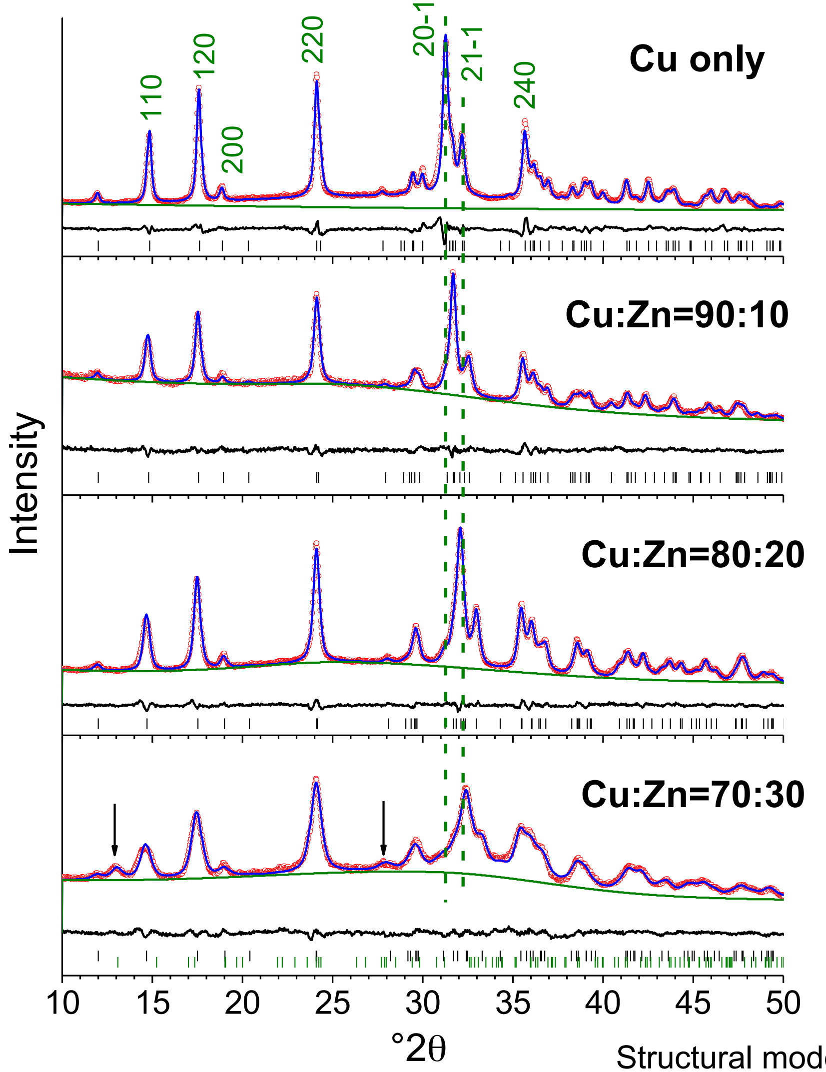
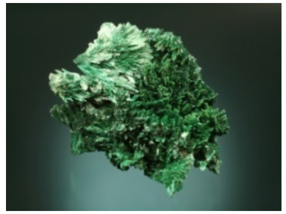
Powder XRD of the precursor compound

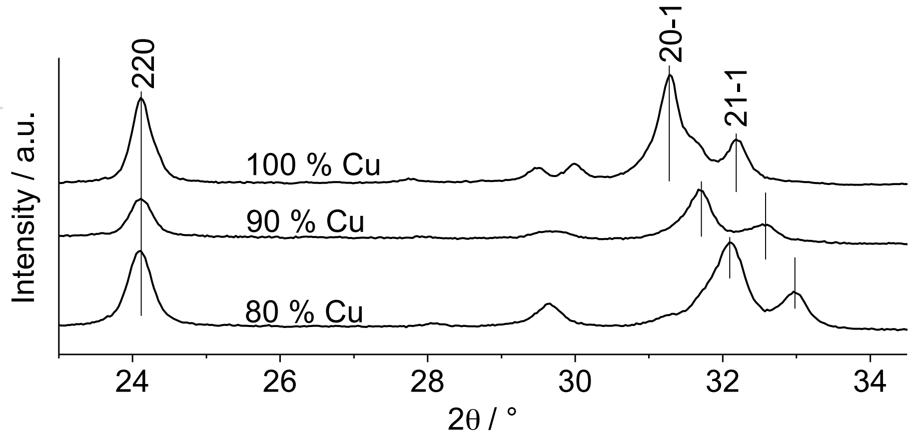


Malachite $\mathbf{Cu_2(OH)_2CO_3}$: $P2_1/a$

a=9.502 Å b=11.974 Å

c=3.240 Å β=98.75°





93 % malachite

+

7 % aurichalcite $(Zn,Cu)_5(OH)_6(CO_3)_2$

M. Behrens, F. Girgsdies, *Z. Anorg. Allg. Chem.* 636 (2010) 919.

Structural model: F. Zigan, W. Joswig, H.D. Schuster, S.A. Mason, *Z. Krist.* 145 (1977) 412.

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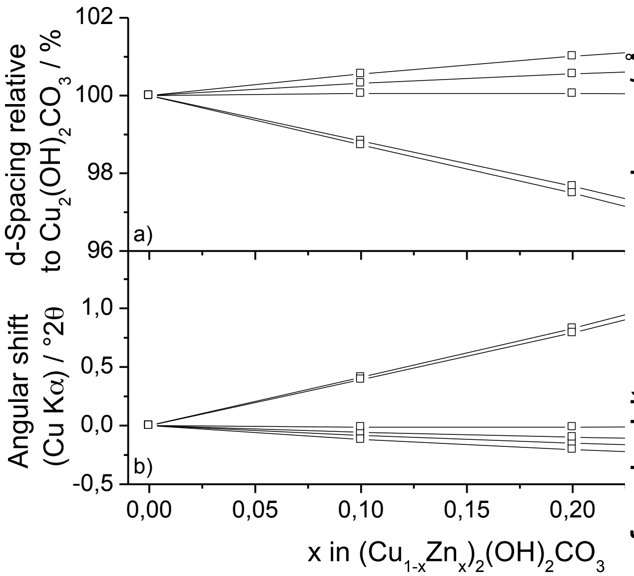
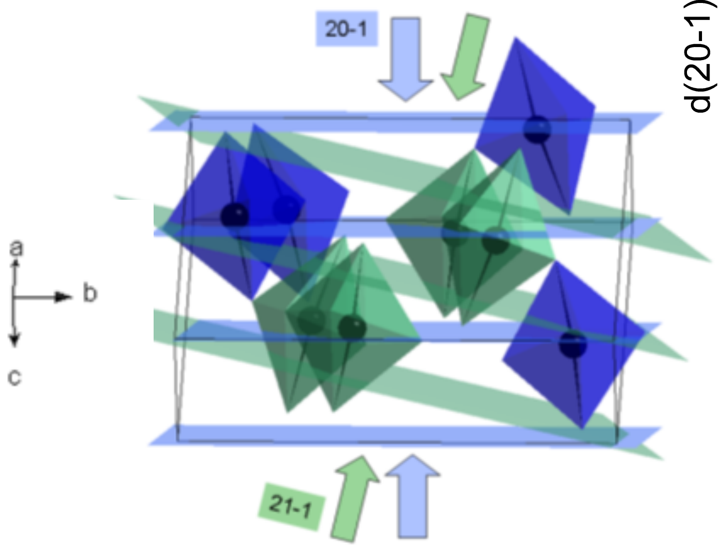
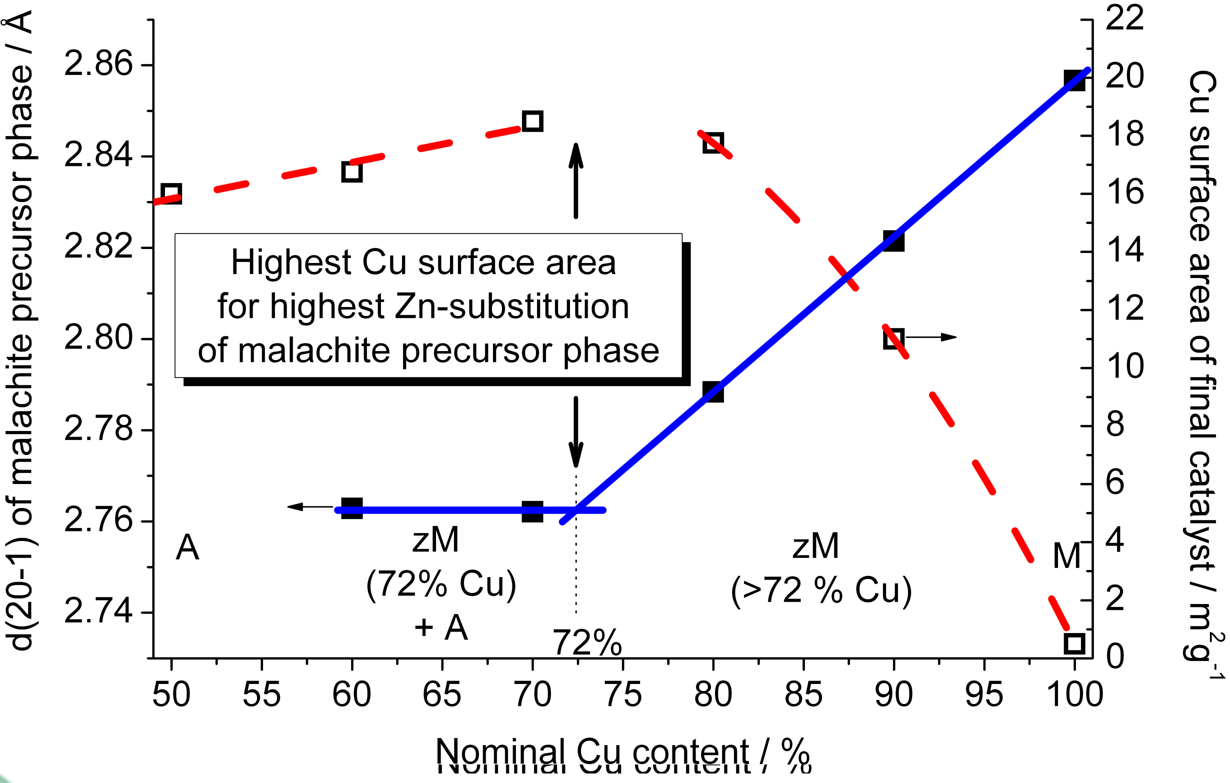
Precursor crystal chemistry controls catalyst function

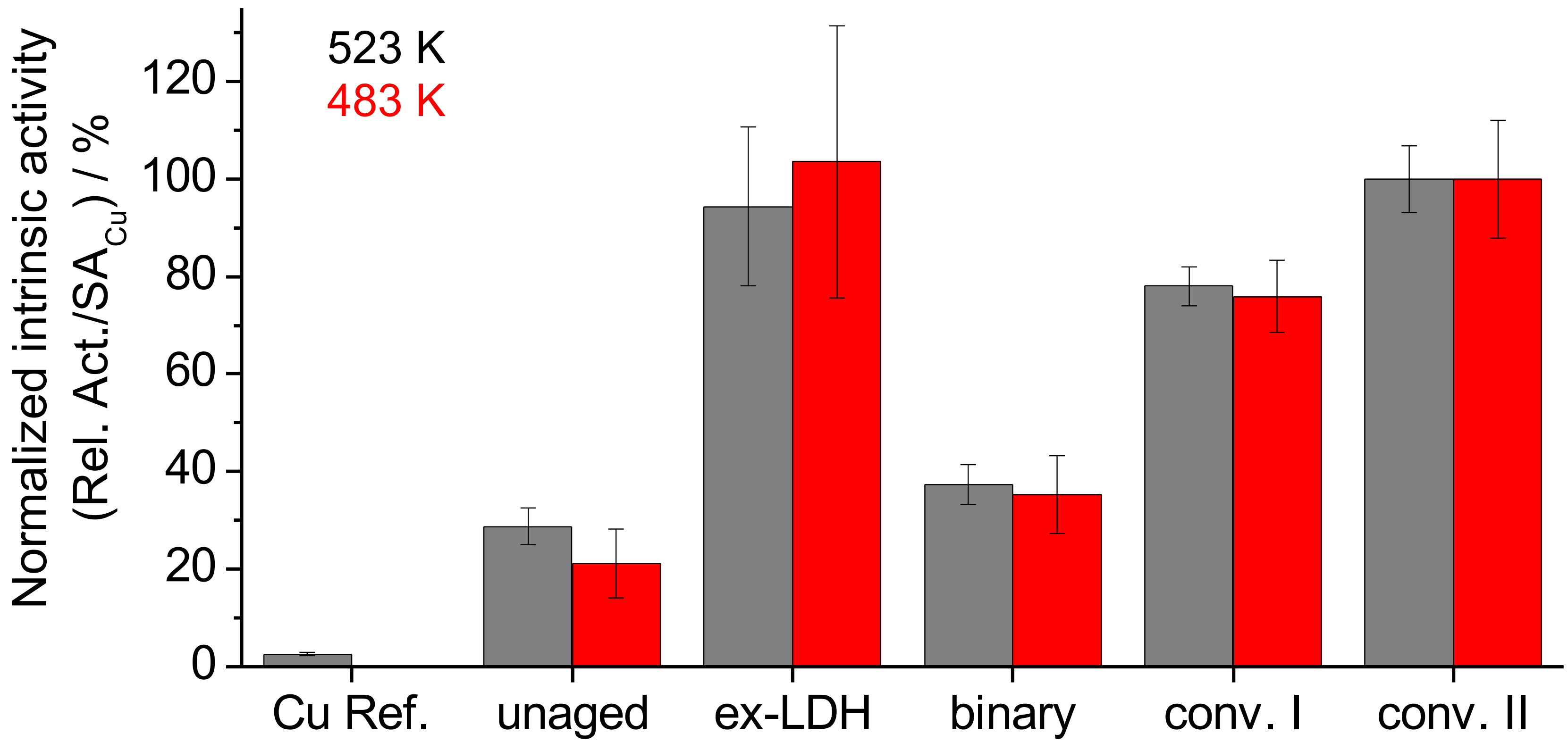






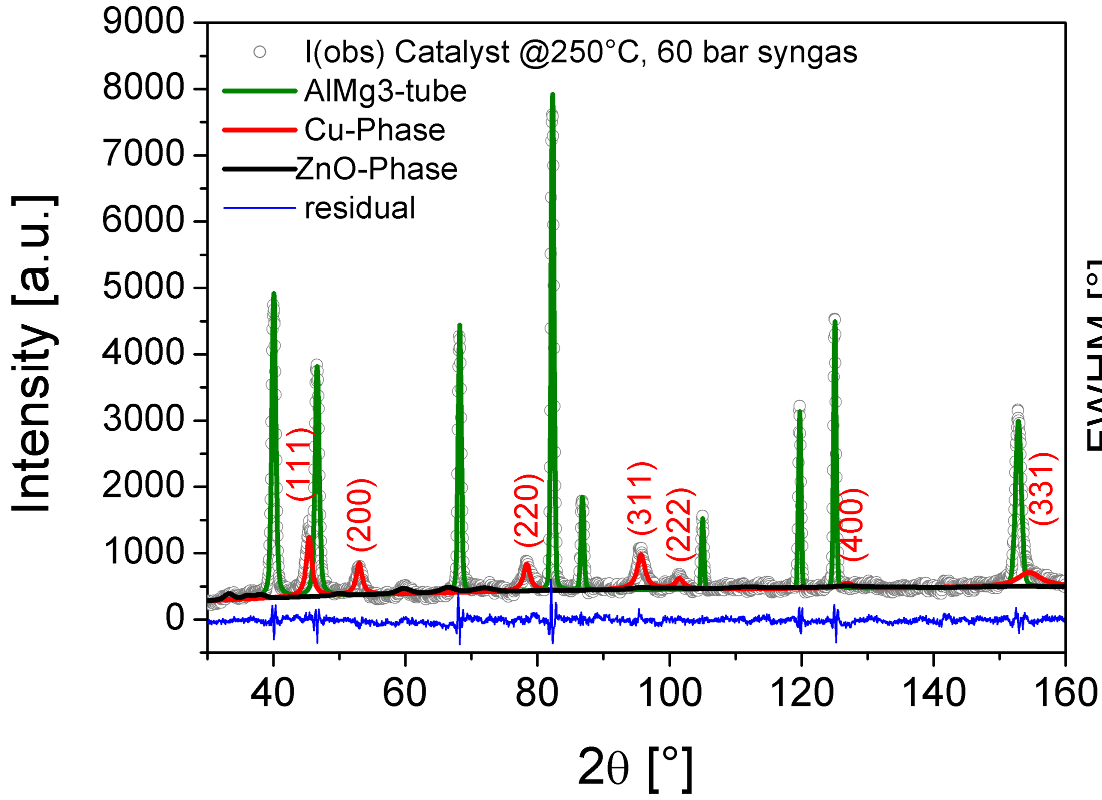
With this concept of nanostructuring by touching spheres the precursor chemistry limits size distribution

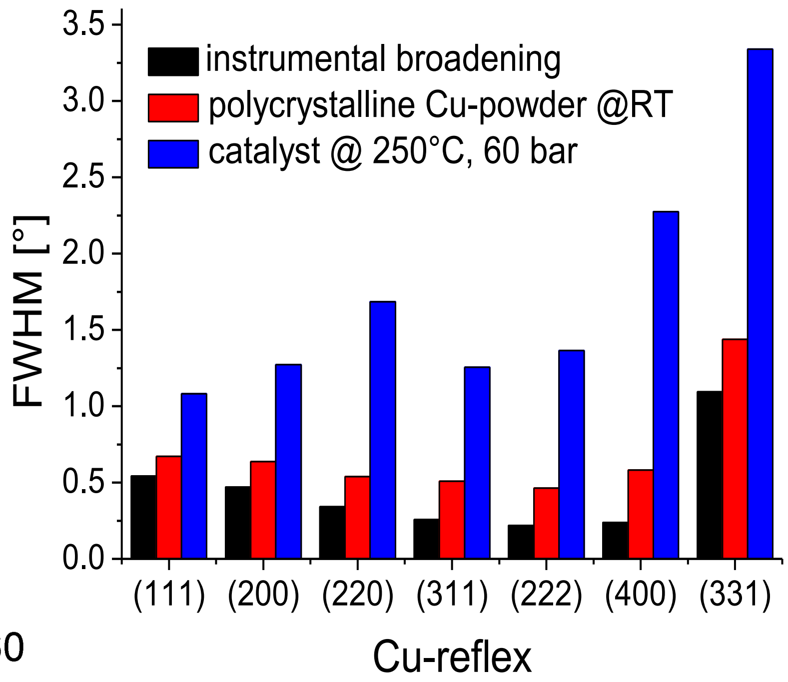
Intrinsic activities



Substantial variation in intrinsic activities over reproductions of synthesis and testing in two laboratories: pure Cu particles are almost inactive (model?)

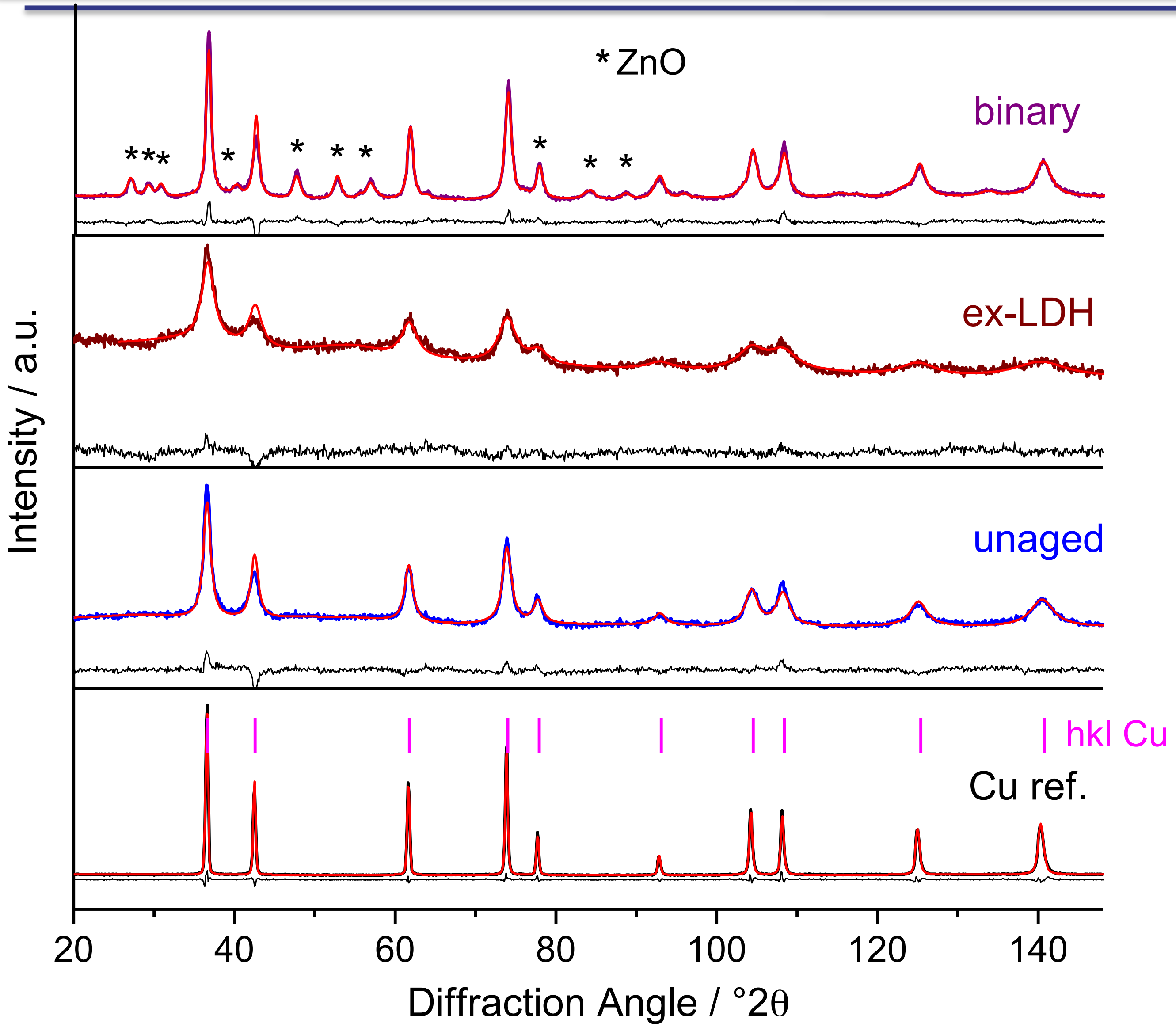
Methanol copper





No brass at reaction temperature:
At 573 K slow conversion to brass

High quality diffraction data: quite variable phase integrity



The Al promoter reduces the crystallinity of the synergy phase ZnO

Neutrons give ample access to high angle reflections: structural precision.

Defect analysis of neutron diffraction data

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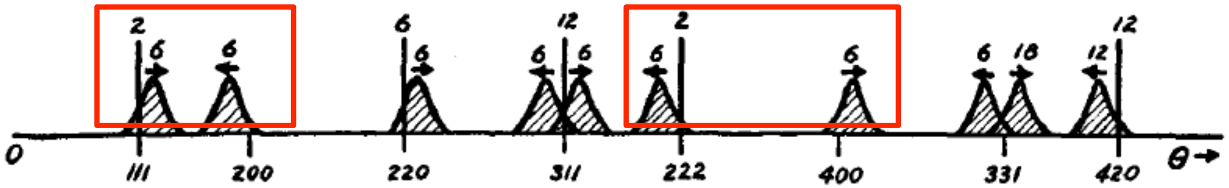
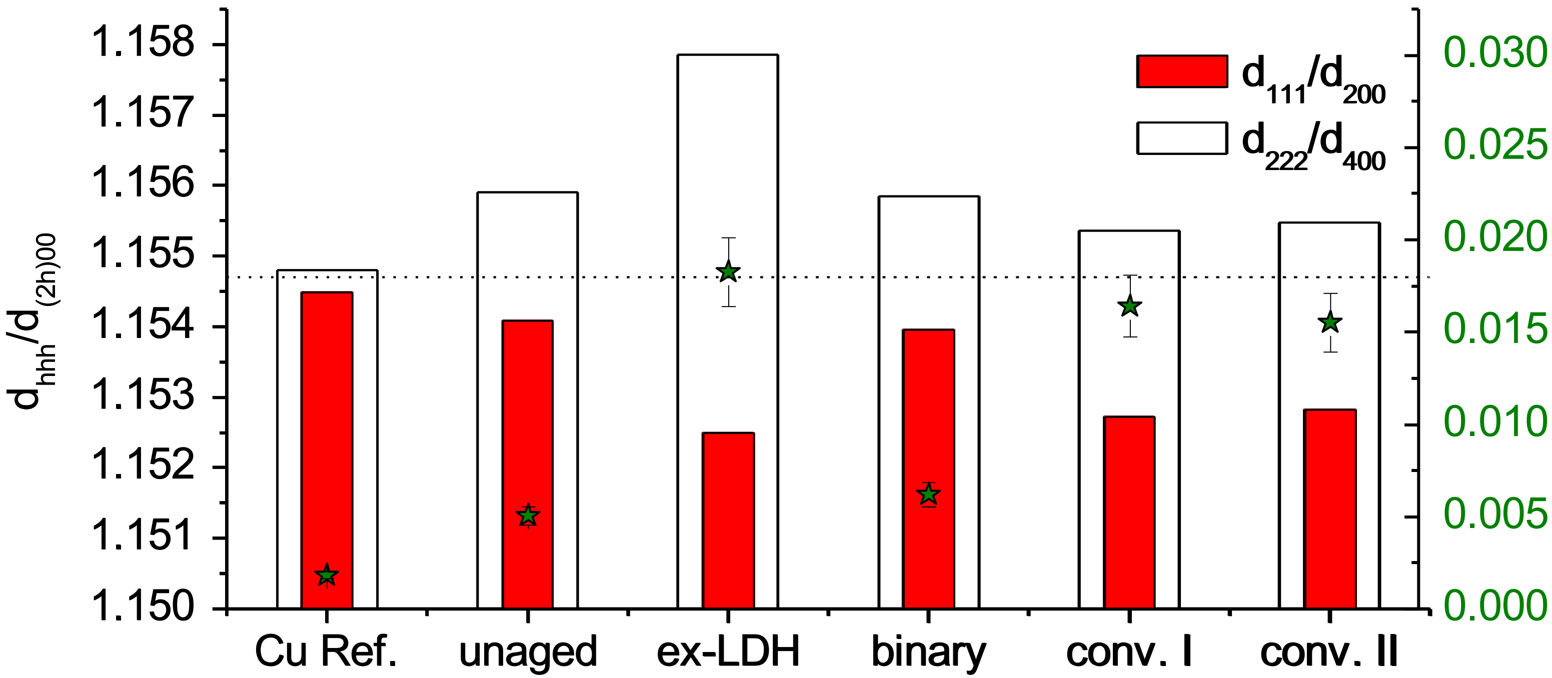
M.S. Paterson, J. Appl. Phys. 23, 1952, 805: (h+k+l = 3N±1) broadened and shifted; (h+k+l = 3N) not affected





$$\alpha = 8.3\left(2/\sqrt{3} - \sin\theta_{200} / \sin\theta_{111}\right)$$

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

Defect structure – function relationship

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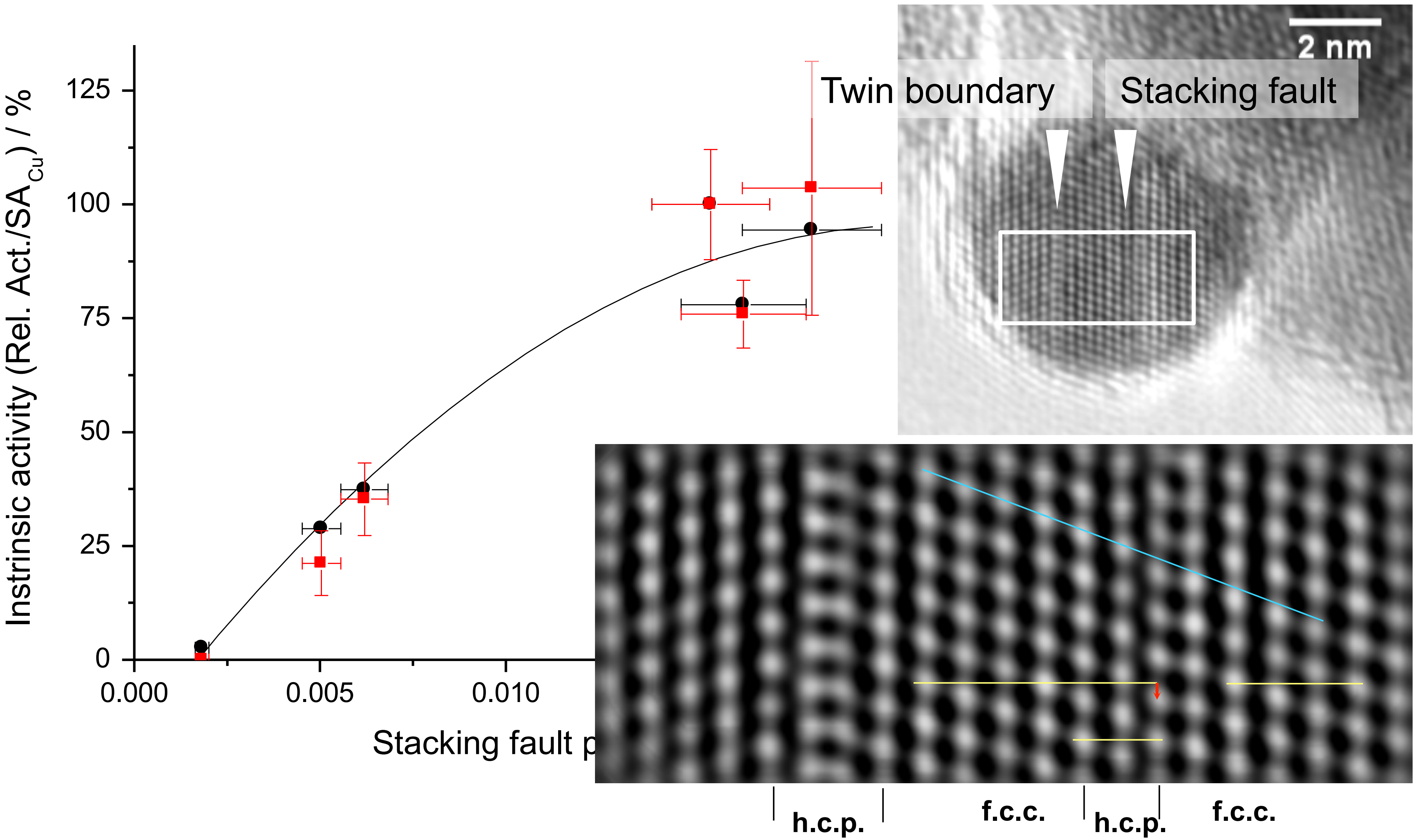

Active Cu
How we get more sites

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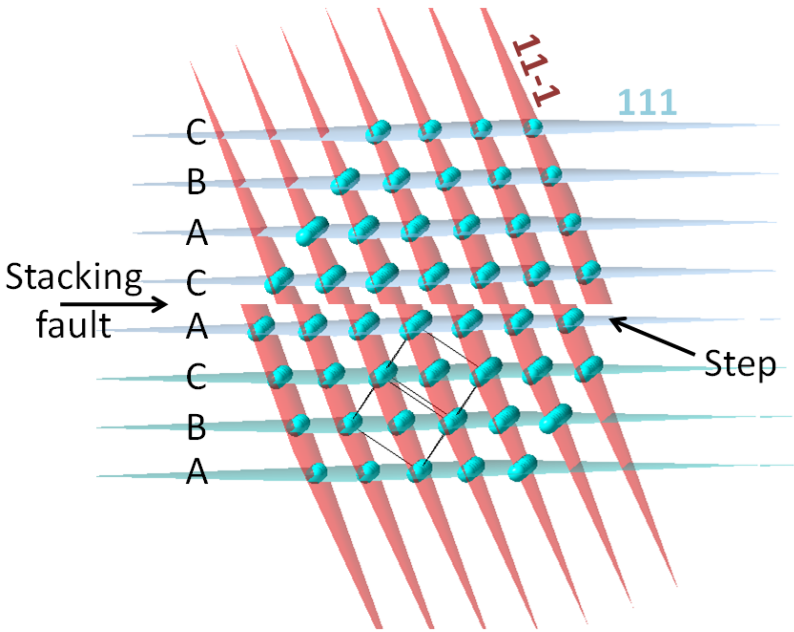

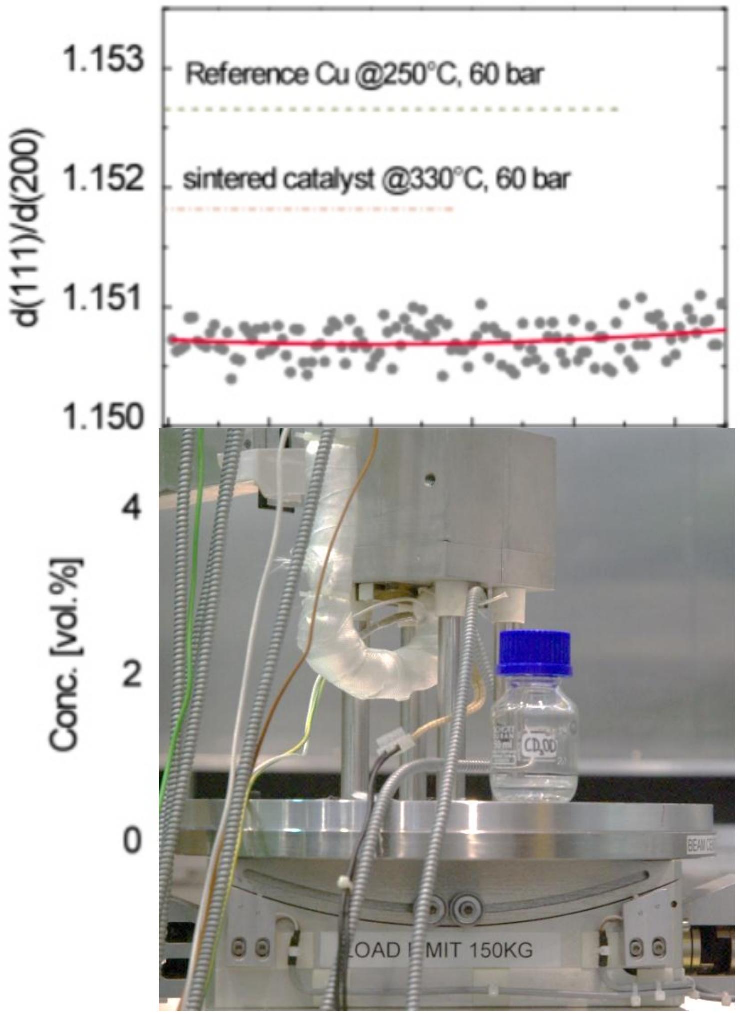

In-situ neutron diffraction:

Activity scales with defect density (terminating at the surface)…

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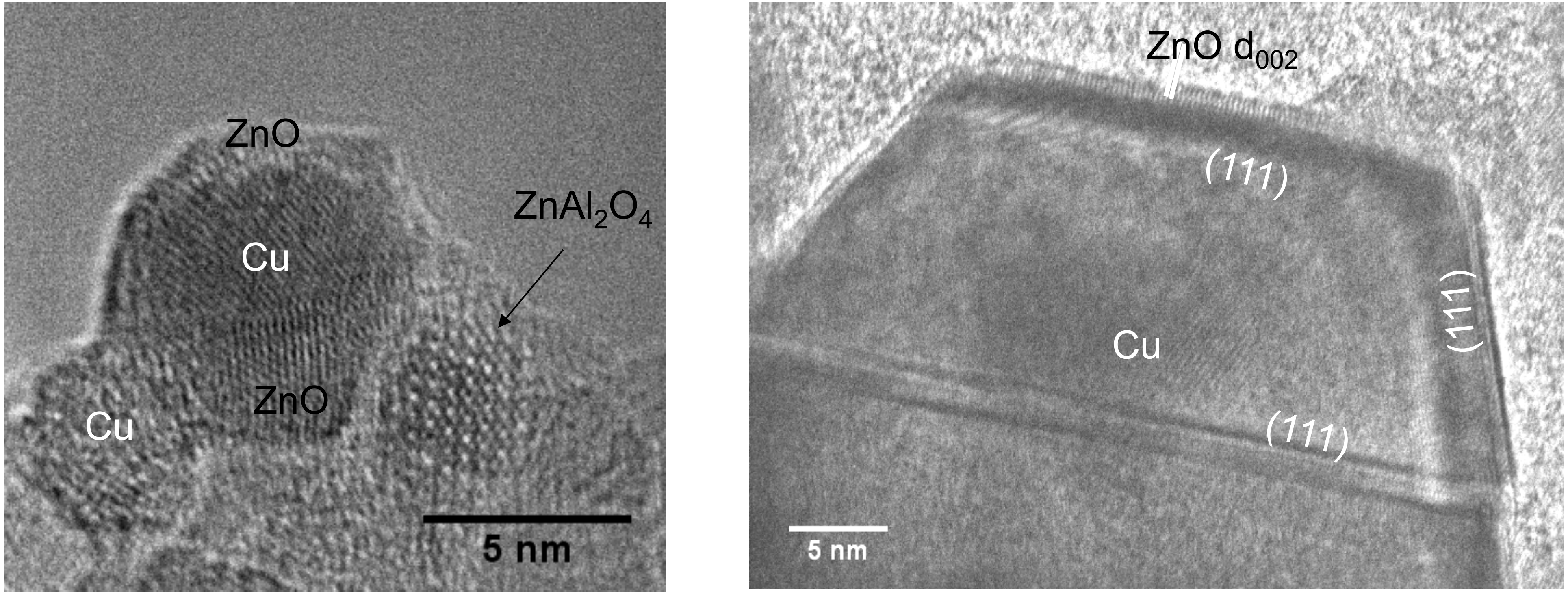
The sintered catalyst for reference



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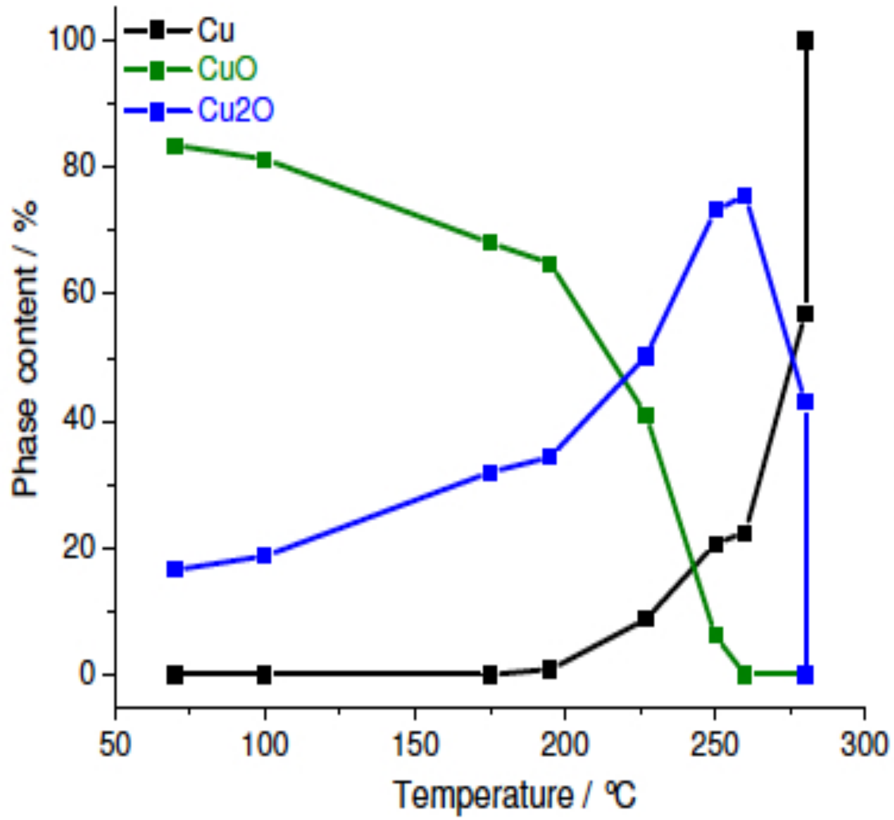
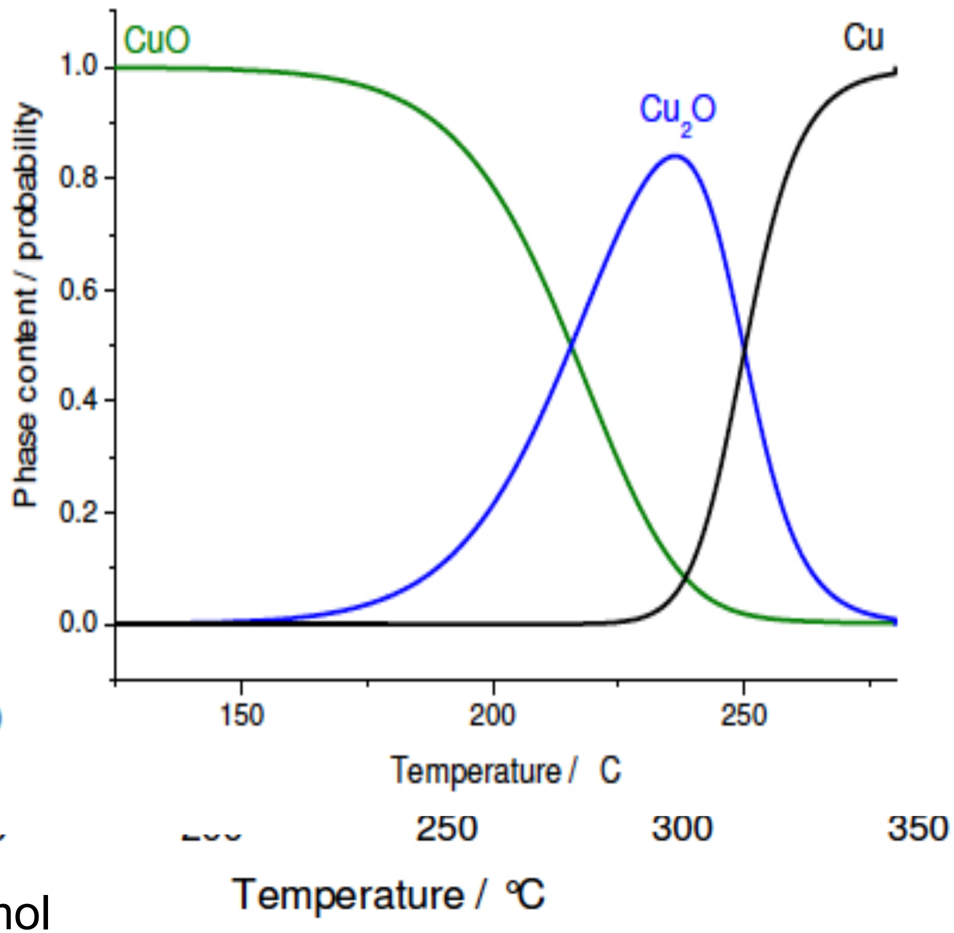
Where come the defects from?





Thermal analysis and modelling.
A➔B➔C, E_{a1}= 56 kJ/mol, E_{a2} = 63 kJ/mol
Autocatalytic process with 1-D reaction front

The intermediate oxide

The issue of crystallinity for diffraction methods

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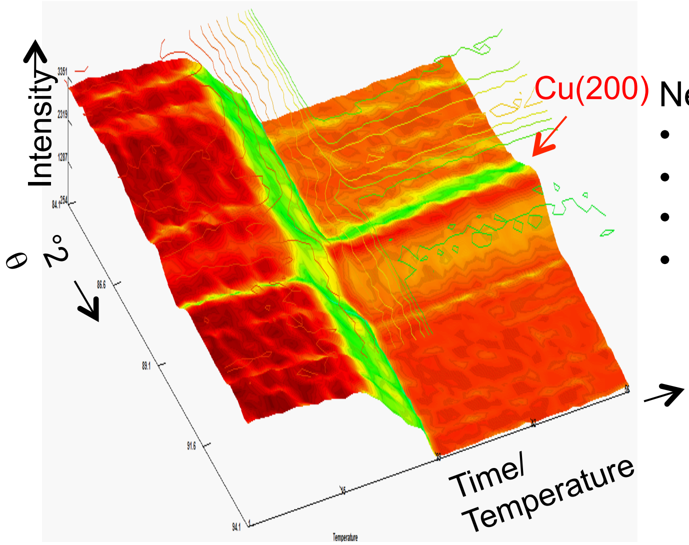
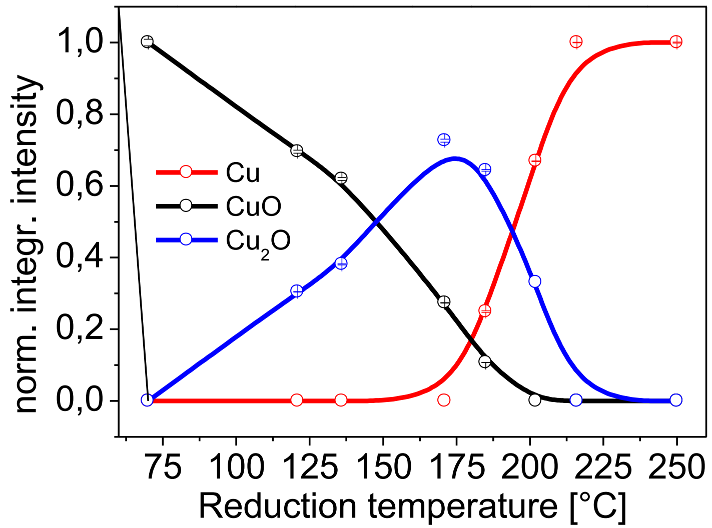


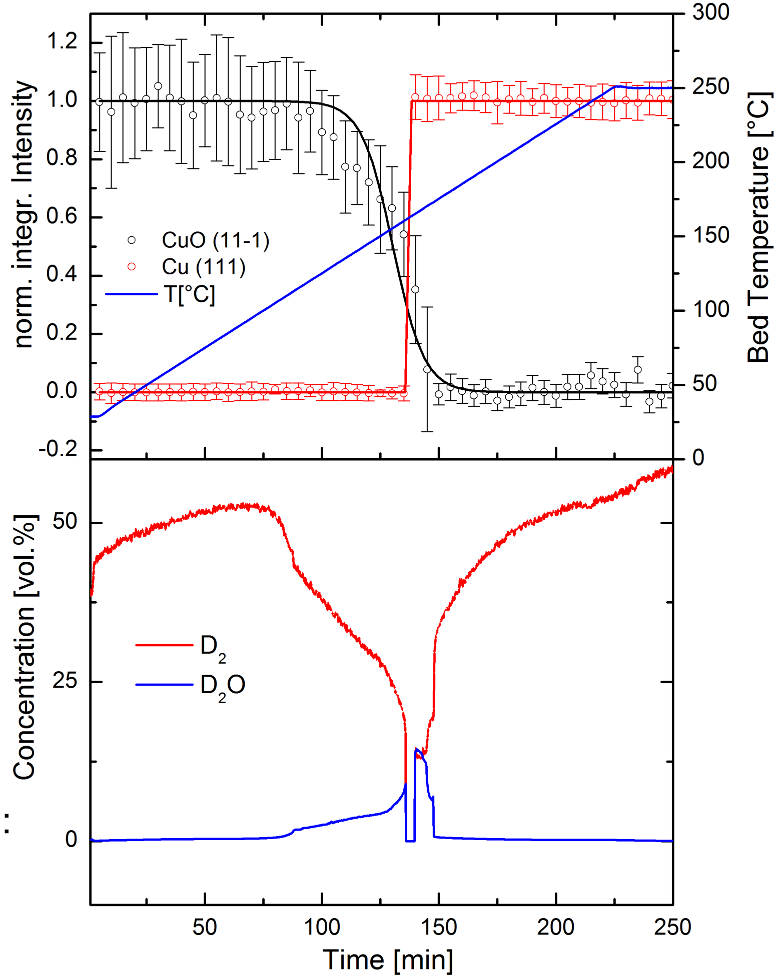
Neutrons:

- Reduction conditions:
- 100% D_2
- 1 Kpm to 250°C
- 1 pattern every 5 minutes



NEXAFS:

- Reduction conditions:
- 100% H_2
- 2 Kpm to 250°C



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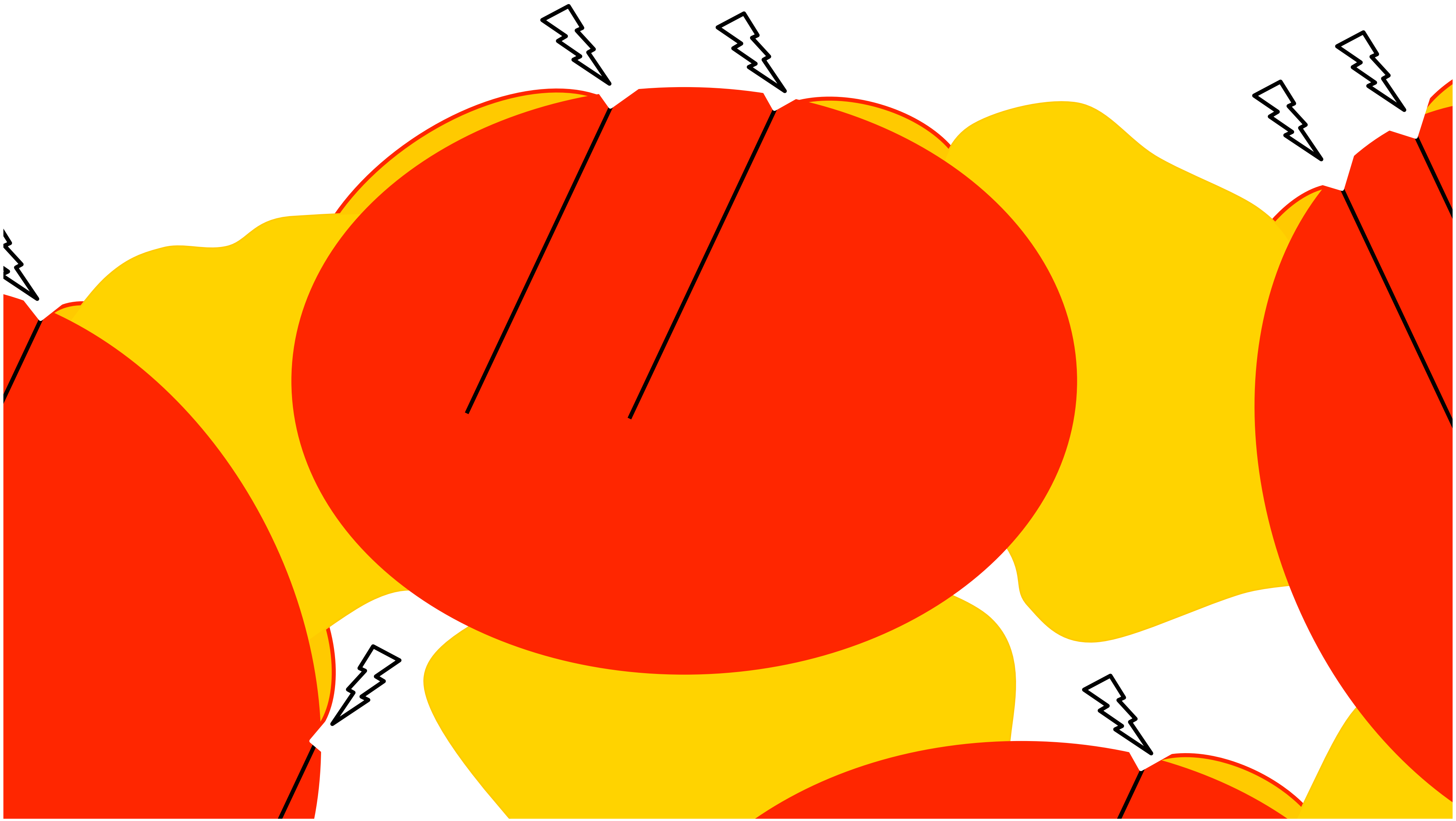
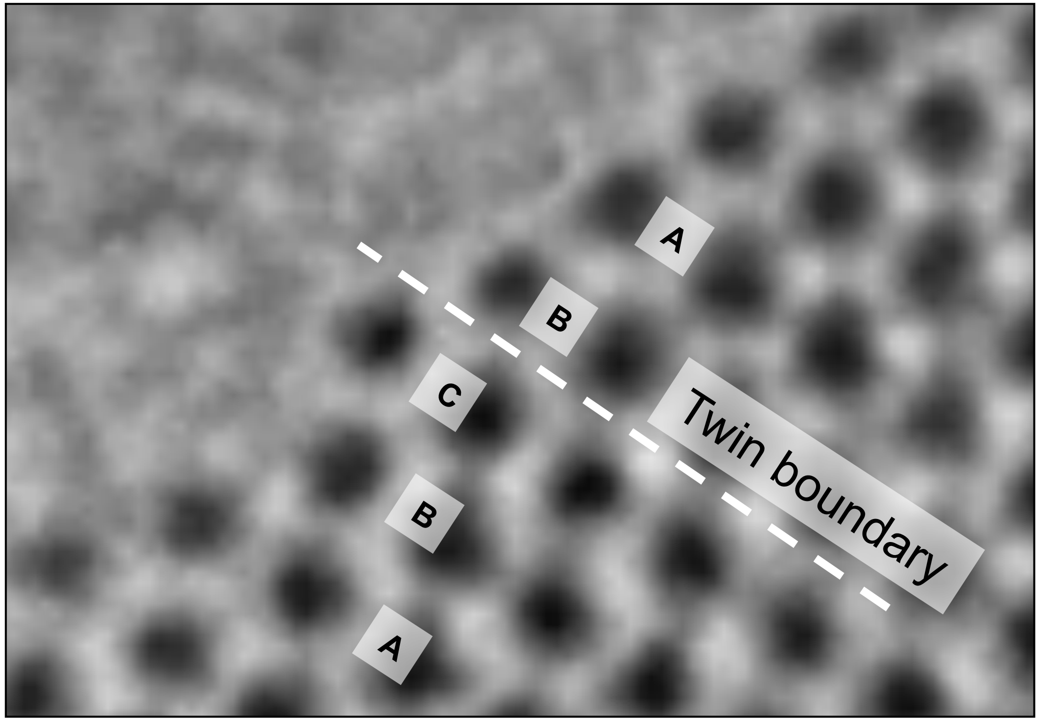
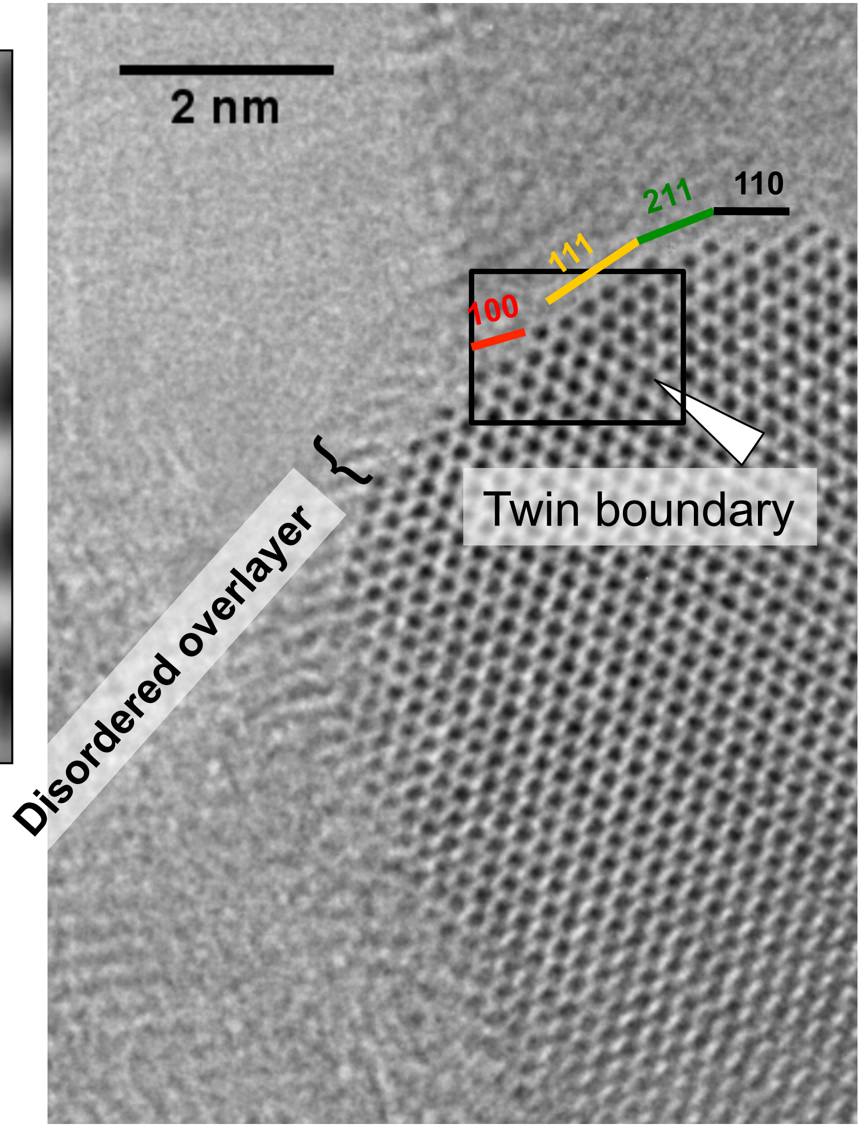
The active site model for Cu/ZnO
Synergy at work



Can we see the active sites?





Summary

- Translational phases and their low-energy termination are not active as catalysts (also not stable products with reagents: nitrides, brass).
- Reactive are high energy sites arising from local defects of the translational structure terminating at the surface (step formers).
- Kinetics of catalyst synthesis controls defects and hence reactivity (black magic).
- Bulk nanostructure (defects) control activation of as-synthesized catalyst precursor through reactants (N in Fe, O in Cu: planar defects).

Dem Anwenden muss das Erkennen vorausgehen

Max Planck

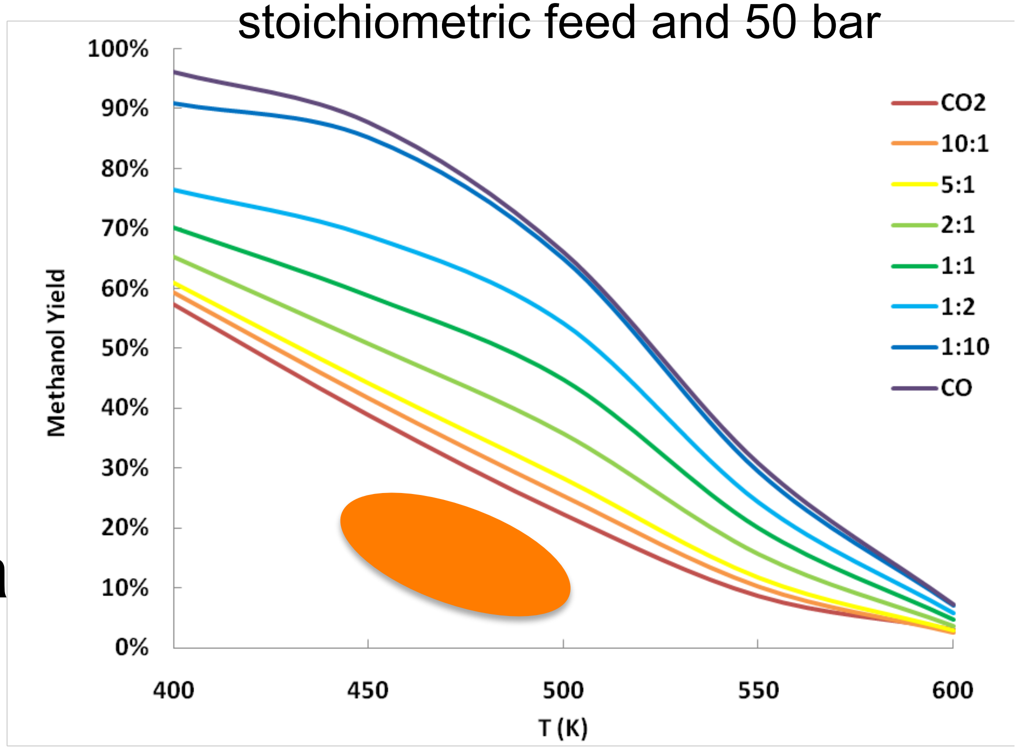
Thank You

[redacted]

Use of solar hydrogen: CO_2 hydrogenation to MeOH

- Methanol from solar hydrogen and CO_2.
- The “power-to-gas” option also for high volume energy transport (global).
- Methanol synthesis is a known technology with 100Mtons/a volume.

Equilibrium conversion for CO_x at stoichiometric feed and 50 bar



G. Olah: Synthesis of MeOH from CO_2 is facile and known technology

Materials basis for reactivity studies

Sample	Preparation	Precursor	Pretreatment	Reference
Cu	Co-ppt + ageing	Malachite	Calcination (330°C) + Reduction (5 % H_2)	[1]
Cu/ZnO		Zincian malachite		[2,3]
$Cu/ZnAl_2O_4$		Cu,Zn,Al-LDH		[4]
$Cu/ZnO/Al_2O_3$ unaged	Co-ppt w/o ageing	Amorphous		[5]
$Cu/ZnO/Al_2O_3$ conventional I	Co-ppt + ageing	Zincian malachite		[6]
$Cu/ZnO/Al_2O_3$ conventional II				

[1] F. Zigan, W. Josig, H. D. Schuster, *Z. Kristallogr.* 145 (1977) 412.

[2] M. Behrens; *J. Catal. 267 (*2009) 24.

[3] M. Behrens, F. Girgsdies*, Z. Anorg. Allg. Chem.* 636 (2010) 919-927.

[4] M: Behrens, I. Kasatkin, S. Kühl. G. Weinberg, *Chem. Mater.* 22 (2010) 386-397.

[5] B. L. Kniep, T. Ressler, A. Rabis, F. Girgsdies, M. Baenitz, F. Steglich, R. Schlögl, Angew. Chem Intern. Ed. 43 (2003) 112.

[6] I. Kasatkin, P. Kurr, B. Kniep, A Trunschke, R. Schlögl, *Angew. Chem.* 119 (2007) 7465.

Sample	Cu content (metal basis)	Average TEM particle size	N_2O SA_{Cu}
Cu	100	-	6 m^2g^{-1}
Cu/ZnO	70	13.3 ± 0.1 nm	26 m^2g^{-1}
$Cu/ZnAl_2O_4$	50	6.9 ± 0.1 nm	10 m^2g^{-1}
$Cu/ZnO/Al_2O_3$ unaged	70	9.5 ± 0.5 nm	24 m^2g^{-1}
$Cu/ZnO/Al_2O_3$ conv. I	70	10.0 ± 0.7 nm	30 m^2g^{-1}
$Cu/ZnO/Al_2O_3$ conv. II	70	12.7 ± 0.4 nm	43 m^2g^{-1}

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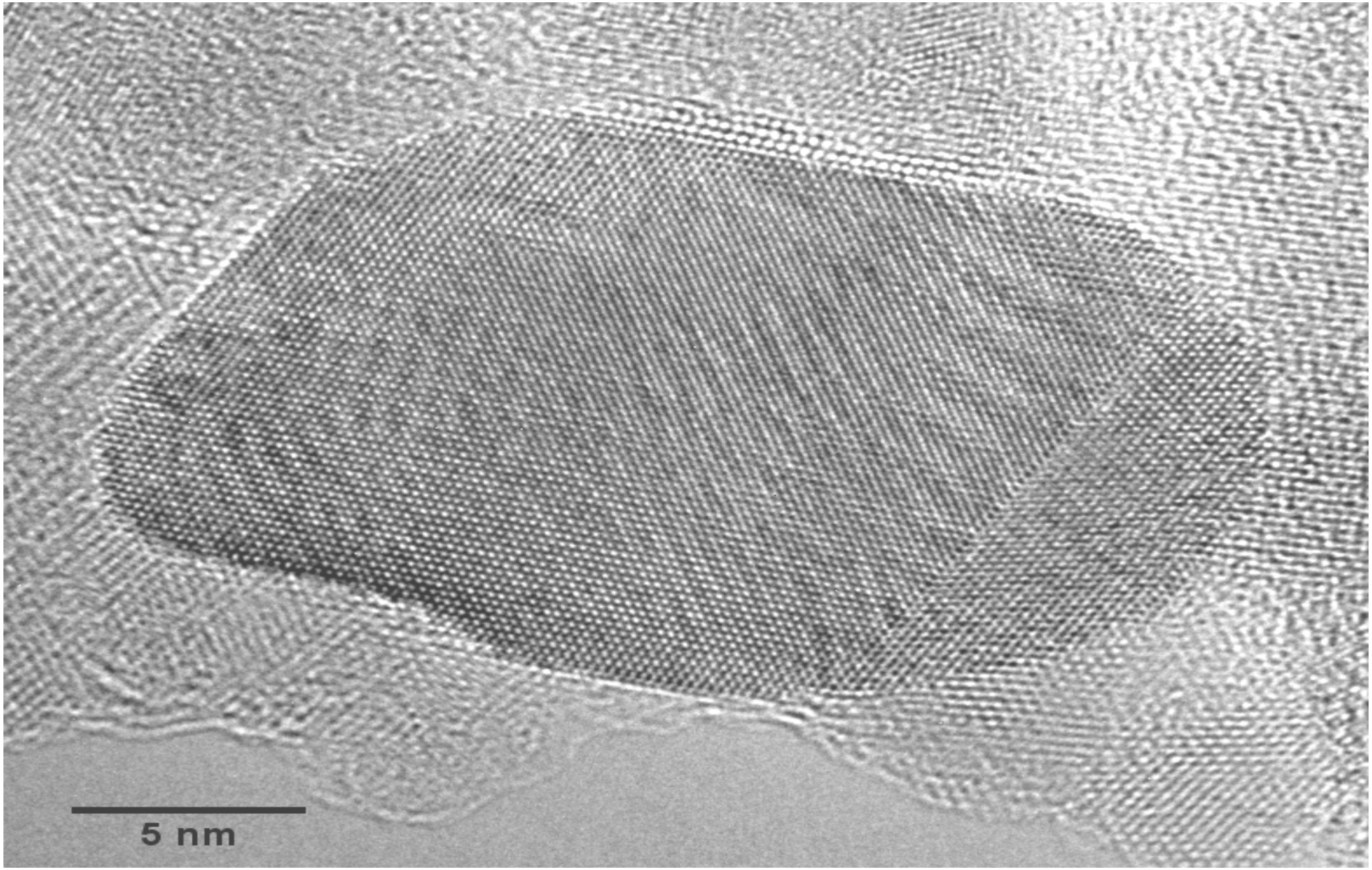
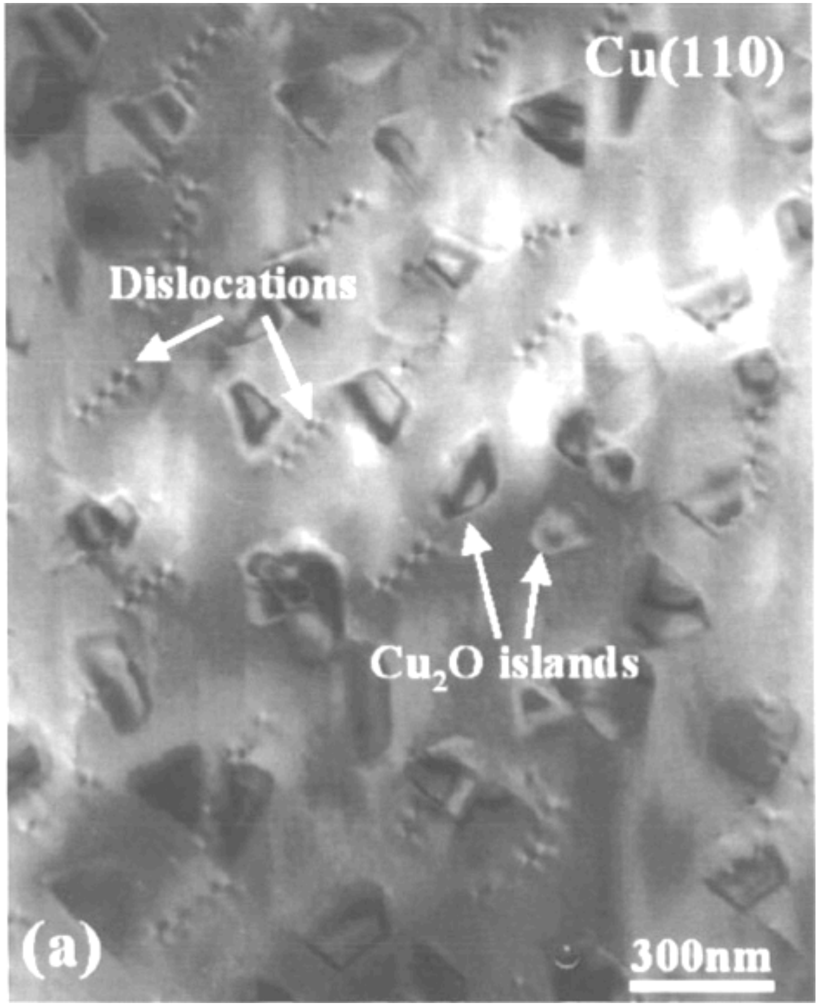
Seeing the defects





Active oxygen located at strained sites

Zhuo et al, J. Appl. Phys, 2006