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2269-20

Workshop on New Materials for Renewable Energy

17 - 21 October 2011

Heterogeneous catalysis for chemical energy storage

Robert SCHLOEGL
Dept. of Inorganic Chemistry
Fritz-Haber-Institut der MPG, Berlin
Germany

Heterogeneous Catalysis for Chemical energy storage

The largest challenge for catalysis ever?

Robert Schlögl

Fritz-Haber-Institut der MPG

www.fhi-berlin.mpg.de

Special thanks to:

M. Behrens, R. Horn, A. Knop-Gericke, D. Su, J. Tornow, A. Trunschke, M. Willinger

Mother nature on earth
provides all our energy needs?

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- We generate today in 60000 world-scale power stations about 18 TW electricity.
- All biological life on earth generates 250 TW energy equivalents. Man can use a maximum of 25 % of it.
- All agriculture and fishing consumes 25 TW.
- With the increase of population there is little extra energy extractable from the biosphere without damaging it.
- Biomass is no global solution for storable energy.
- We need non-biological sustainable energy storage when using regenerative (solar) energy.

- ENERCHEM with MPI Biogeochemistry, Jena

Mother nature on earth provides all our energy needs?

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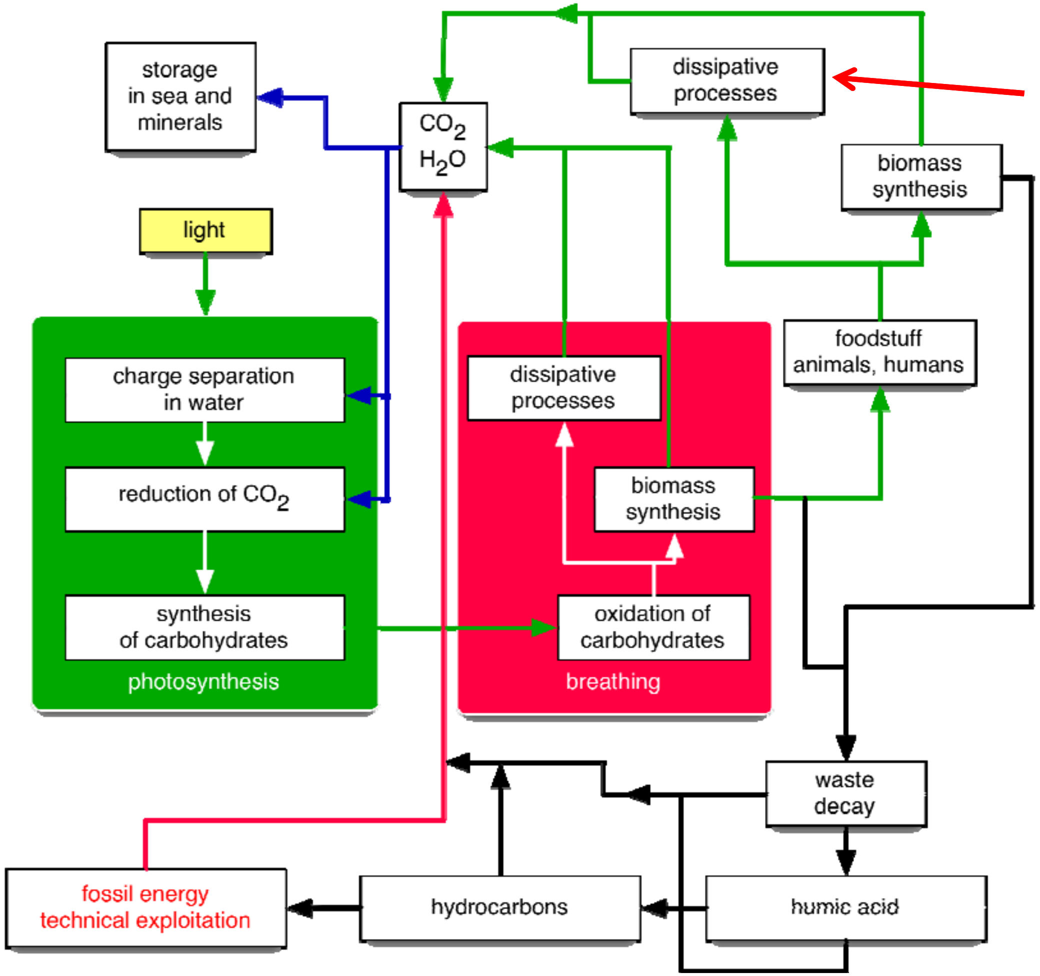

One human brain requires 6 g glucose/h

- ENERCHEM with MPI Biogeochemistry, Jena

Some observations

- All “first world” constant in energy consumption and CO_2 emission (effects of globalization).
- True challenge in Asia.
- In the global energy (emission) market Germany is a regional player (2%), the US is global (x10).
- Chance for Germany to develop role models: but only when implemented here!
- The “Energiewende” is a prototype example for energy changes being necessary everywhere for economic pressures from fossil resources (and for climate protection).

Some observations

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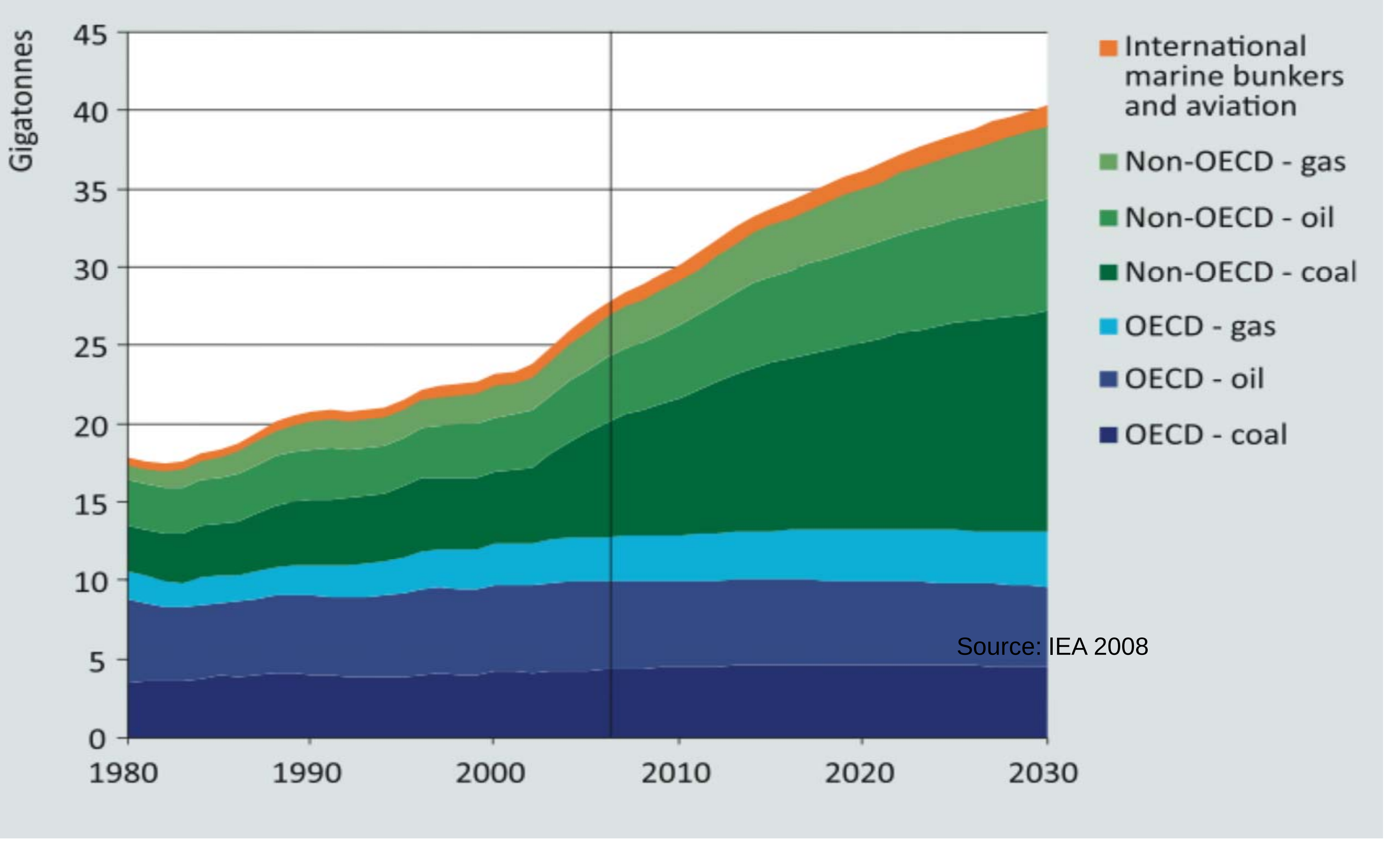

Source: IEA 2008

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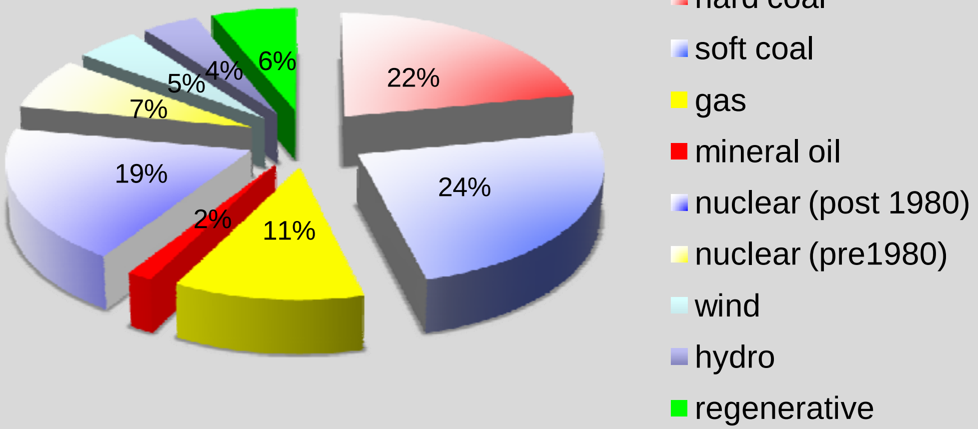
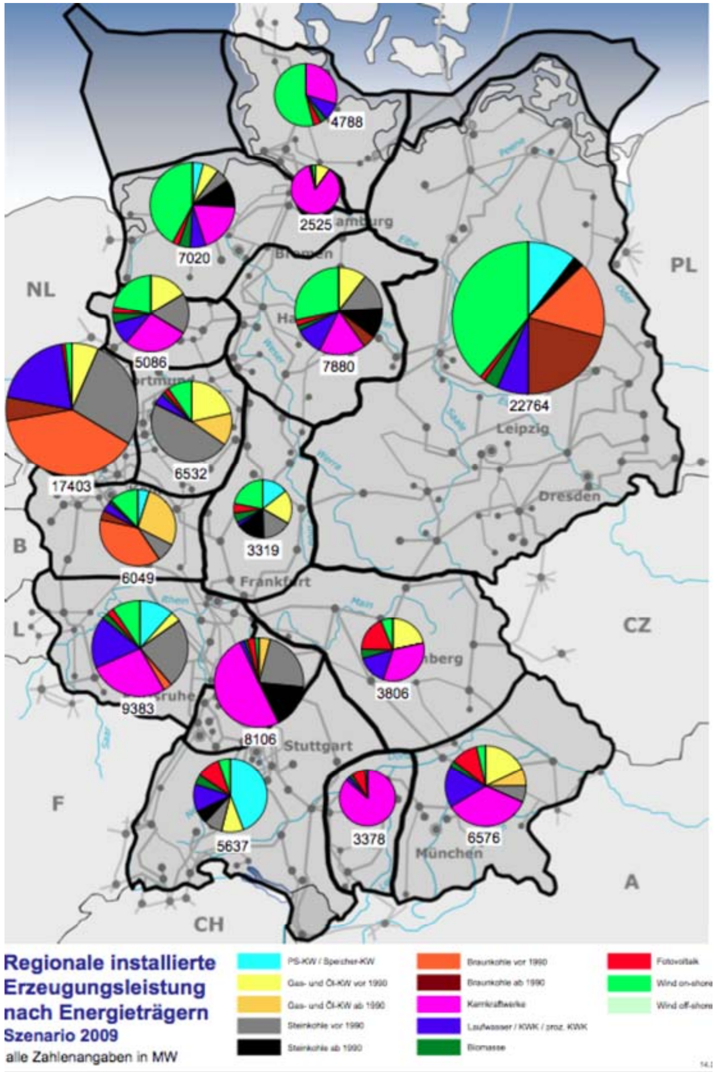
In 2010 about 600 TWh



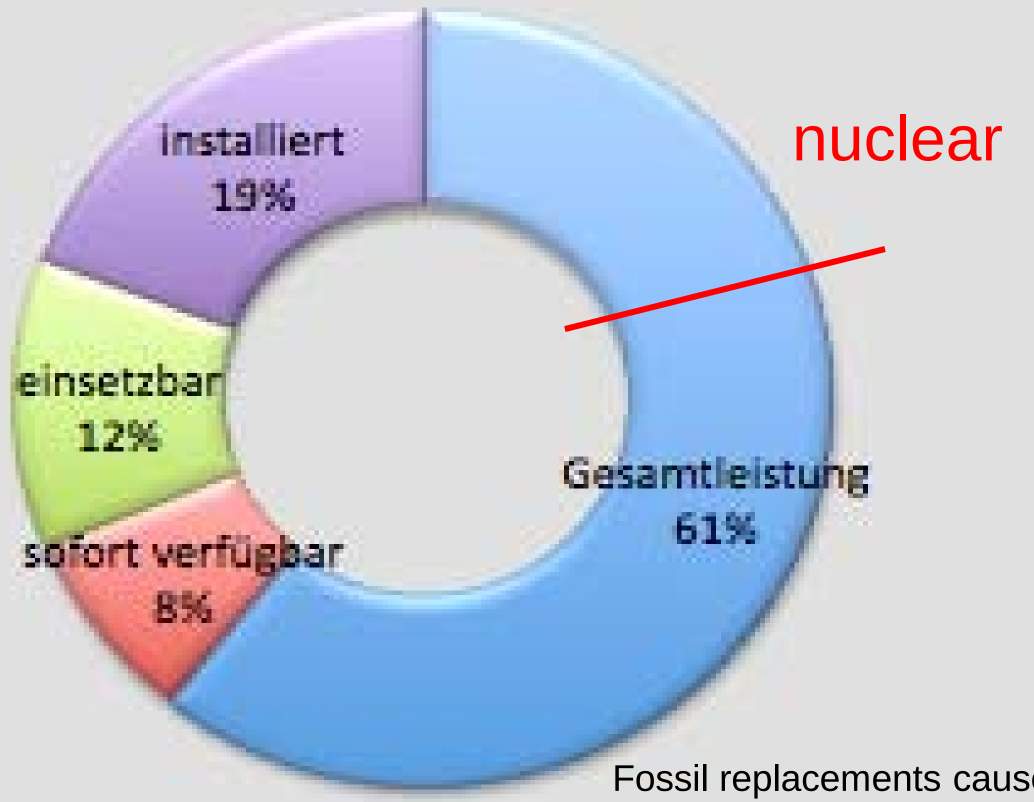
Energy carriers for German electricity (2008)
BMWI



In 2010 about 16% EE

Enormous dimension of energy use

German electricity



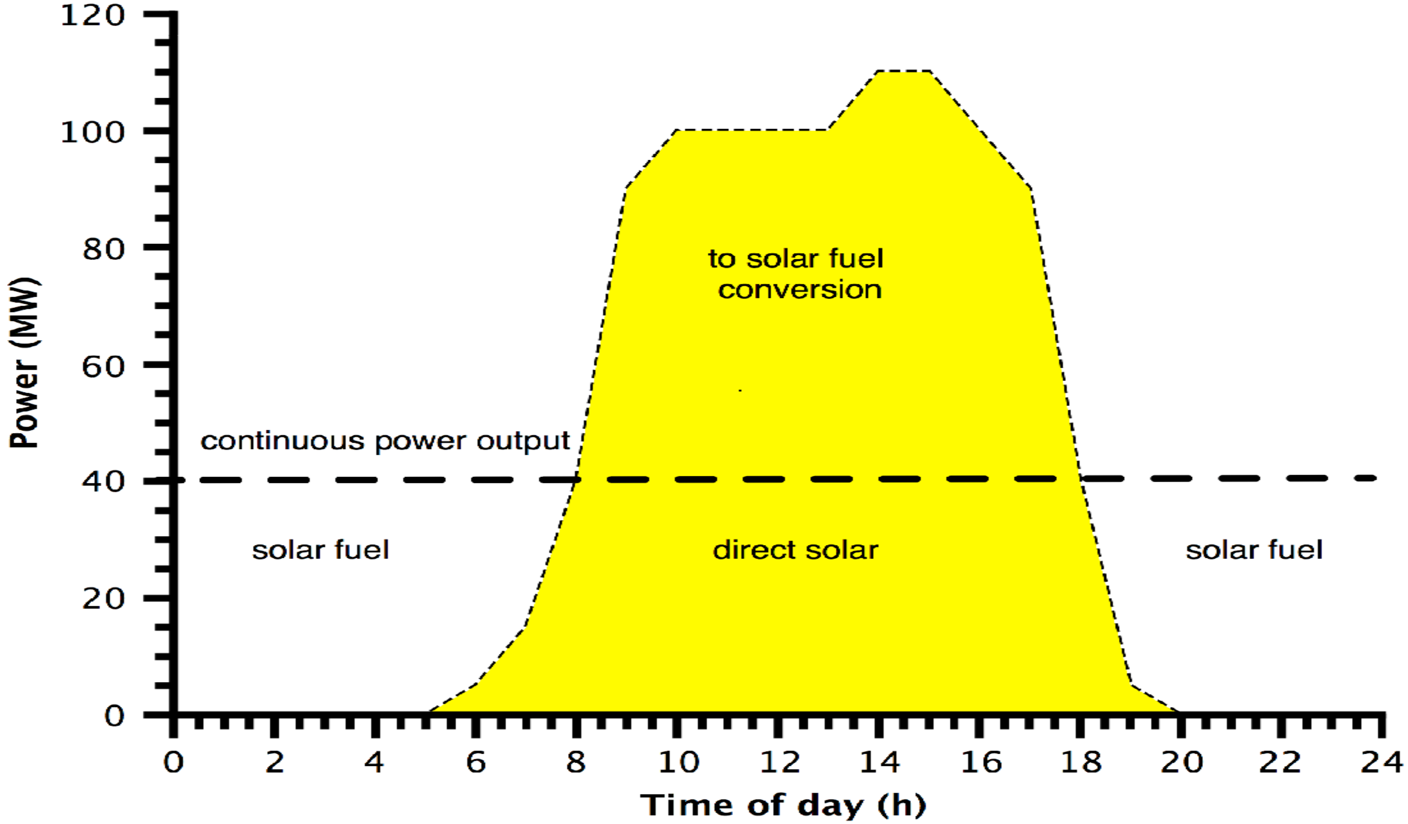
Fossil replacements cause additional emission of 65 - 100 Mio. t/a CO_2

- The use of renewable energies without large admixtures of fossil sources for electricity is impossible without chemical energy storage, even when a “smart grid” exists.
- In addition, chemical energy carriers are needed.
- Chemical storage is essential: “Solar hydrogen” may be used to generate chemical energy carriers through catalysis.
- Saving strategies are useful and helpful for short times but cannot replace missing base supply.

Tabelle 2: Nutzungsdauer von Kraftwerkstypen im Jahr 2007 (BDEW)

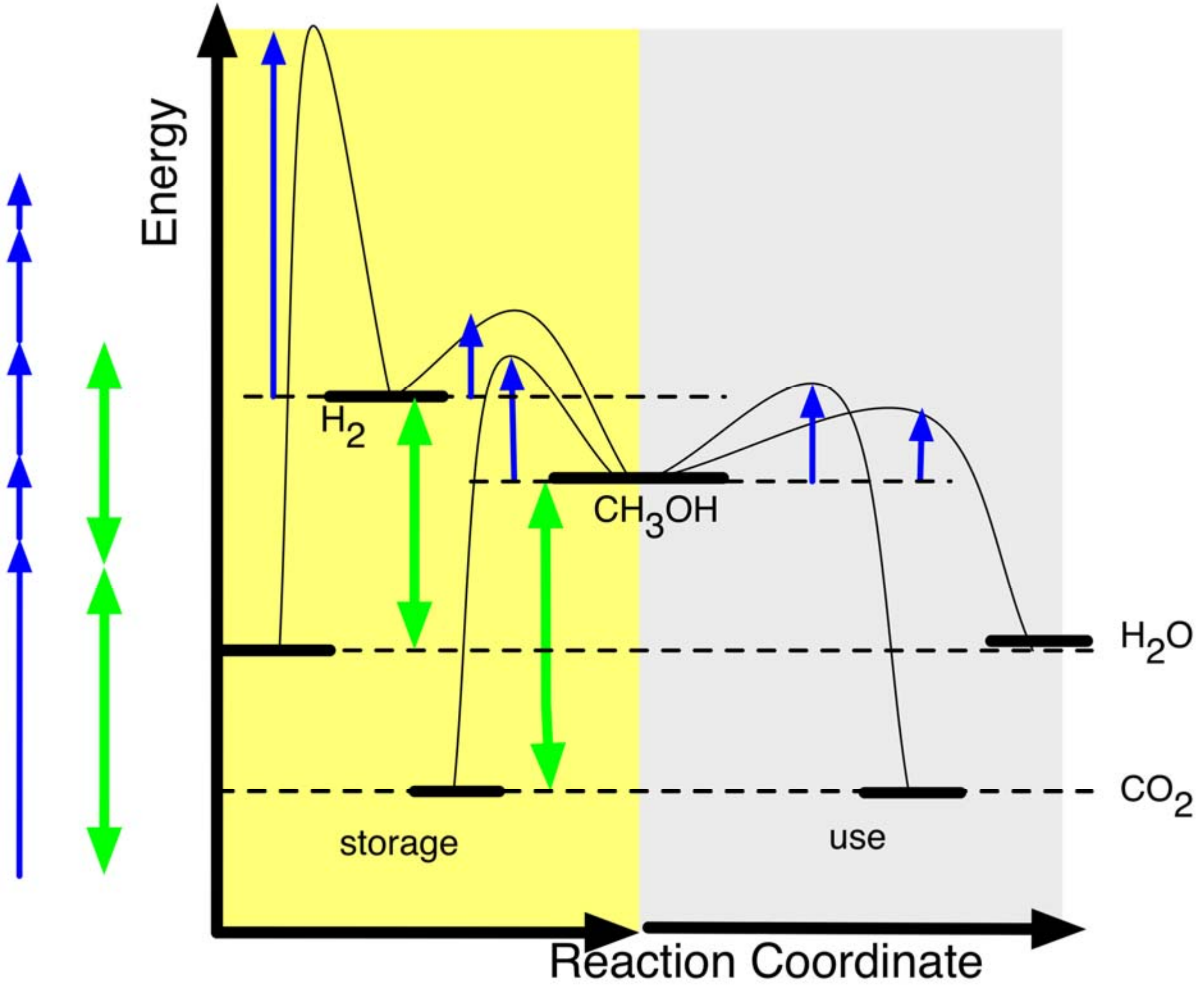
Kraftwerksart	*Volllastnutzung in Stunden*
Kernkraft	7710
Steinkohle	3650
Braunkohle	6640
Erdgas	3170
Erdöl	1640
Wind	1550
Speicherwasser	970
Photovoltaik	910

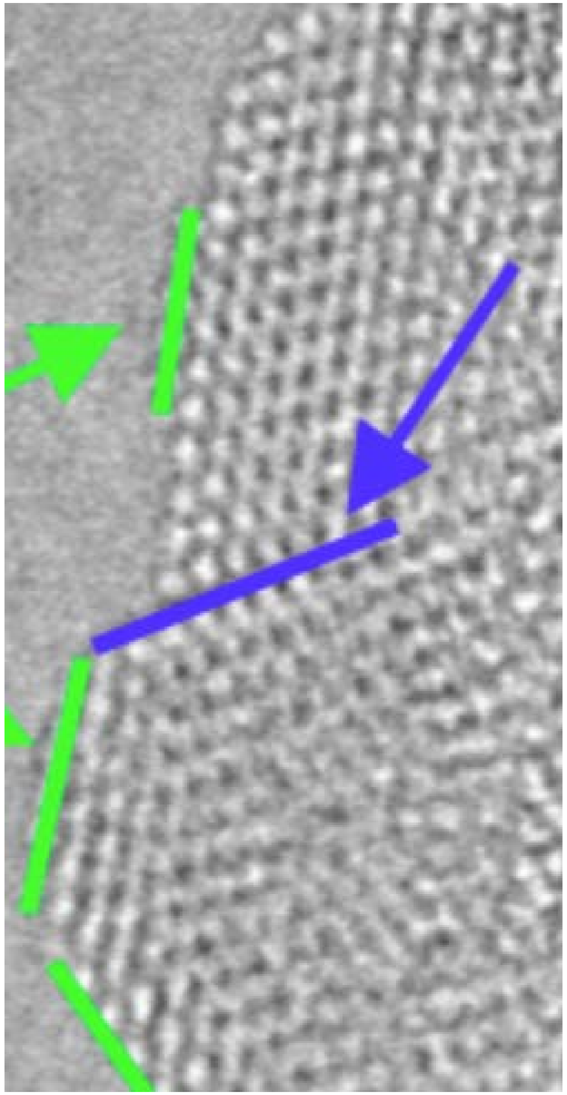
The energy challenge for chemistry



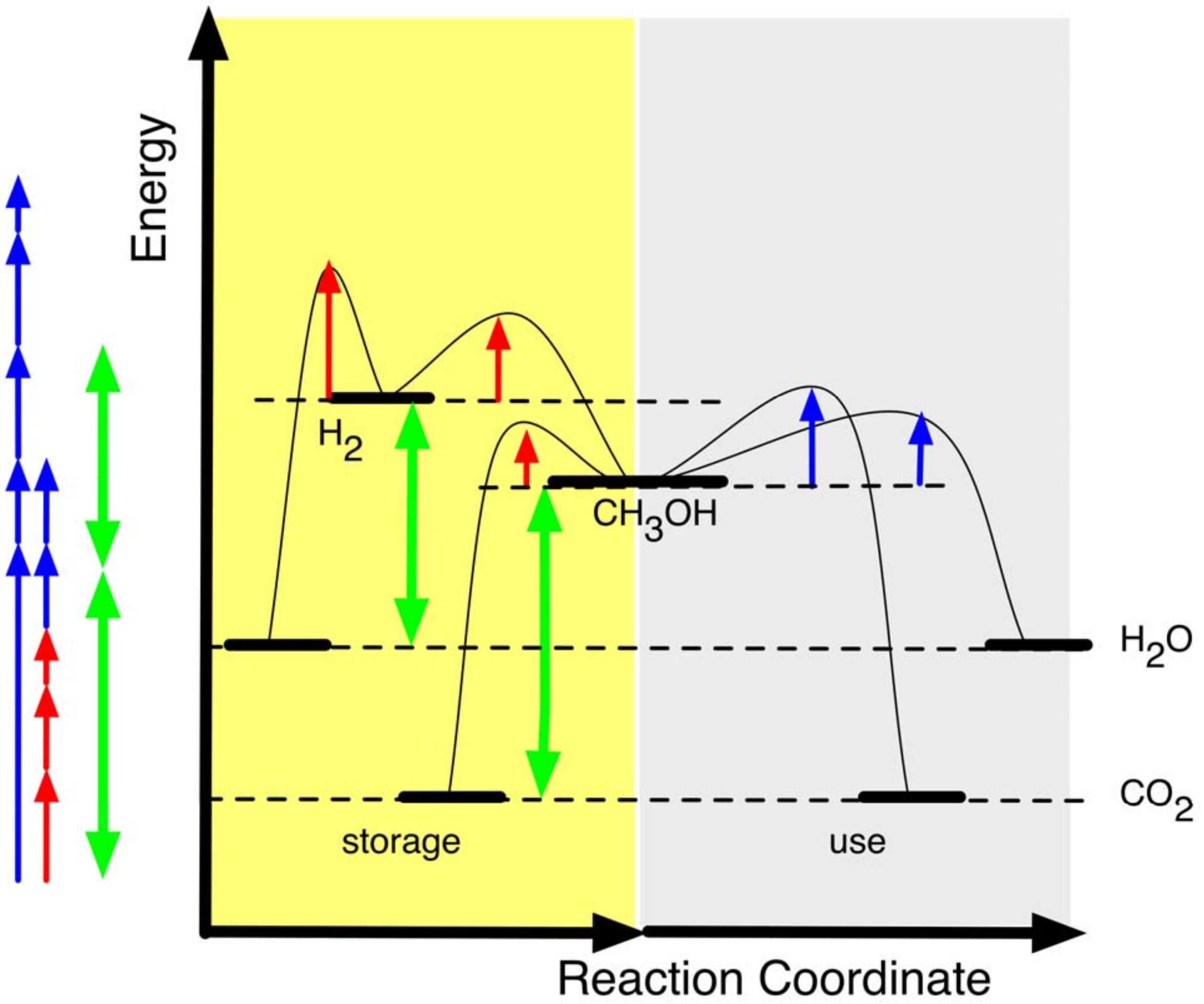
An effective regenerative power station
With 24/7 production.

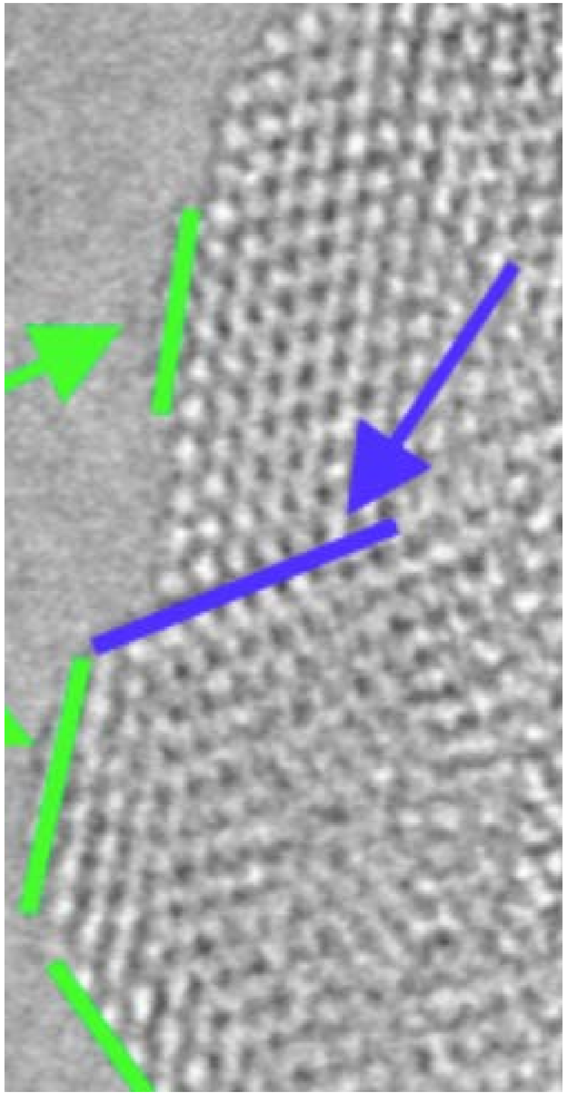
Concept of chemical energy storage



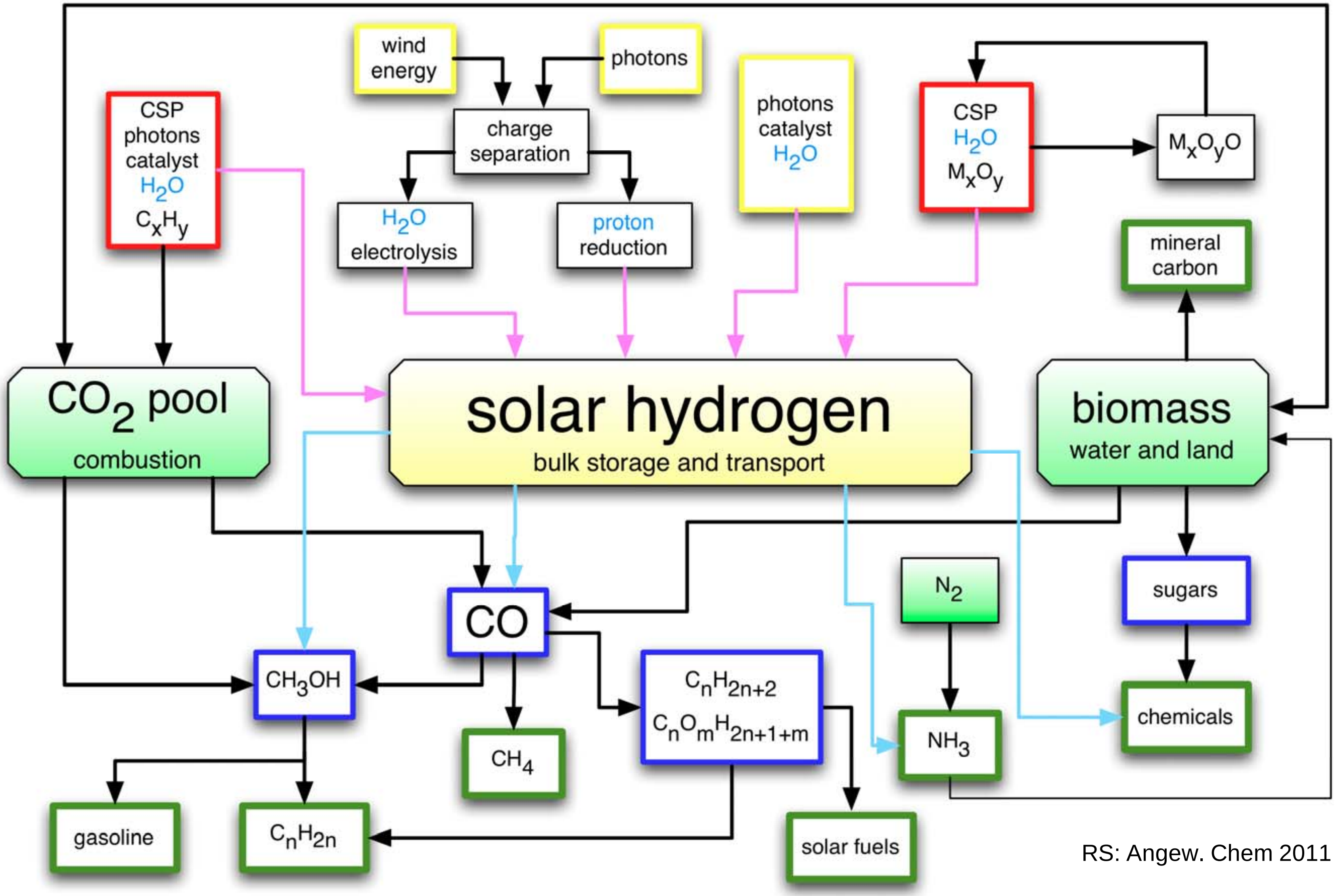


Concept of chemical energy storage



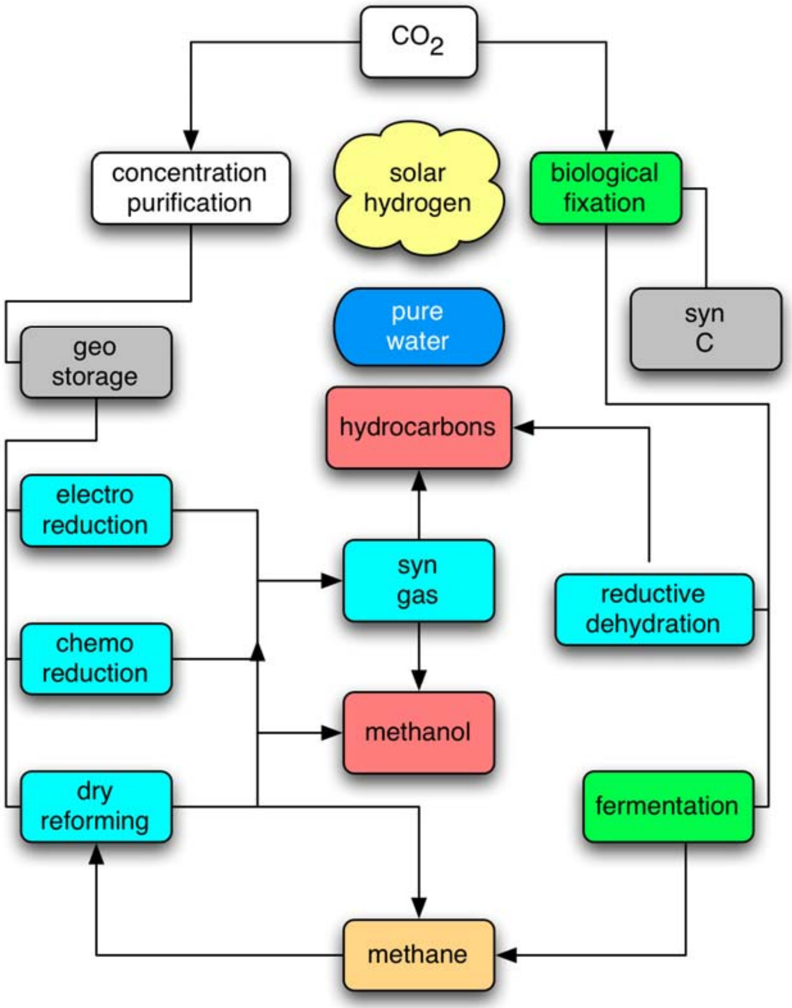


Energy supply: a systemic challenge
Catalysis is the core technology

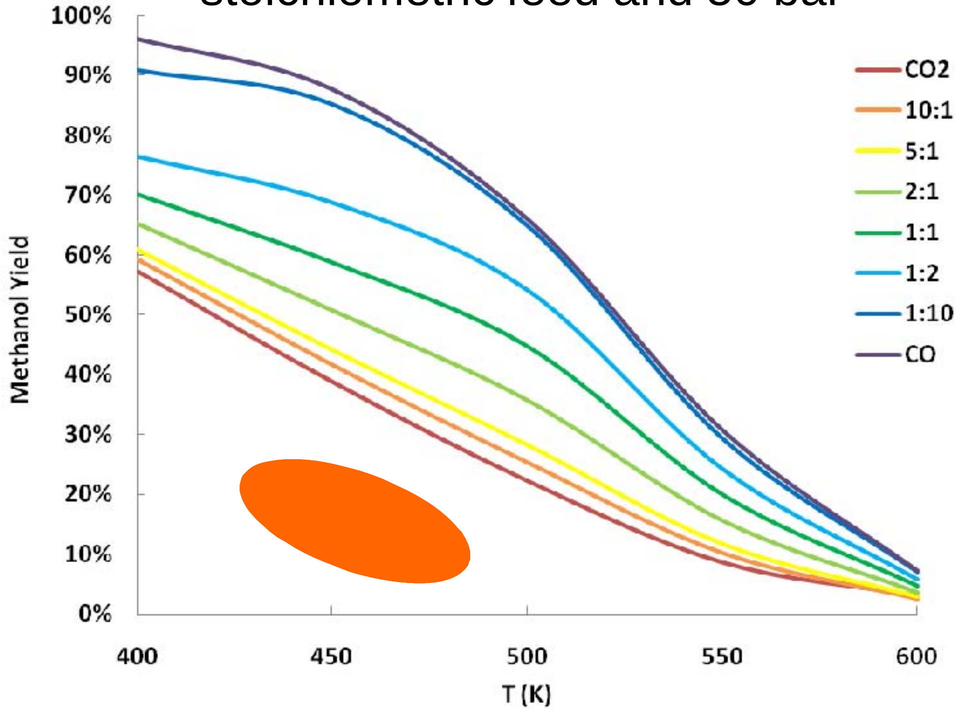


RS: Angew. Chem 2011

Use of solar hydrogen: CO_2 hydrogenation



Equilibrium conversion for CO_x at stoichiometric feed and 50 bar



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

Catalyst Preparation

Ageing

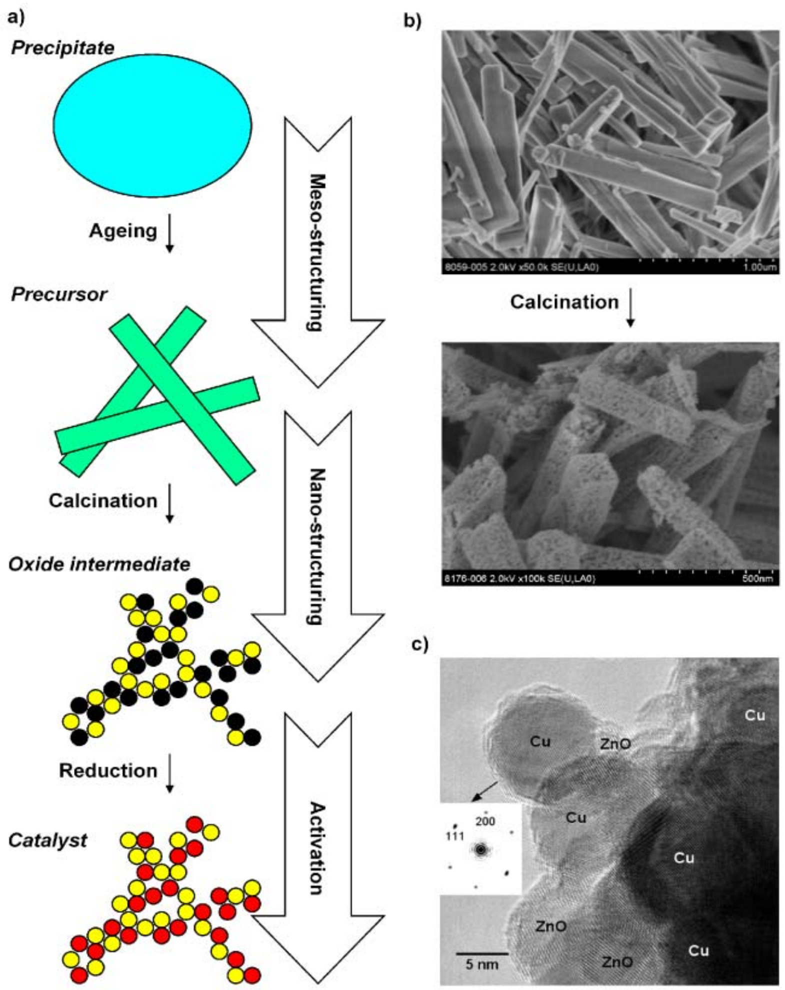
Washing / drying

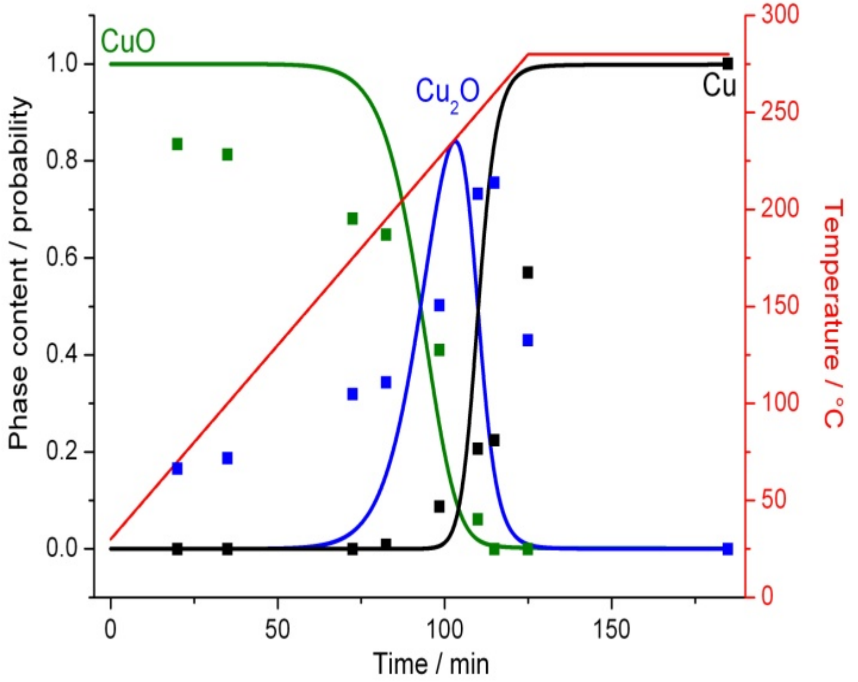
Calcination

Reduction

$Cu/ZnO/Al_2O_3$

M. Behrens et al, 2011





Reduction profile from NEXAFS (points and from a 3-d model derived from TPR analysis: intermediate!

Synergy: Alternatives for ZnO?

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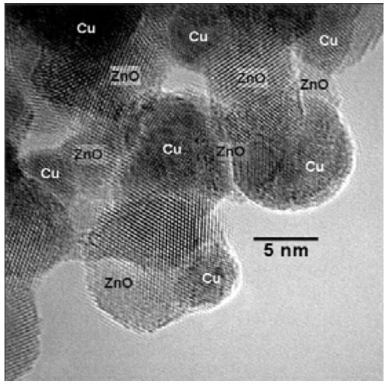
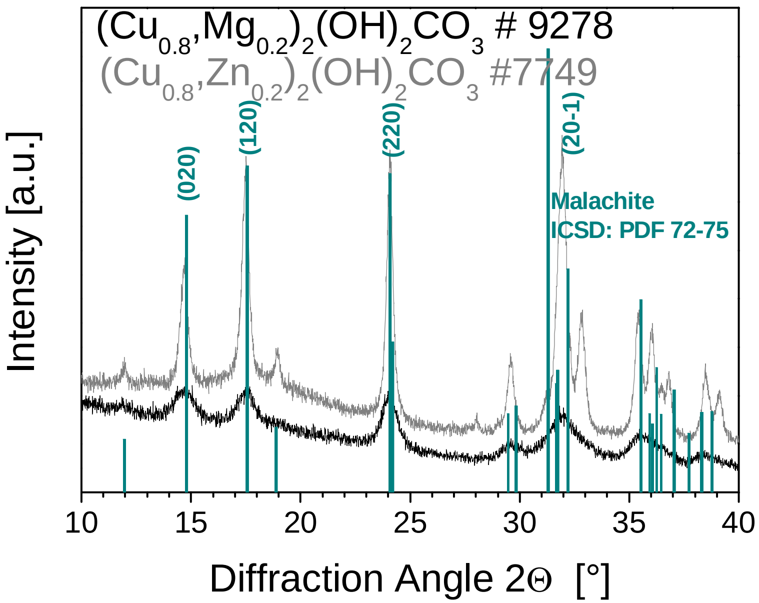
$(Cu_{1-x}M_x)_2(OH)_2CO_3$
$x = 0.2$

M = Zn

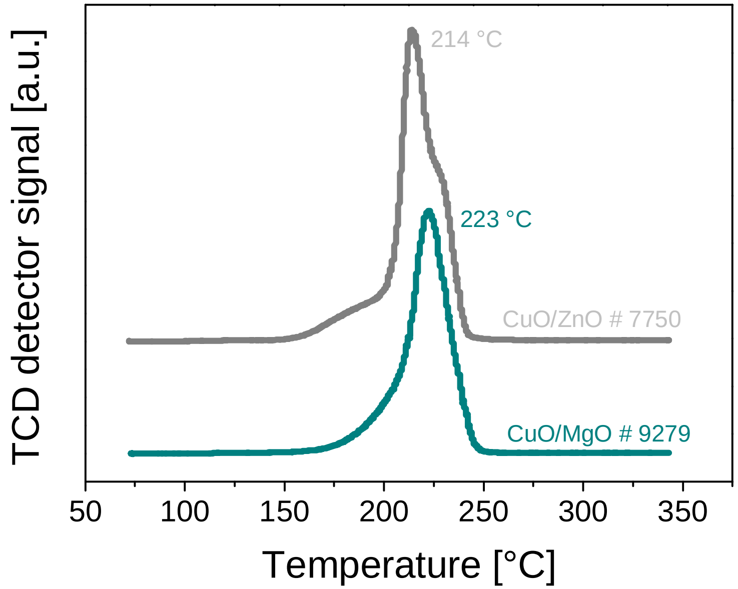


M = Mg



Calcination

Reduction



Synergy: Geometric effect + …

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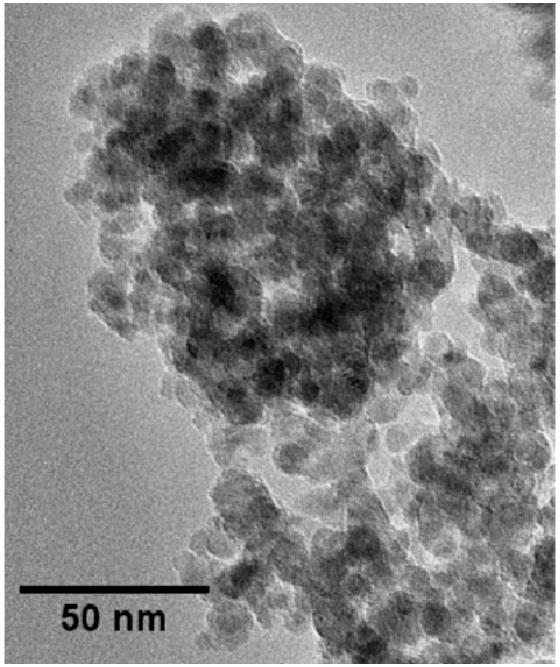

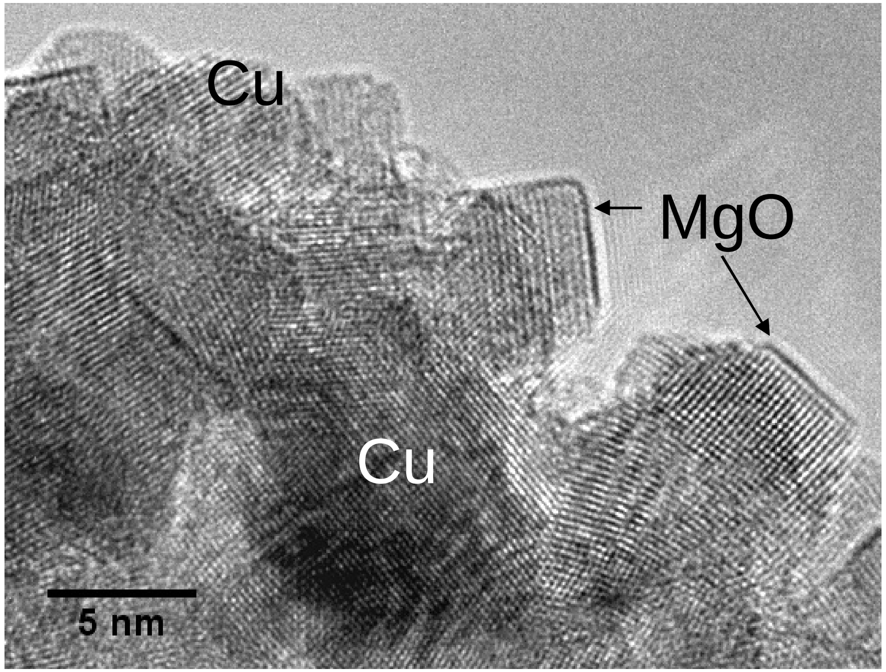

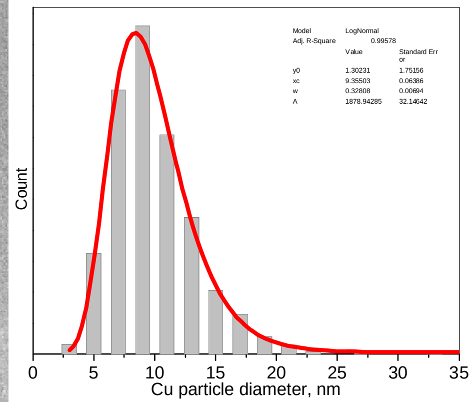

d = 10.4 nm

	Catalyst	Cu surface area [m²/g]	Activity [mmol/h*g_{cat} MeOH]	Intrinsic activity [mmol/h/m² MeOH]
2980	$Cu_xZnO_y(Al_2O_3)_z$ (NGM-Std.)	33 (100 %)	0.45 (100 %)	0.014 (100 %)
9279	$Cu_{0.83}MgO_{0.17}$	39 (119 %)	0.03 (6 %)	0.001 (5 %)
7750	$Cu_{0.8}ZnO_{0.2}$	27 (83 %)	0.22 (49 %)	0.008 (60 %)

Kinetic observations

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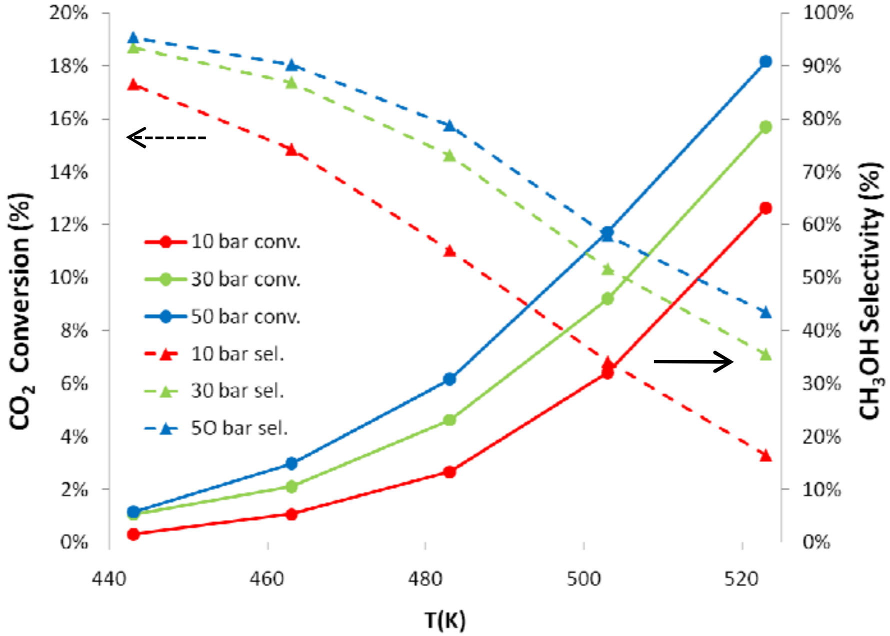
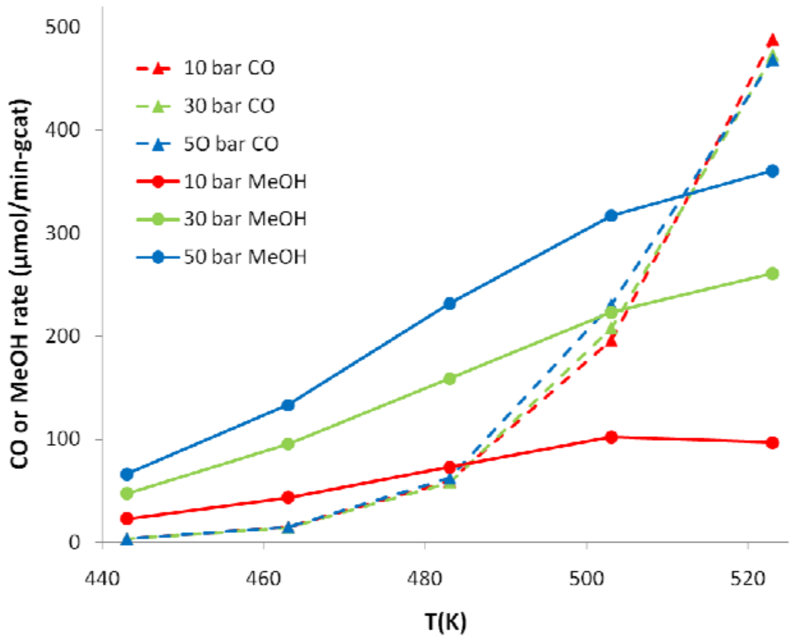
$$CO_2 + 3H_2 \longrightarrow CH_3OH + H_2O$$

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





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

availability of hydrogen at a hypothetical common active intermediate is the problem

Search for active sites: Intrinsic activities in MeOH synthesis at 60 bar

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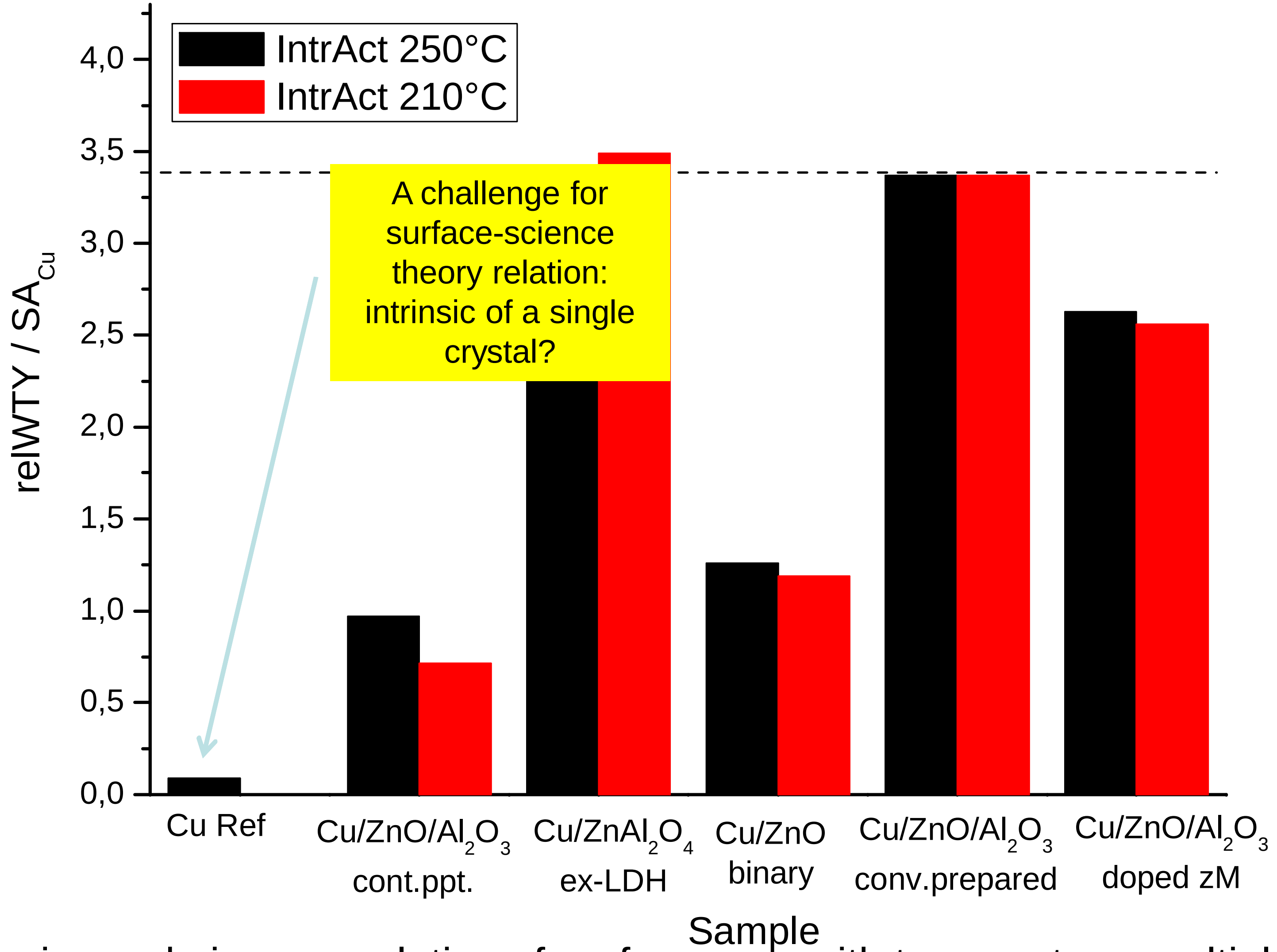

There is no obvious correlation of performance with temperature; multiple processes

Cu-ZnO dynamics

unicat
Unifying Concepts in Catalysis

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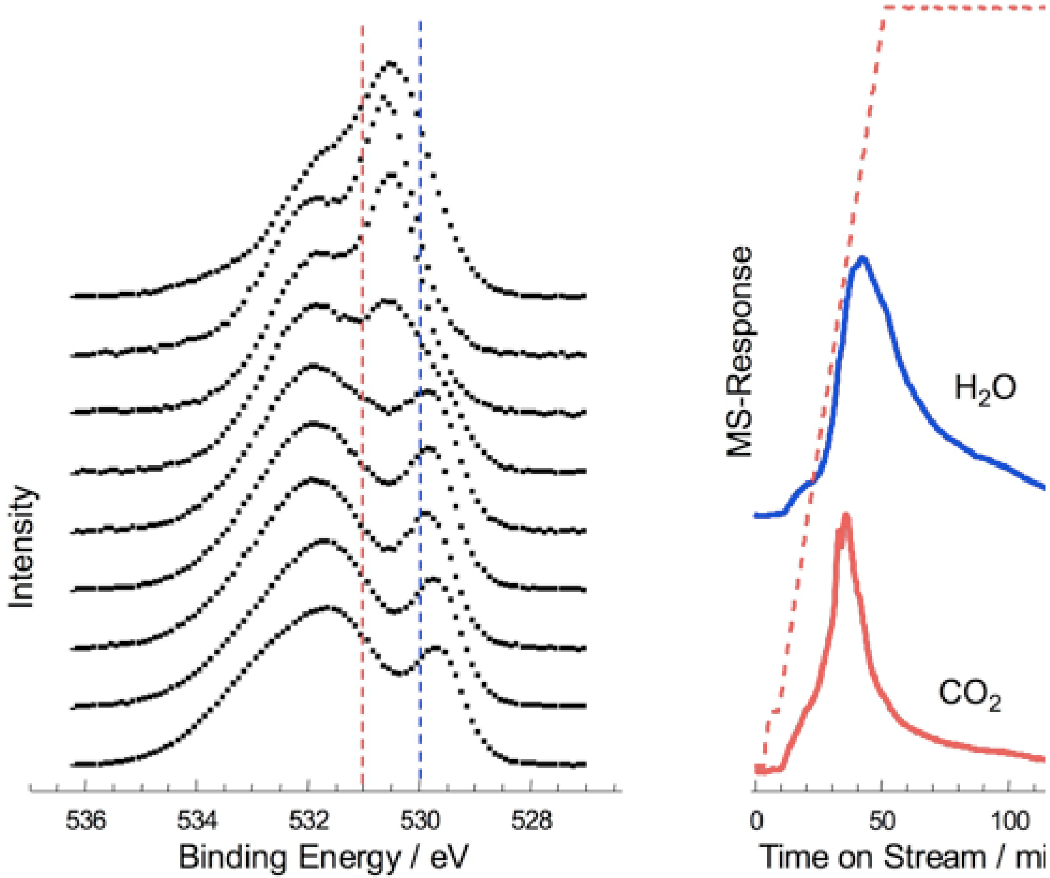
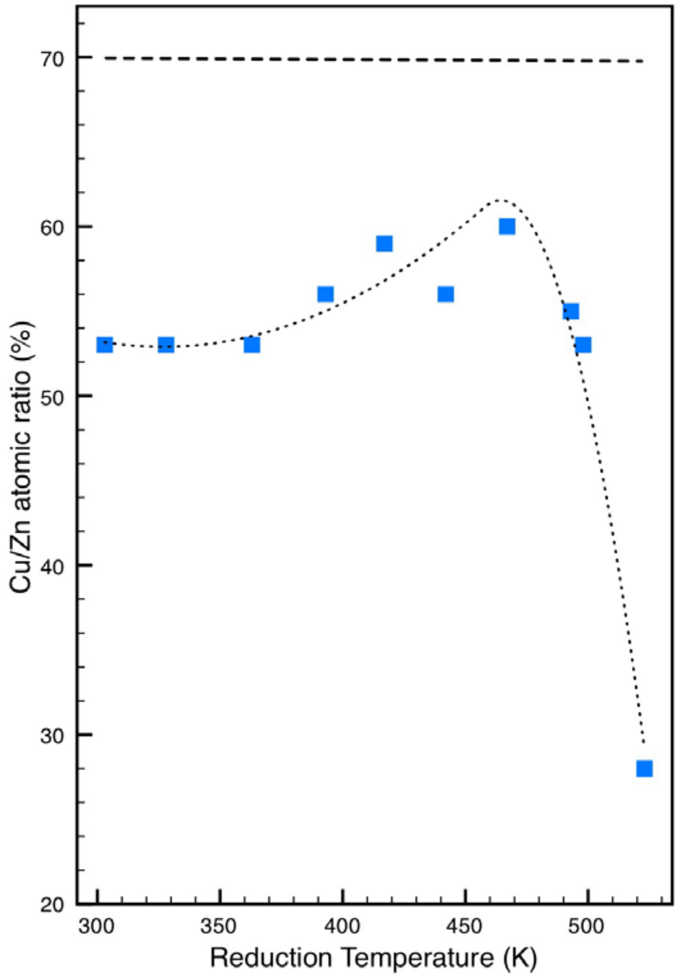


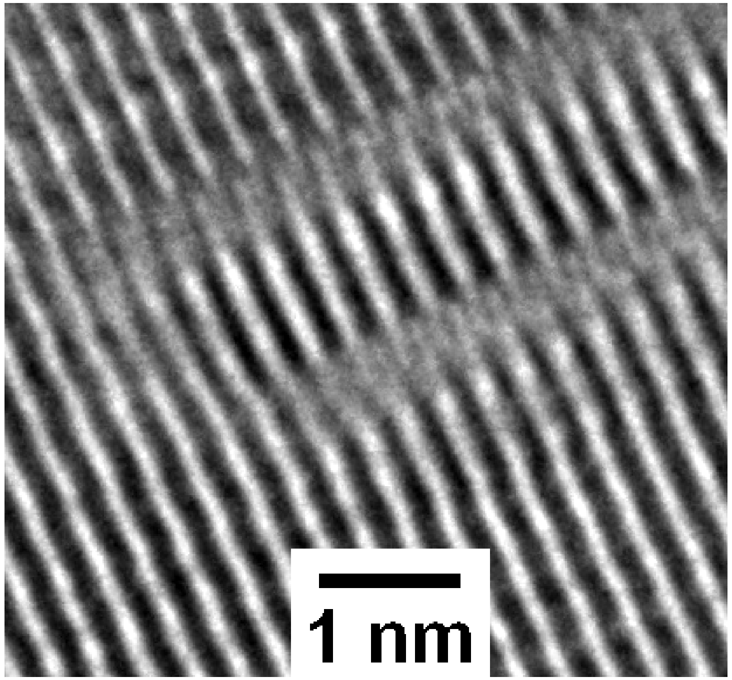
Disperse ZnO_{1-x} on Cu metal

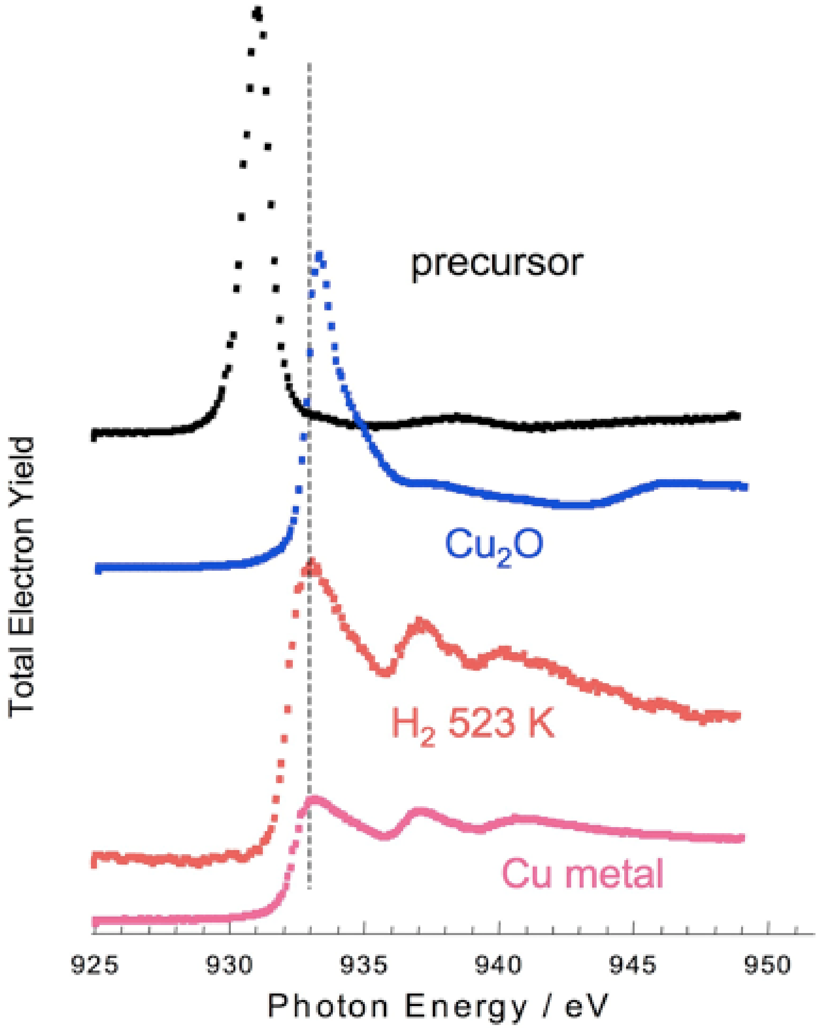


Cu-Zn neighbouring sites likely to exist

Cu-ZnO dynamics

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





Alumina in lattice controls SMSI

In-situ XPS is not sufficient…..

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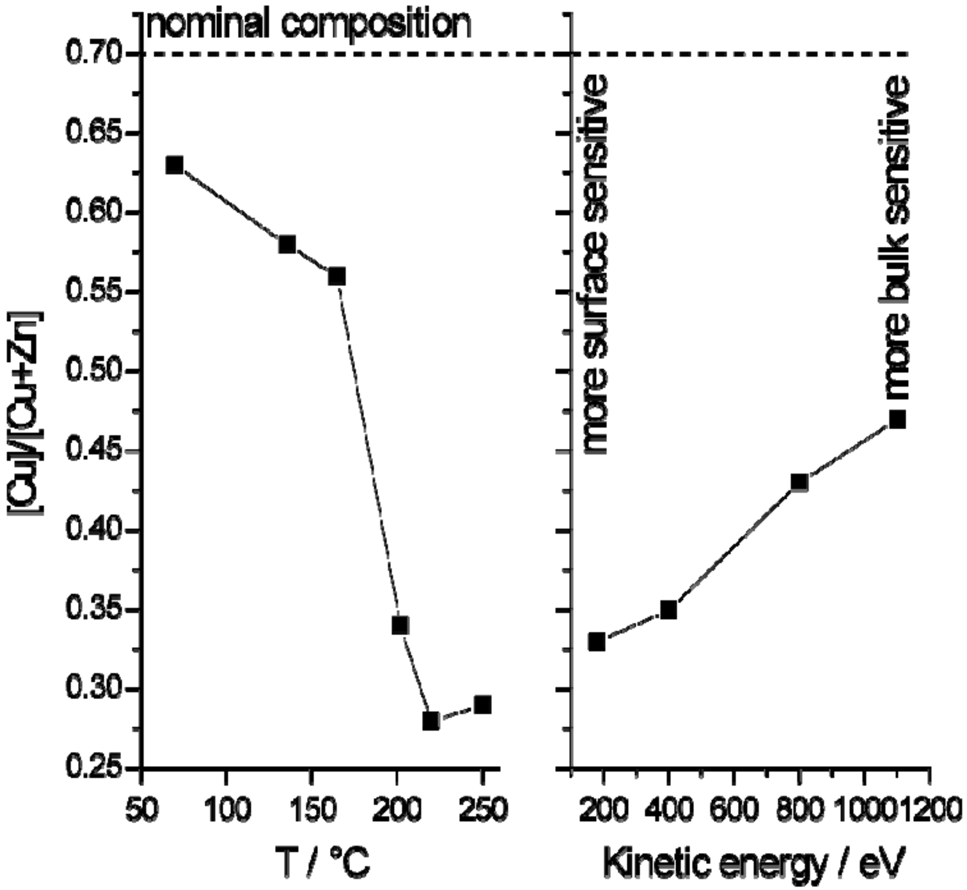

The ZnO overlayer is less than 2 nm thick!!

Spectroscopy is still not sufficient: In-situ neutrons for structure-function

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Unifying Concepts in Catalysis

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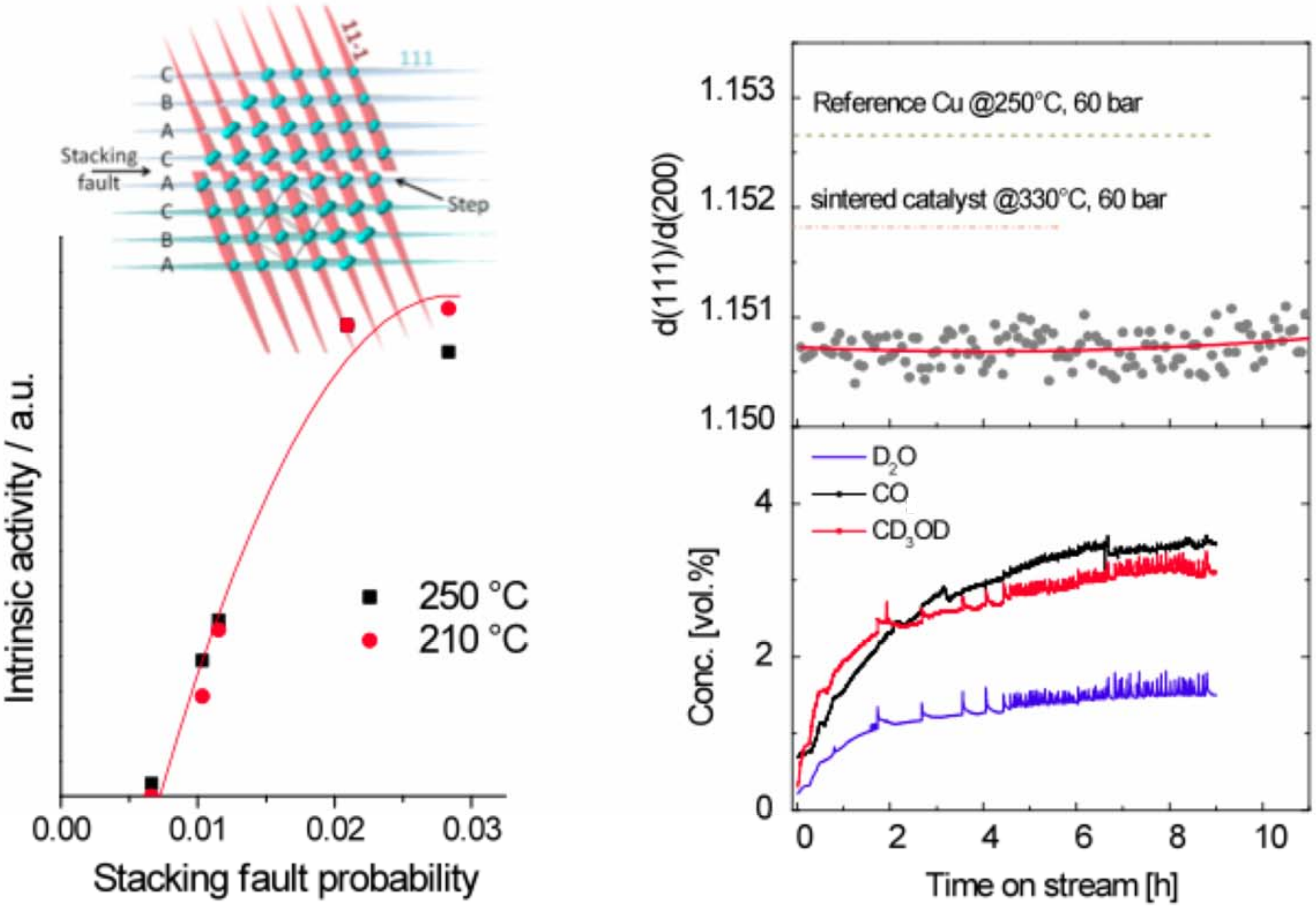
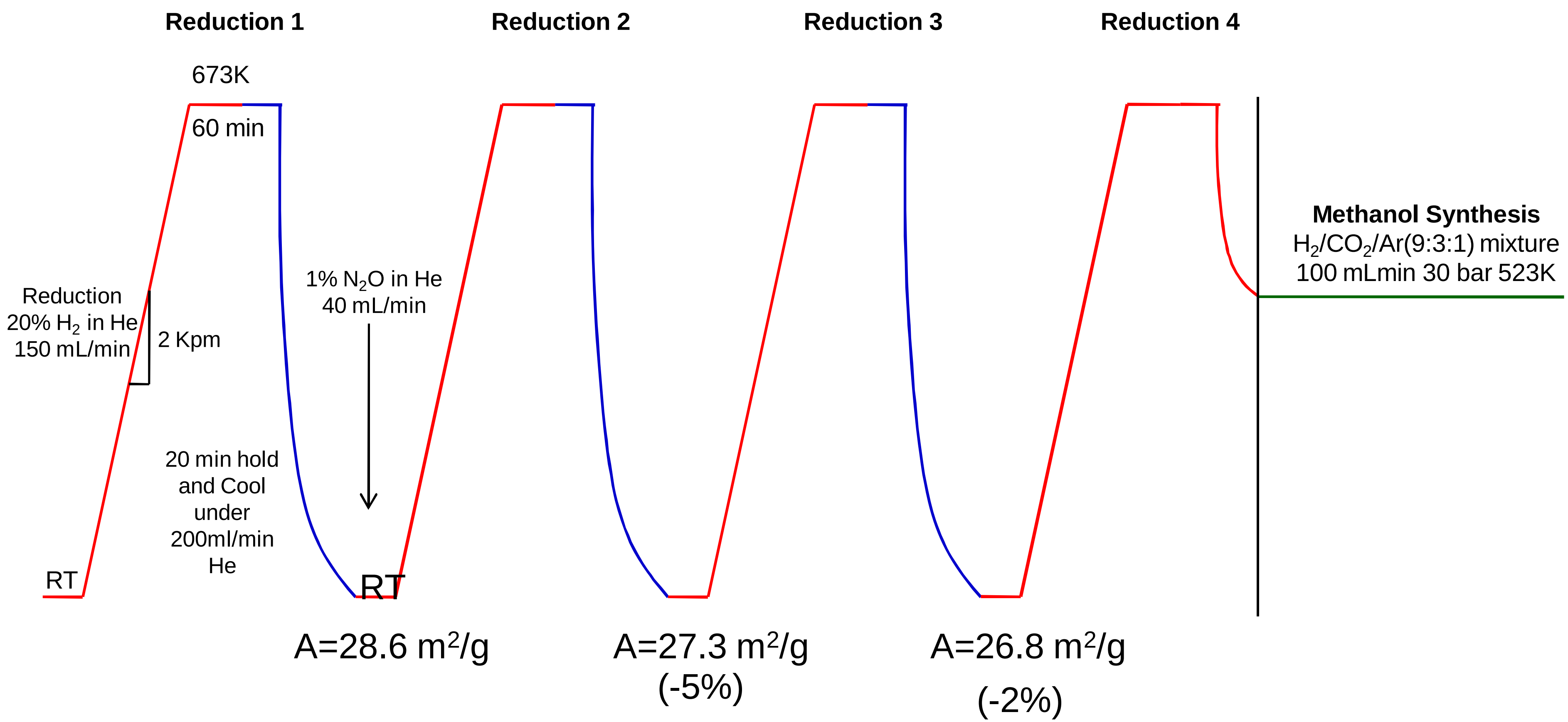


In-situ surface area measurement



In-situ surface area measurement

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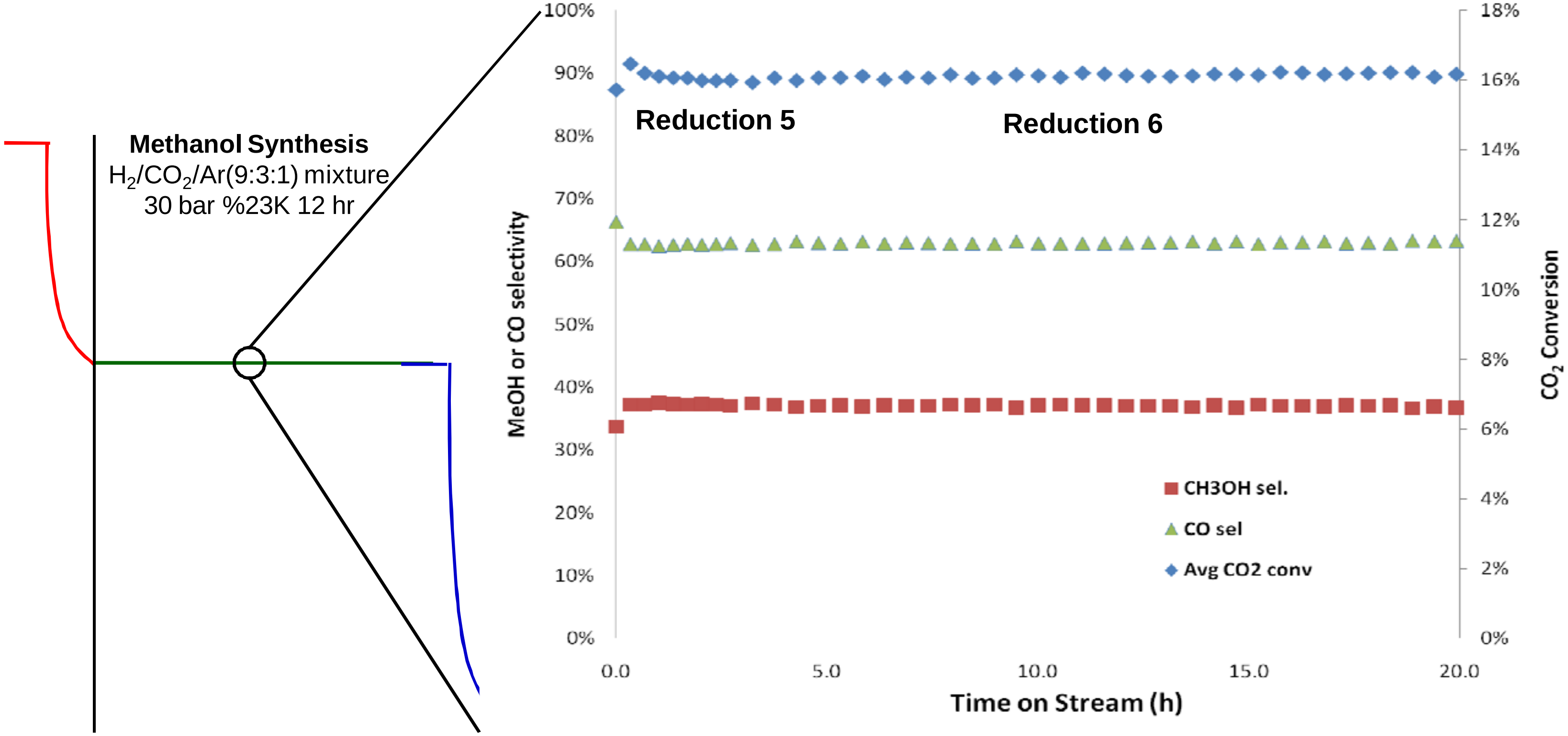
	After 1 std. Reduction	Current Test
X_{CO2}	15.7%	16.1%
S_{MeOH}	35.5%	36.7%



A=12.4 m²/g A=19.2 m²/g A=19.1 m²/g

In-situ surface area measurement

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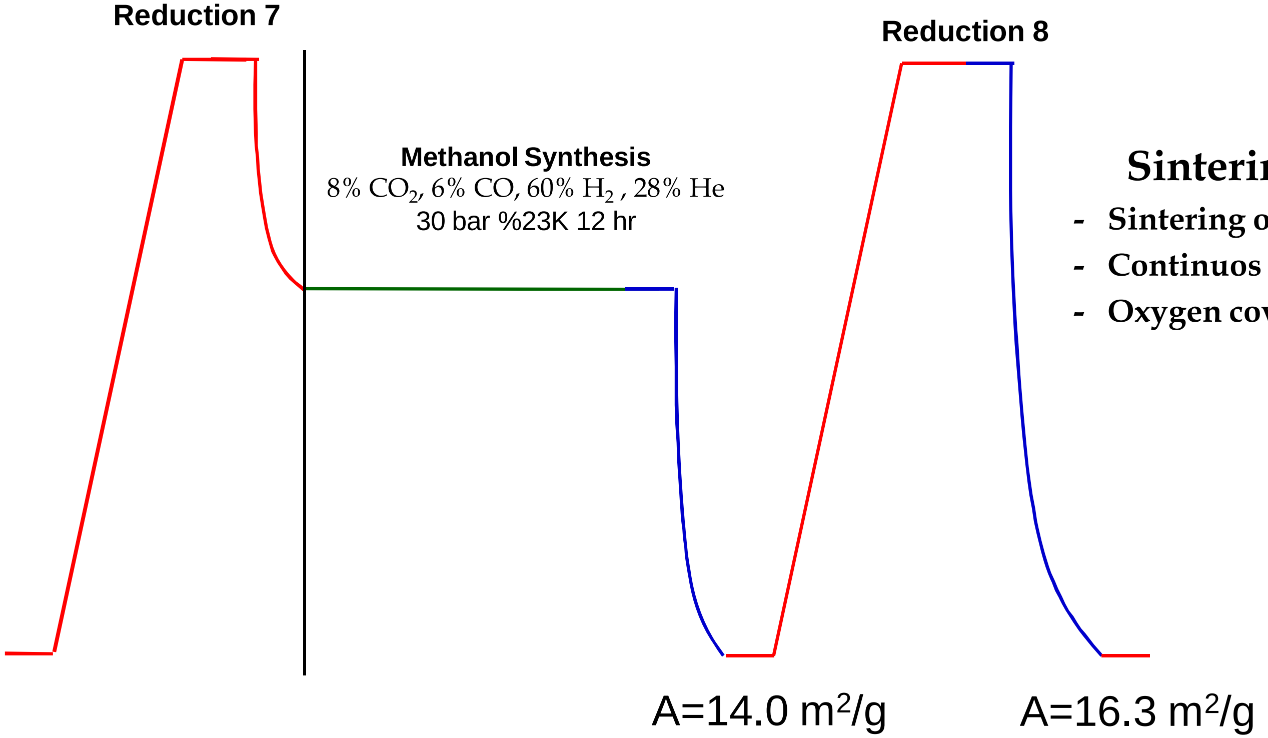
Gas mixture	$A_{rxn}/A_{re\text{-}reduced}$	M.L. O coverage	$A_{re\text{-}red}/A_{pre\text{-}react}$
H2/CO2	65%	18%	71%
H2/CO2/CO	86%	7%	61%



Sintering and oxygen converage

- **Sintering occurs upon initial exposure to RXN**
- **Continuos sintering not observed (no activity loss)**
- **Oxygen coverage dependent on gas composition**

Is Cu + O the same as Cu_2O?

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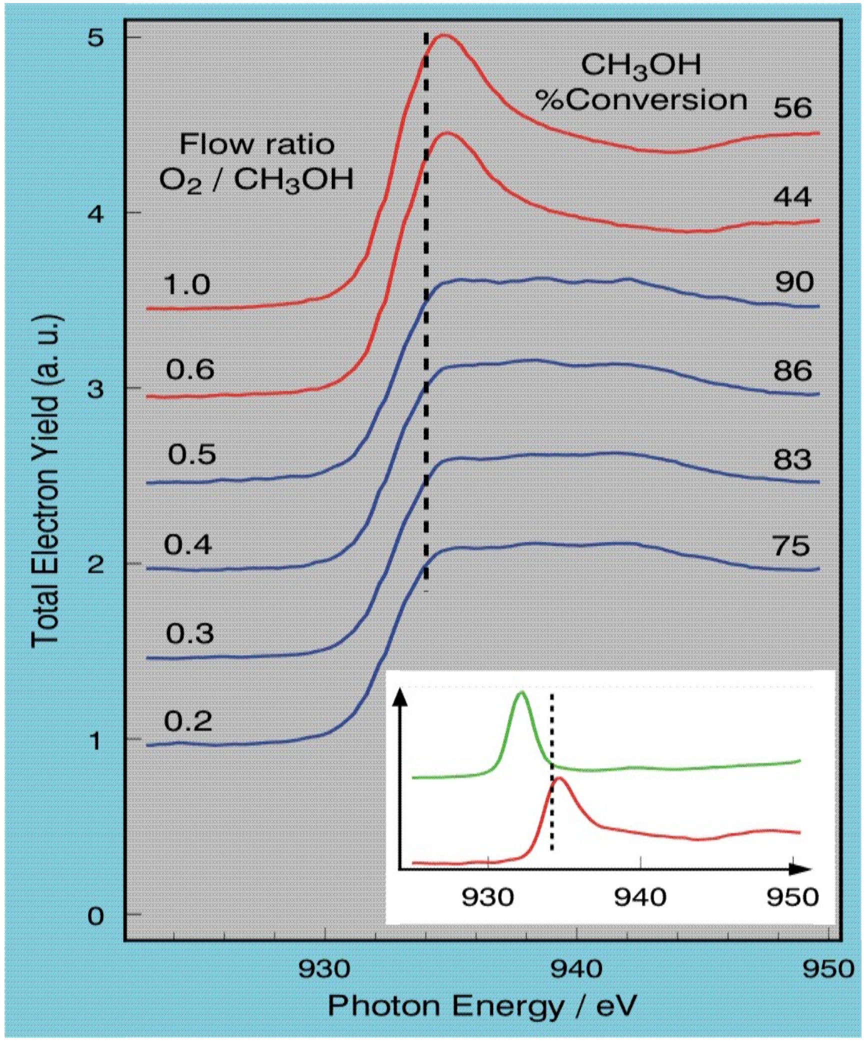
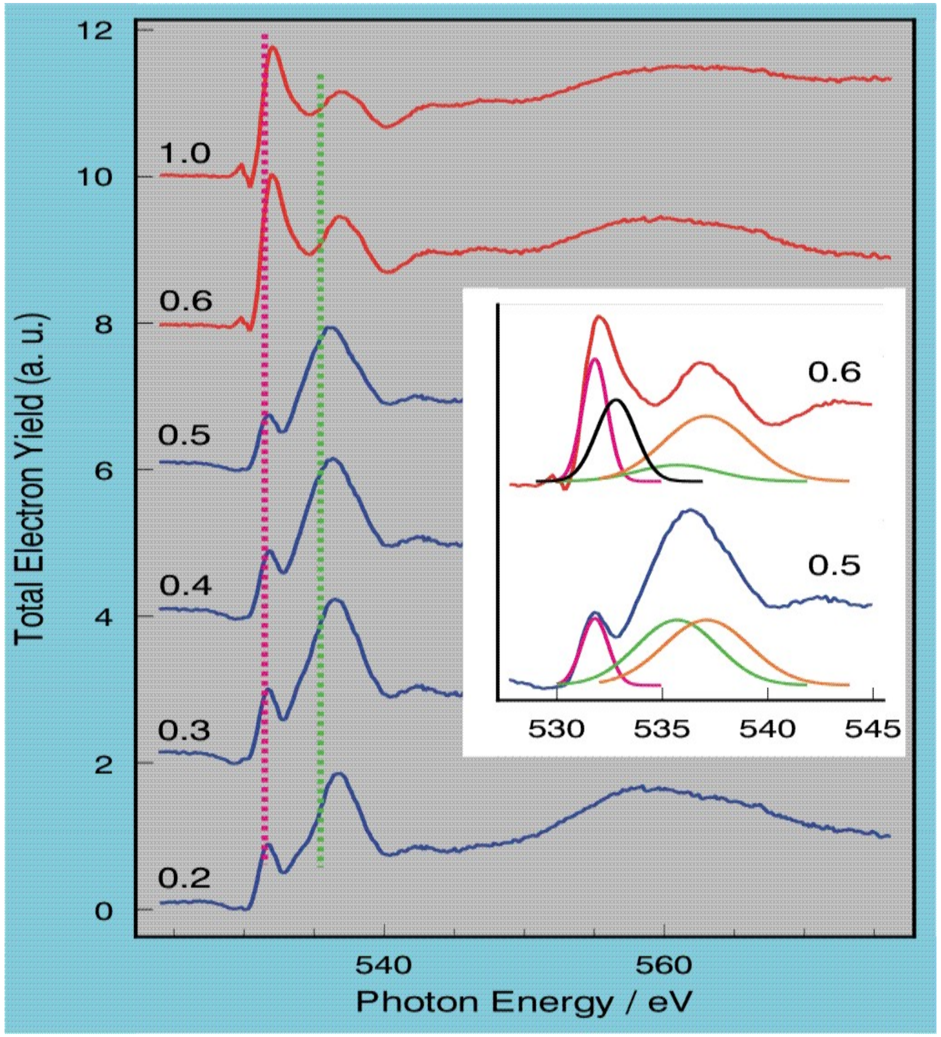
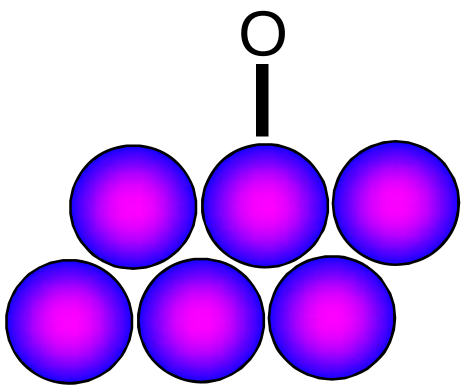




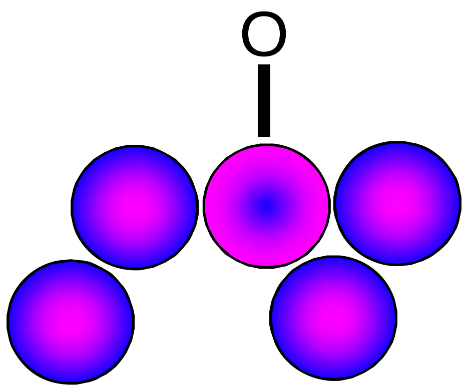
The critical step

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)

Surface oxygen coverage

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50 bar , 523K 3:1 CO_2:H_2

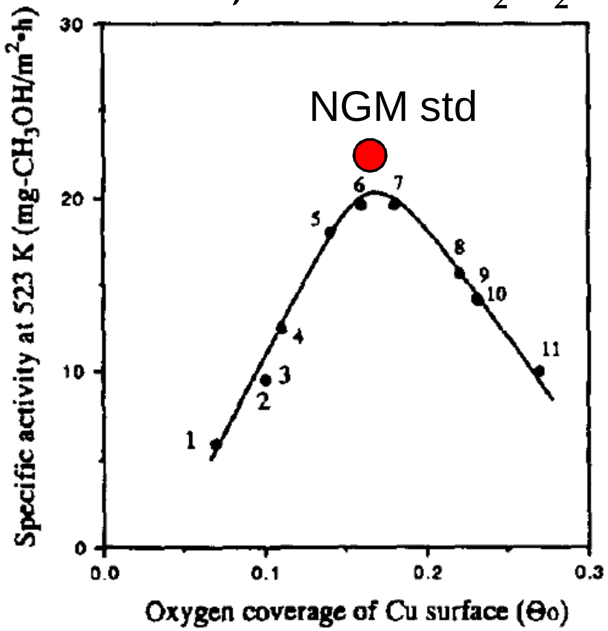
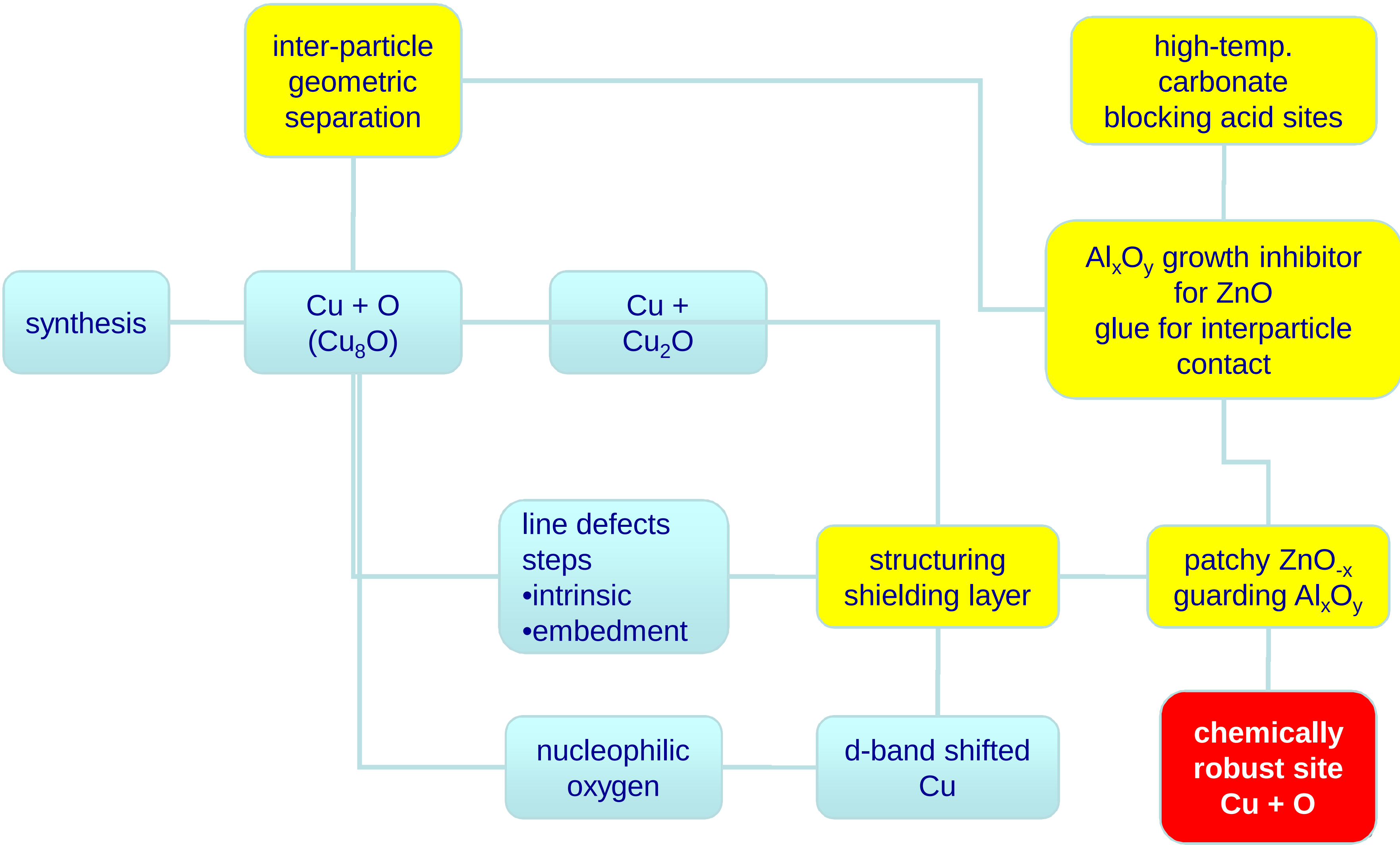


Fig. 4. Specific activity at 523 K as a function of oxygen coverage of Cu surface. Reaction conditions were the same as shown in Table 1. Catalysts composition (wt.-%): (1) Cu/SiO_2 (30/70), (2) Cu/Al_2O_3 (50/50), (3) Cu/ZrO_2 (50/50), (4) Cu/Cr_2O_3 (50/50), (5) Cu/ZnO/Cr_2O_3 (50/40/10), (6) Cu/ZnO/Ga_2O_3 (50/25/25), (7) Cu/Ga_2O_3 (50/50), (8) Cu/ZnO/Al_2O_3 (50/45/5), (9) Cu/ZnO (50/50), (10) Cu/ZnO/ZrO_2 (50/25/25), (11) Cu/ZnO/La_2O_3 (50/40/10).

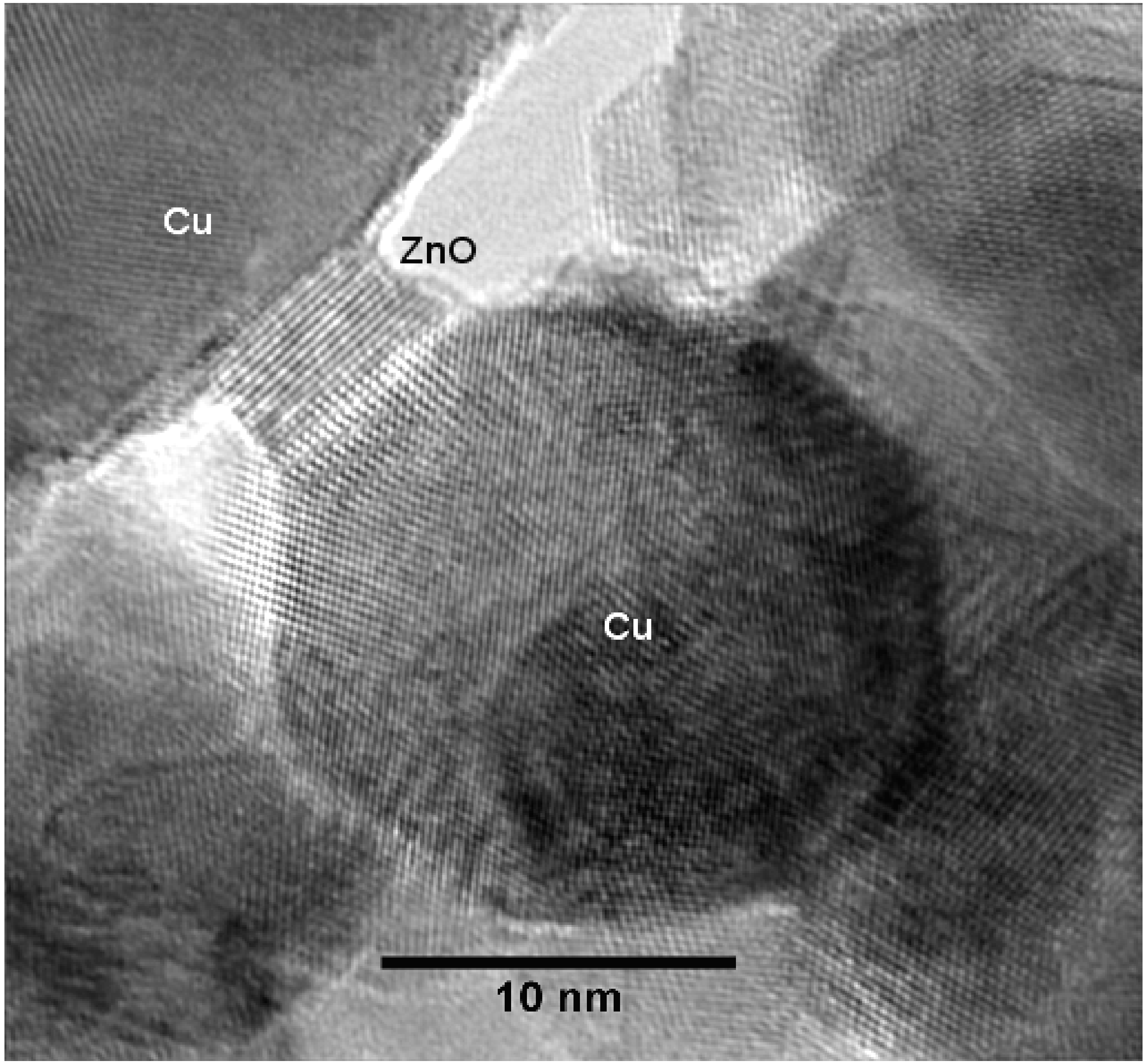
- **Synergy between Cu^0/Cu^{+1} sites controls specific activity**
- **Our result is consistant with literature**

M. Saito, et. al, Applied Catalysis A: General **138** *(1996) 311-318*

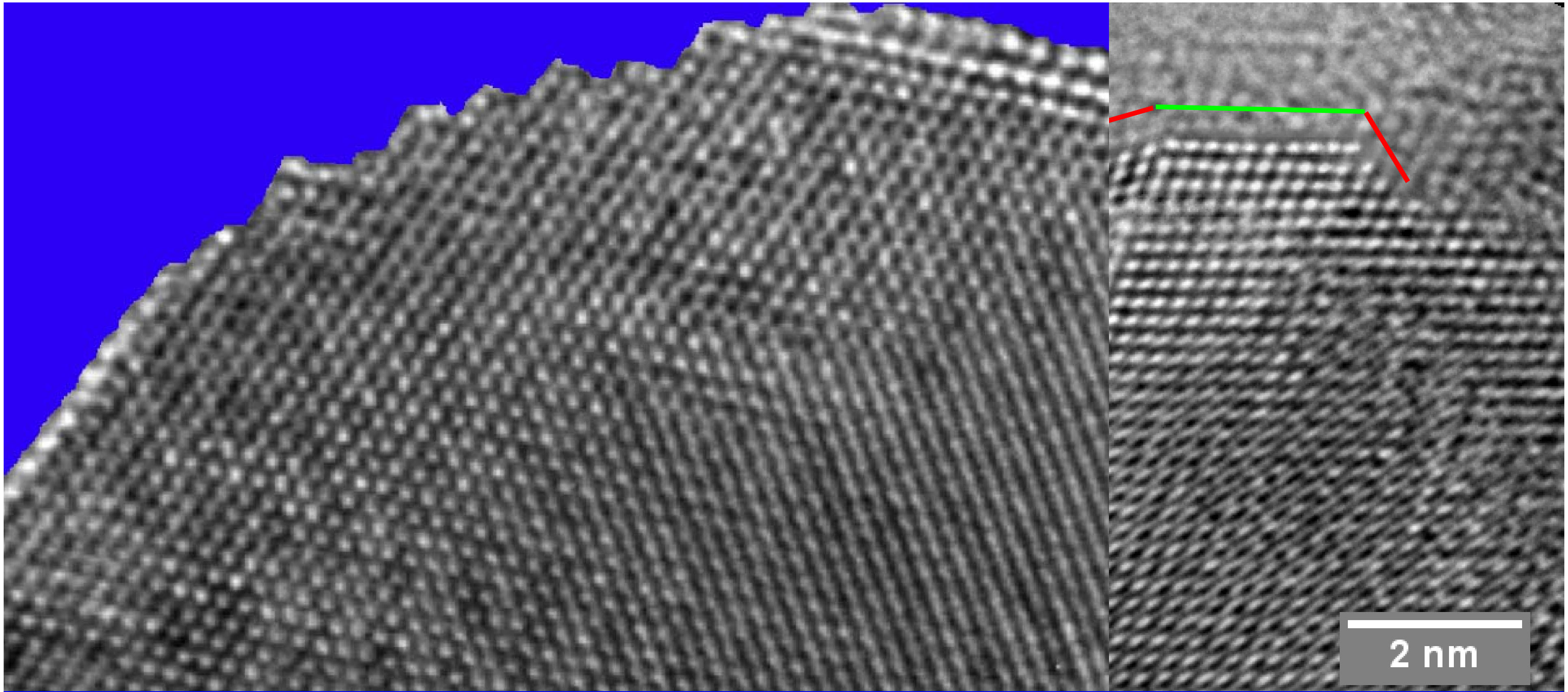
High performance catalysis: rational design or a labyrinth?



High performance catalysis: rational design or a labyrinth?



Can we see?
Yes, we can…



….. active sites?

To take home

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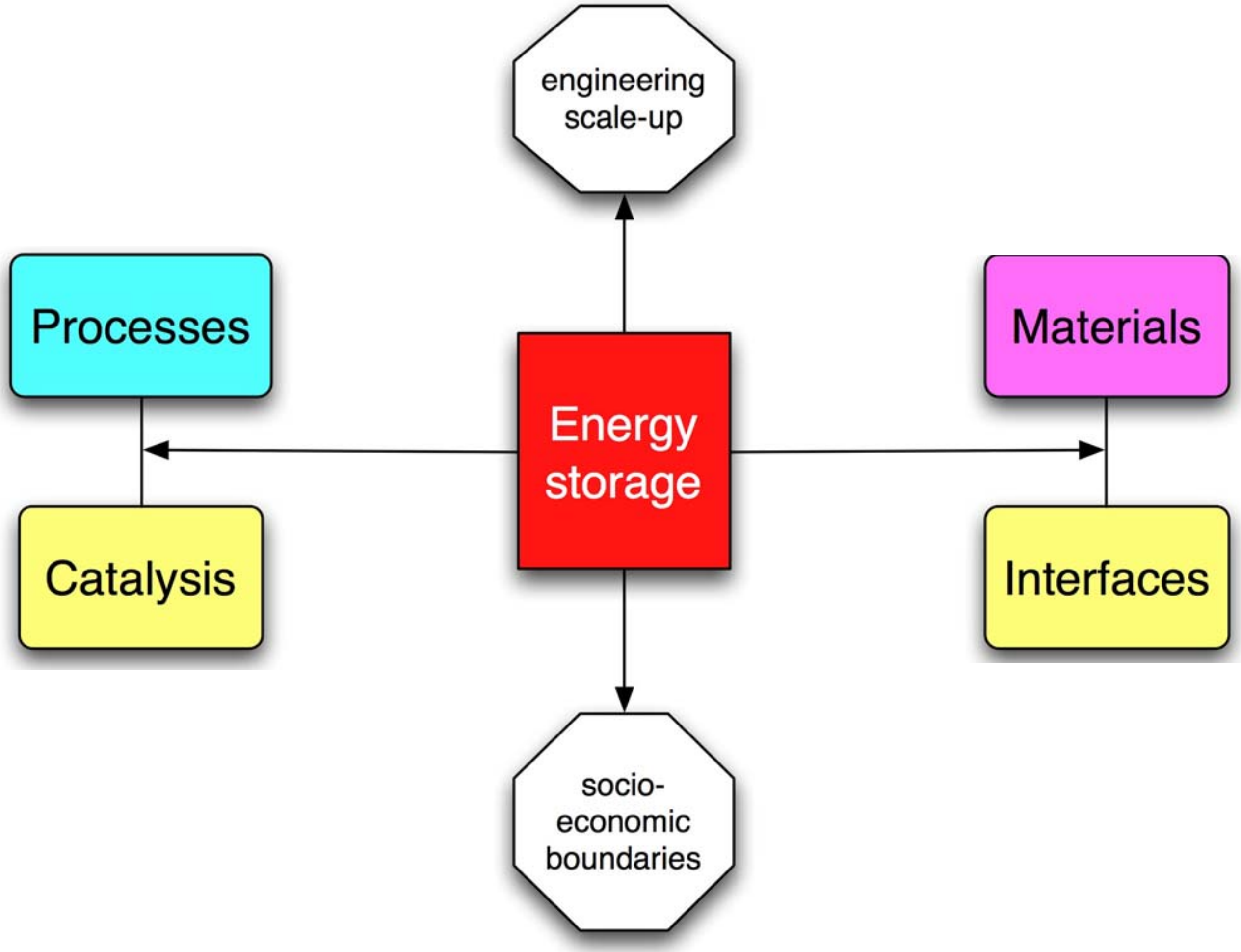
- Catalysis is strategic for the energy challenge.
- Classical problems of catalysis need sustainable large-scale solutions.
- Traditional development strategies not efficient.
- Systemic multi-scale approach between surface science and high-performance catalysis is the solution.
- Multi-disciplinary approach within chemistry (experimental and theoretical) together with engineering is needed.
- In-situ analysis is a core toolbox (besides advanced chemical synthesis) helping to give us the picture of dynamically working systems.

Finale


engineering
scale-up
Processes
Materials
Energy
storage
Catalysis
Interfaces
socio-
economic
boundaries

Geometric effect of promoter?

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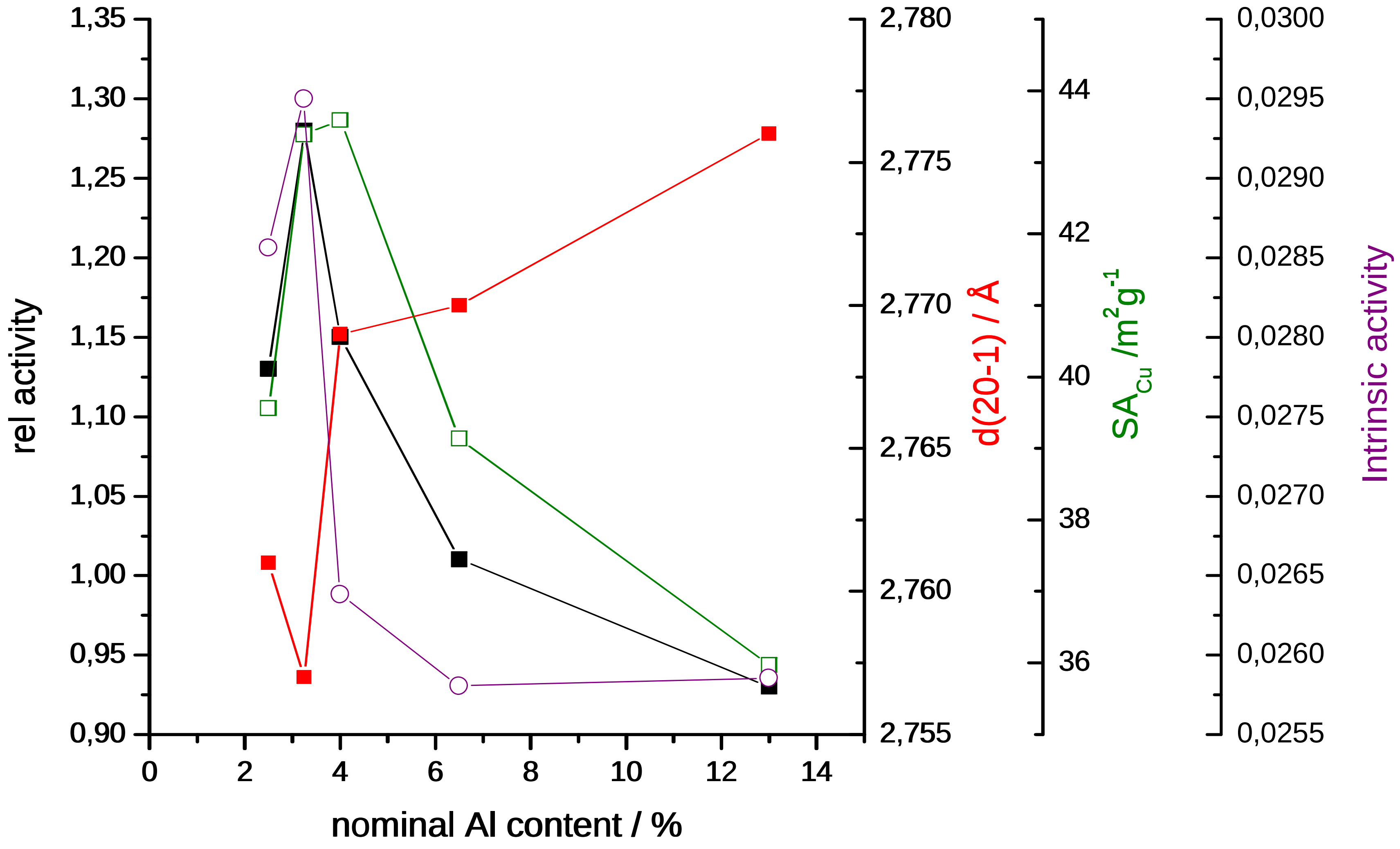

^{27}Al-MAS-NMR study

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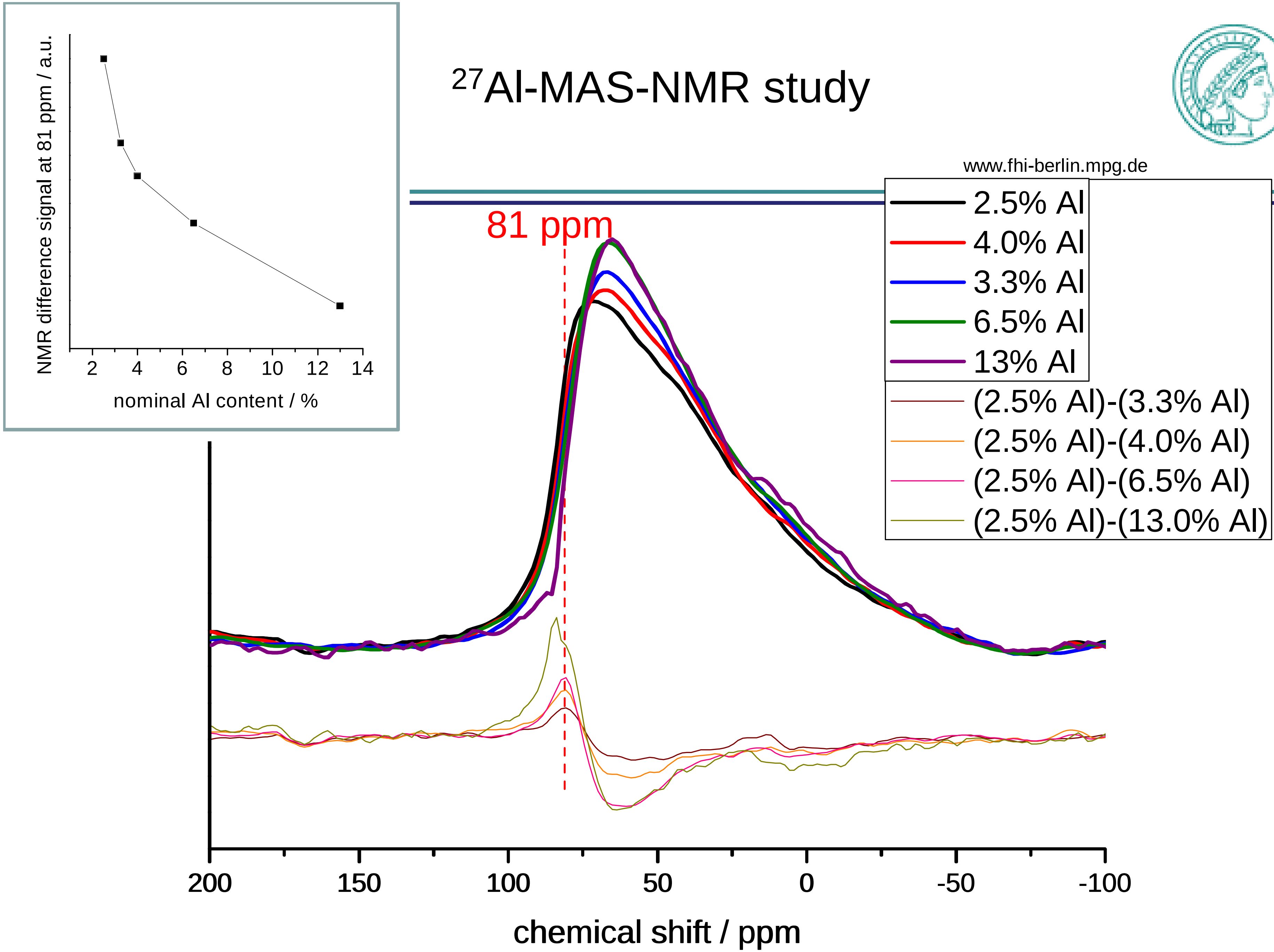

Electricity consumption and CO_2 emission
Saving potentials

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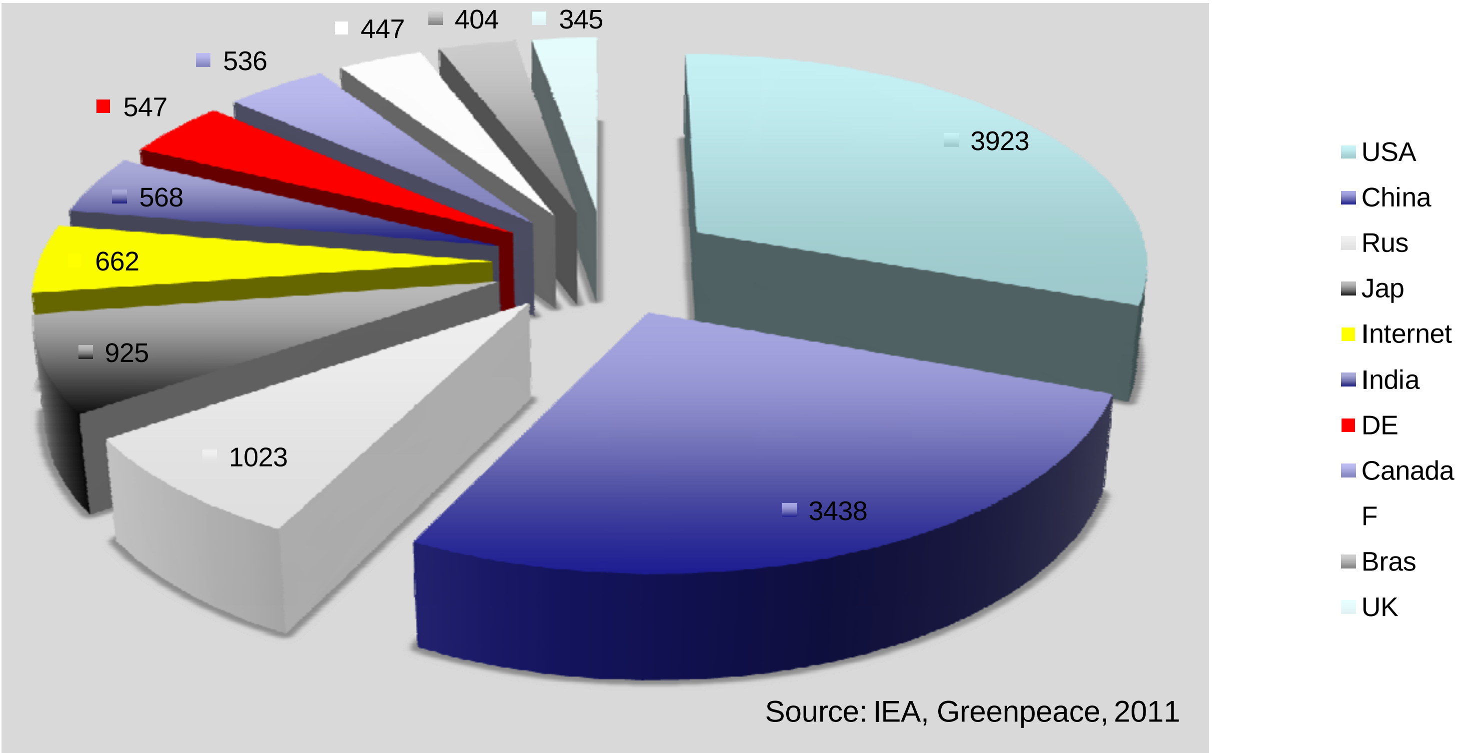
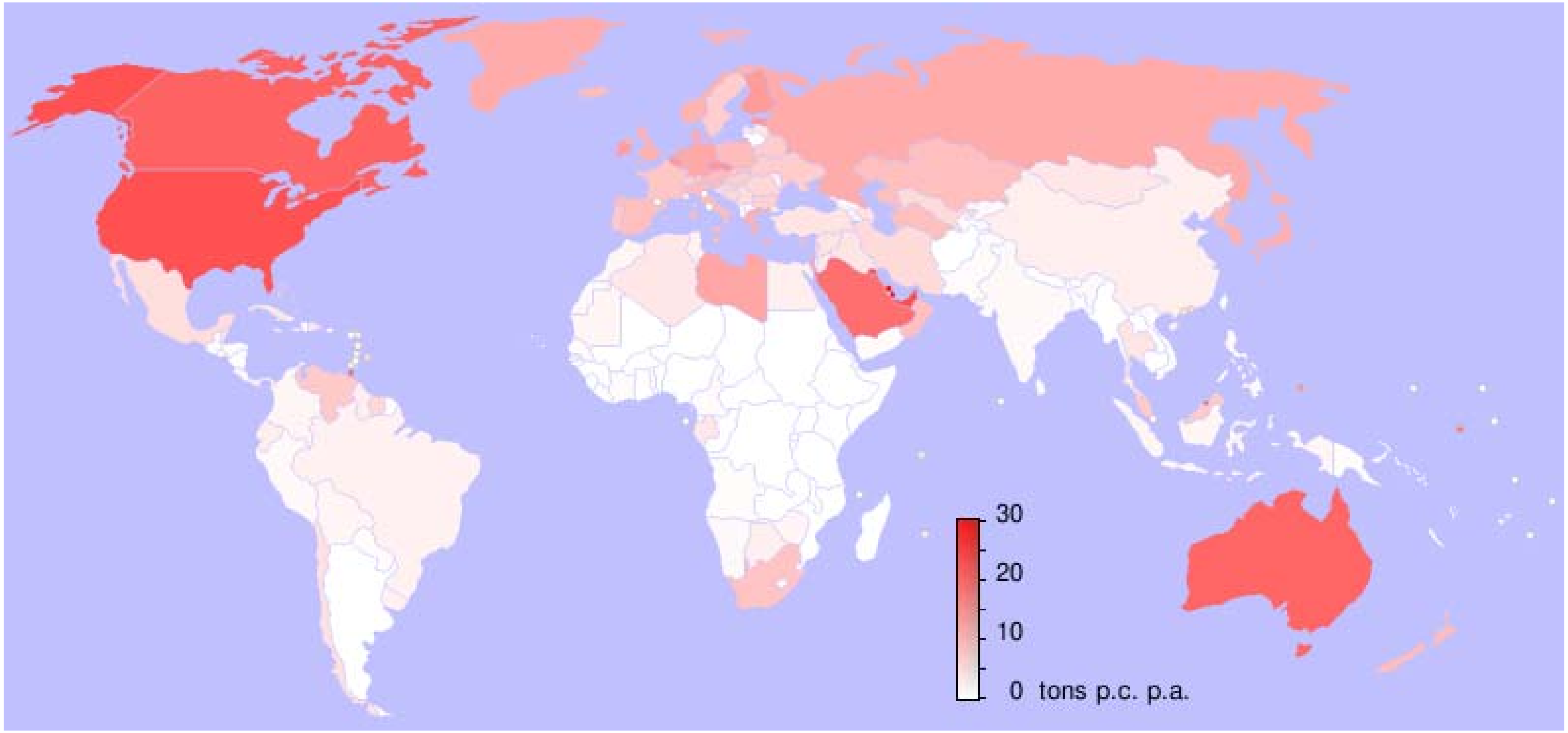


Source: US DOE

The German electricity production gave rise to ca 400 Mtons CO_2

Who emits the CO_2 in the world



Basic energy science and its environment

Common for all areas in the world

Different for regions in the world

Politics
Scenarios
Programs
Fragmented efforts

Climate
Chemical resources
Biological resources

Technologies:
Energy conversion
Energy distribution
Energy consumption

geosphere

BES

anthroposphere

Politics
Economics
Legal

Behaviour
Decision making
Value orders

Technologies
Systemic knowledge
Scenarios

Science in close contact to society: Ivory tower?

Beware of false expectations Educate and inform without bias

Post "Energiewende"
Regenerative Energy: the solution?

- Energy needs are very different in their usage profiles.
- Domestic distributed vs. industrial centralized.
- Current centralized supply chain unidirectional and inflexible in response to profiles.
- Regenerative energy is largely electricity: transportation and many other applications need material energy carriers:
- The low-carbon-all electrical solution is not realistic in long dimensions of time.

Post “Energiewende”
Regenerative Energy: the solution?

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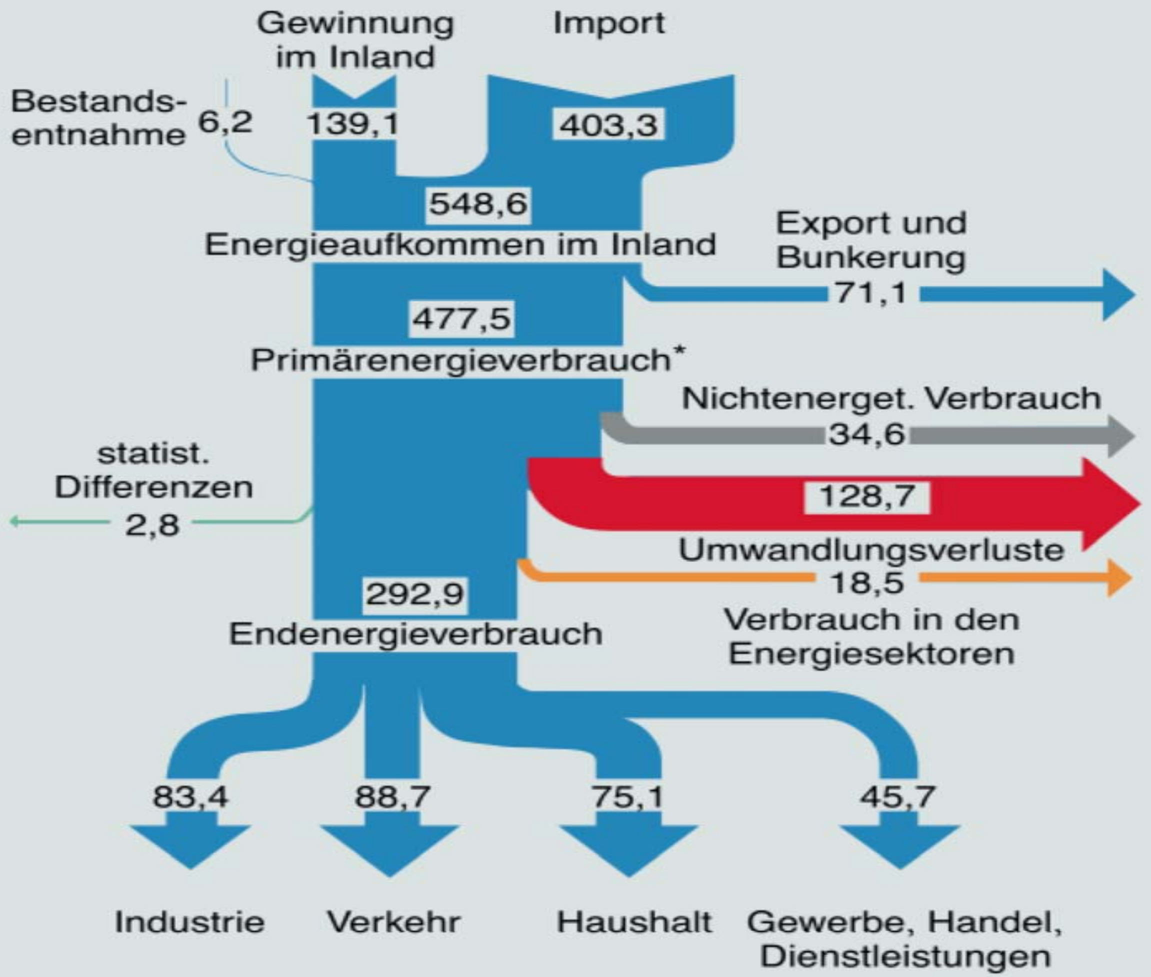

*Der Anteil der erneuerbaren Energieträger liegt bei 7,2%.
Alle Zahlen vorläufig/geschätzt.
Quelle: Arbeitsgemeinschaft Energiebilanzen 08/2008