Functional analysis of the Cu/ZnO system

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Acknowledgements

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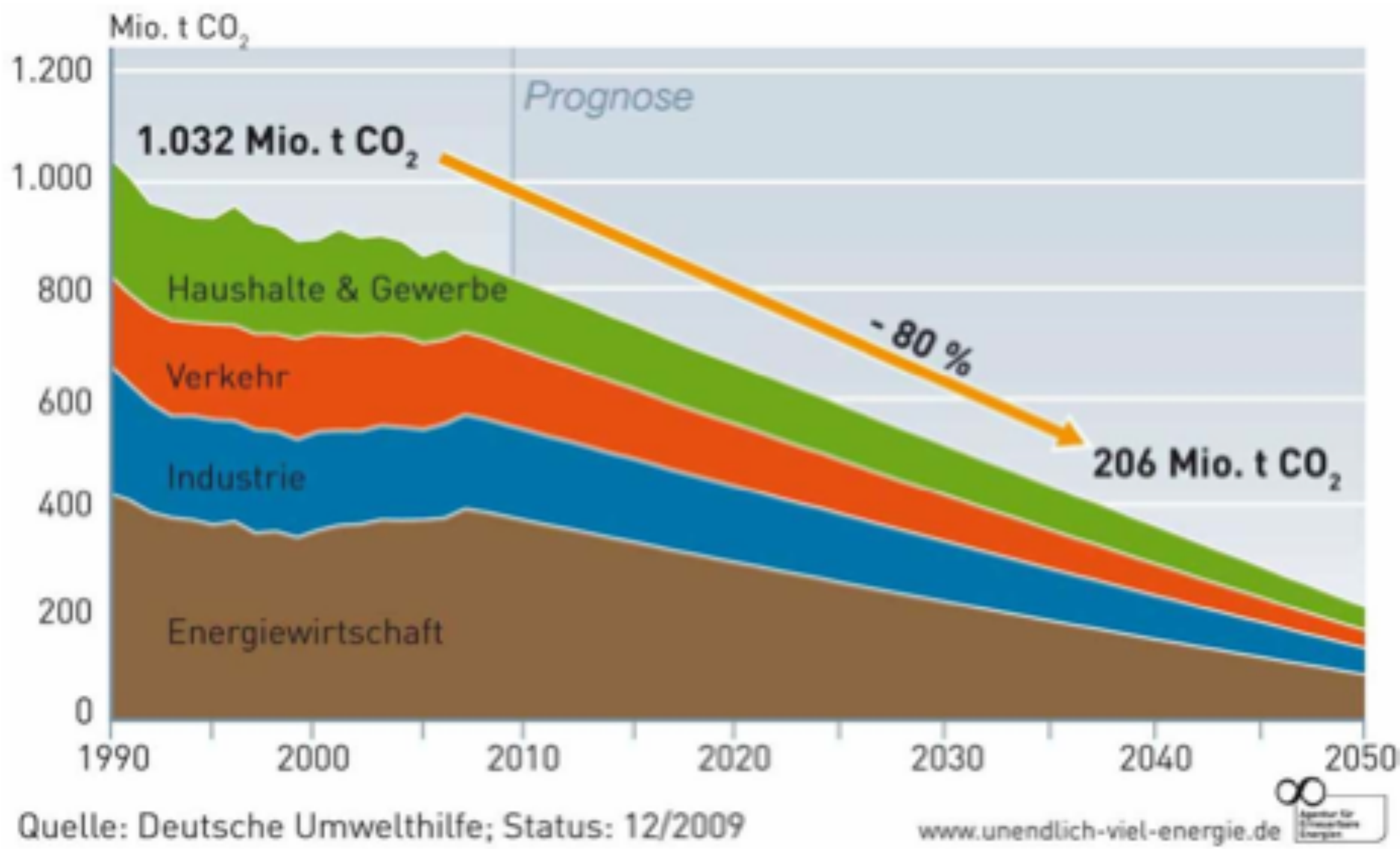
…..and the excellent longstanding collaboration with RUB AG Muhler

Atomausstieg in Deutschland

- AKW tragen 14% des Kraftwerksparkes und ca. 25% der erzeugten Leistung bei.
- In 10 Jahren: Abschaltung und Abbau (wäre immer nötig, nur wann?).
- Ersatz durch konventionelle KW: technisch unproblematisch aber 65-100 Mio. t CO_2 zusätzlich pro Jahr!
- Energiekonzept D sieht Ausstieg vor.
- Maßnahmen: Sparen und regenerative Energie (sehr „windlastig“).

  - Reicht das aus?



Mio. t CO2
1.200
1.000
800
600
400
200
0
Prognose
1.032 Mio. t CO2
- 80 %
206 Mio. t CO2
Haushalte & Gewerbe
Verkehr
Industrie
Energiewirtschaft
1990
2000
2010
2020
2030
2040
2050
Quelle: Deutsche Umwelthilfe; Status: 12/2009
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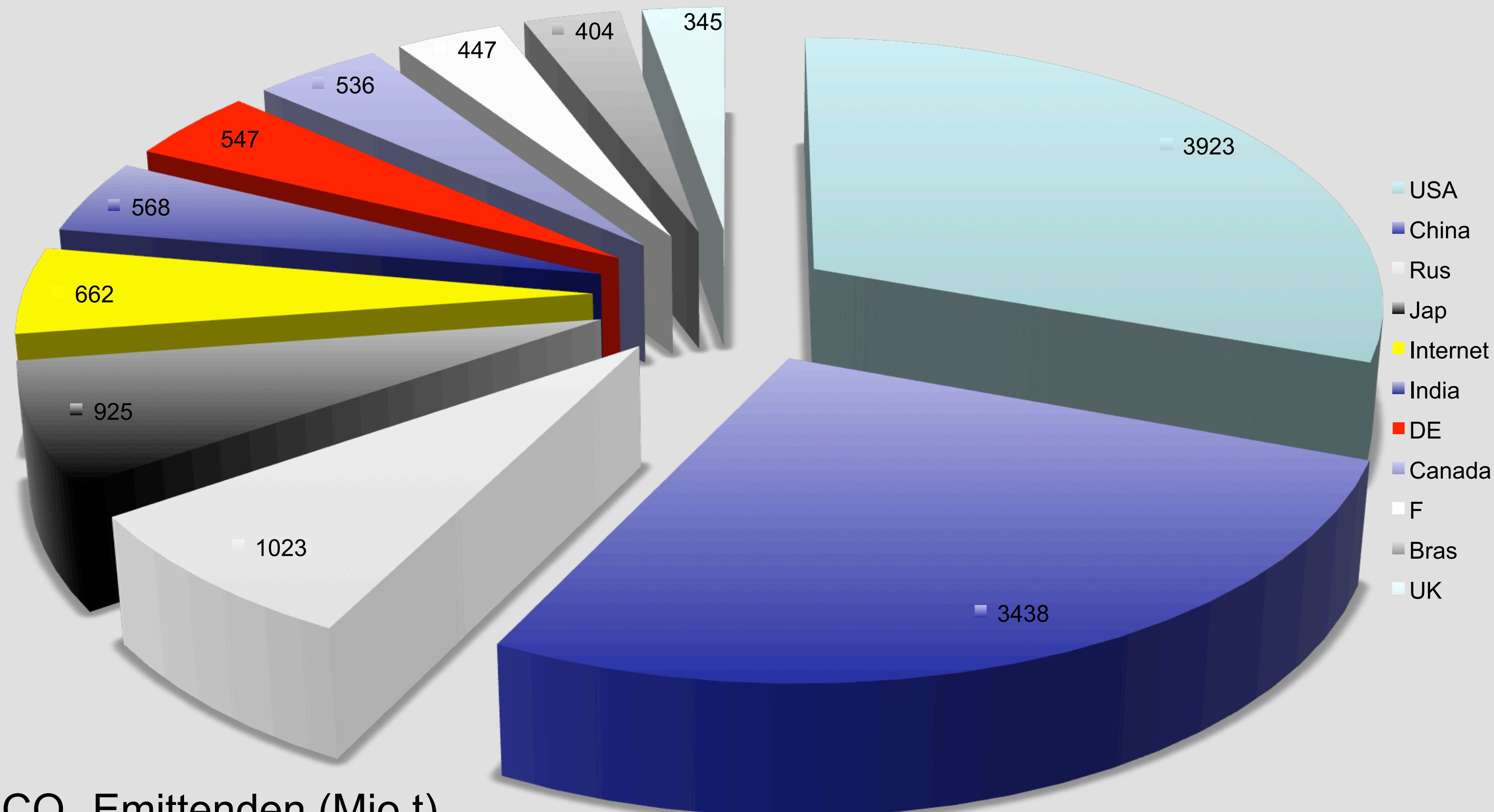

CO_2 Emittenden (Mio t)
Für Strom

Source: IEA, Greenpeace, 2011

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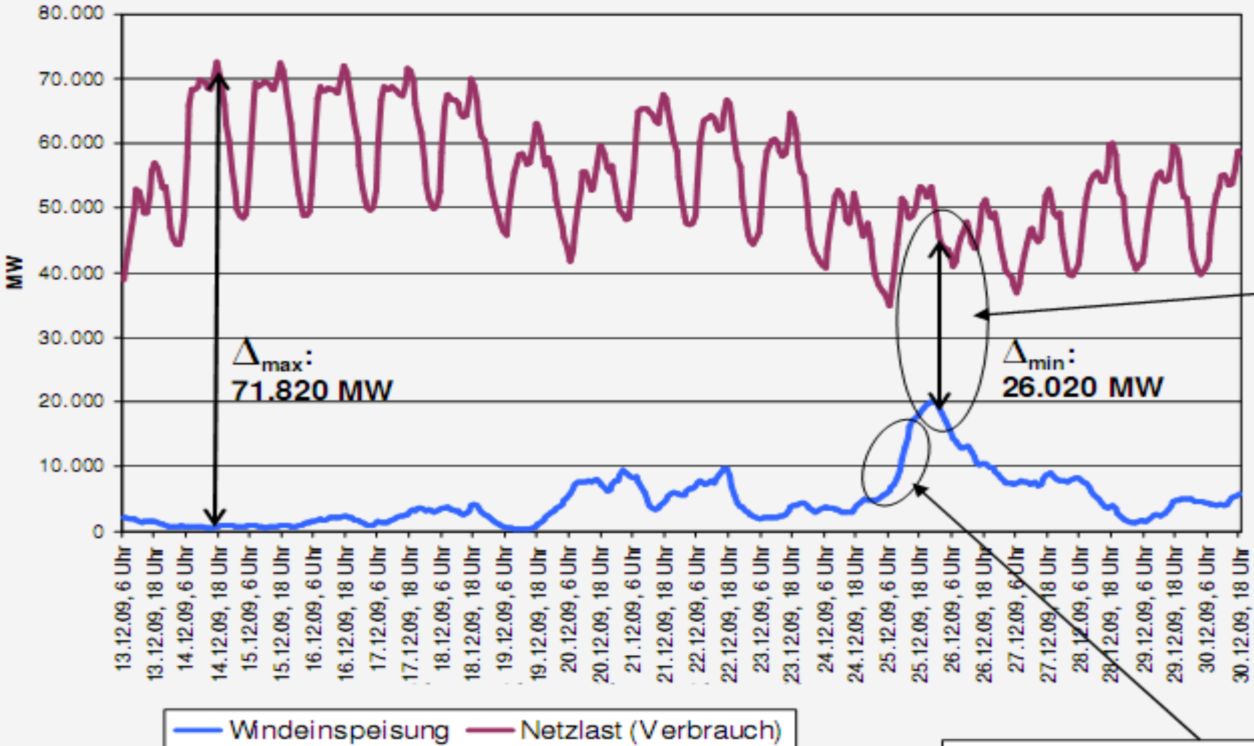
Stromverbrauch und Windeinspeisung: Flexibler Kraftwerkspark notwendig

bdew Energie. Wasser. Leben.



Hohe Windeinspeisung bei Schwachlast (26.12.09, 2 Uhr):

- KWK muss im Winter am Netz bleiben
- Gas-KW teilweise für Systemdienstleistungen notwendig
- Drosselung der KKW auf 55%
- Kohle-KW größtenteils abgefahren oder stark gedrosselt
- Erzeugungsüberschüsse als Stromexport

Leistungsanstieg Windeinspeisung: 11.800 MW in 12 h (25.12.09, 5h bis 17h), allerdings gleichlaufend mit Netzlast.

Quellen: BDEW, entso-e

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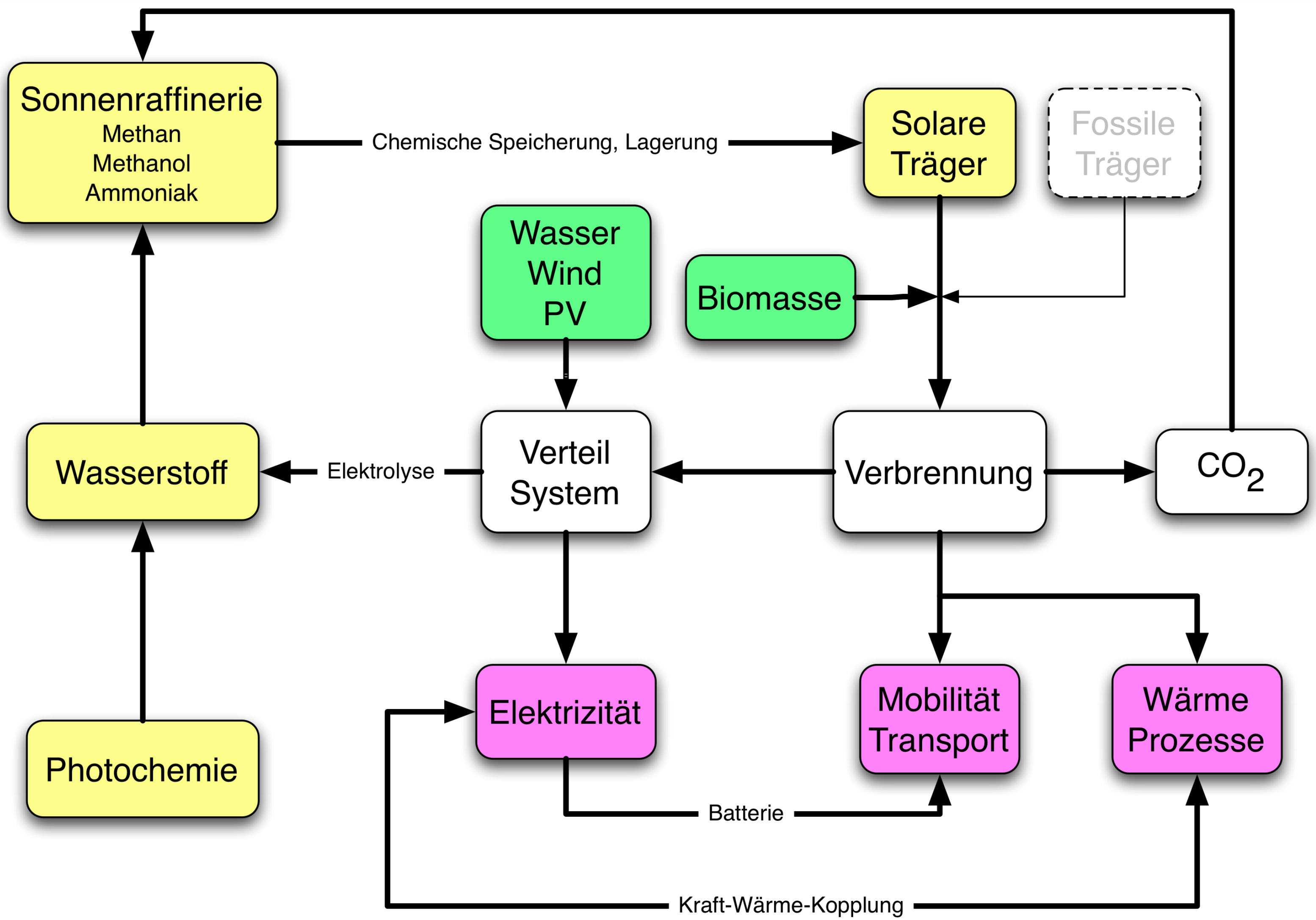
Regenerative Energie
Nur mit Speichertechnik

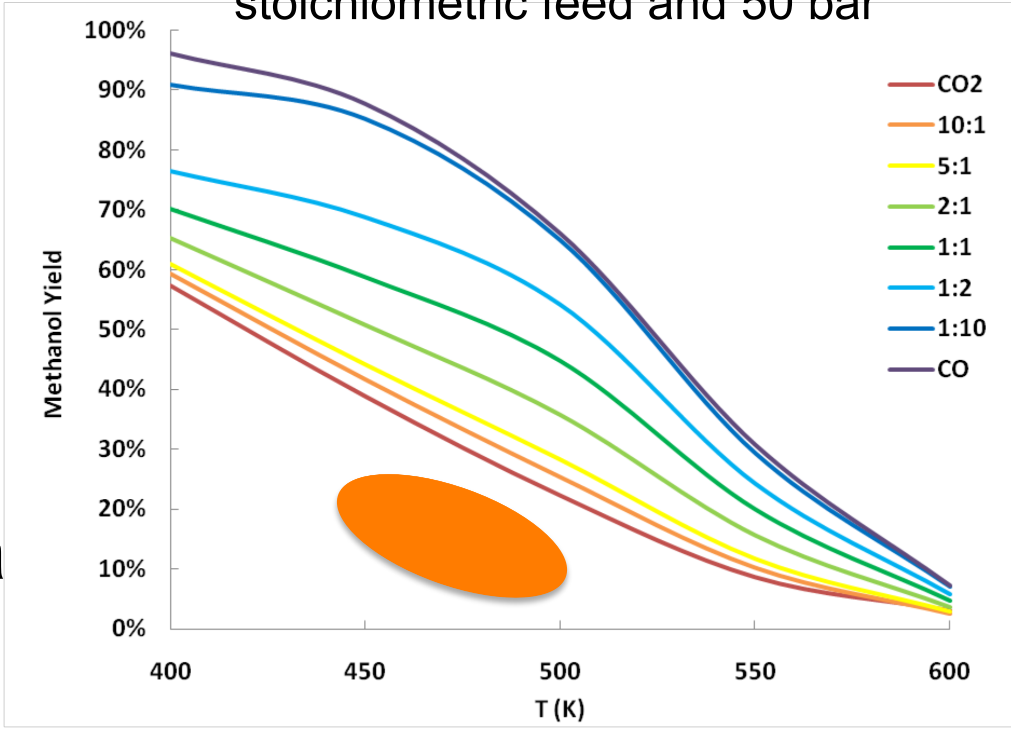


Nicht ohne Grundlagenforschung für Wandler und Speicher

Use of solar hydrogen: CO_2 hydrogenation

- 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

Mixing Copper Nanoparticles and ZnO Nanocrystals: A Route towards Understanding the Hydrogenation of CO_2 to Methanol?

*Frederic C. Meunier**

Cu–ZnO-based materials,[5a] while stressing that those could yet be important in the case of copper-free ZnO. Tsang et al.[1] suggest a model remotely derived from the junction effect as described by Frost[8] to explain the improved activity of their Cu–ZnO platelets, in which some electrons and oxygen atoms migrate from the ZnO to Cu to form CuO and oxygen vacancies in the ZnO phase near to the interface.

The comments above underline that further studies will be needed to ascertain the origin of the selectivity differences observed by Tsang and co-workers.[1] In particular, operando techniques need to be used, since Grunwaldt et al.[9] showed that Cu wetted differently ZnO depending on the experimental conditions. It would be interesting to assess 1) possible changes in shape and size of the copper particles under reaction conditions, 2) the possibility of Zn–Cu surface alloys formation, and 3) the Cu surface area in situ after reaction (by N_2O reactive frontal chromatography[5a]) in the case of Cu–ZnO platelets and Cu–ZnO rods.

The marked difference of selectivity observed is related to the difference in the structure of the catalytic materials derived from the original mechanical mixtures.[1] The water–

Berg. M. Farle, Y. Wang, R. A. Fischer, M. Muhler, *ChemCatChem* **2010**, *2*, 214–222.

[3] a) M. Saito, *Catal. Surv. Jpn.* **1998**, *2*, 175–184; b) M. Saito, T. Fujitani, M. Takeuchi, T. Watanabe, *Appl. Catal.* **1996**, *138*, 311–318.

[4] S. Fujita, M. Usui, H. Ito, N. Takezawa, *J. Catal.* **1995**, *157*, 403–413.

[5] a) K. C. Waugh, *Catal. Today* **1992**, *15*, 51–75; b) W. X. Pan, R. Cao, D. L. Roberts, G. L. Griffin, *J. Catal.* **1988**, *114*, 440–446; c) S. Polarz, J. Strunk, V. Ischenko, M. W. E. van den Berg, O. Hinrichsen, M. Muhler, M. Driess, *Angew. Chem.* **2006**, *118*, 3031–3035; *Angew. Chem. Int. Ed.* **2006**, *45*, 2965–2969; d) I. Kasatkin, P. Kurr, B. Kniep, A. Trunschke, R. Schlögl, *Angew. Chem.* **2007**, *119*, 7465–7468; *Angew. Chem. Int. Ed.* **2007**, *46*, 7324–7327.

[6] M. Behrens, *J. Catal.* **2009**, *267*, 24–29.

[7] a) Y. Choi, K. Futagami, T. Fujitani, J. Nakamura, *Appl. Catal. A* **2001**, *208*, 163–167; b) N.-Y. Topsøe, H. Topsøe, *Top. Catal.* **1999**, *8*, 267–270.

[8] J. C. Frost, *Nature* **1988**, *334*, 577–580.

[9] J.-D. Grunwaldt, A. M. Molenbroek, N.-Y. Topsøe, H. Topsøe, B. S. Clausen, *J. Catal.* **2000**, *194*, 452–460.

[10] a) R. A. Hadden, P. J. Lambert, C. Ranson, *Appl. Catal. A* **1995**, *122*, L1–L4; b) K. C. Waugh, *Catal. Lett.* **1999**, *58*, 163–165.

Microstructure of $Cu/ZnO/(Al_2O_3)$ catalysts

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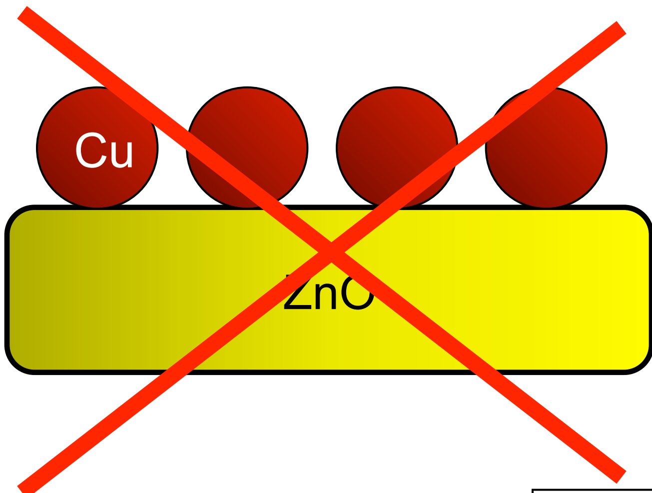
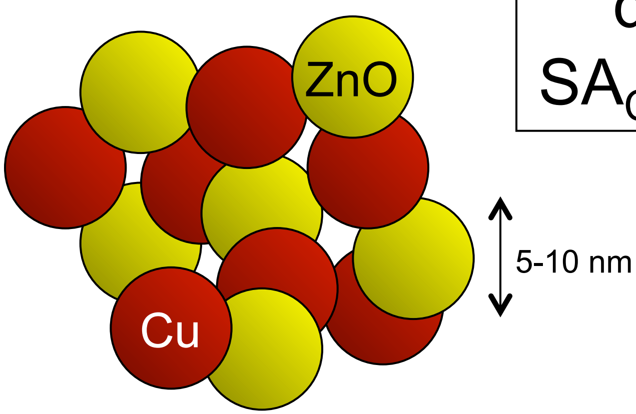
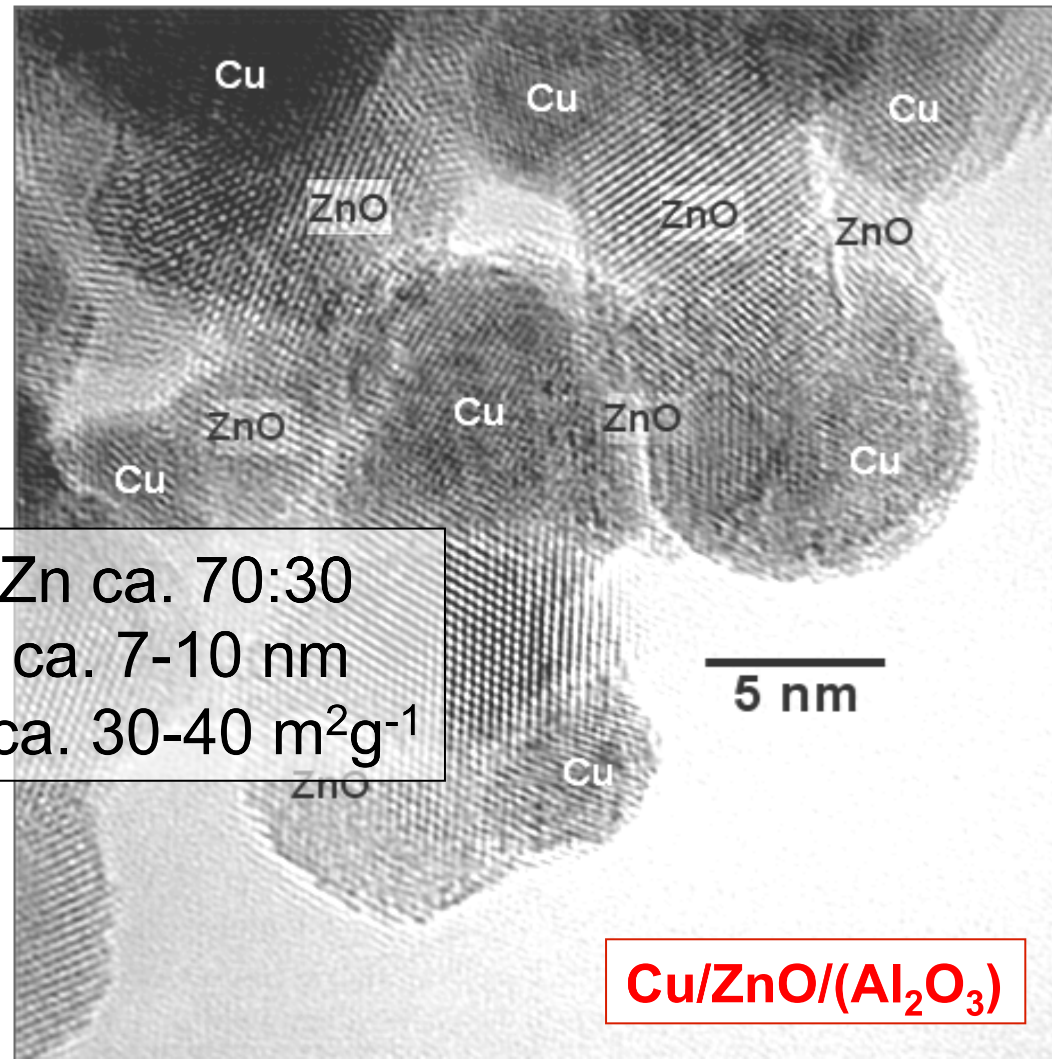


Cu:Zn ca. 70:30
d_{Cu} ca. 7-10 nm
SA_{Cu} ca. 30-40 m^2g^{-1}

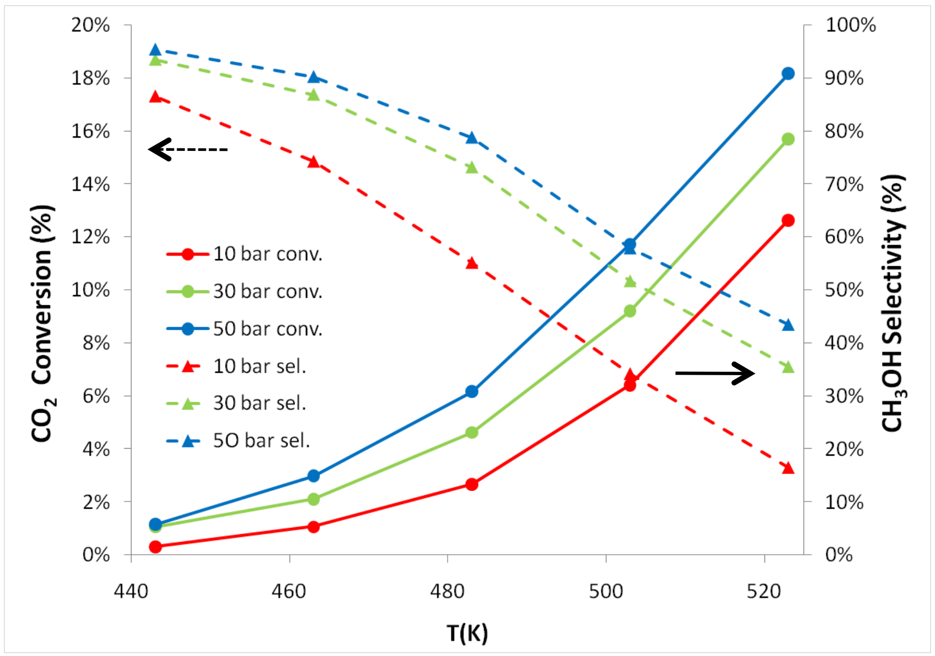


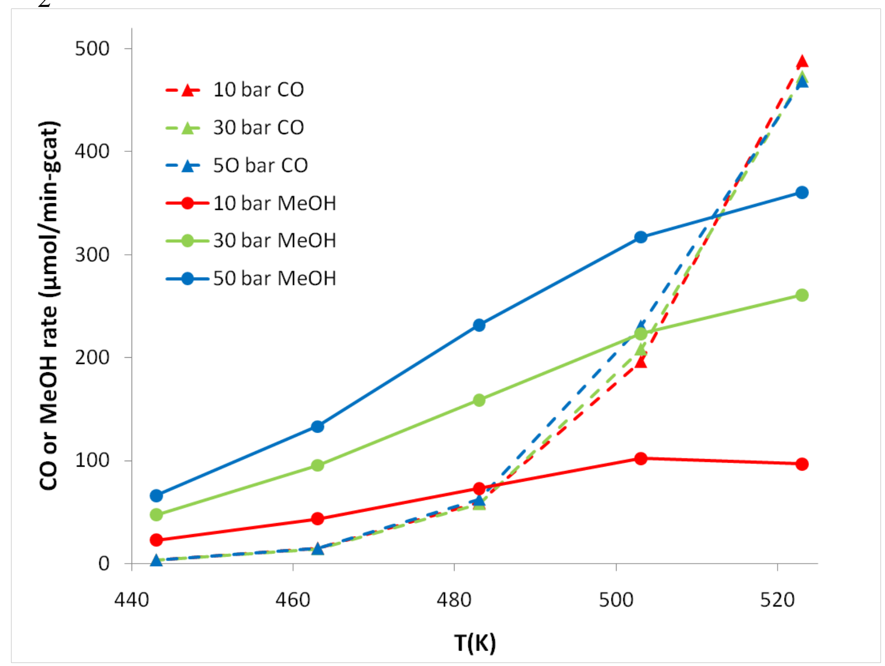


Kinetic observations

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

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





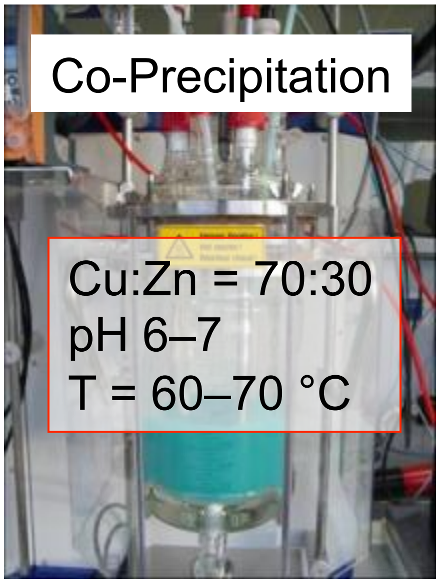
Pressure and Temperature Studies with 200 mg NGM std. Catalyst 20 µm powder
(a representative malachite-derived catalyst) 100 ml/min CO_2/H_2/Ar (3:9:1) in 10 mm OD reactor

The CO shift chemistry is faster than the MeOH synthesis

Synthesis: How to get there

A multi-step synthesis is controlled by the kinetics of precipitation to form a single-phase meta-stable intermediate zM (zincian malachite)

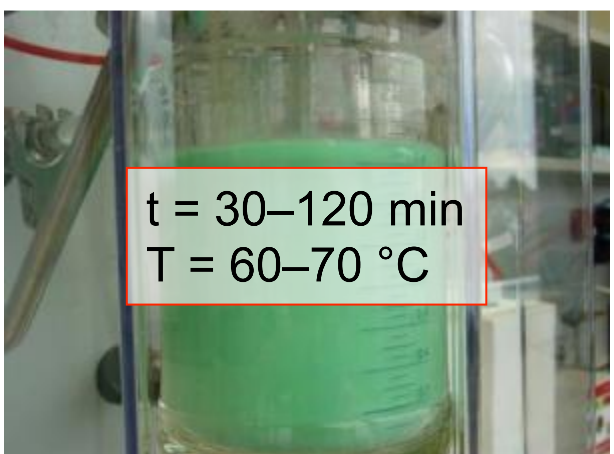
Catalyst synthesis



Co-Precipitation

Cu:Zn = 70:30
pH 6–7
T = 60–70 °C

Ageing

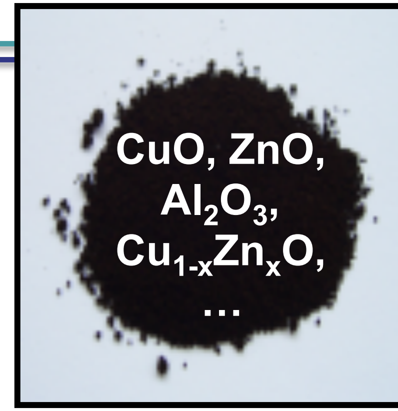


t = 30–120 min
T = 60–70 °C

Washing
Drying

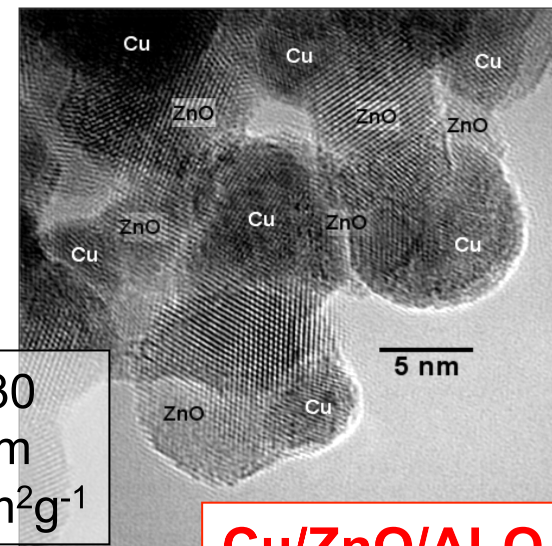
Malachite
Rosasite
Aurichalcite
Hydrotalcite
...

Calcination



CuO, ZnO,
Al_2O_3,
$Cu_{1-x}Zn_xO$,
...

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)

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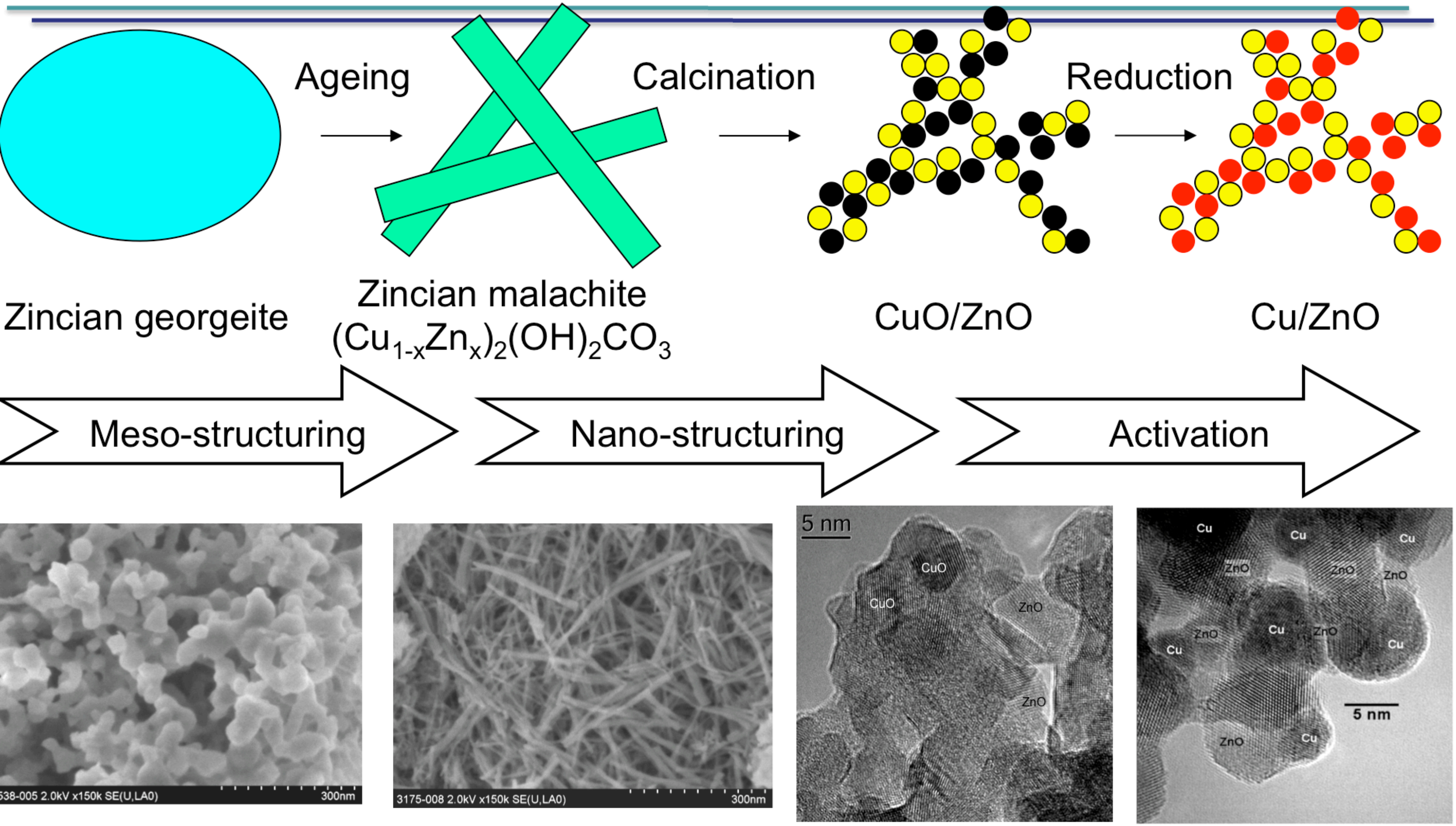
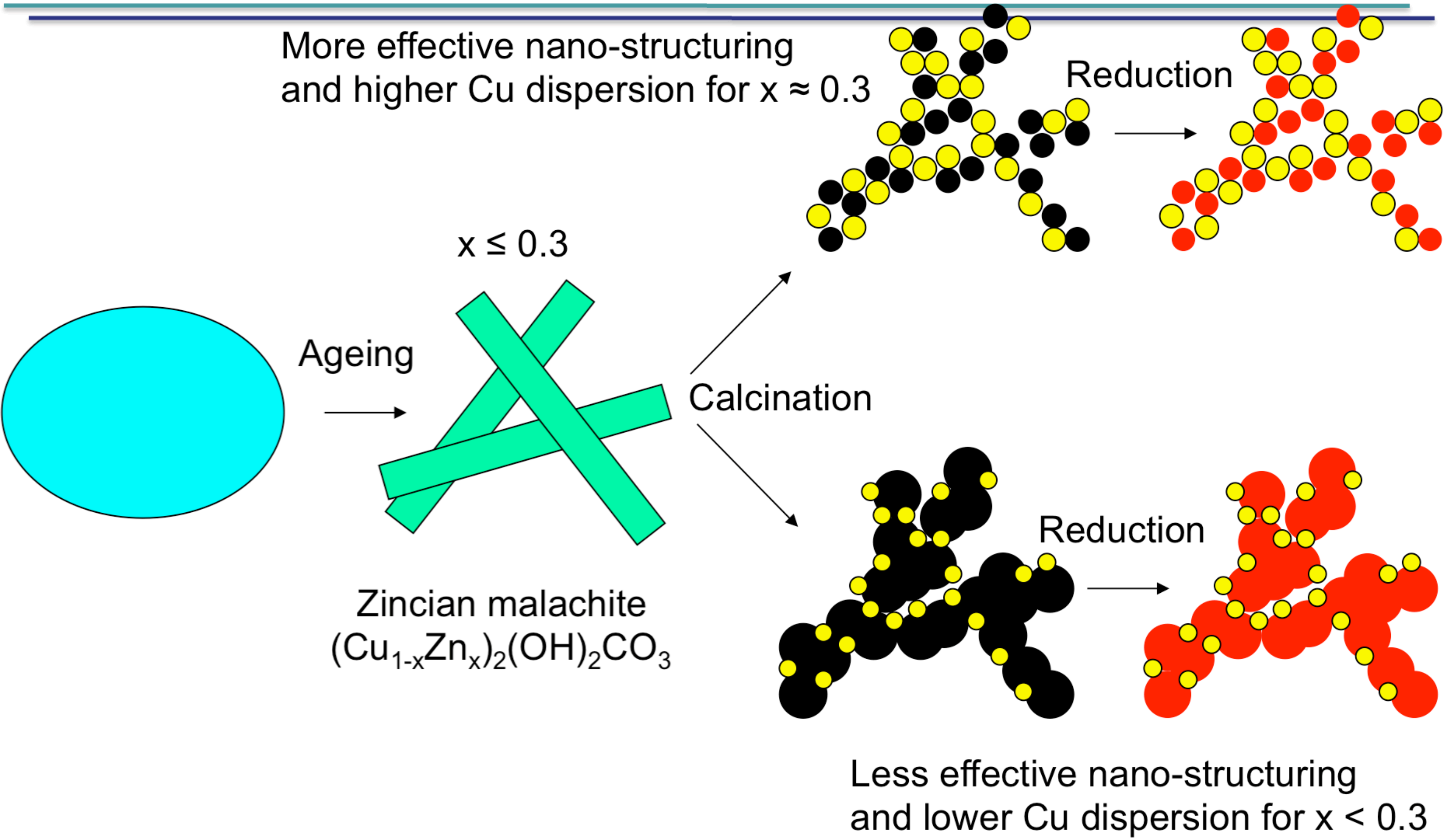


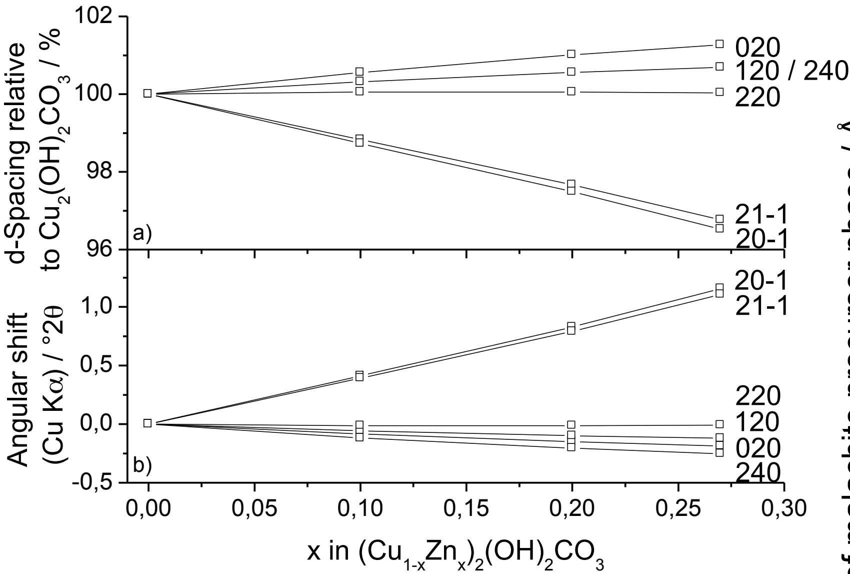
Undefinied compact shape
size ca. 100 nm

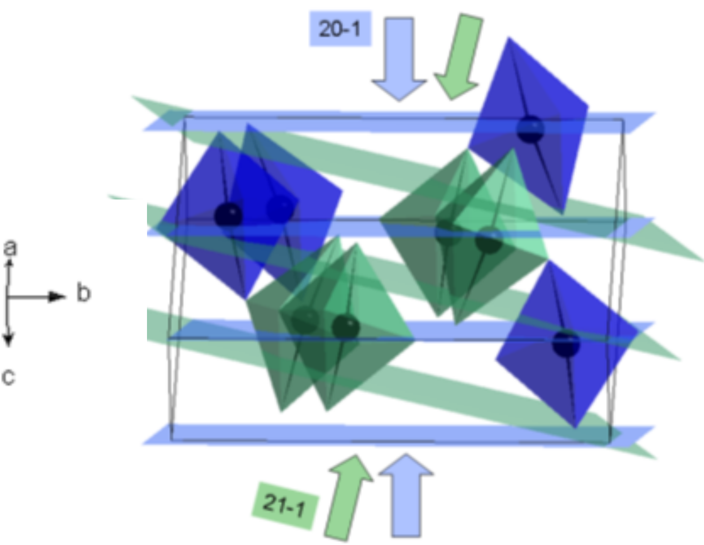
Thin needles
size ca. 20 × 200 nm

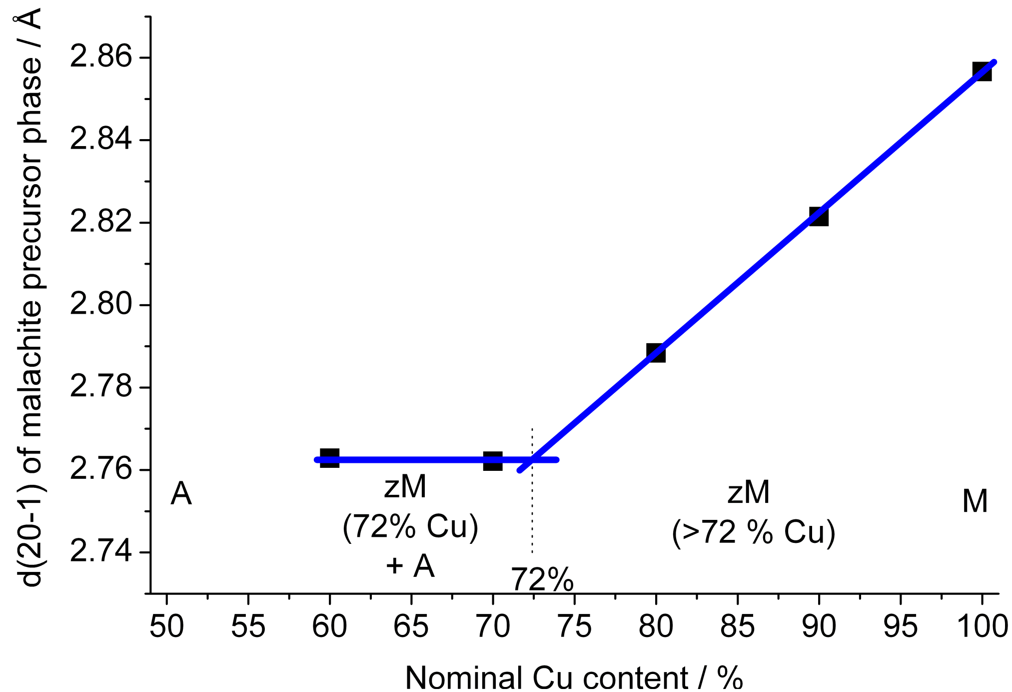
Spherical shaped particles
size ca. 10 nm


More effective nano-structuring
and higher Cu dispersion for x ≈ 0.3
Reduction
x ≤ 0.3
Ageing
Calcination
Reduction
Zincian malachite
$(Cu_{1-x}Zn_x)_2(OH)_2CO_3$
Less effective nano-structuring
and lower Cu dispersion for x < 0.3

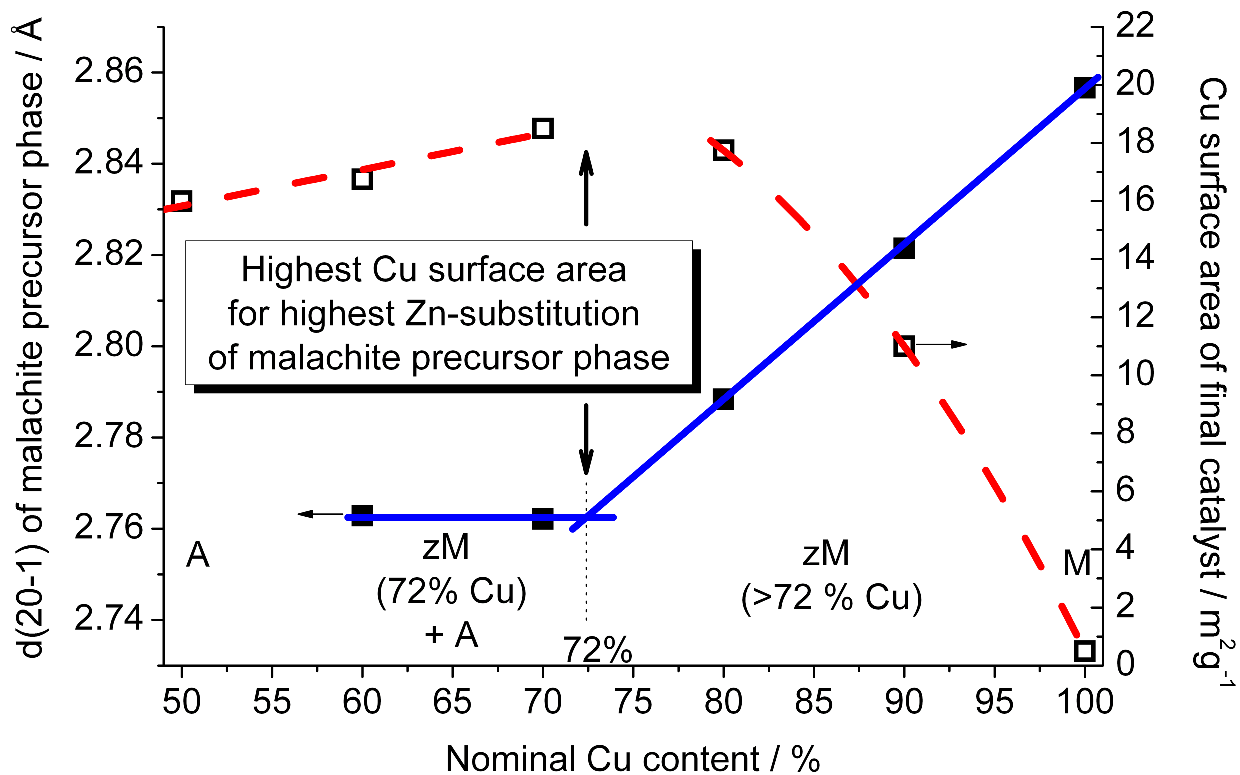
Precursor solid state chemistry







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



Highest Cu surface area
for highest Zn-substitution
of malachite precursor phase
d(20-1) of malachite precursor phase / Å
Cu surface area of final catalyst / m2g-1
Nominal Cu content / %
A
zM
(72% Cu)
+ A
72%
zM
(>72 % Cu)
M

The “universal” catalysis trick: a promoter

Al does much more to the active phase than serving as spacer between Cu NP

$Cu/ZnO/(Al_2O_3)$ in MeOH synthesis

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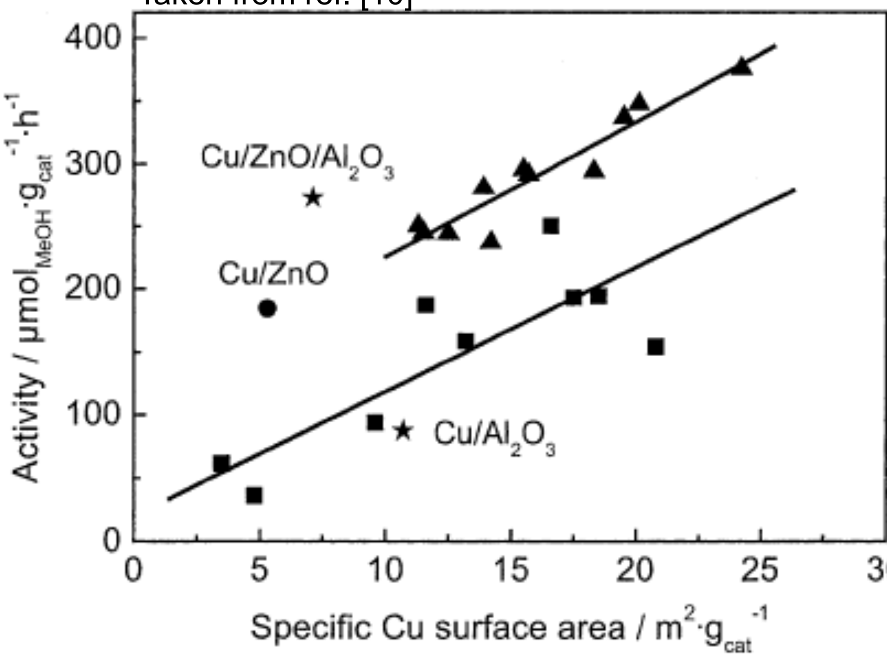
Taken from ref. [10]



- Cu/Zn Catalysts exhibit higher specific activity than Cu/SiO_2 systems [1,2]
- Synergetic effect of ZnO
  - as geometric spacer
  - on active Species:
    - Cu(0) surface[3]
      - with lattice strain[4]
      - with planar defects[5]
    - Dynamic processes („Topsøe-Model“)[6]
    - Cu^+ in the ZnO lattice[7]
    - Electron-rich Cu at Schottky-junction[8]
    - H-Spillover from ZnO involved[9]
- Promoting effect of Al_2O_3[10]

[1] Y. Kanai, T. Wanatabe, T. Fujitani, T. Uchijima, J. Nakamura, Catal. Lett. 38 (1996) 157.

[2] R. Burch, R. J. Chappell, S. E. Golunski, J. Chem. Soc. Faraday Trans. 85 (1989) 3569.

[3] K. C. Waugh, *Catal. Today* 15 (1992) 51-75.

[4] M. M. Günter, T. Ressler, B. Bems, C. Büscher, T. Genger, O. Hinrichsen, M. Muhler, R. Schlögl, *Catal. Lett.* 71 (2001) 37.

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

[6] J.-D. Grunwaldt, A.M. Molenbroek, N.-Y. Topsøe, H. Topsøe, B.S. Clausen, J. Catal. 194 (2000) 452.

[7] K. Klier, *Adv. Catal.* 31 (1982) 243.

[8] J. C. Frost, *Nature* 334 (1988) 577-580.

[9] M. S. Spencer, *Catal. Lett.* 50 (1998) 37-40.

[10] M. Kurtz, N. Bauer, C. Büscher, H. Wilmer, O. Hinrichsen, R. Becker, S. Rabe, K. Merz, M. Driess, R. A. Fischer, M. Muhler, *Catal. Lett.* **2004**, *92*, 49.

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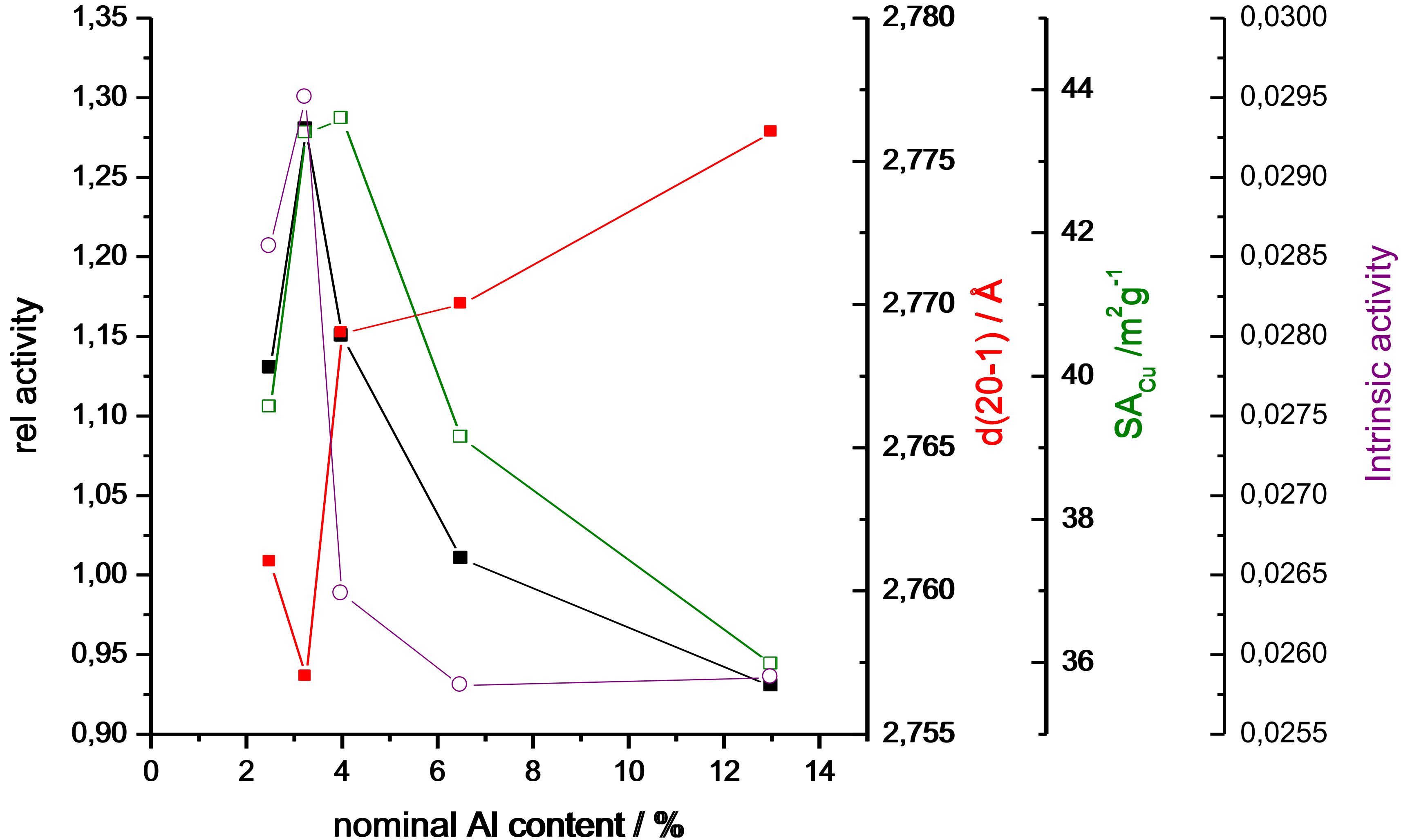
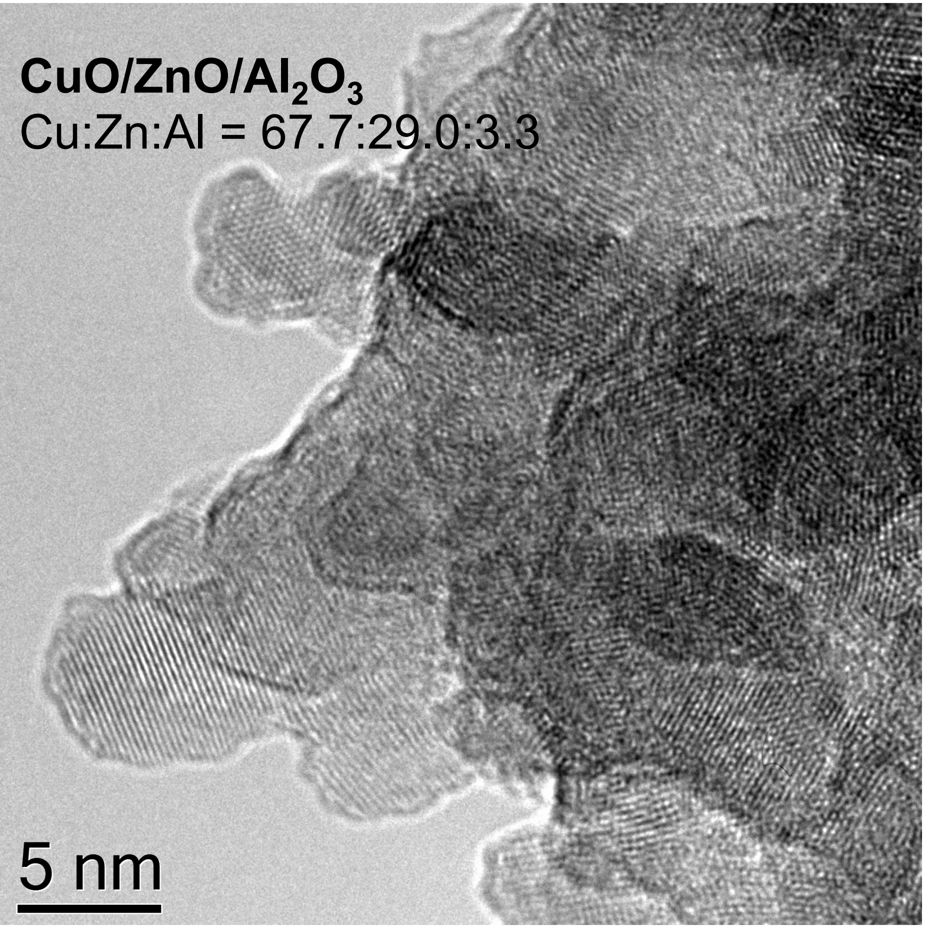
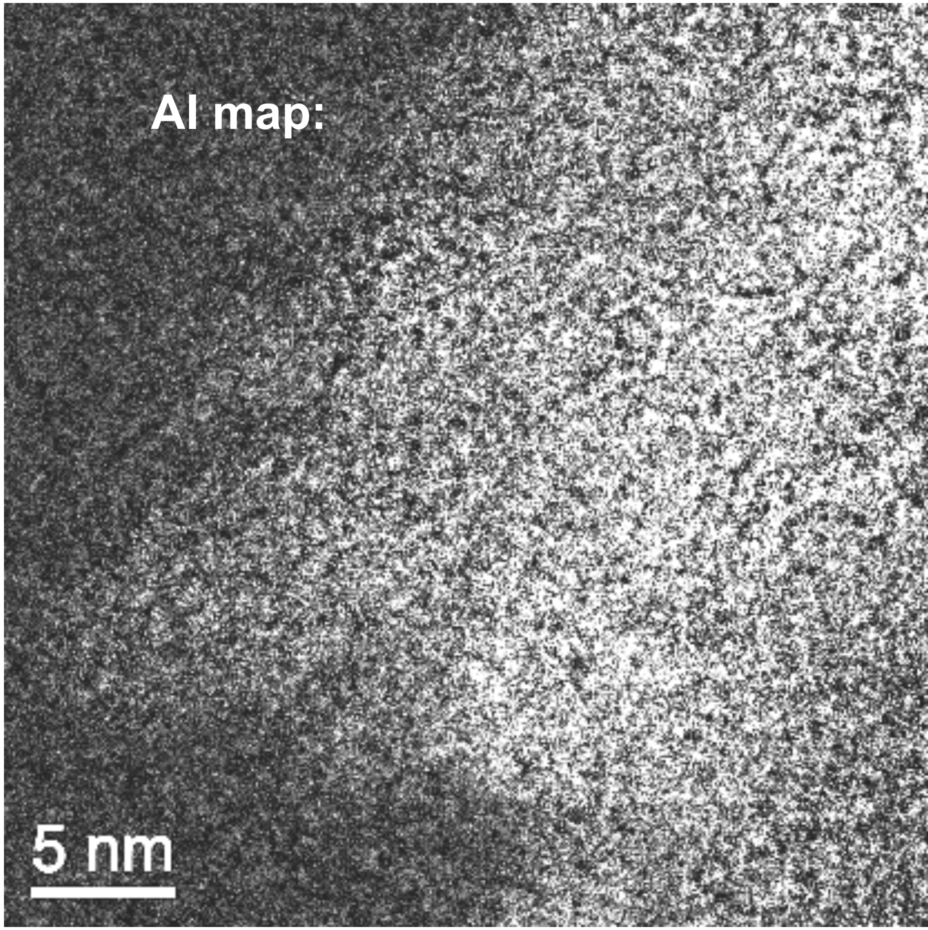
Geometric effect of promoter?



The fate of the promoter





Al is well dispersed, above 3% solubility limit in ZnO reached and spinel formation

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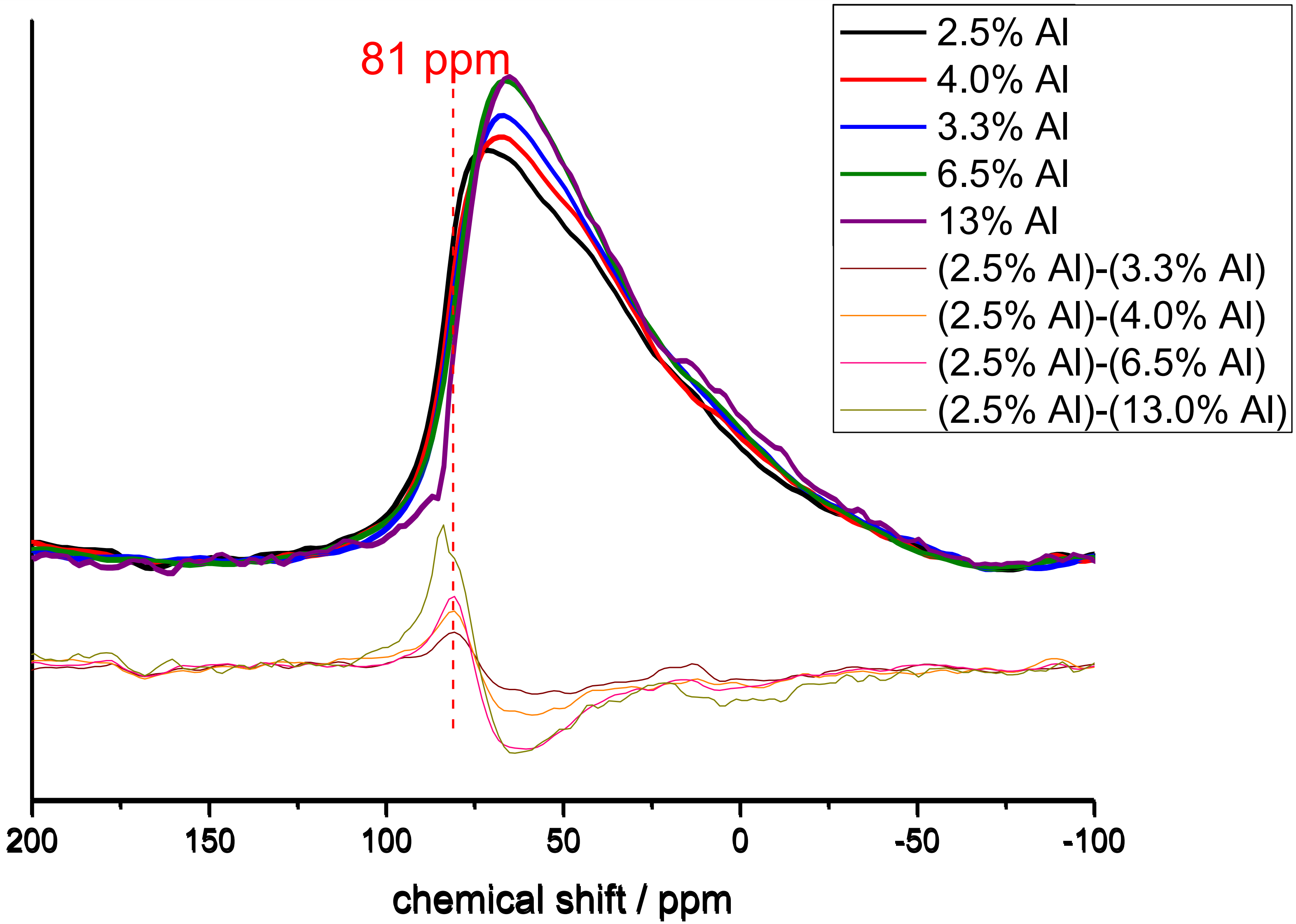
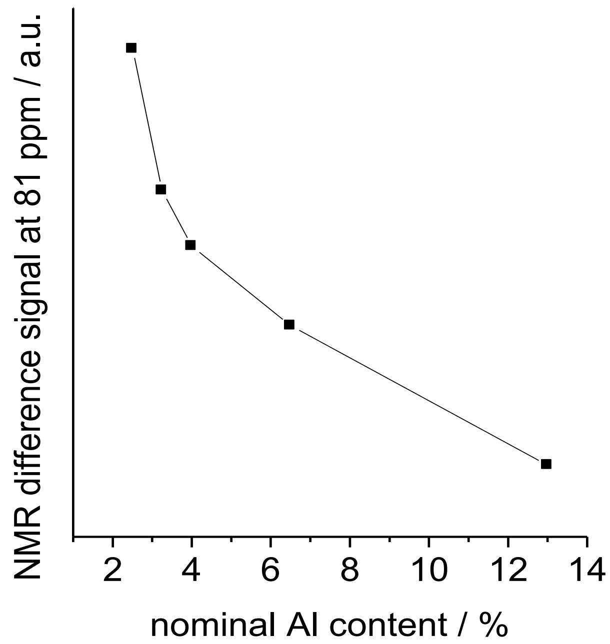
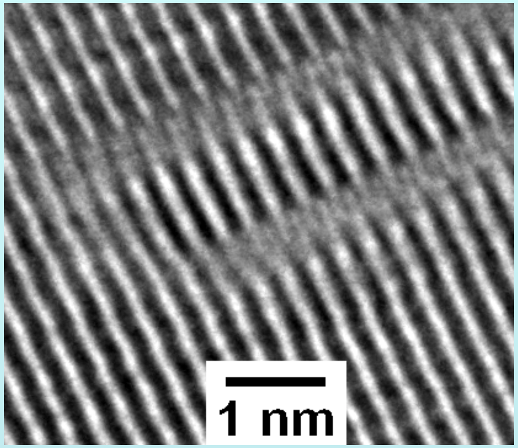
^{27}Al-MAS-NMR study





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



Nano-Cu with a non-reducible oxide

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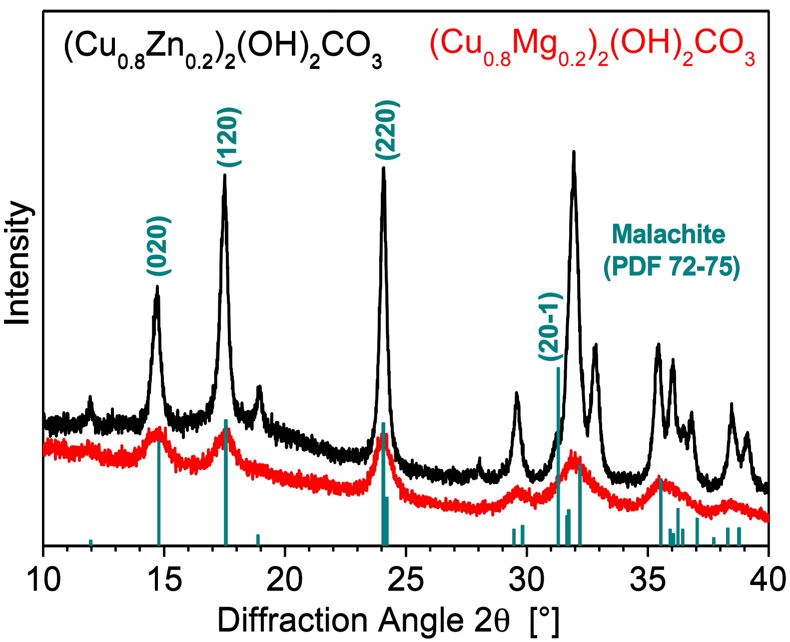
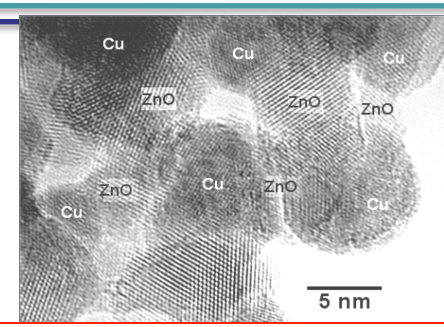
$(Cu_{1-x}M_x)_2(OH)_2CO_3$
$x = 0.2$

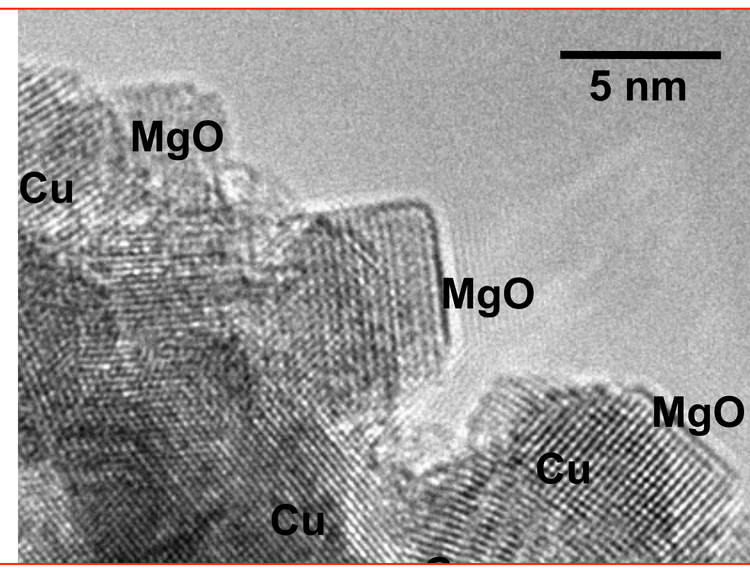


M = Zn



$SA_{Cu} = 27\ m^2g^{-1}$
WTY_{MeOH} = **0.22** $mmol_{MeOH}h^{-1}g_{cat}^{-1}$

M = Mg



$SA_{Cu} = 39\ m^2g^{-1}$
WTY_{MeOH} = **0.03** $mmol_{MeOH}h^{-1}g_{cat}^{-1}$

Time for models: not as you may expect

A series of polycrystalline phase-pure systems with Cu/Zn constant and pure Cu NP are prepared by varying the kinetics

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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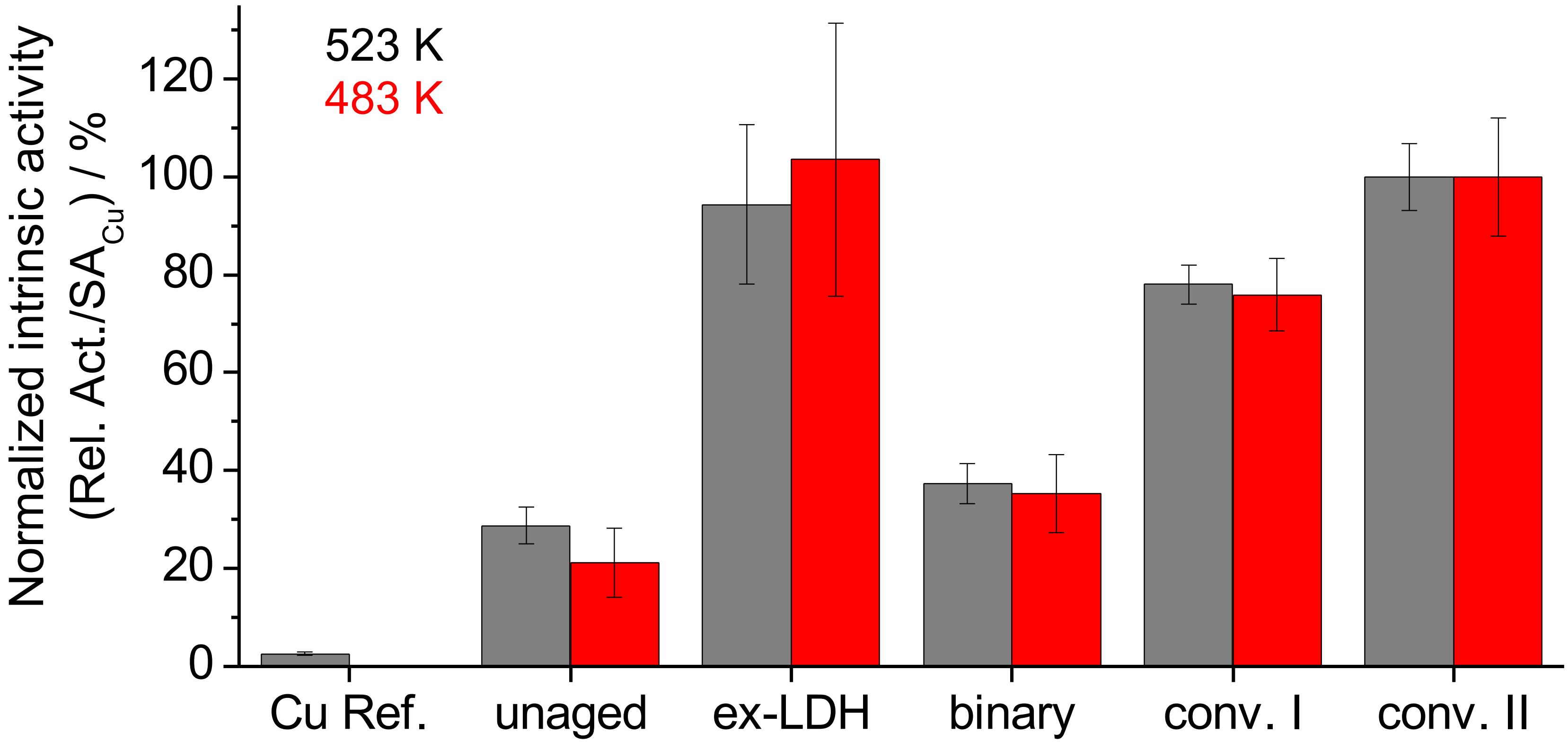
Intrinsic activities



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

Defect analysis of neutron diffraction data

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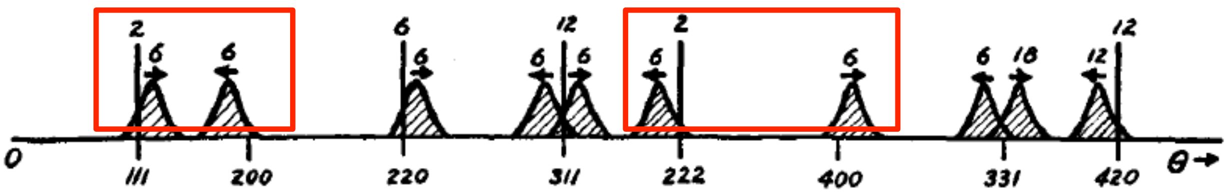
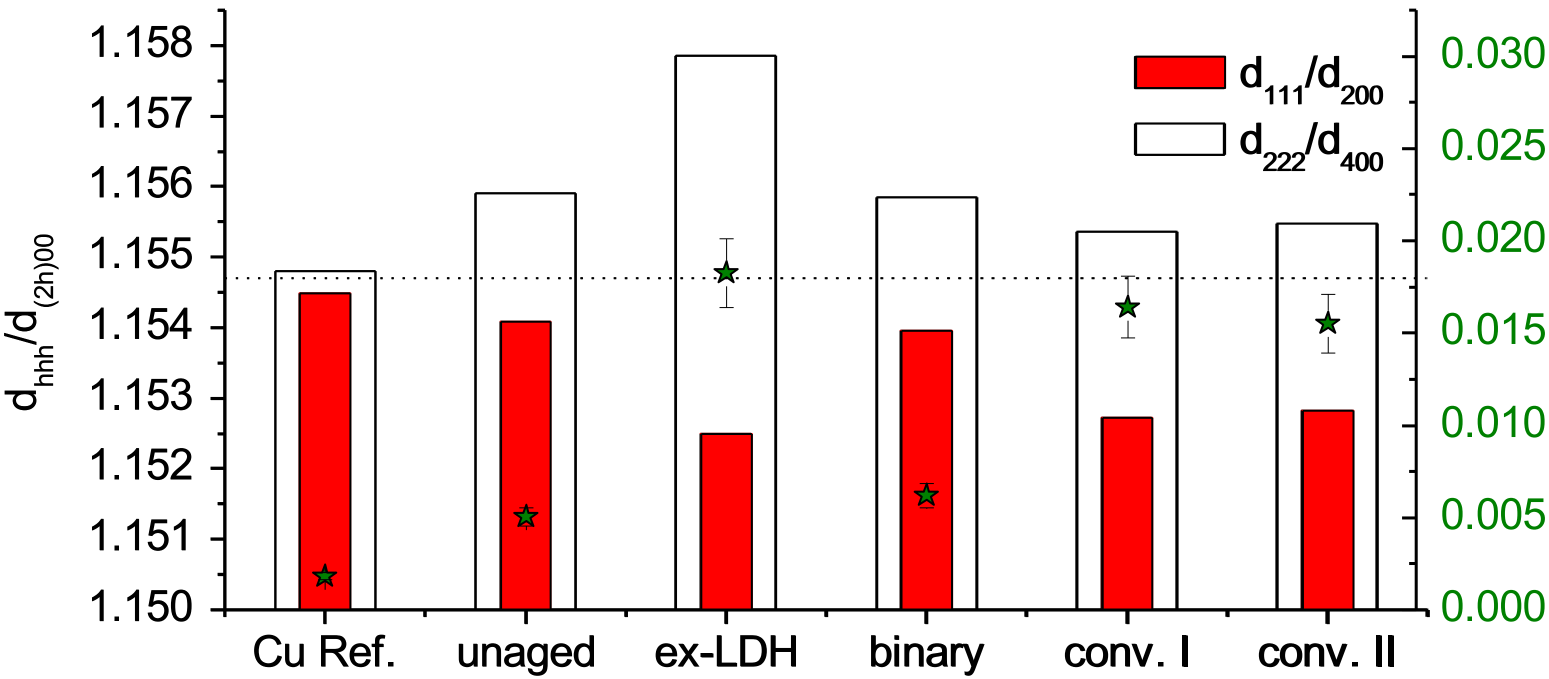
M.S. Paterson, J. Appl. Phys. 23, 1952, 805: (h+k+l = 3N±1) broadened and shifted; (h+k+l = 3N) not affected





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

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

Defect structure – function relationship

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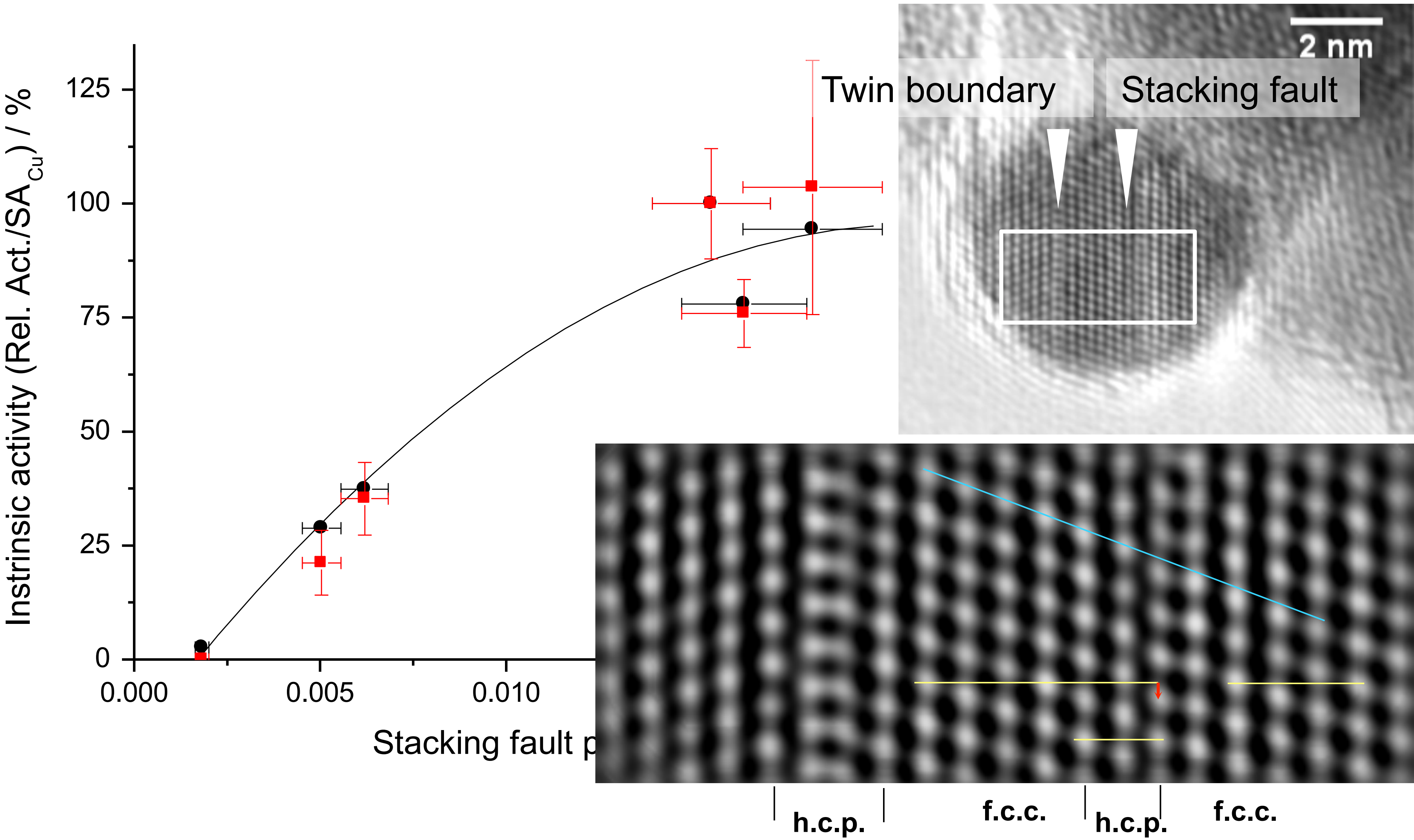
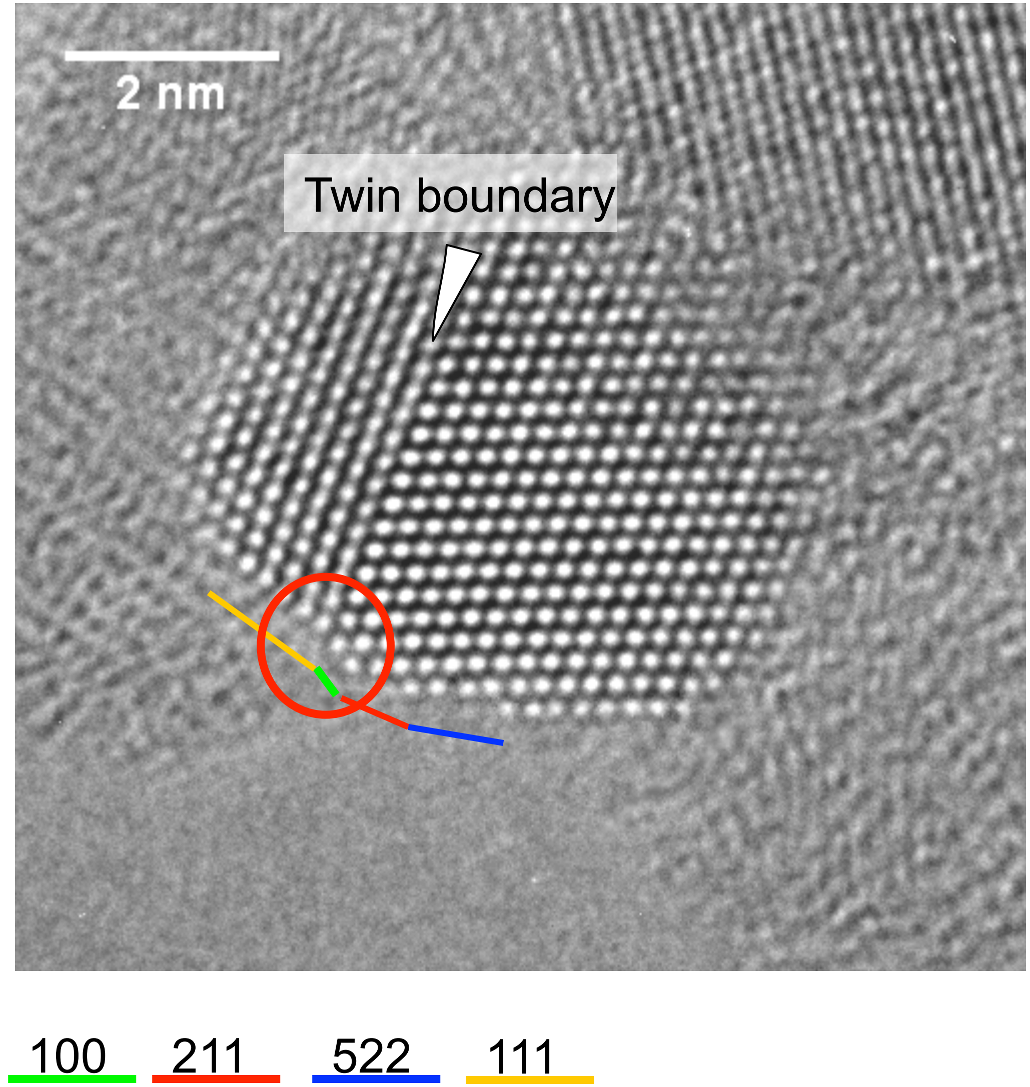


HRTEM study of $Cu/ZnO/Al_2O_3$: Defects

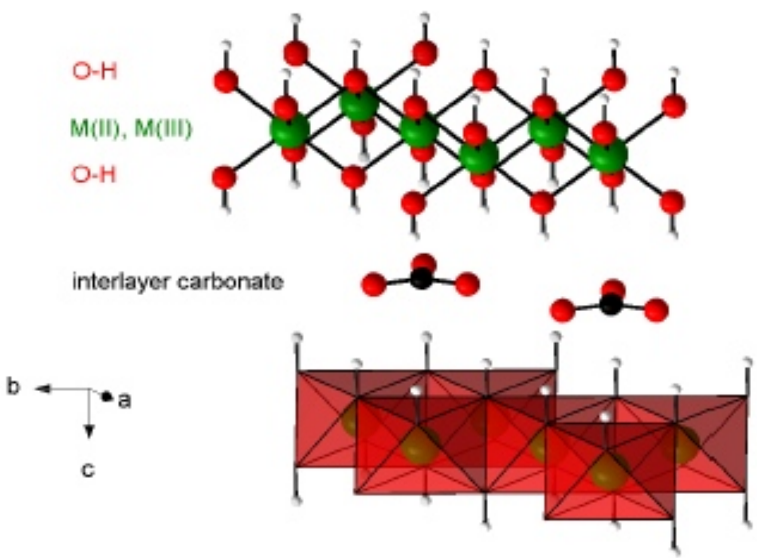
Reduced in 5% H_2
6 Kpm, 250 °C, 30 min



A functional model Cu/ZnO ex LDH

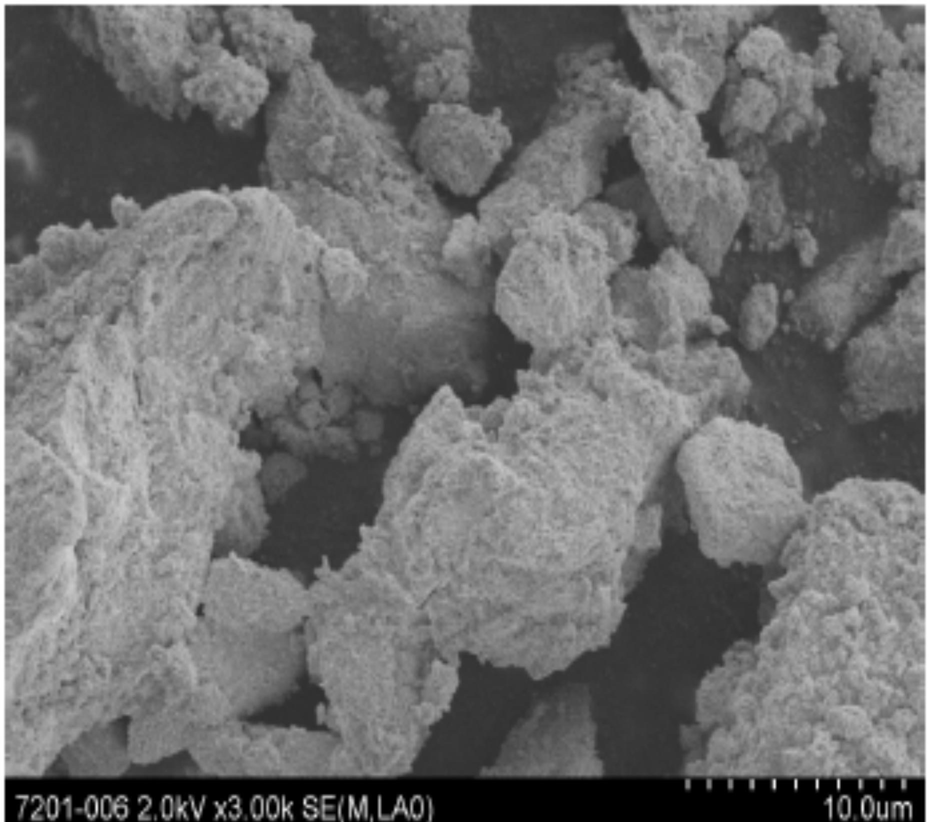
$$[M(II)_{1-x}M(III)_x(OH)_2]^{x+}(A^{n-}_{x/n})\cdot mH_2O$$

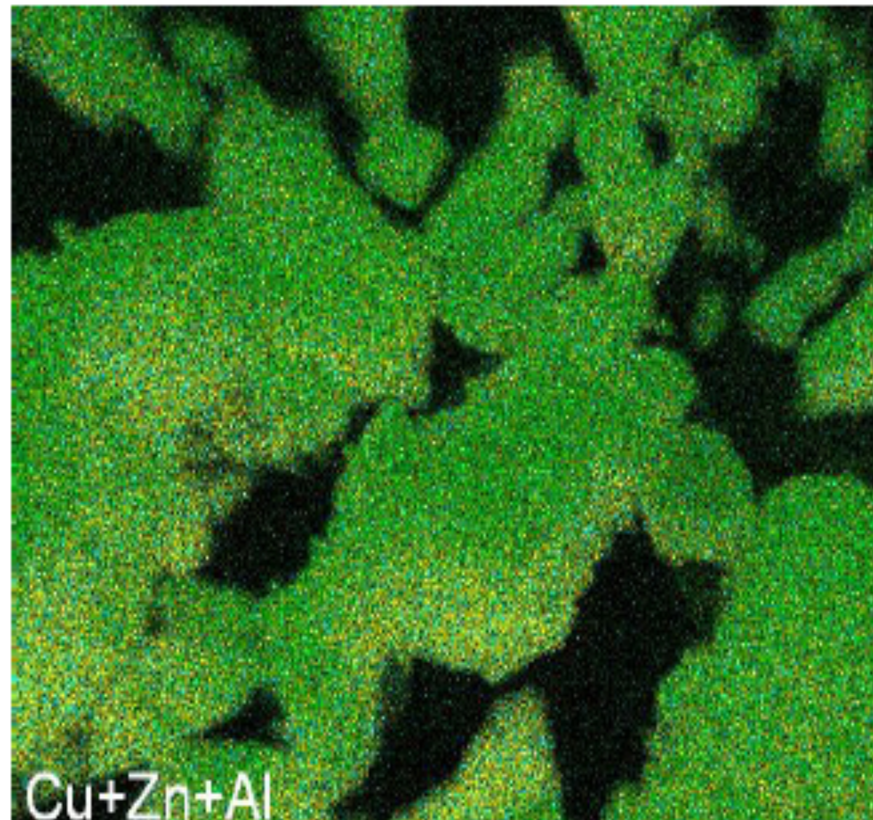
- Cu,Zn,Al hydrotalcite-like compounds (LDH) formed as by-phase during synthesis of $Cu/ZnO/Al_2O_3$ catalysts for methanol synthesis



- expectations:
  - formation of catalysts with homogeneous microstructure
  - high dispersion of the metal species
  - enhanced metal-oxide interaction after reduction

A functional model Cu/ZnO ex LDH





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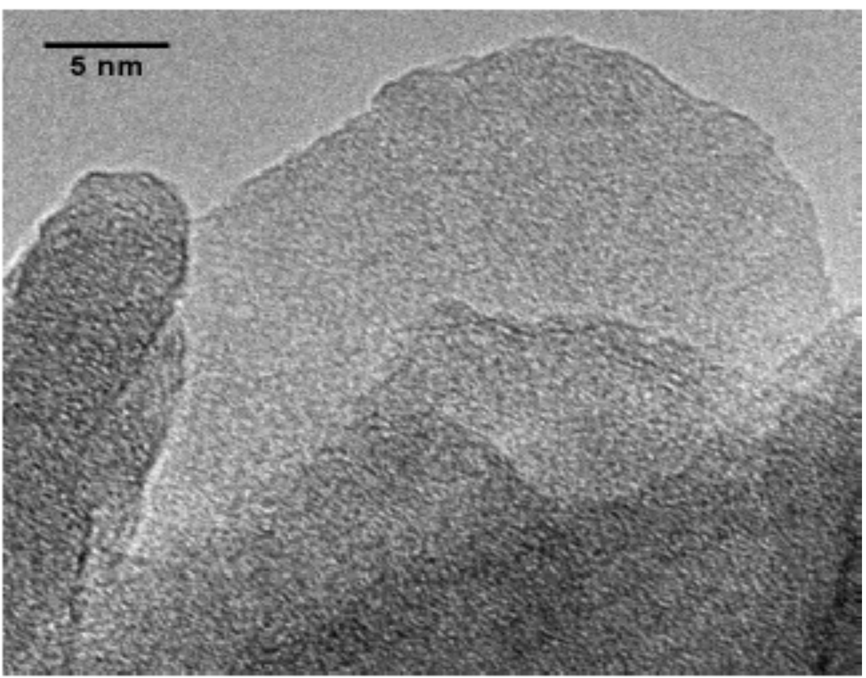
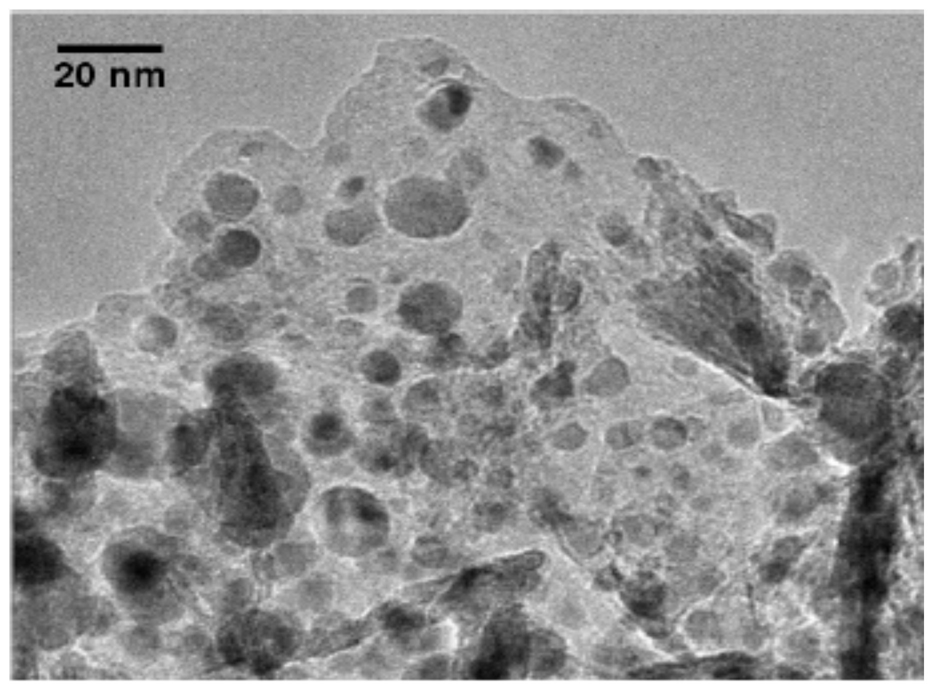
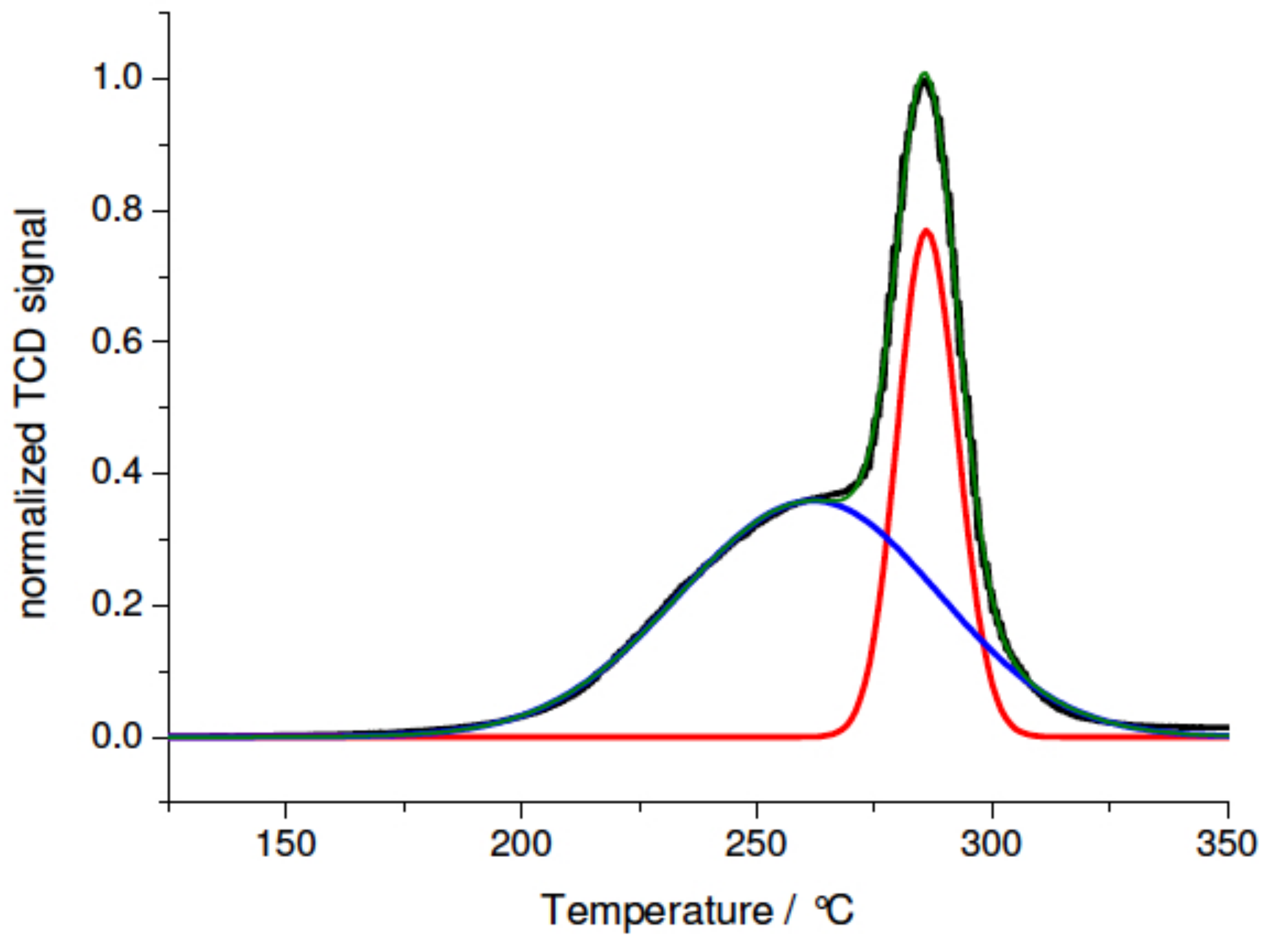
A functional model Cu/ZnO ex LDH





Where come the defects from?



The intermediate oxide

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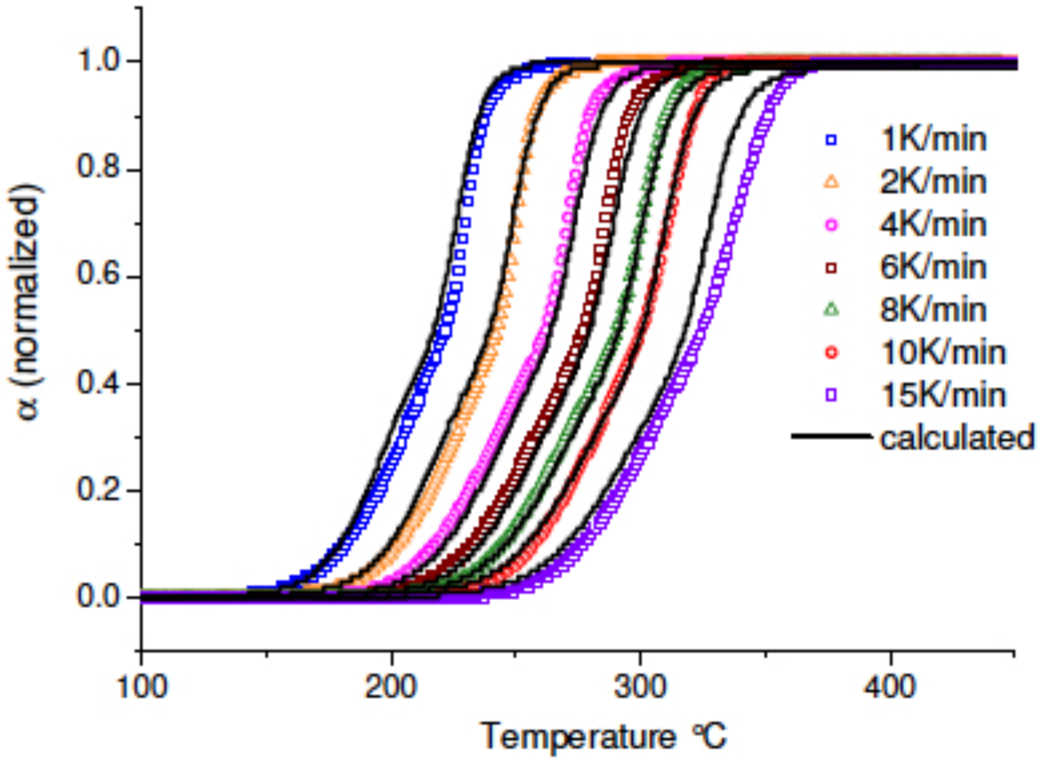
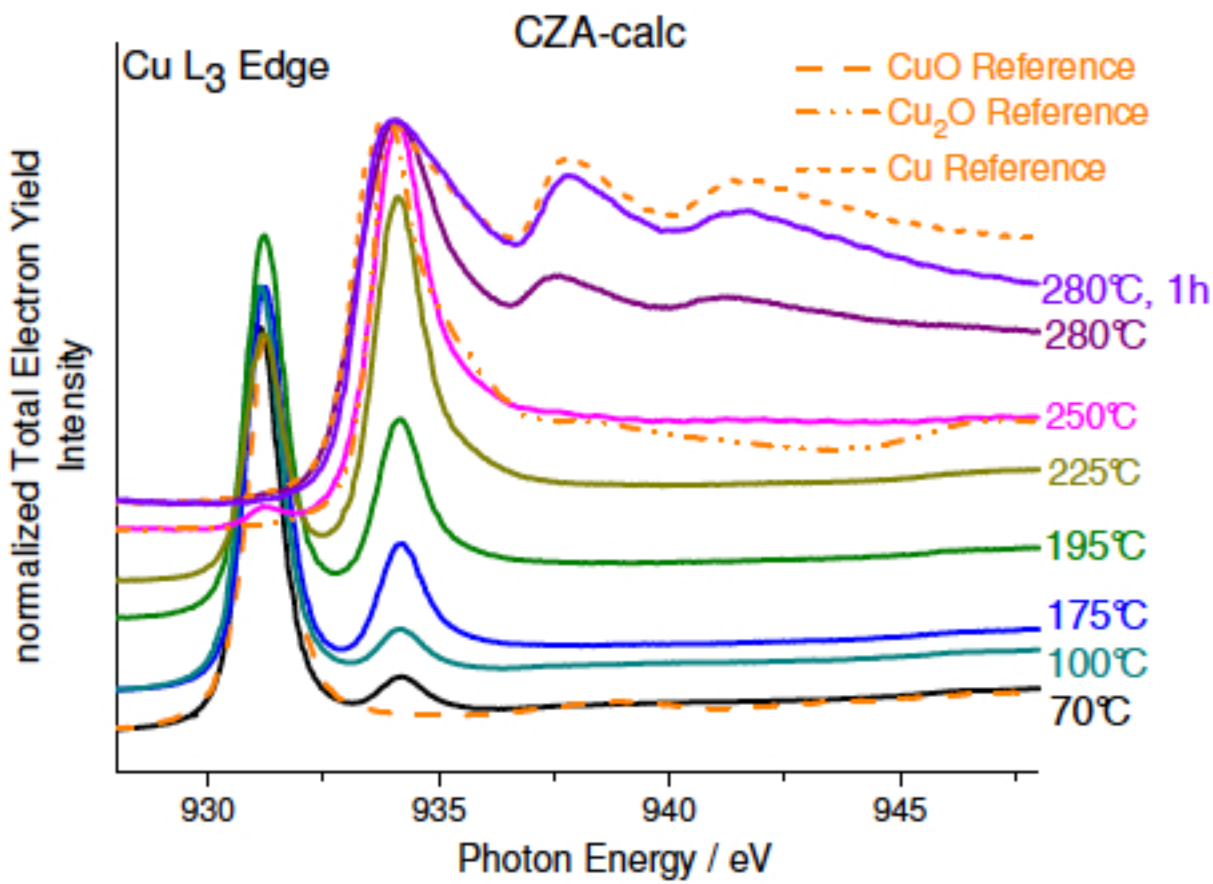
Where come the defects from?

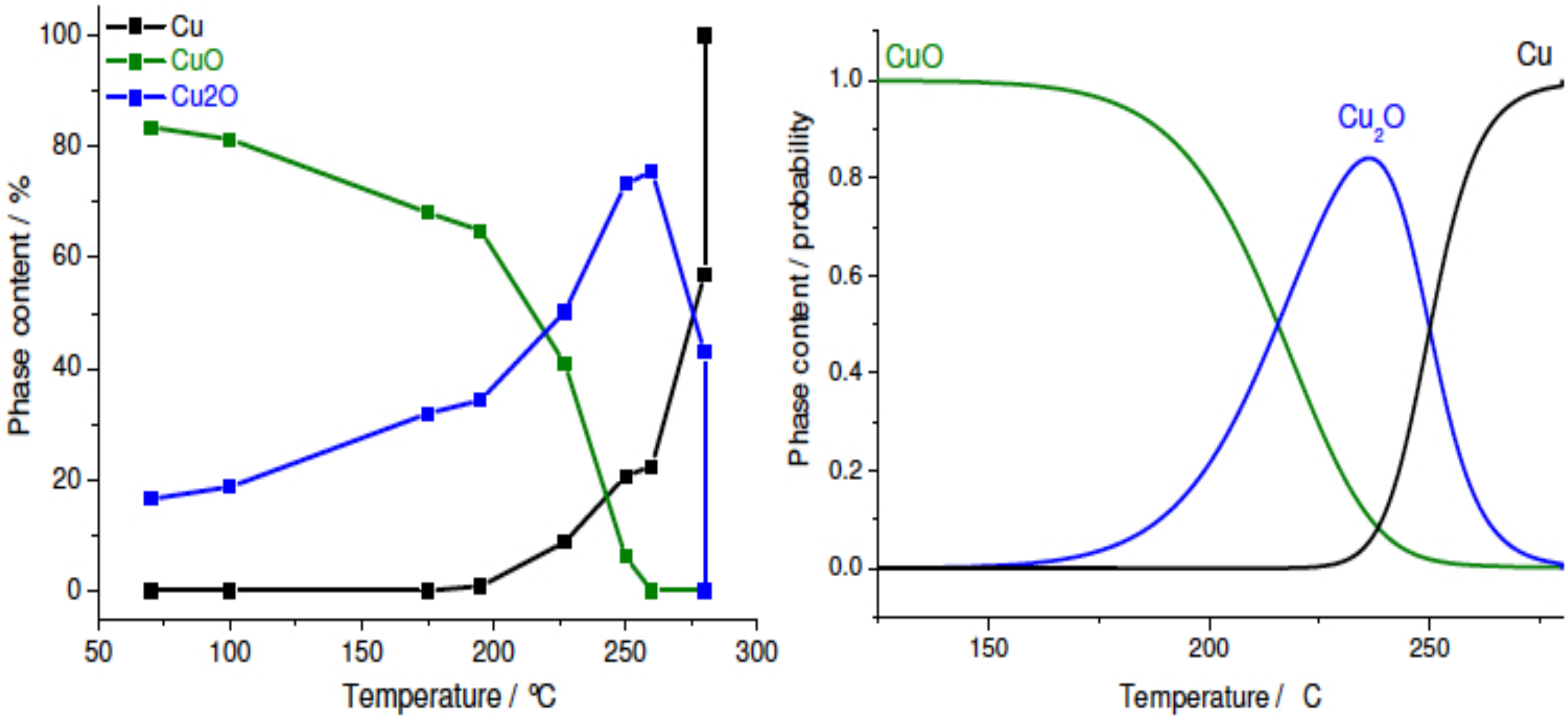


Thermal analysis and modelling.
A➔B➔C, E_{a1}= 56 kJ/mol, E_{a2} = 63 kJ/mol
Autocatalytic process with 1-D reaction front

Where come the defects from?



Where come the defects from?



Seeing the defects

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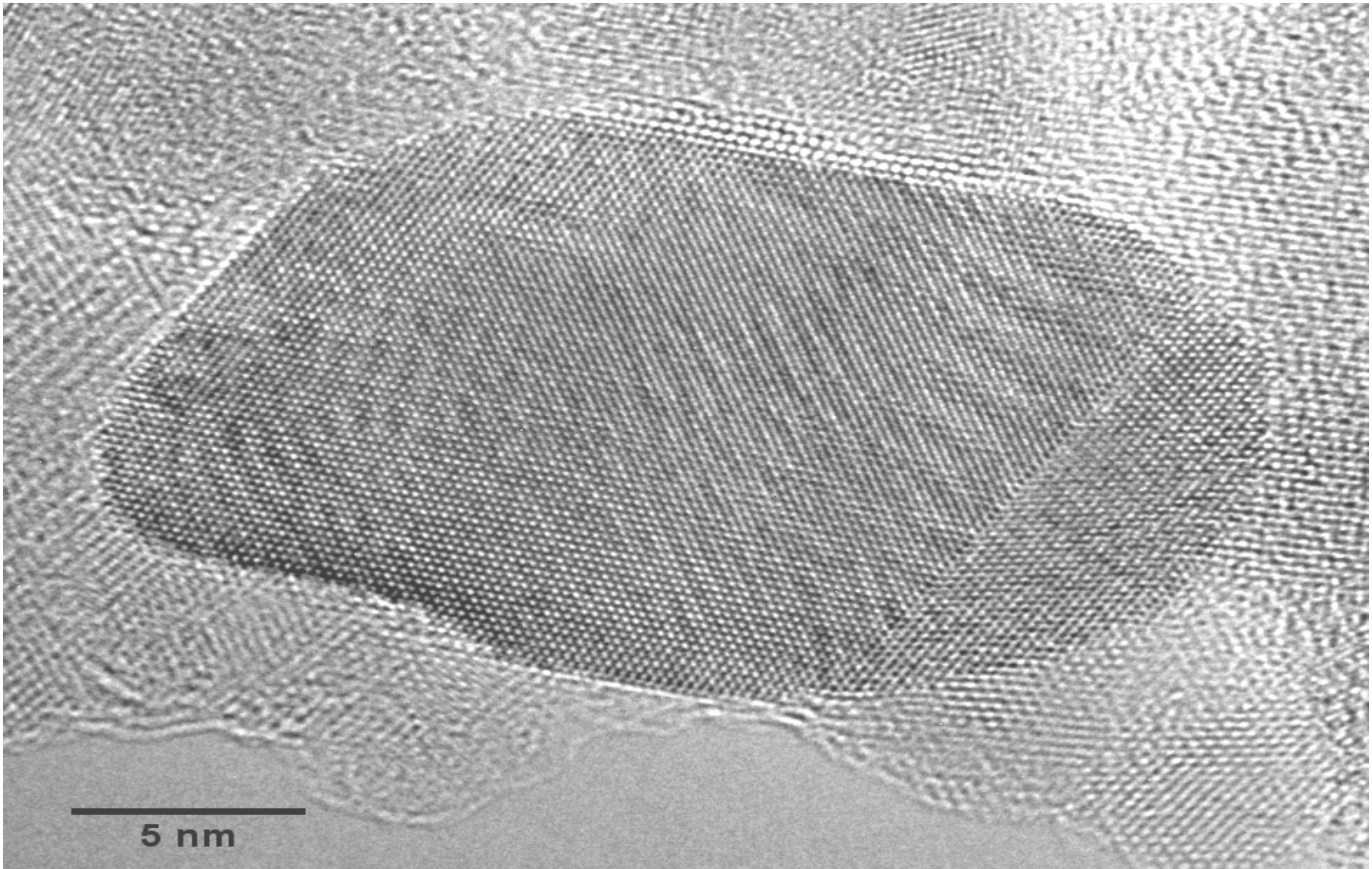
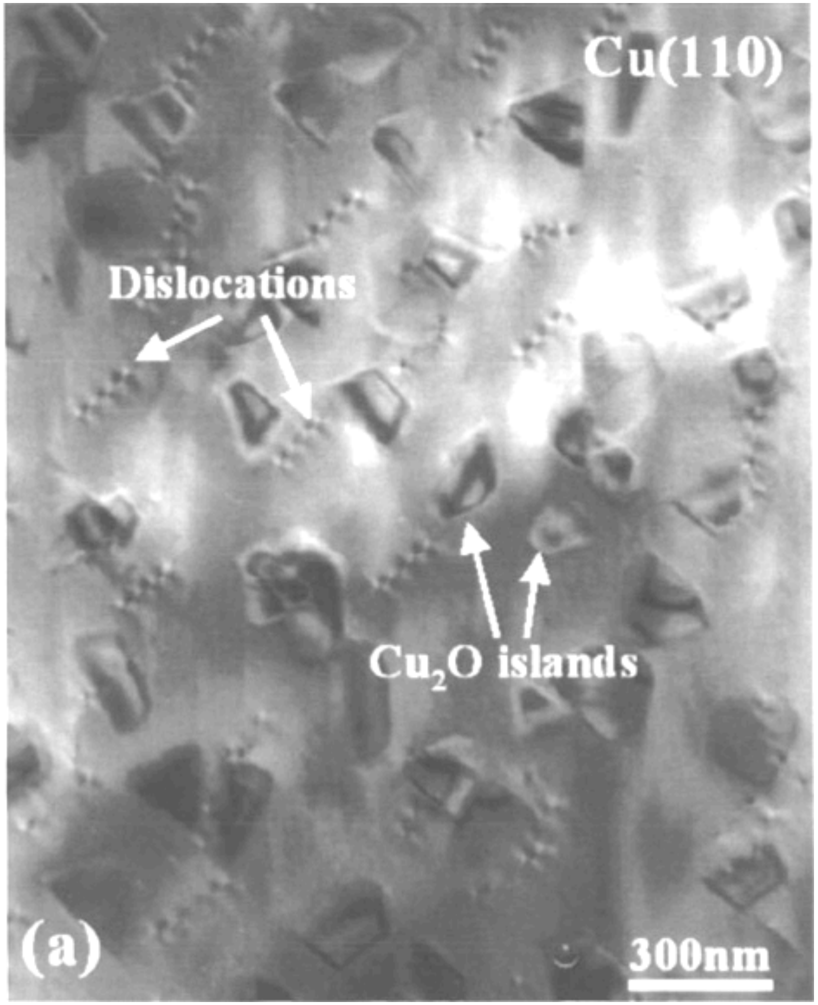


Summary models: bulk

- Pure copper is not the active phase: some defects are critical.
- Point defects and “roughness” are not directly connected.
- It is the line defects (twins and dislocations) that correlate well with the intrinsic performance.
- What is the effect of synergy:
  - Stabilizing defects?
  - Decorating the surface as co-catalyst
  - Forming a surface alloy?



Active oxygen located at strained sites

Zhuo et al, J. Appl. Phys, 2006

Surface analysis: what we can learn from in-situ studies

ambient pressure photoemission allows connection to structural data and gives us a complementary picture to microscopy

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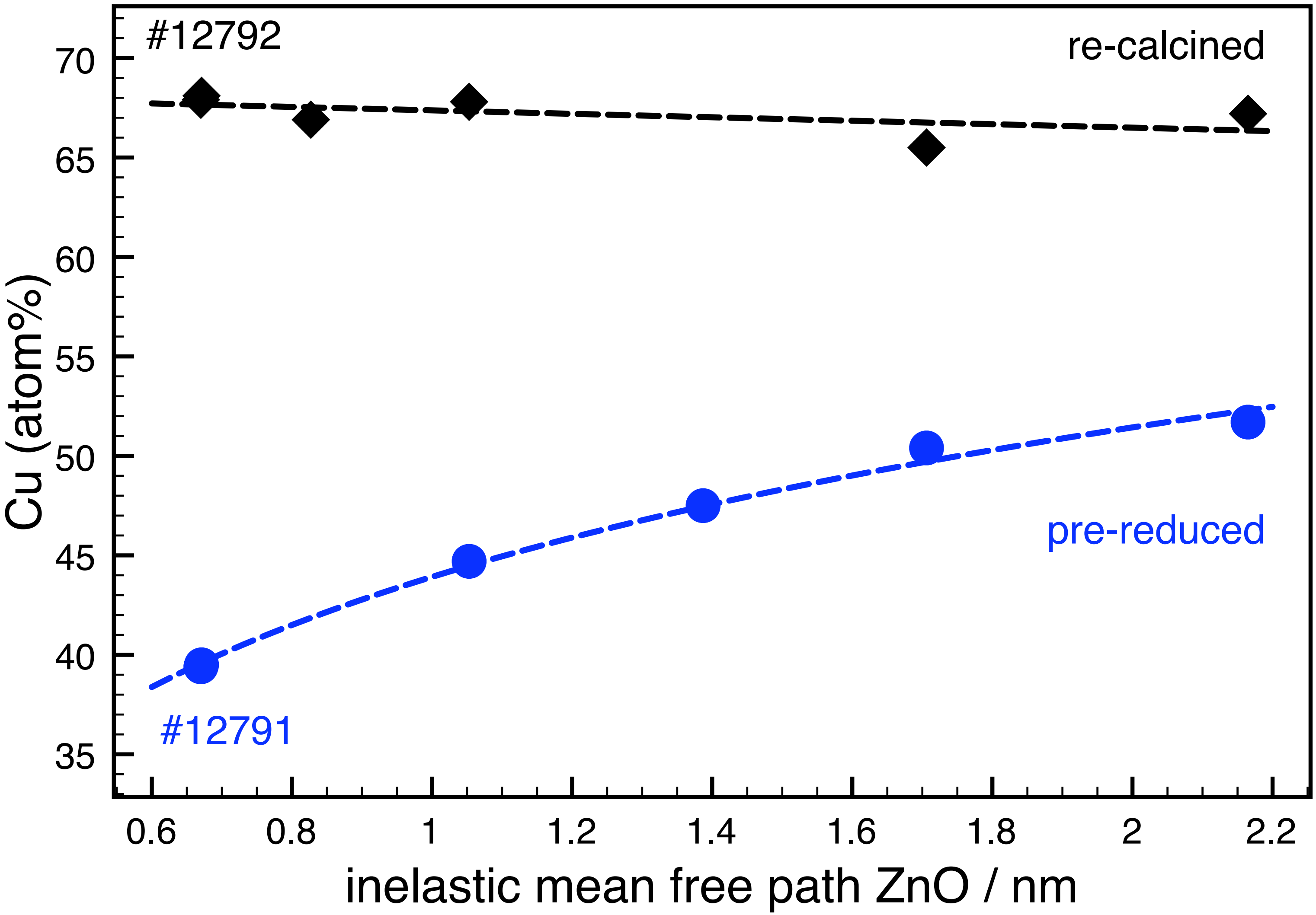
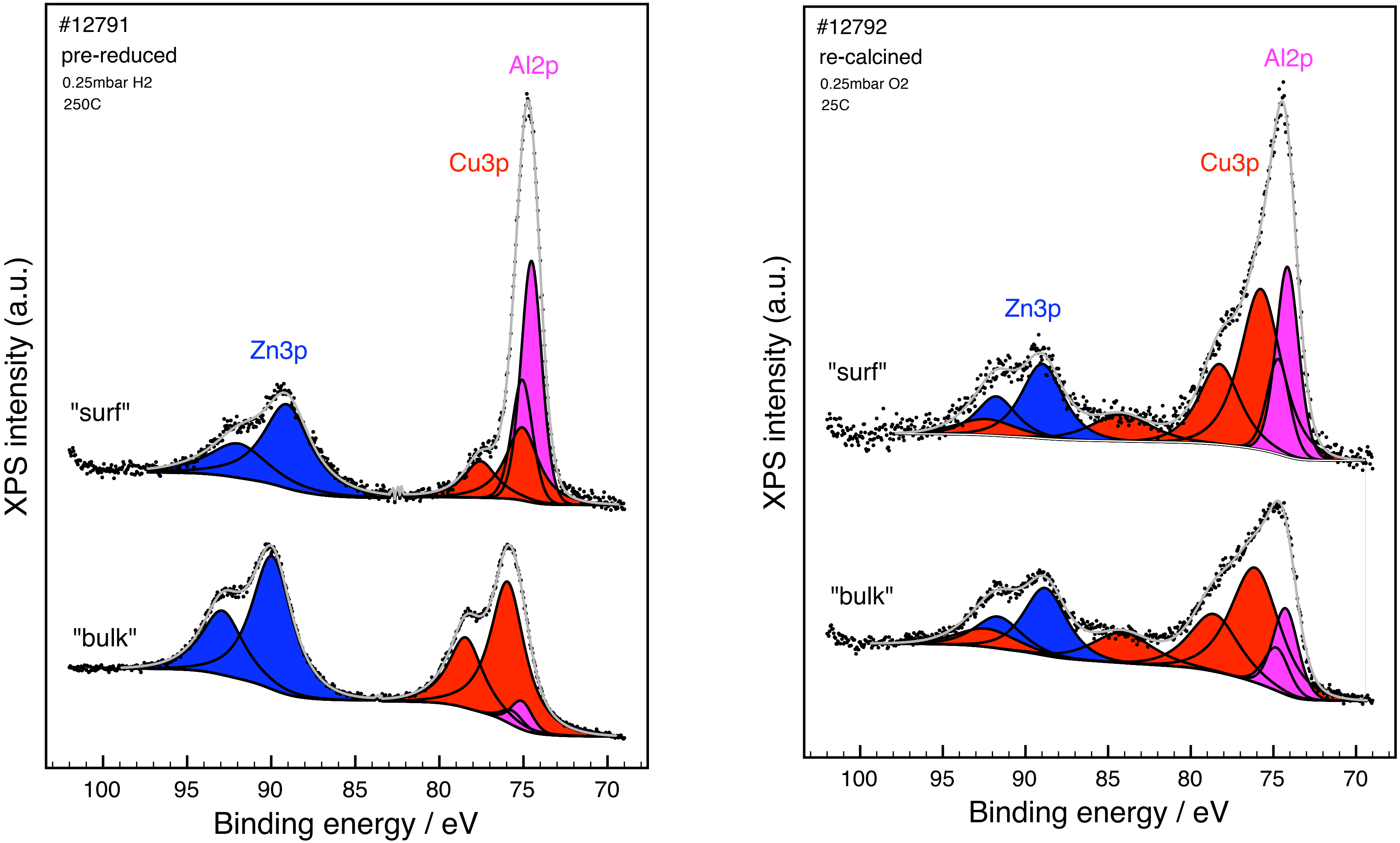
Depth-resolved surface composition



Termination layer



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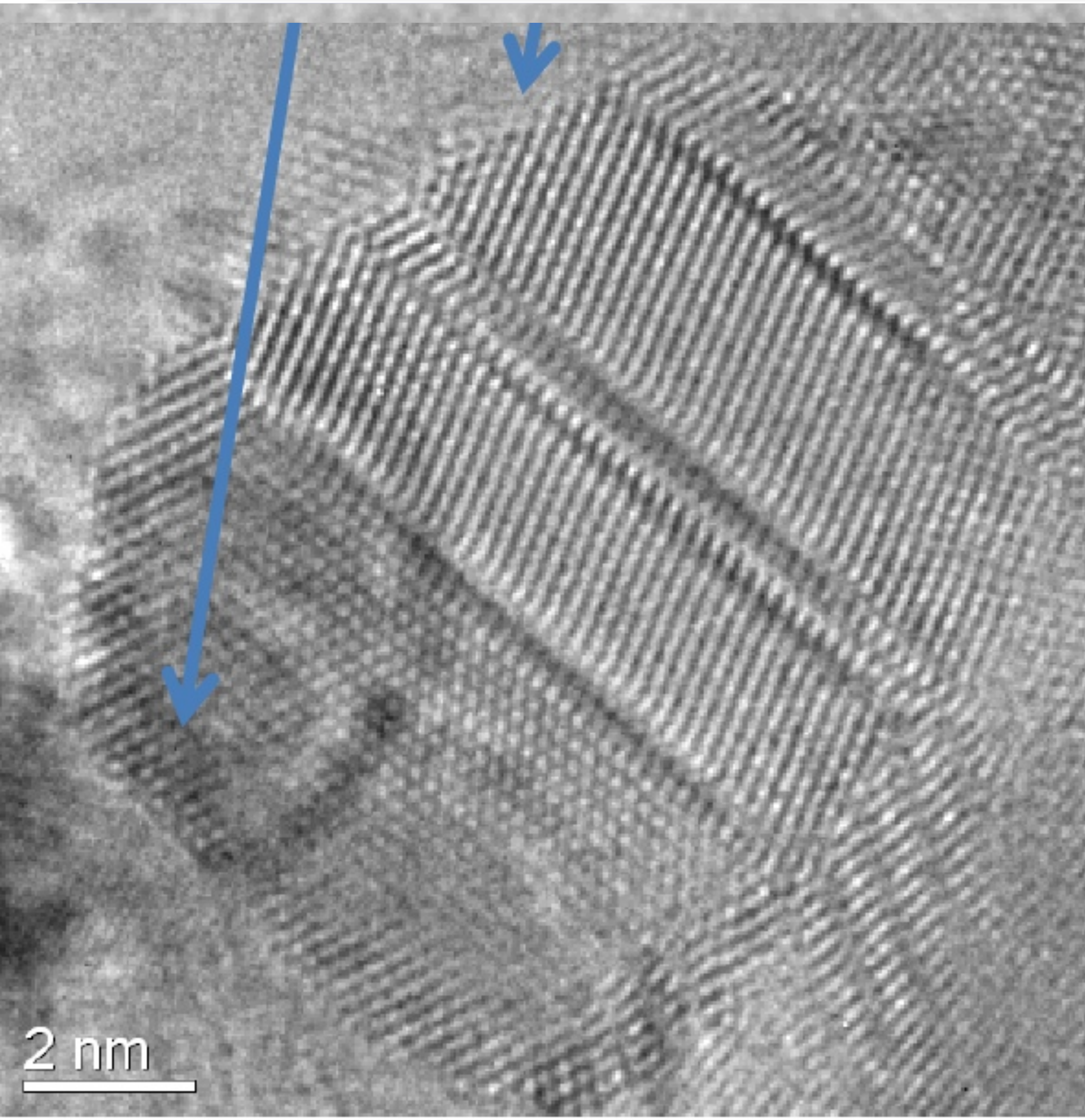
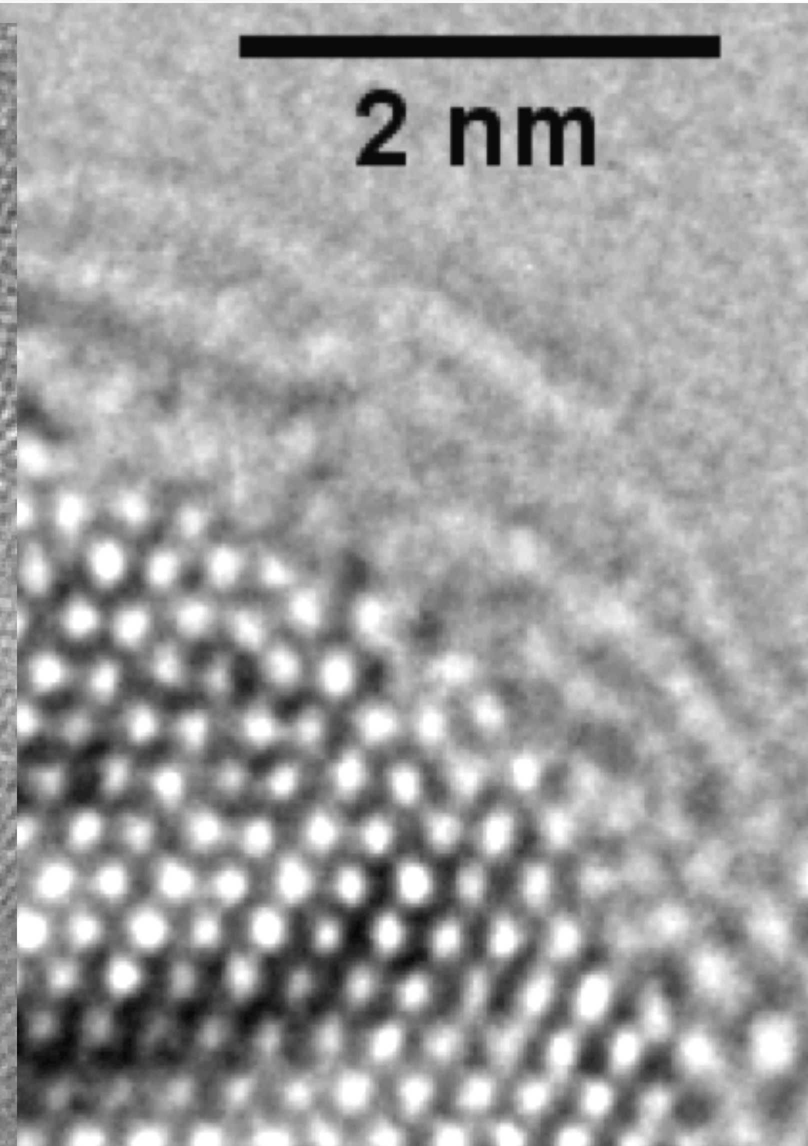
Seeing the surface termination





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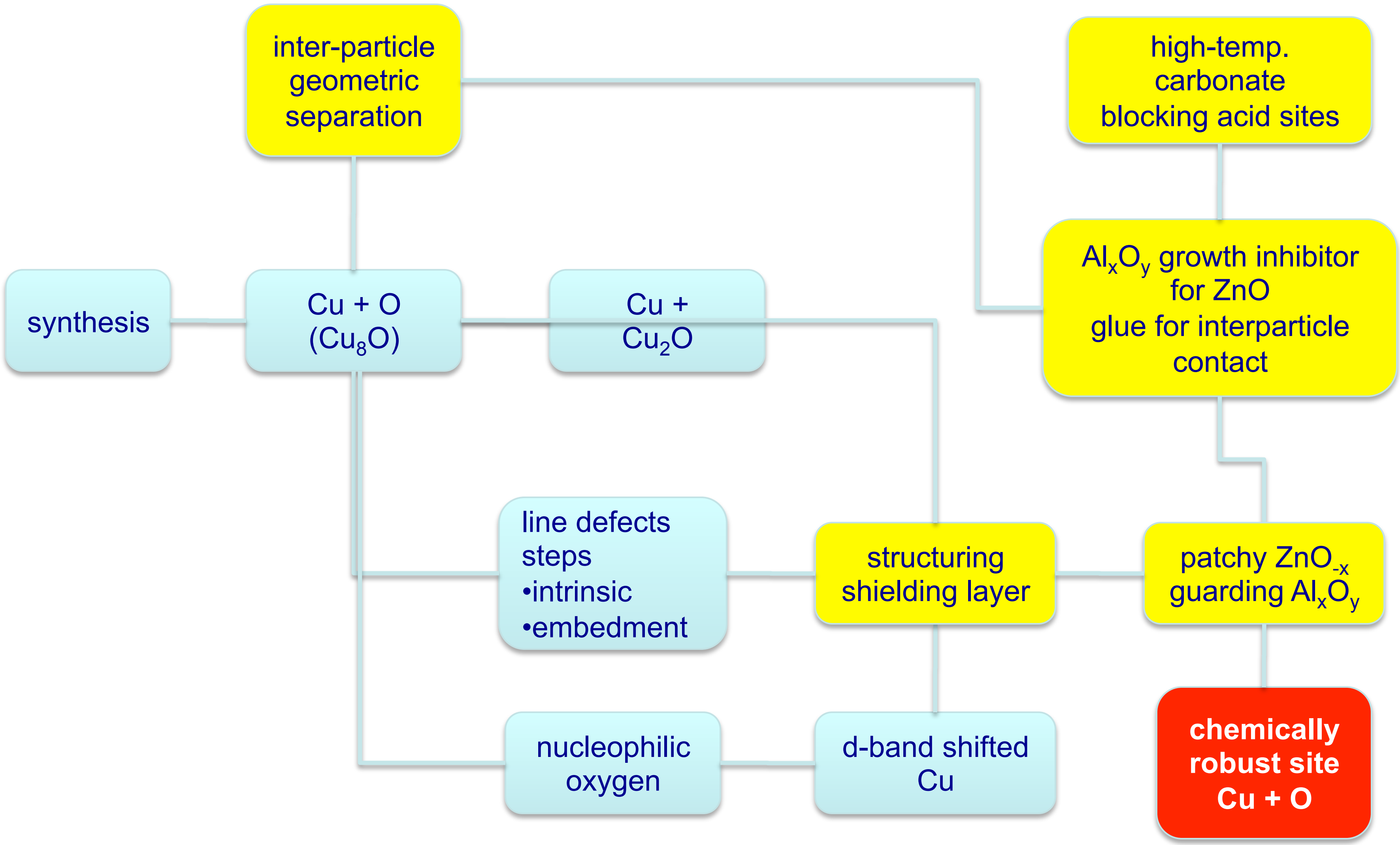
Conclusion: elements of a puzzle: or a catalyst labyrinth



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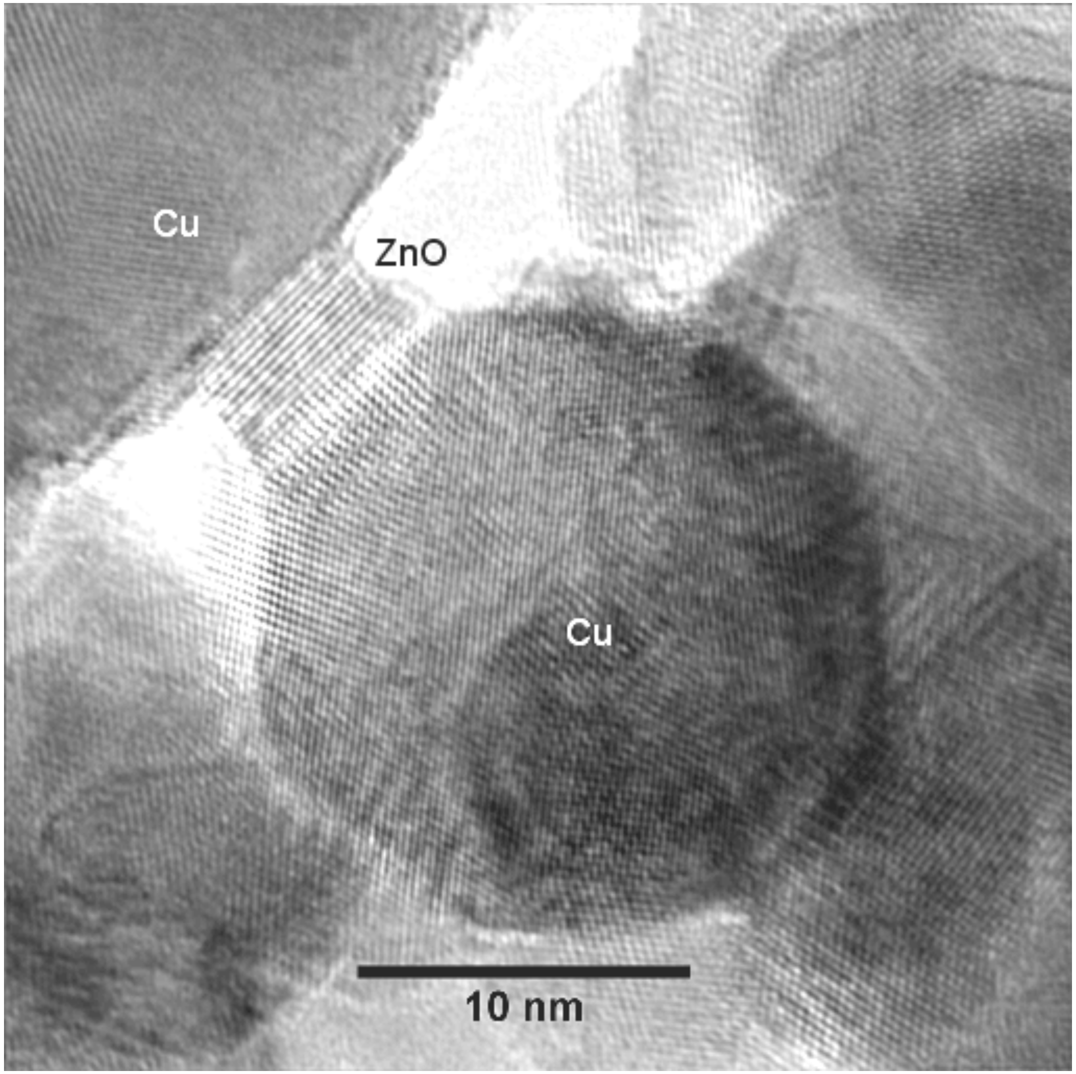
Conclusion: elements of a puzzle: or a catalyst labyrinth



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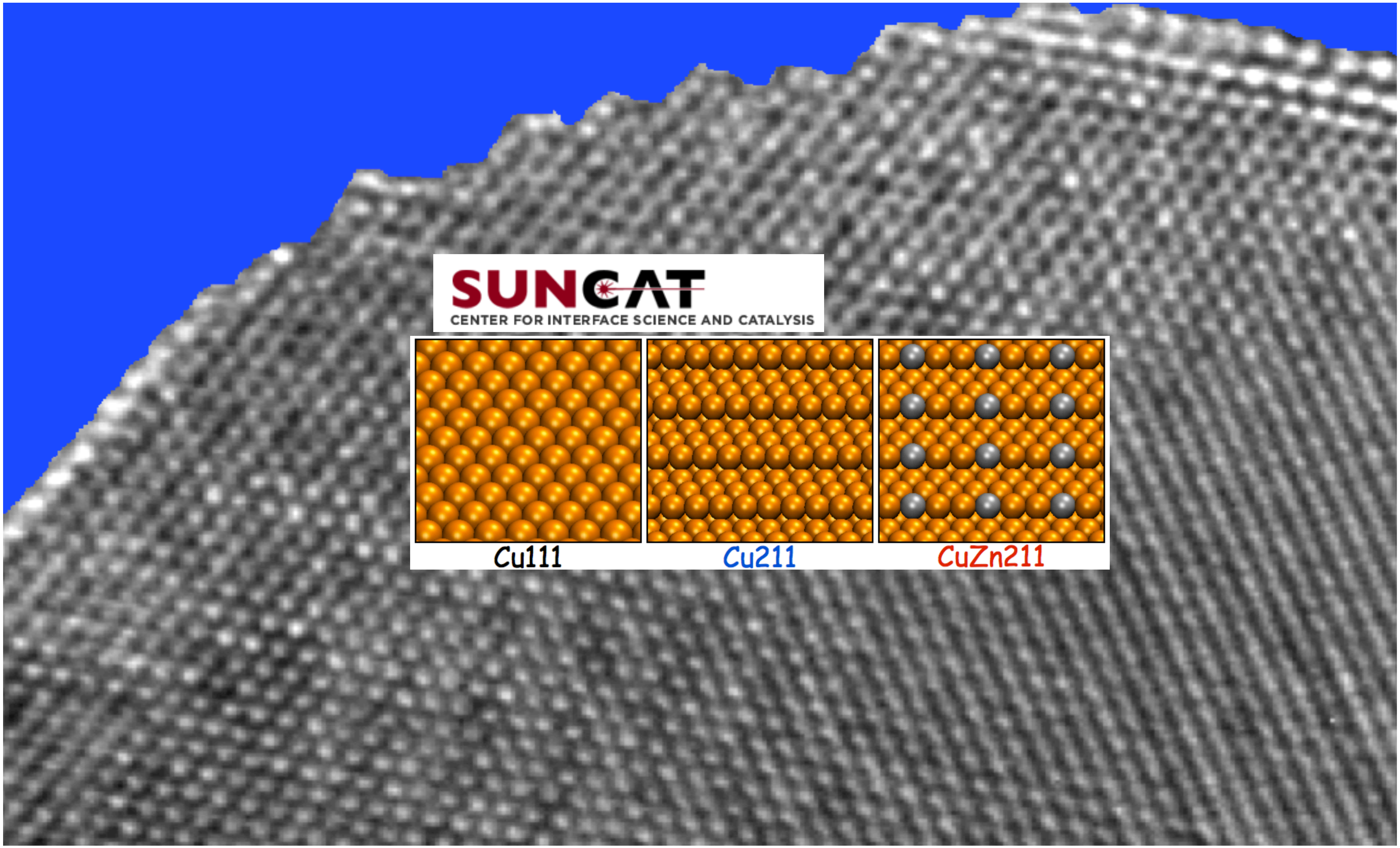
Relation to mechanism



Relation to mechanism

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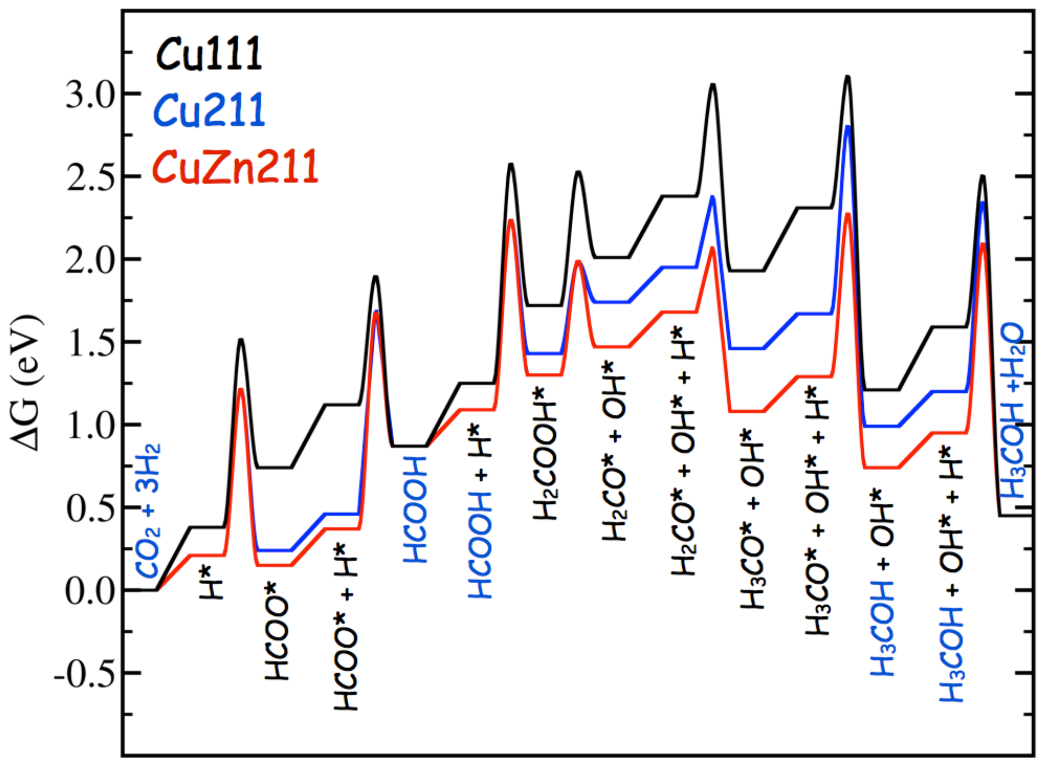

The active site model for Cu/ZnO
Synergy at work

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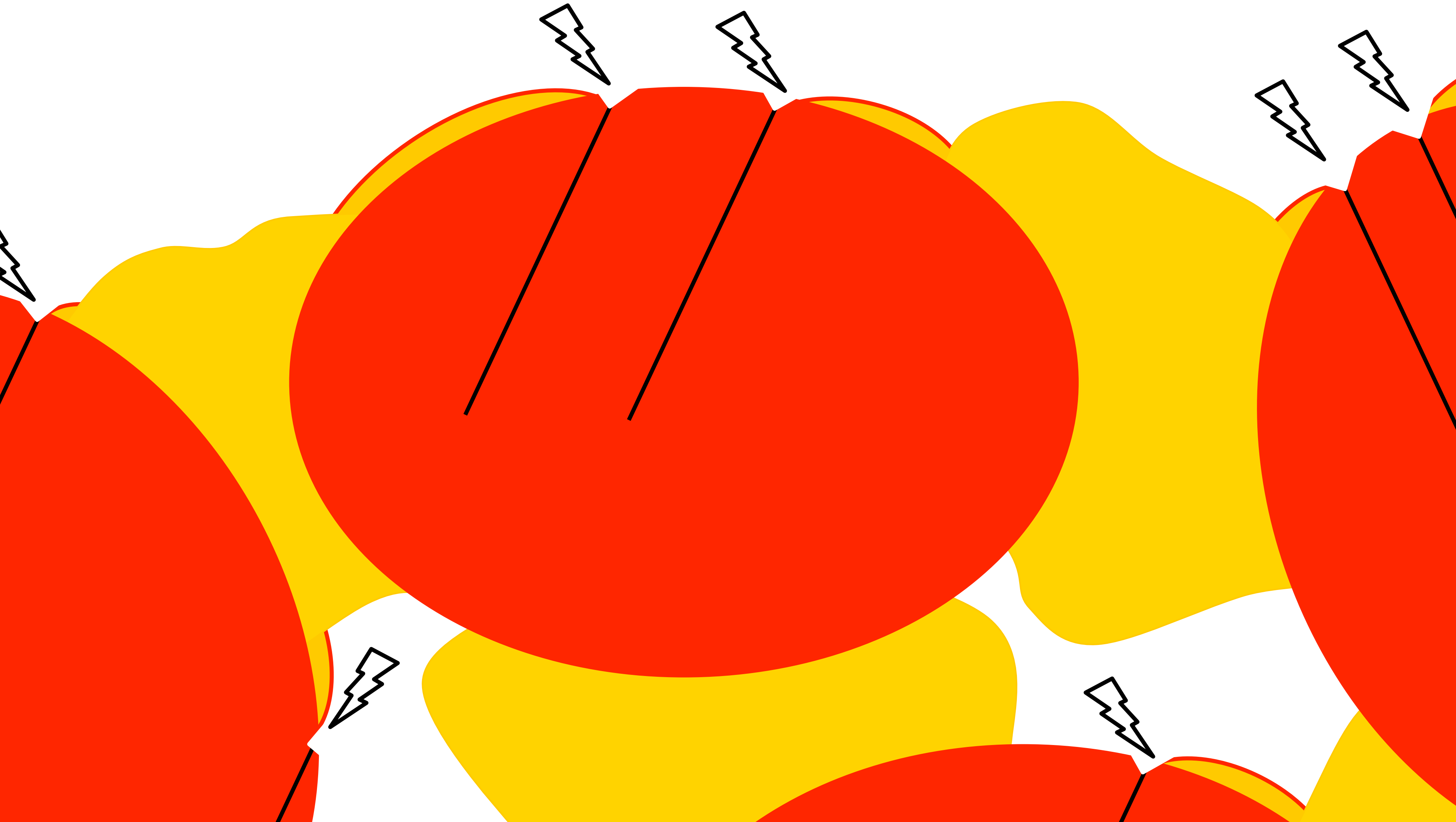
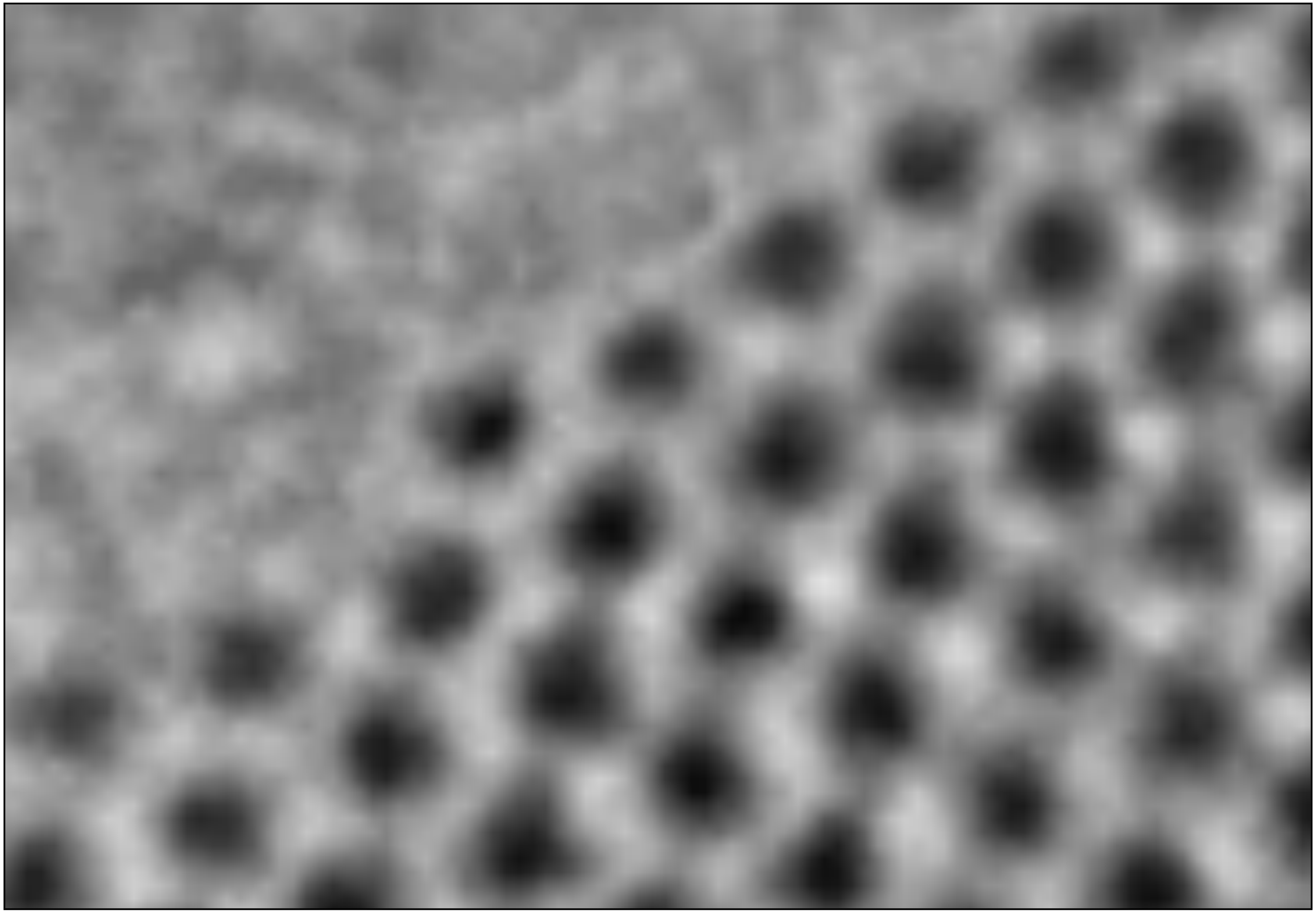
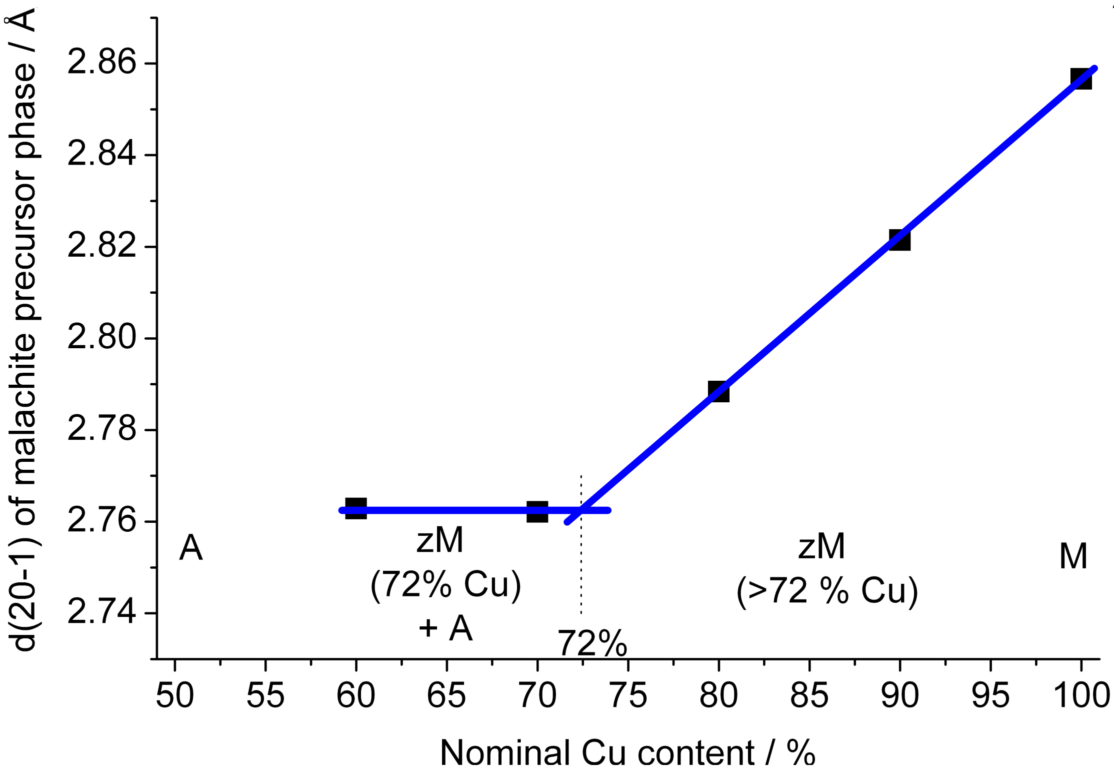


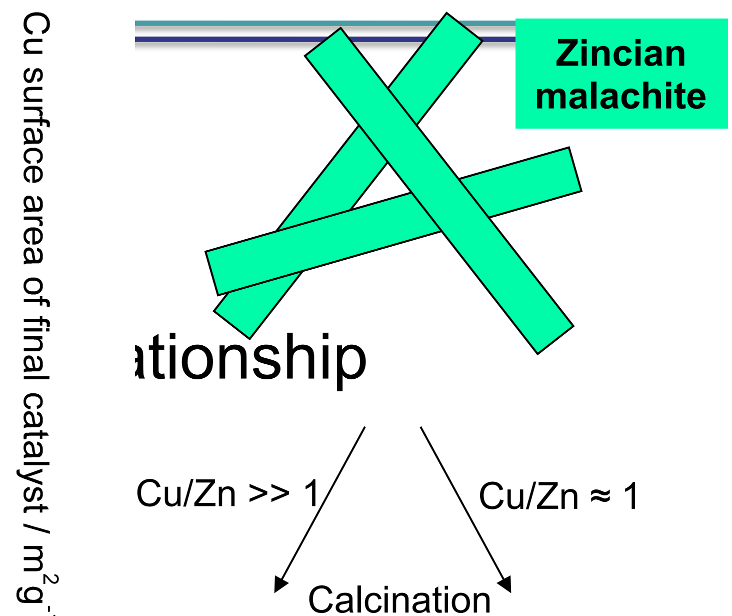


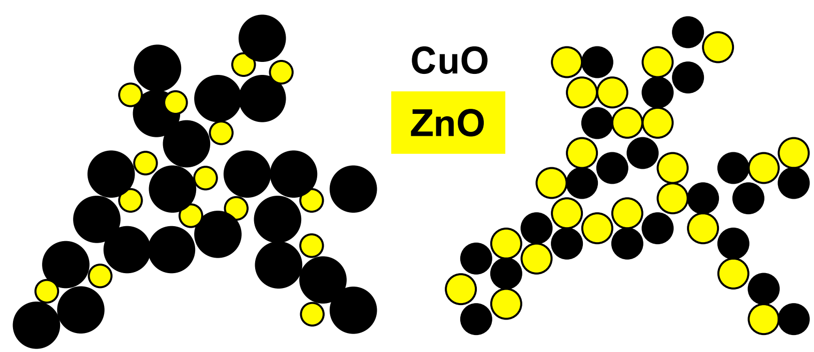
Dem Anwenden muss das Erkennen vorausgehen

Max Planck

Thank You







(Target composition near 1:1)

Dispersion effect is dominated by Cu:Zn ratio in the zincian malachite precursor phase

M. Behrens, *J. Catal.* **2009**, *267*, 24.

We are close to the top, but….

- More active sites
  - More [O] species (synthesis)
  - More strain from matrix (binding).
- More Cu/ZnO synergy
  - Less $(ZnO)_{1-x}$ coverage (promoters)
  - ZnO dispenser matrix (inorganic zincates).
- More TOF
  - Hydrophilic surface (less polar matrix)
  - More [O] species as hydride transfer species (synthesis).
- More macroscopic performance
  - Pre-reaction activation (mechanical stability)
  - Hierarchical homogeneity (density).

Conclusion

Synthesis:

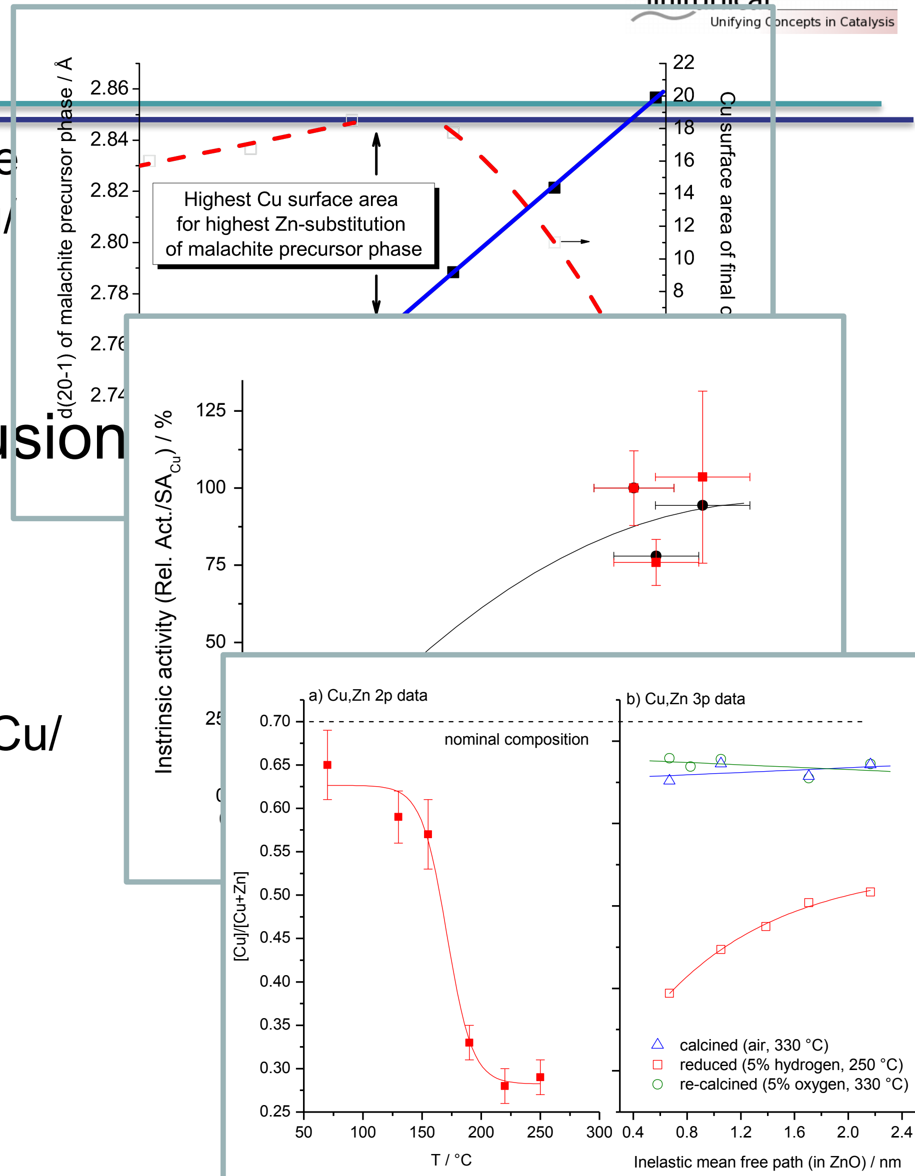
Precursor chemistry is the key to the preparation of high-performance Cu/ ZnO catalysts

Active form of copper:

Intrinsic activity scales with the abundance of planar defects in Cu nanoparticles

Cu-ZnO synergy:

ZnO_x is the dynamic component in Cu/ ZnO and is present at the active Cu surface due to strong metal support interaction



Summary Surface

- Bulk Cu with slight electronic deviations is covered by ZnO and at the top surface also by alumina.
- Bare Cu is a minority species at the surface of the working catalyst.
- An oxygen species is part of the MSR function (and likely also of MS) of Cu.
- A different (OH) species not bonded to Cu is detrimental.
- Cu oxide is not the active phase.
- From calo: methoxide is a frequent intermediate.

How do we store energy chemically?

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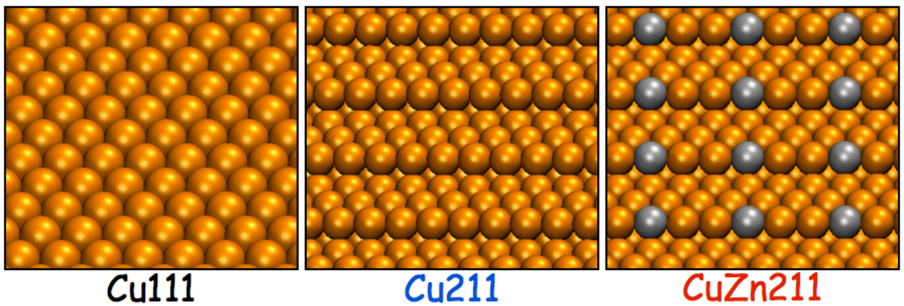
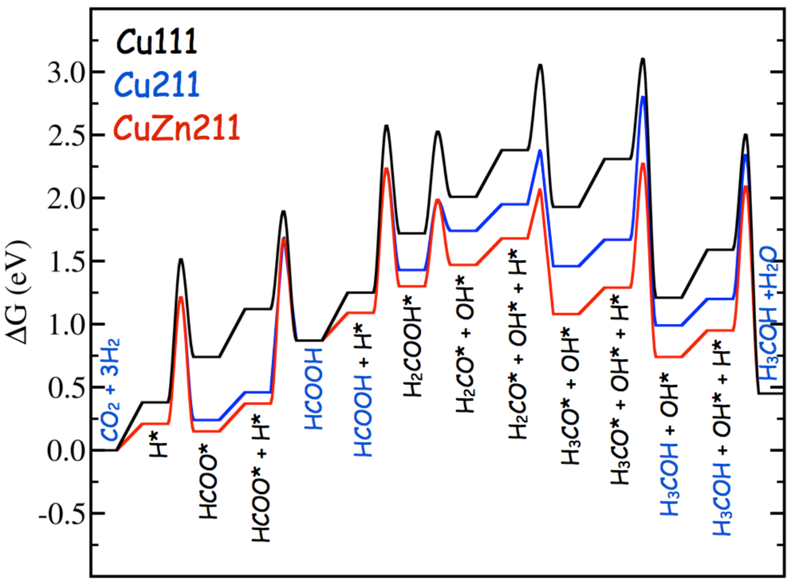
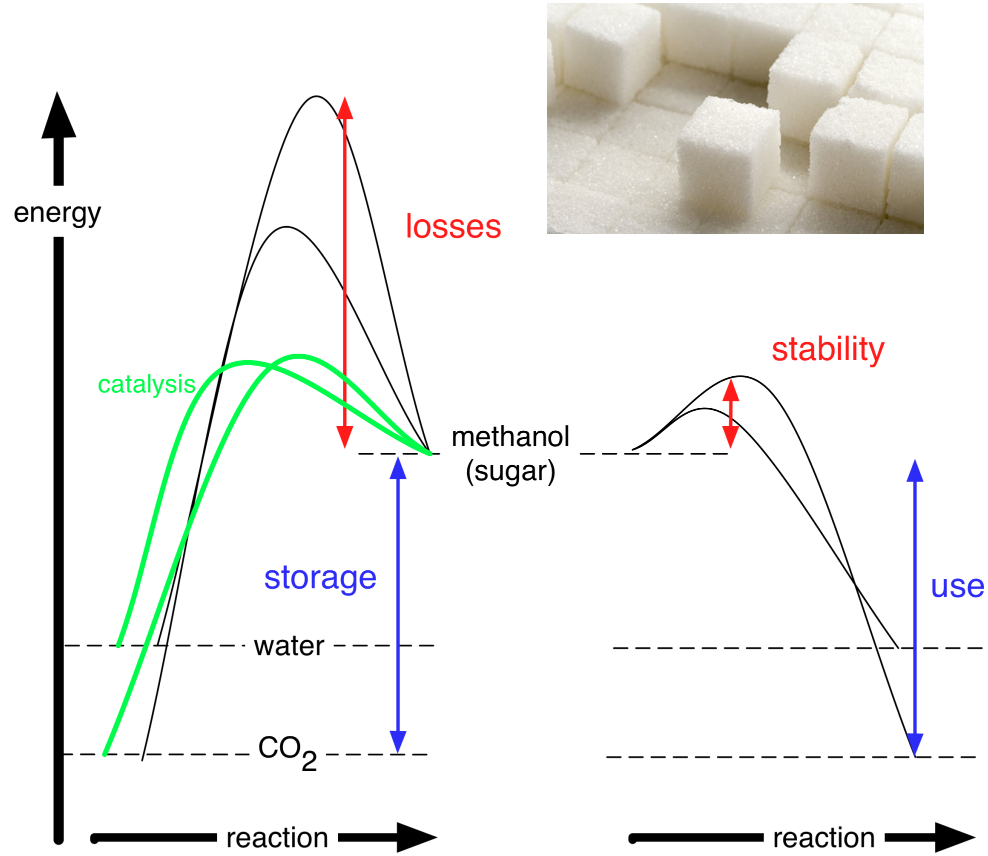
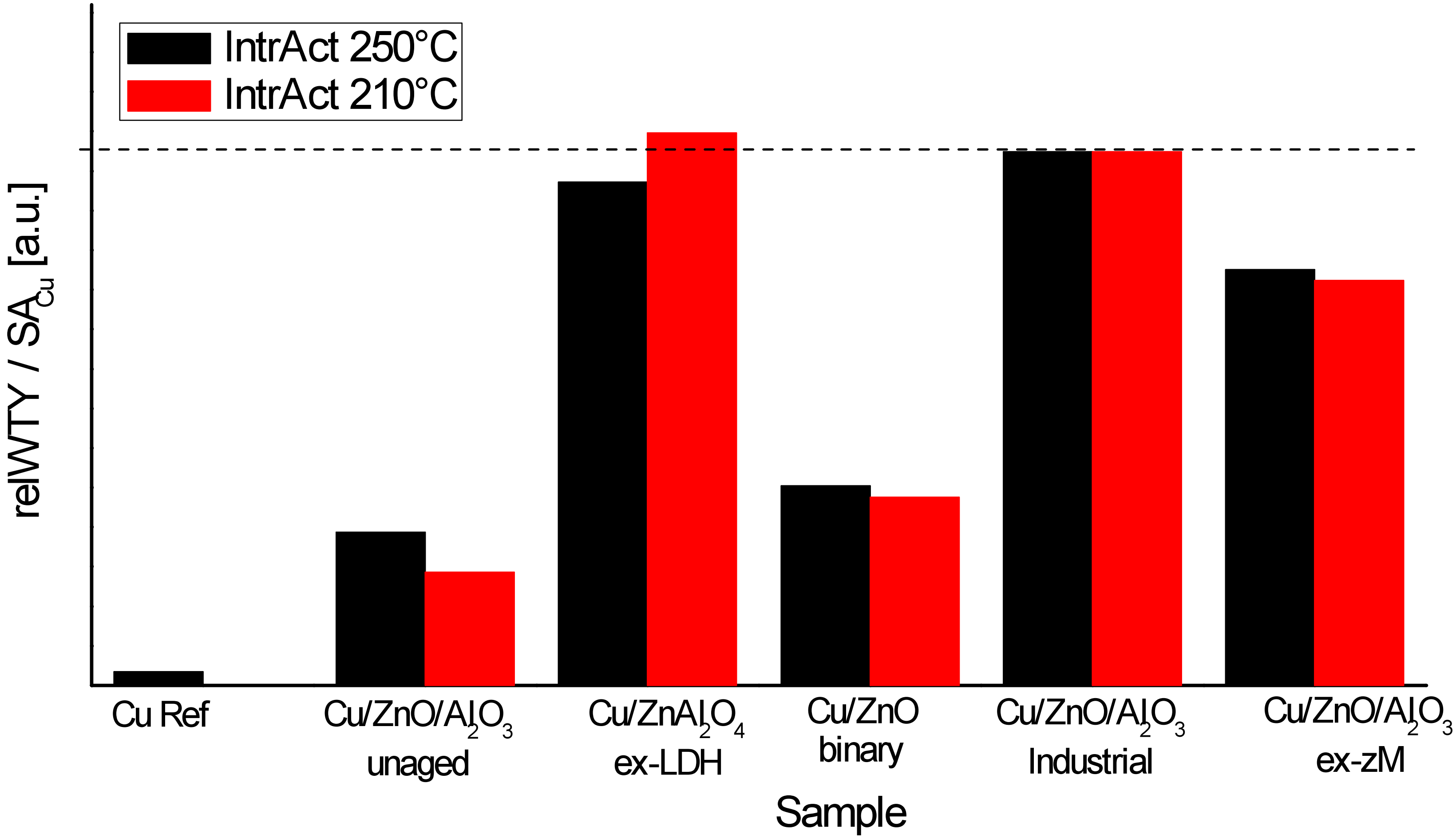
CENTER FOR INTERFACE SCIENCE AND CATALYSIS



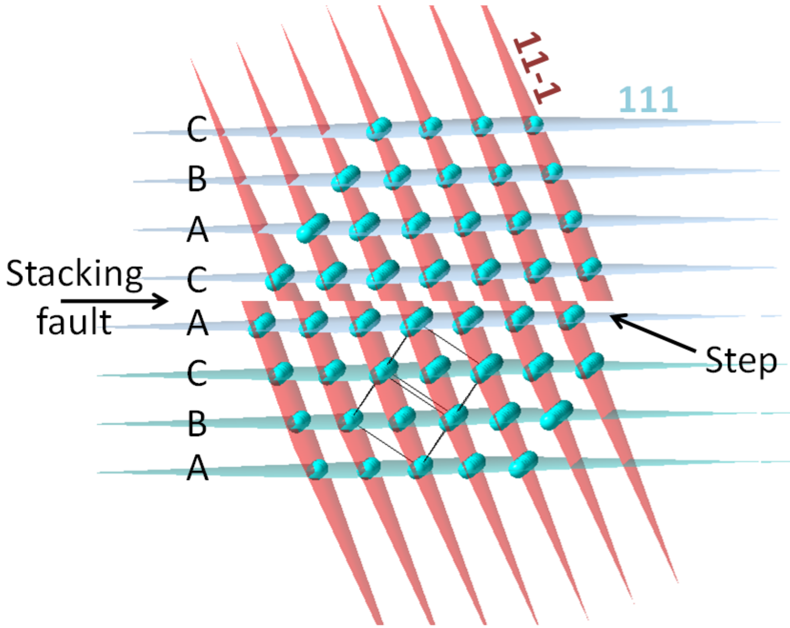


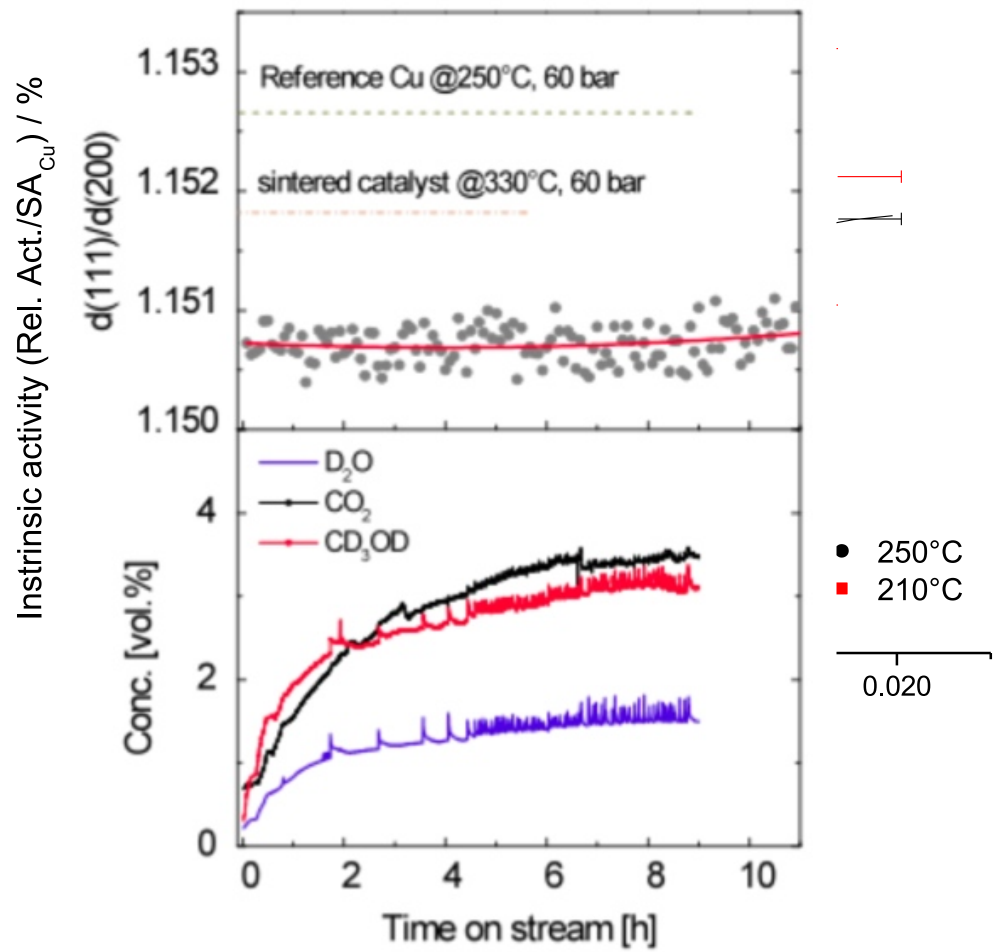


In collab. F. Studt and J. Nørskov, SLAC Standford


IntrAct 250°C
IntrAct 210°C
relWTY / SA_Cu [a.u.]
Cu Ref
Cu/ZnO/Al2O3
unaged
Cu/ZnAl2O4
ex-LDH
Cu/ZnO
binary
Cu/ZnO/Al2O3
Industrial
Cu/ZnO/Al2O3
ex-zM
Sample

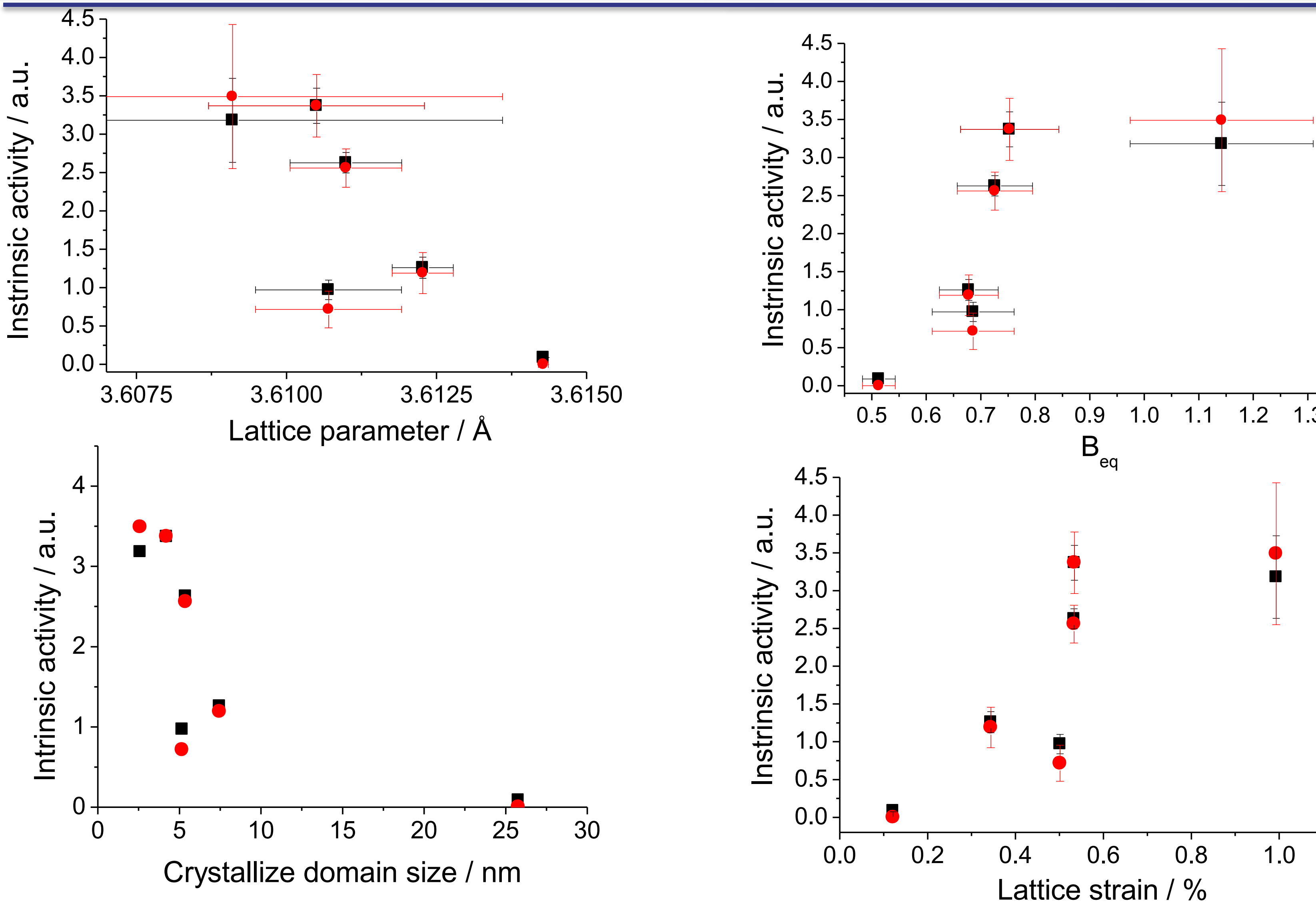
Active Cu
How we get more sites



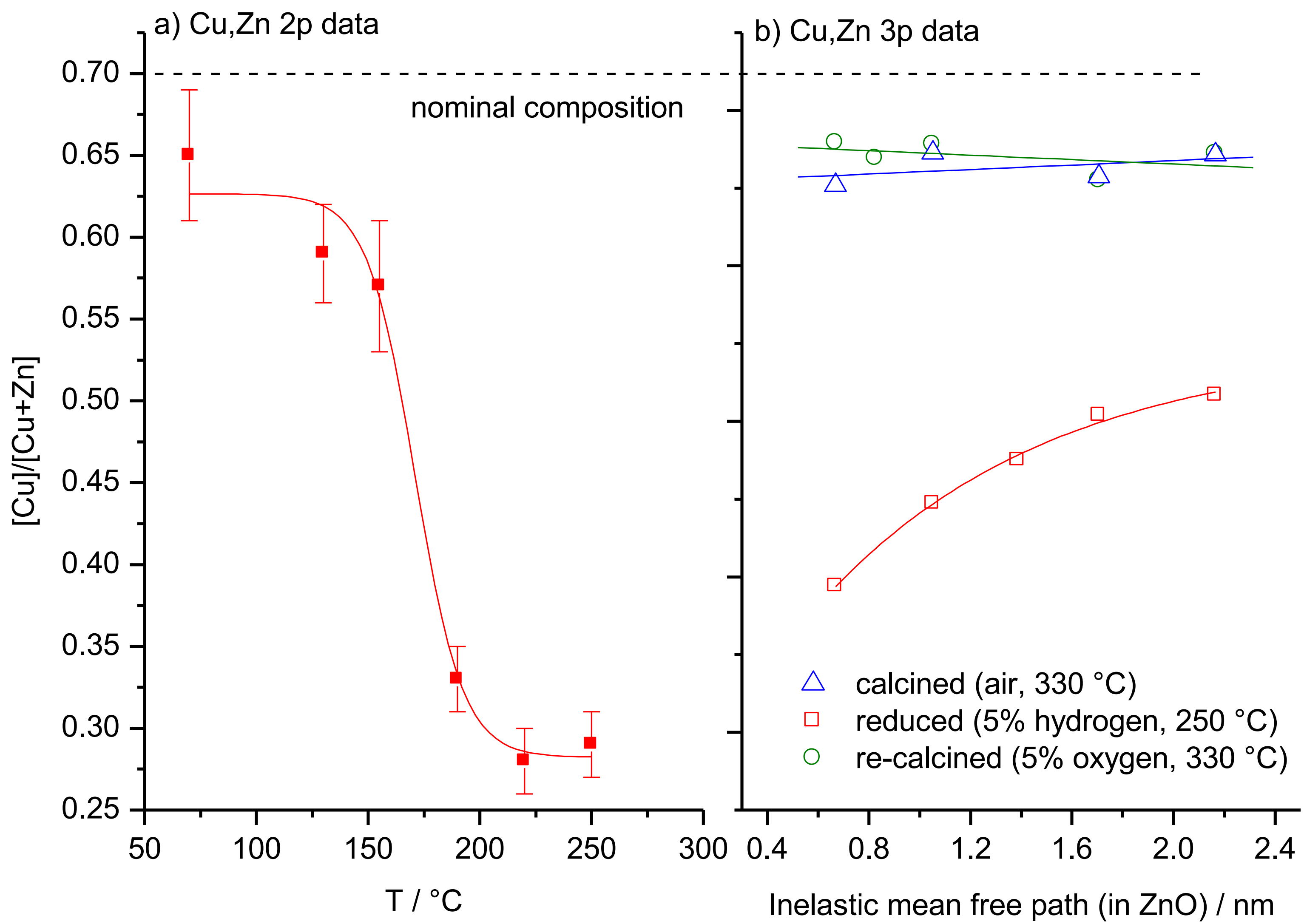


In-situ neutron diffraction:

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


Instrinsic activity / a.u.
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
3.6075
3.6100
3.6125
3.6150
Lattice parameter / Å
Instrinsic activity / a.u.
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
B_{eq}
Intrinsic activity / a.u.
0
1
2
3
4
0
5
10
15
20
25
30
Crystallize domain size / nm
Instrinsic activity / a.u.
0.0
0.2
0.4
0.6
0.8
1.0
Lattice strain / %

The missing bit: activation in situ



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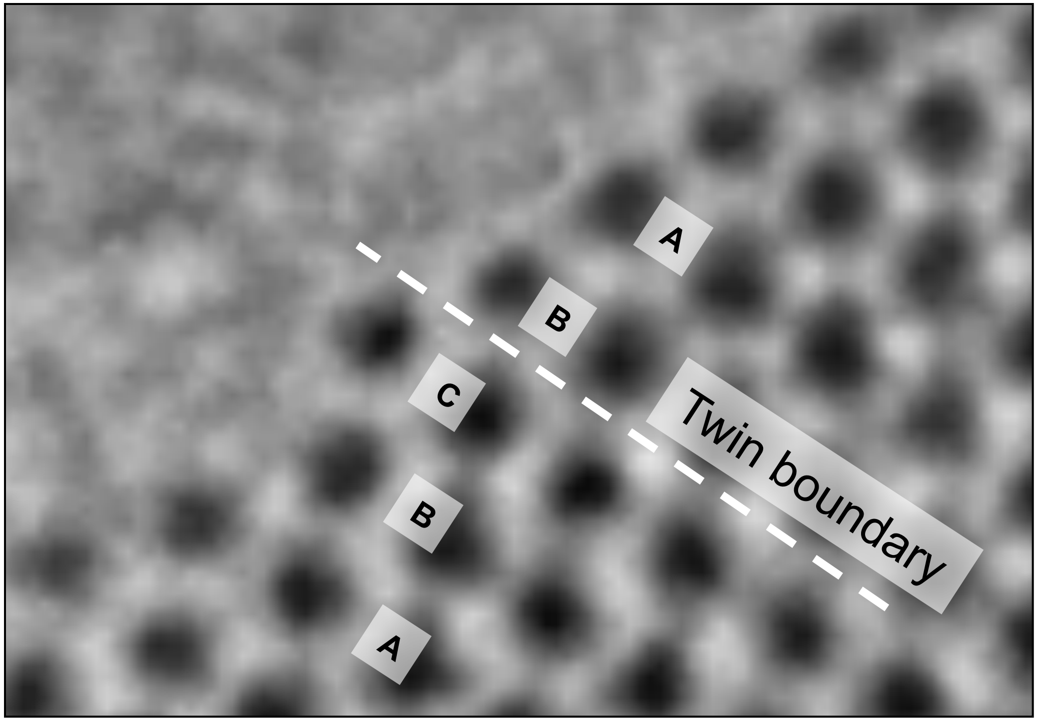
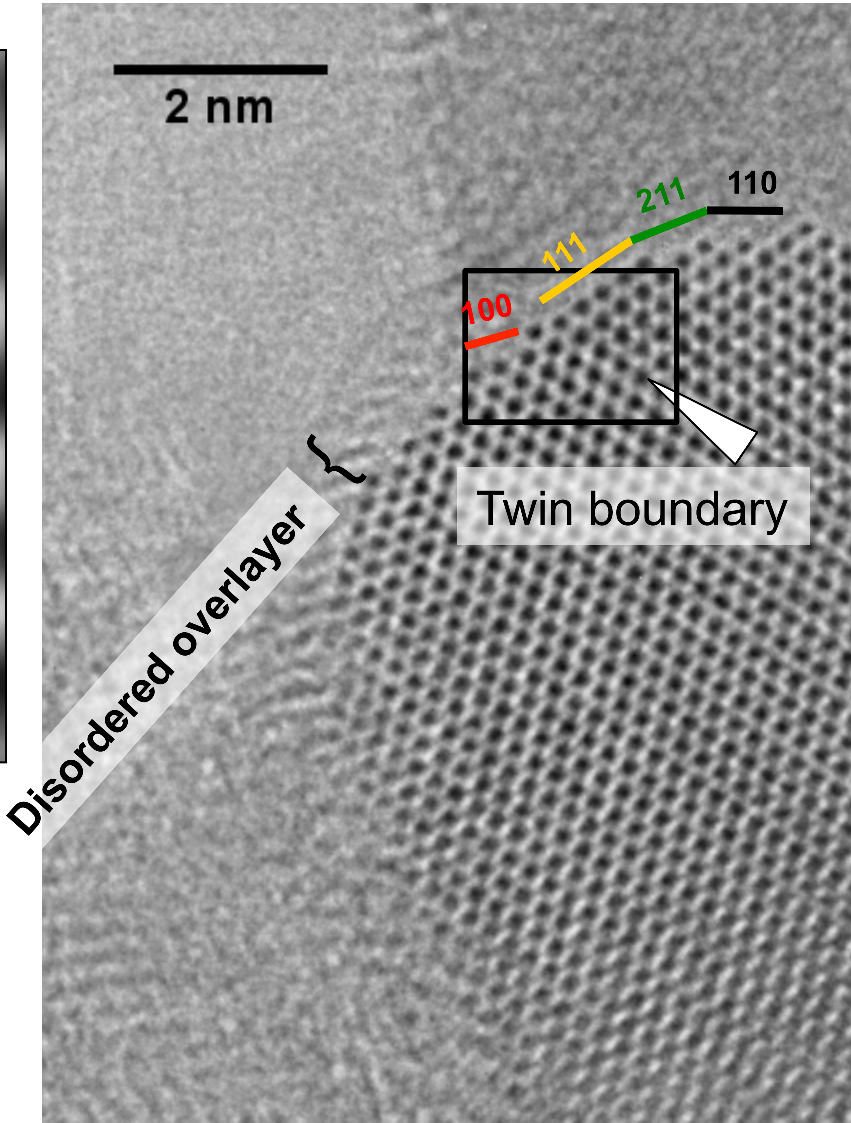
Can we see the active sites?





Was können Sie mitnehmen

- Bisher haben wir nur von der Natur Energieträger „geborgt“: Treibhauseffekt als Preis: nachhaltig ist das nicht!
- Die Energiewende ist nur der Anfang einer großen Umstrukturierung.
- Es gibt genug solare Energie für alle und zudem weitere Alternativen (Fusionsenergie).: regenerative Wandler jetzt!
- Es gibt nicht genug leistungsfähige Speicher (auch nicht die Biomasse).
- Die Grundlagenforschung an Wandlern und Speichern ist erst am Anfang, Vorsicht mit schnellen Entscheidungen (PV).
- Weil die Randbedingungen örtlich und zeitlich verschieden sind brauchen wir mehrere Alternativen für die Energieversorgung.

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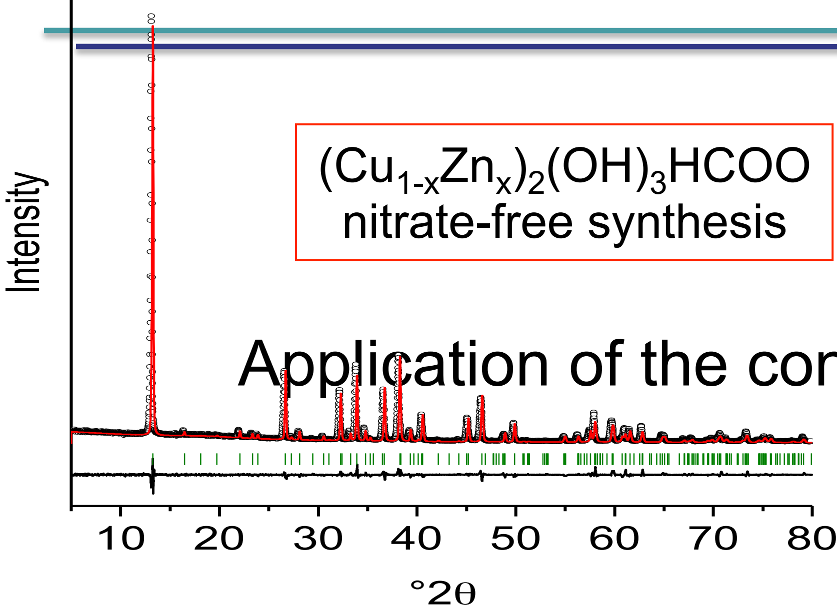
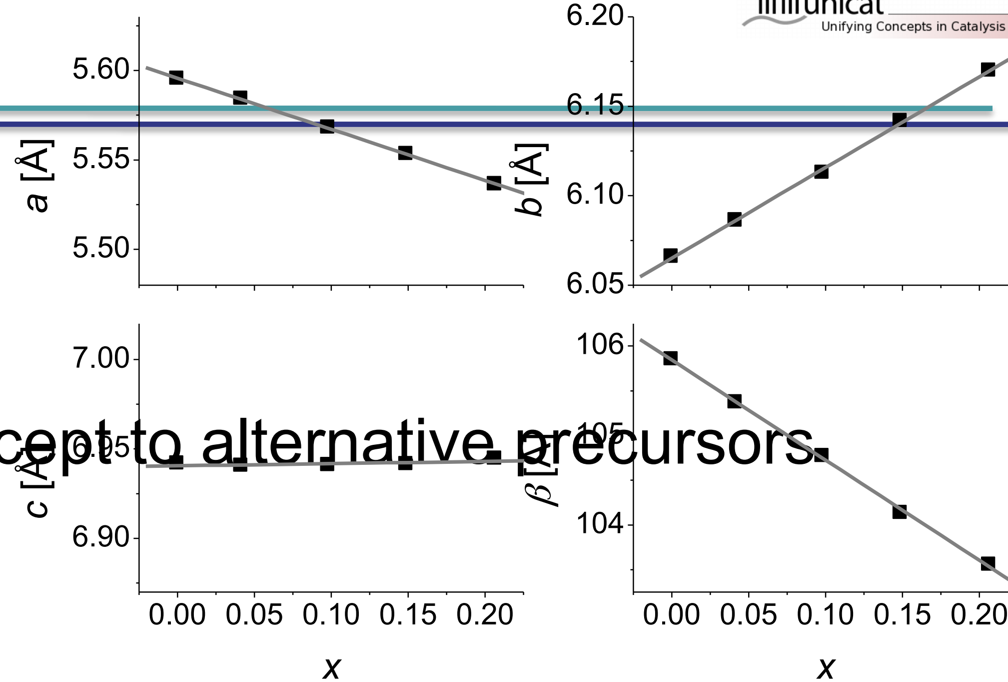
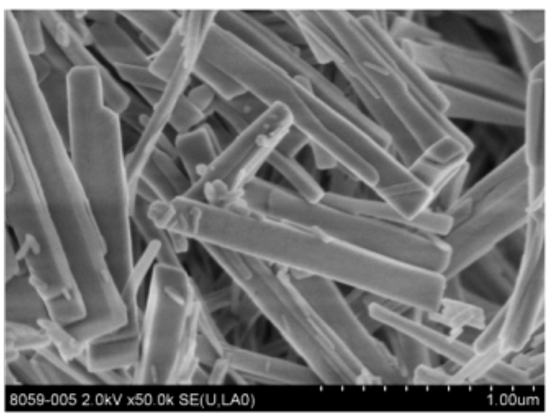
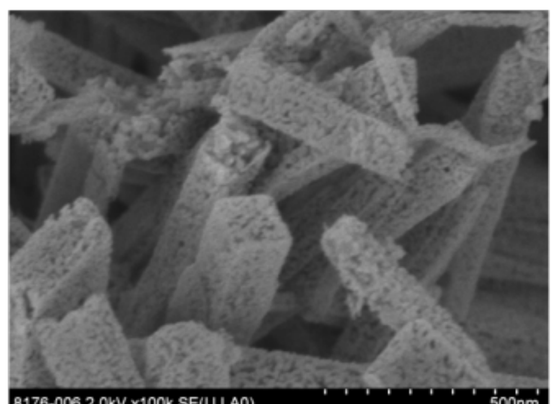
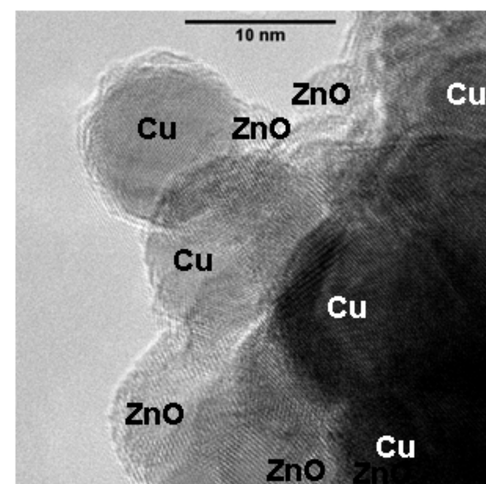
Application of the concept to alternative precursors











M. Behrens, S. Kissner, F. Girgsdies, I. Kasatkin, F. Hermerschmidt, K. Mette, H. Ruland, M. Muhler, Robert Schlögl, Chem. Commun. 47 (2011) 1701.

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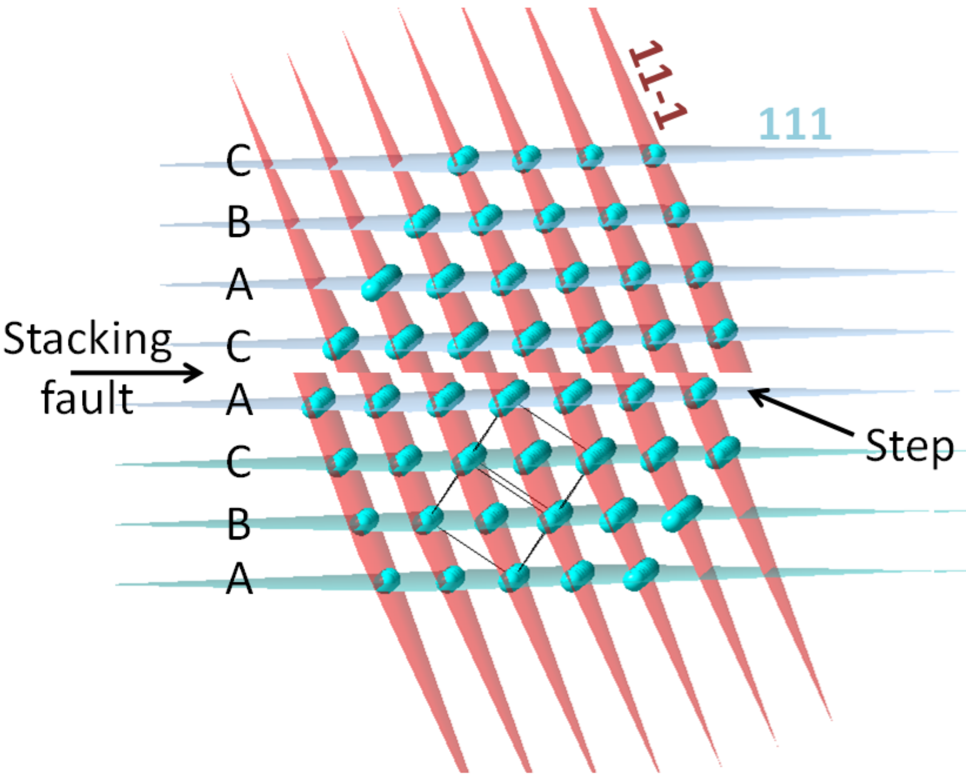
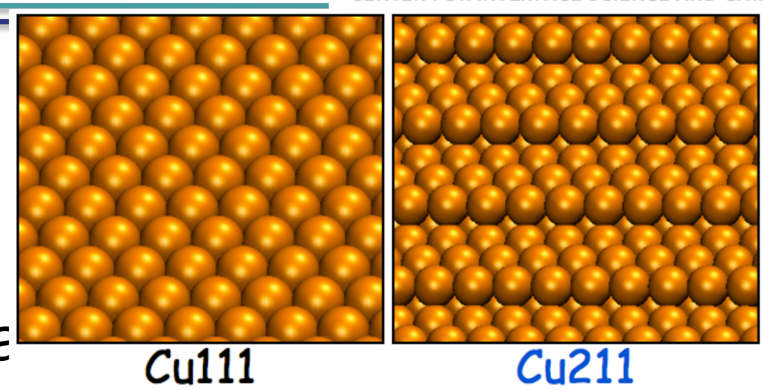
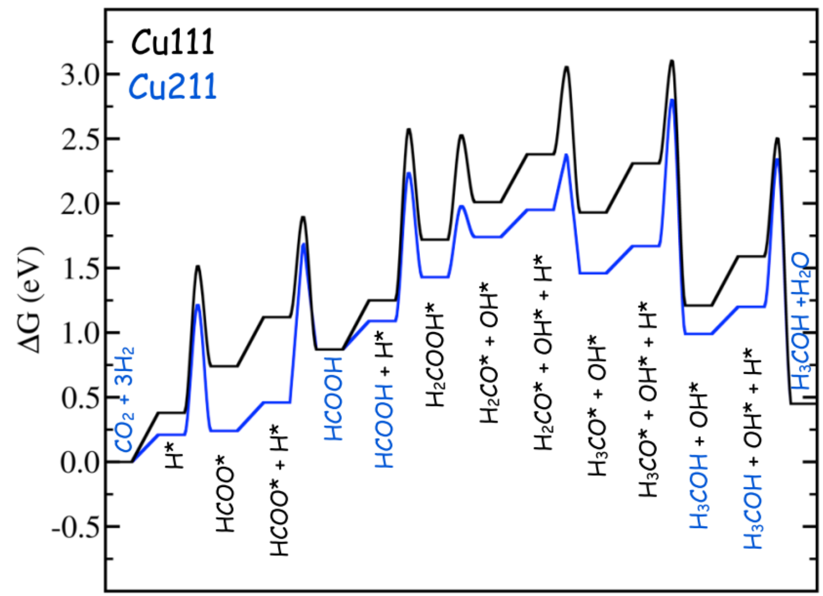


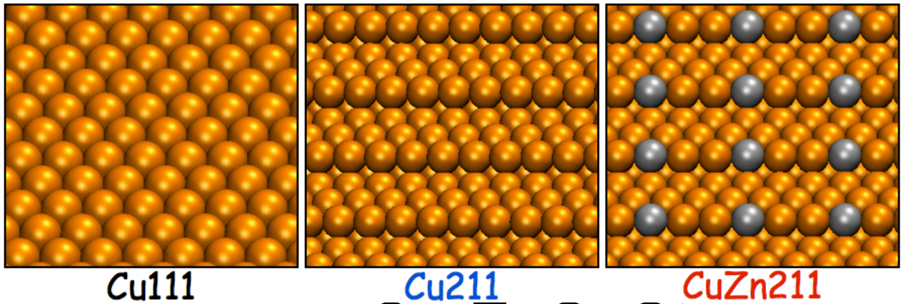


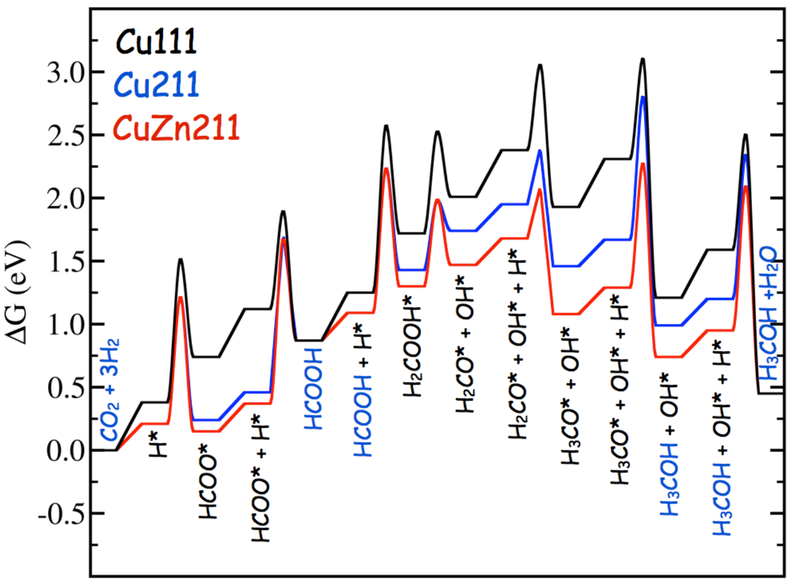


The role of disorder/defects for Cu/ZnO catalysts:
M. M. Günter, T. Ressler, B. Bems, C. Büscher, T. Genger, O. Hinrichsen, M. Muhler, R. Schlögl, *Catal. Lett.* 71 (2001) 37 and I. Kasatkin, P. Kurr, B. Kniep, A. Trunschke, R. Schlögl, *Angew. Chem.* 119 (2007) 7465.

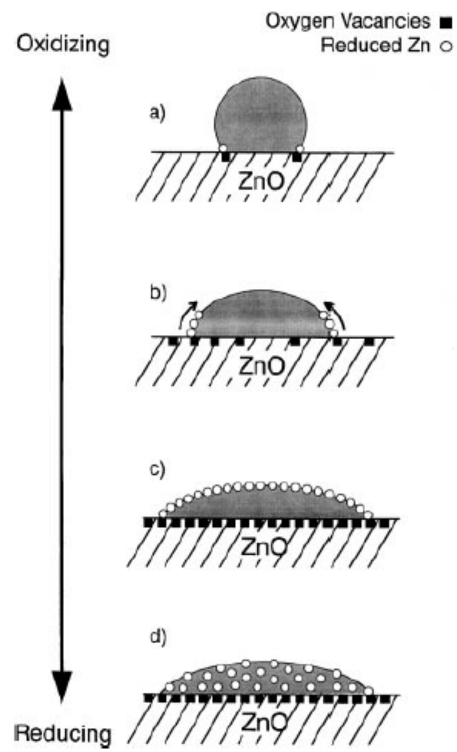
Courtesy of F. Studt and J. Nørskov, SLAC Standford

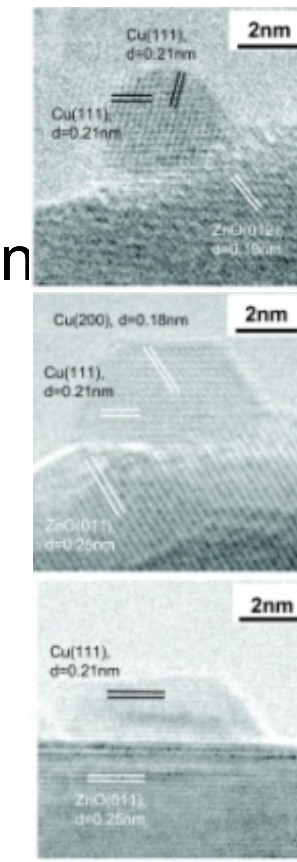
Interaction of Cu and ZnO in Cu/ZnO catalysts (Nakamura, ICI, Frost, Topsøe, SFB 558 Bochum, …)





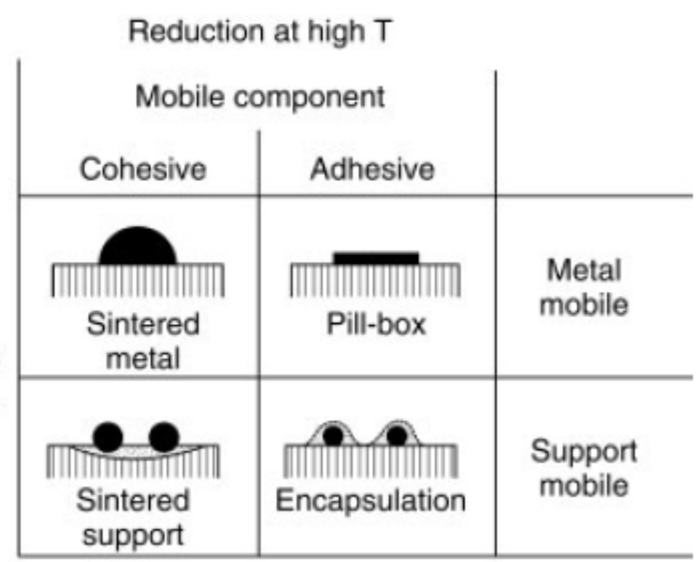
Courtesy of F. Studt and J. Nørskov, SLAC Standford





P.L. Hansen, J.B. Wagner, S. Helveg, J.R. Rostrup-Nielsen, B.S. Clausen, H. Topsøe, *Science* 295 (2002) 2053.
J.-D. Grunwaldt, A.M. Molenbroek, N.-Y. Topsøe, H. Topsøe, B.S. Clausen, *J. Catal.* 194 (2000) 452.

Strong-Metal-Support-Interaction



F. C. M. J. M. van Delft, A. D. van Langefeld, B. E. Nieuwenhuys, *Solid State Ionics* 16, (1985) 233.

Cu/ZnO: Catalyst Preparation

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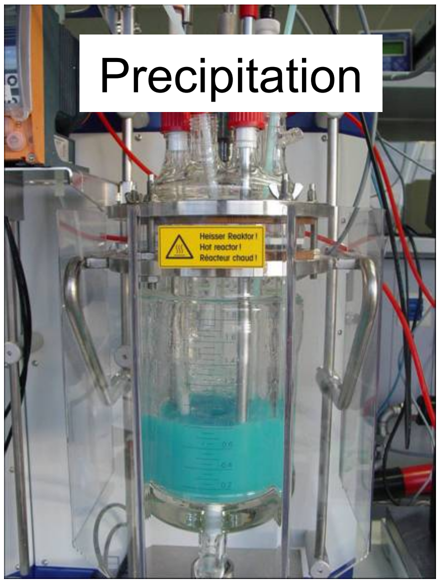
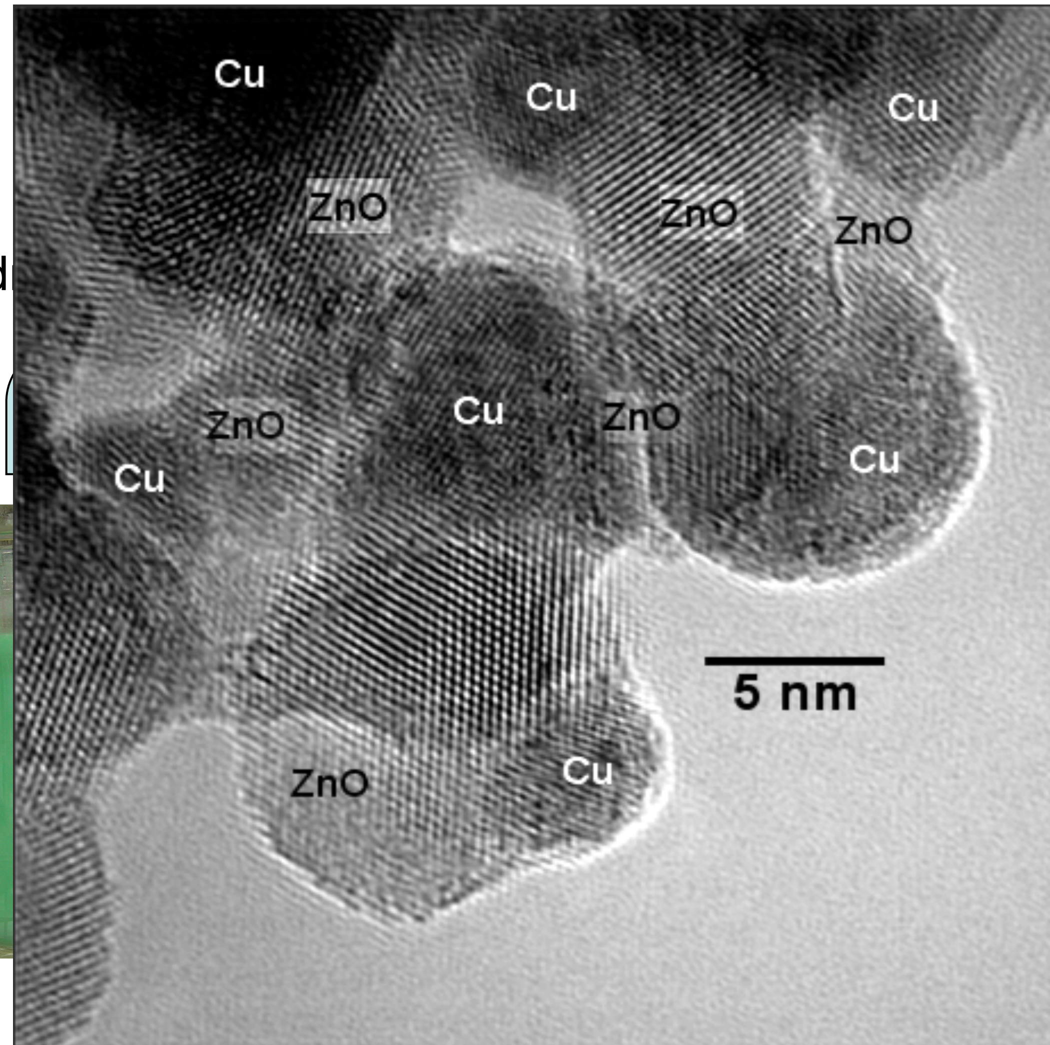


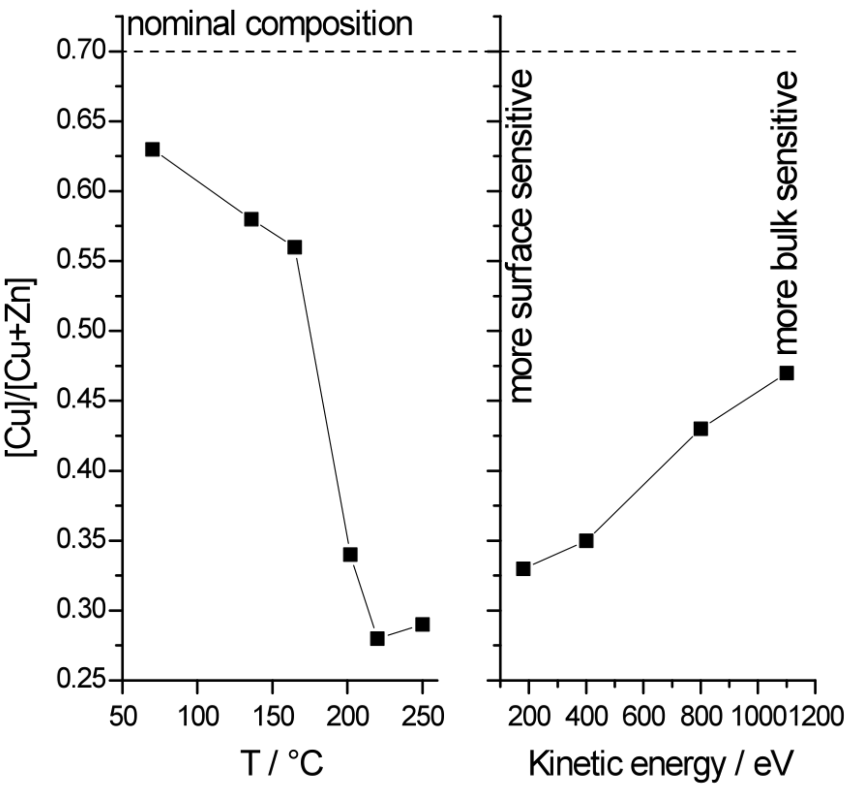
Washing / d

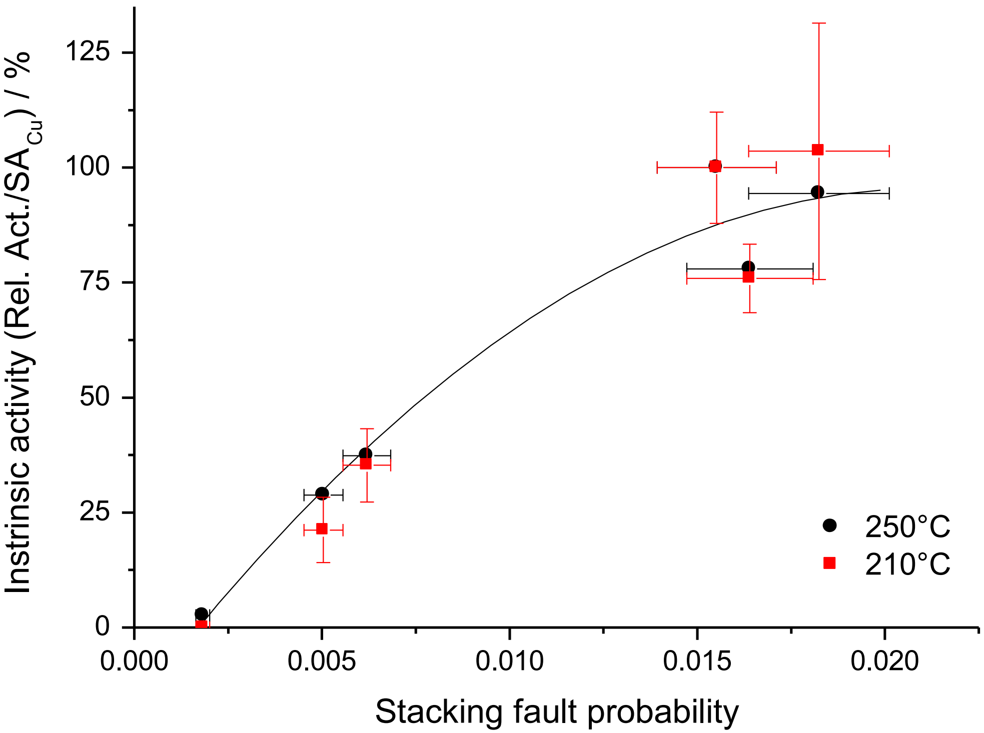
Ageing



M. Behrens et al, 2011

How we get more active sites





Ambient pressure variable energy XPS:
A ZnO overlayer is promoting activity

In-situ neutron diffraction:
Activity scales with defect density (terminating at the surface)…

Can we see the active sites?

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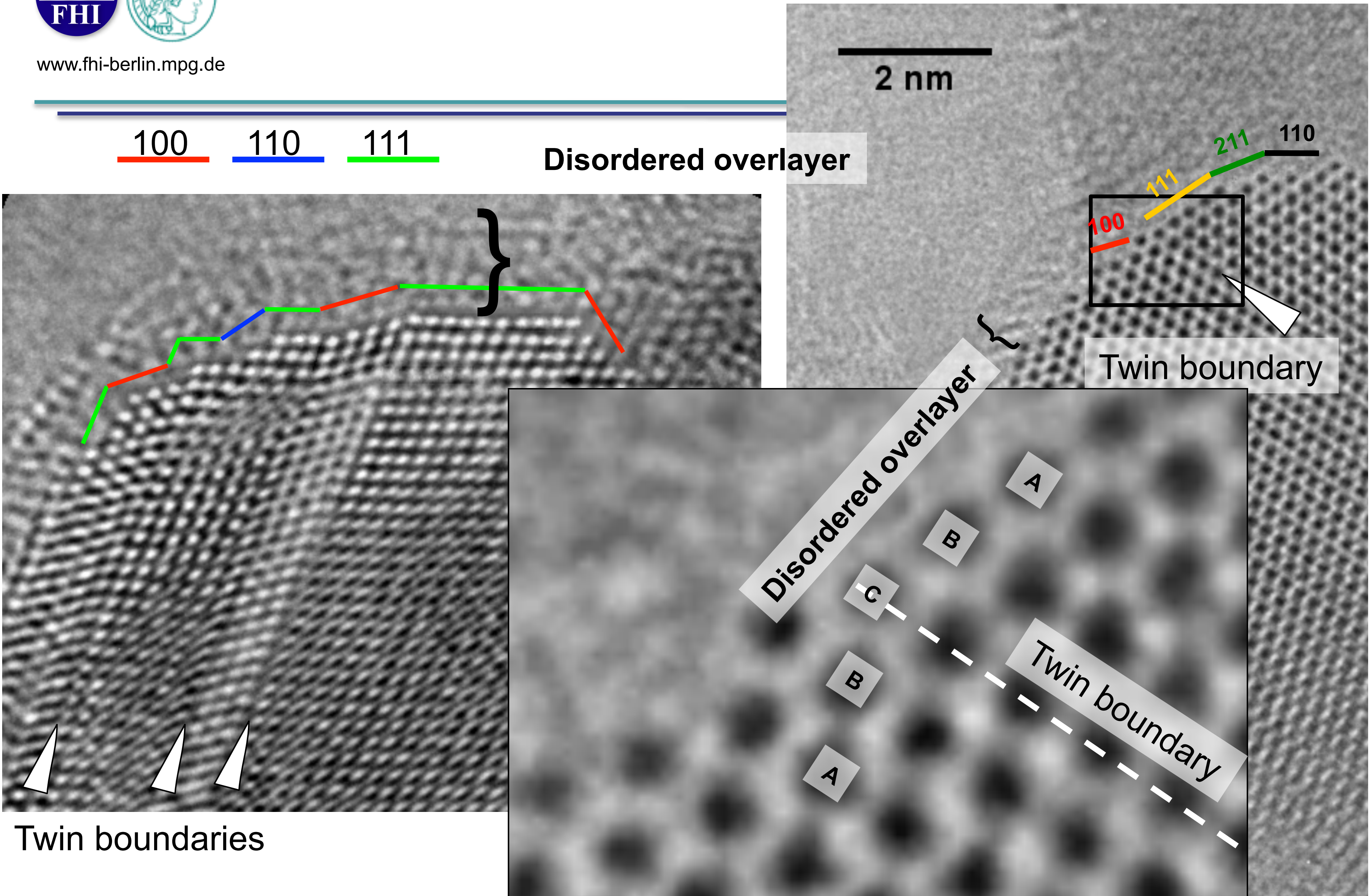

Energieversorgung: Ein System

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