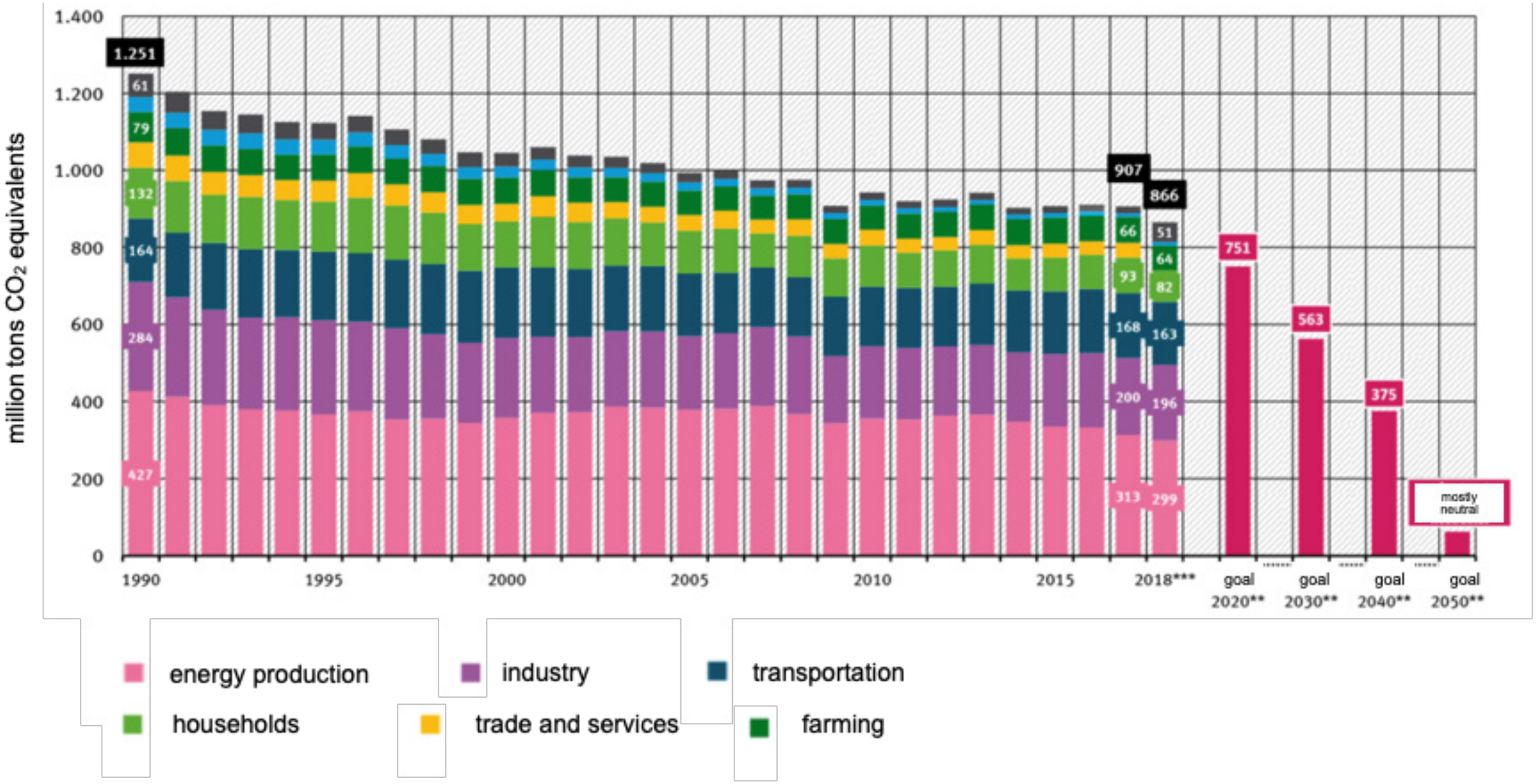
Karlsruher Institut für Technologie

Theory & Experiment in Methanol synthesis and the Methanol-to-Olefin Reaction

7 - Combining Experiment and Theory

Institute of Catalysis Research and Technology
Institute for Chemical Technology and Polymer Chemistry

CO_2 emissions in Germany

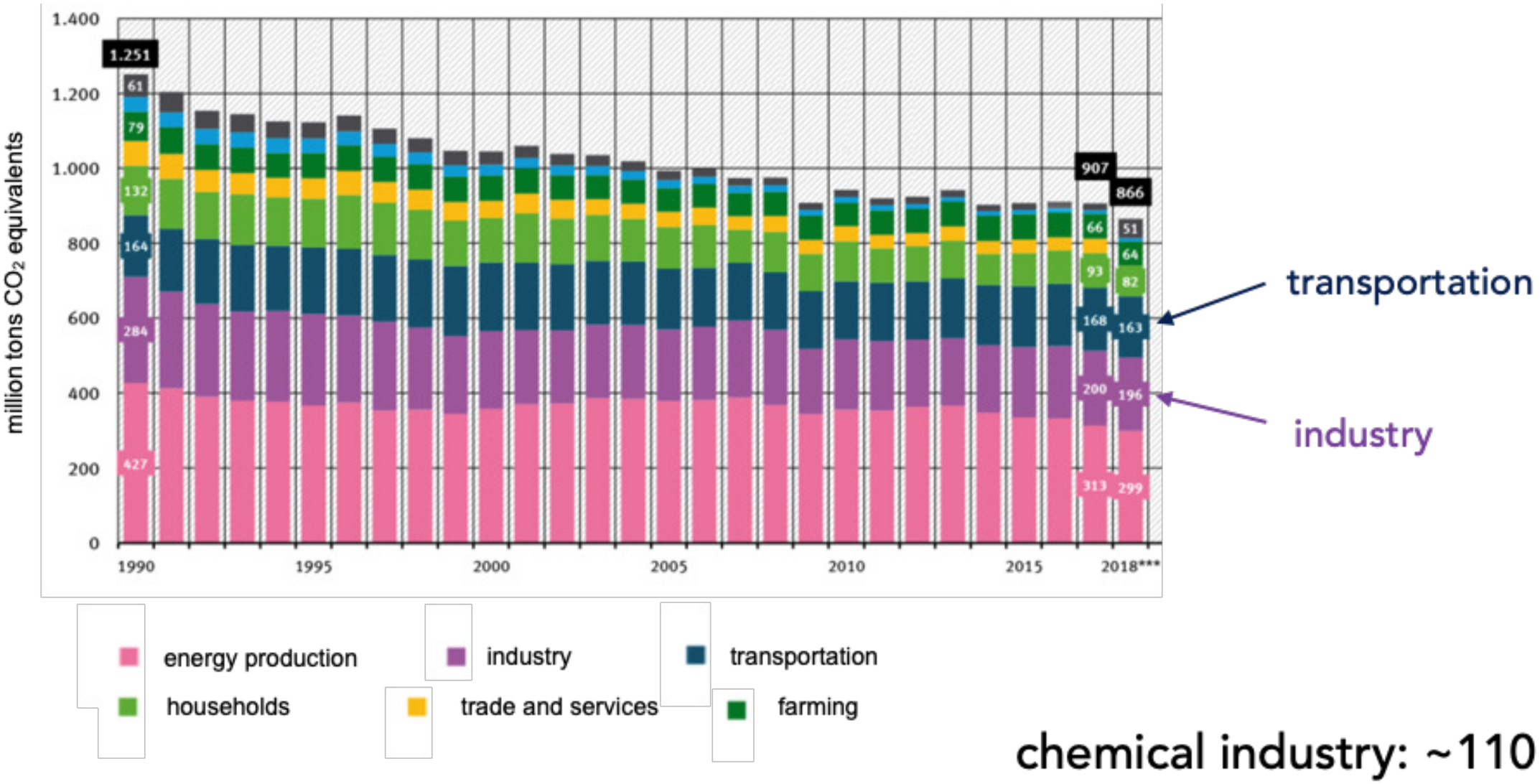


~ 2% of global CO_2 emissions

~ 1% of global population

source: german environmental agency - www.umweltbundesamt.de

CO_2 emissions in Germany



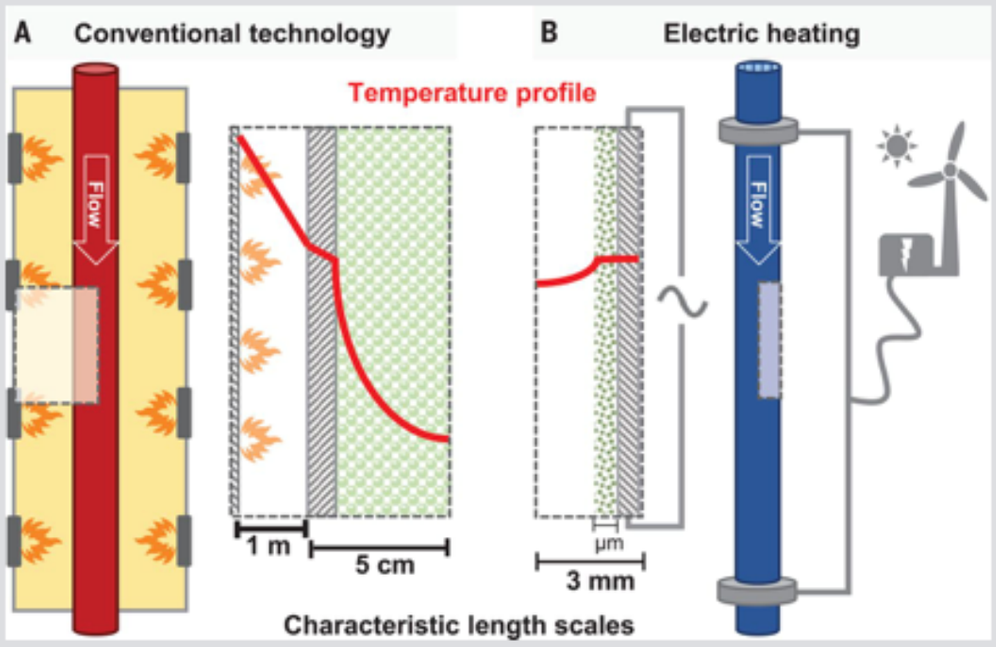
chemical industry: ~110 Mton

—> 30% of CO_2 emissions from (petro-)chemical industry

source: german environmental agency - www.umweltbundesamt.de

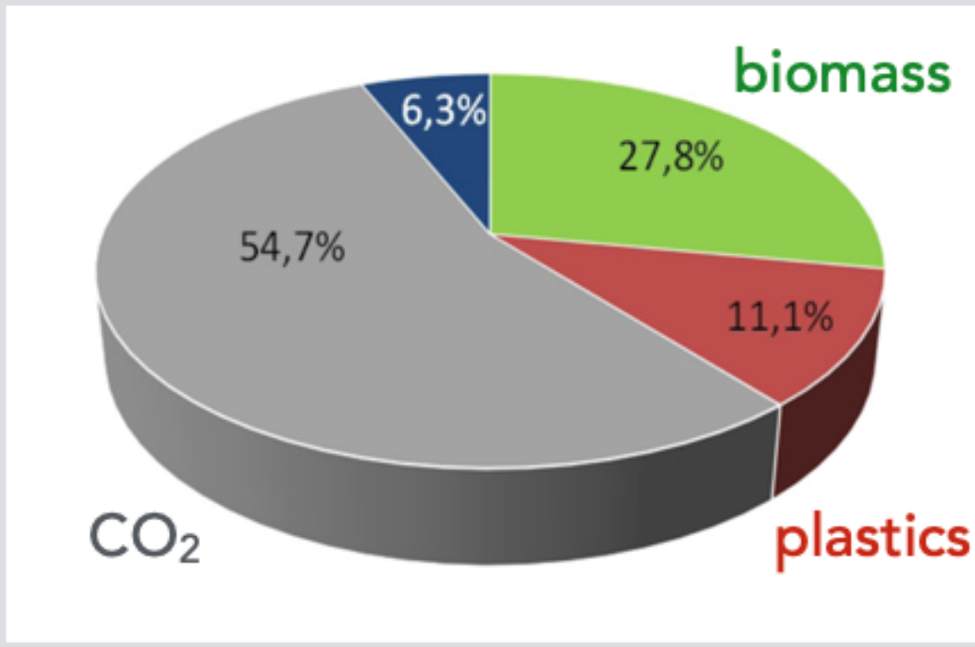
Towards a CO_2 neutral chemical industry

electrification of energy intense processes



Wismann et al., *Science* **2019**, *364*, 756.

drastic shift in resources



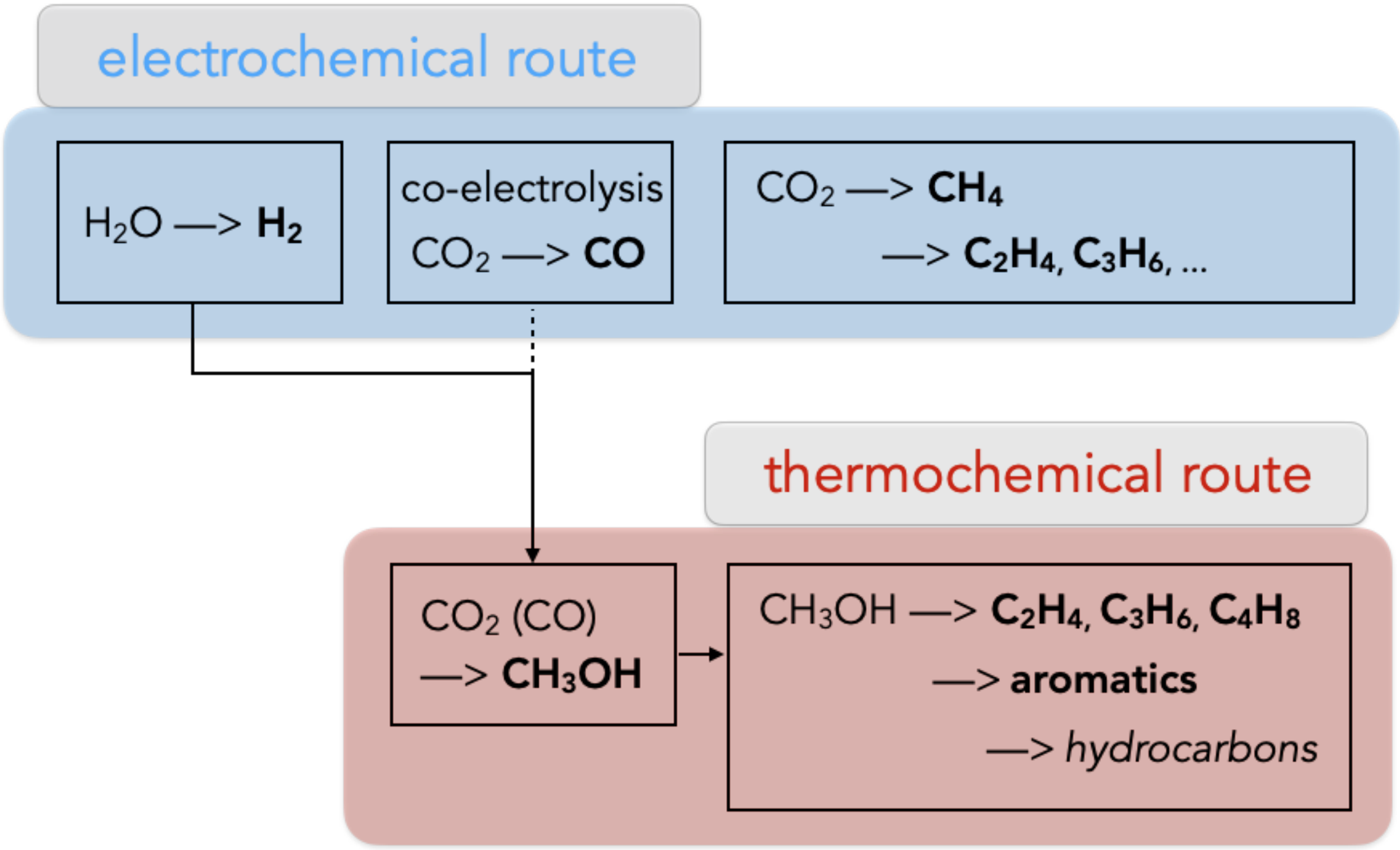
german chemical industry →

628 TWh of electricity

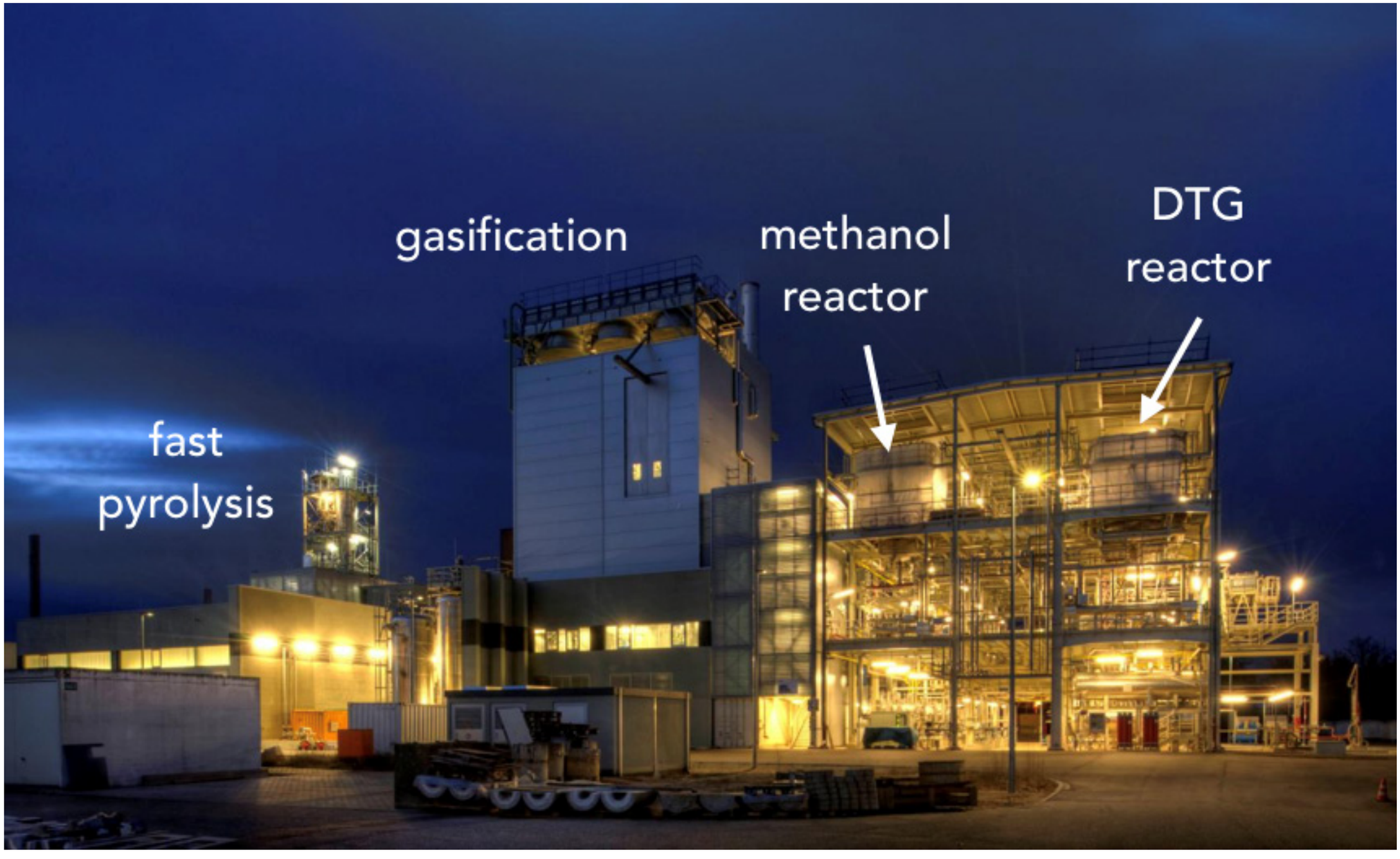
(@ 4 Cent/kWh)

source: Roadmap Chemie 2050 - VCI & DECHEMA (2019)

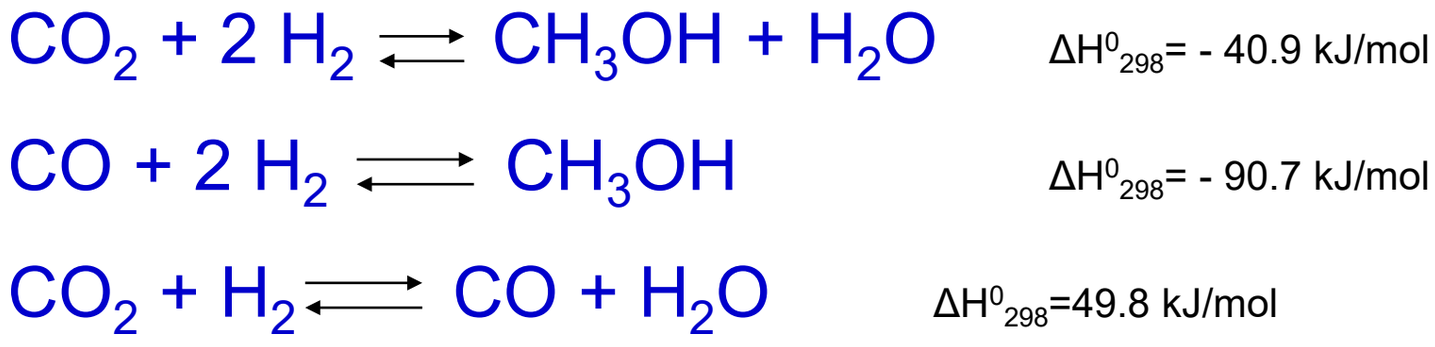
Routes from CO_2 to chemicals



The bioliq plant

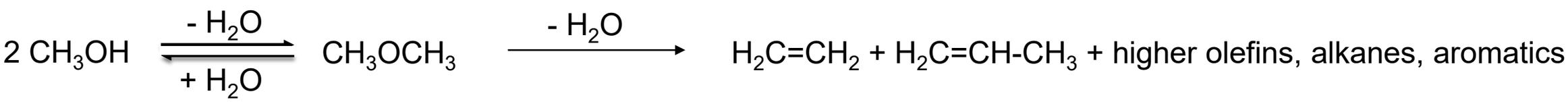


methanol and MTO synthesis



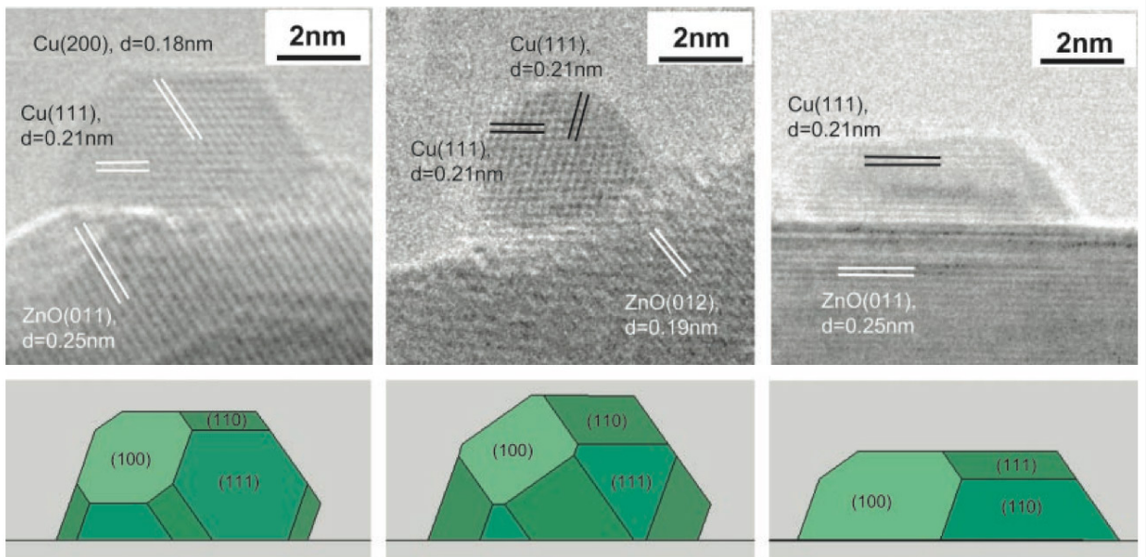
- Methanol: (metal catalyst)

- MTO: (zeolite catalyst)



- Take-away: the catalysis is a system of energy-based manipulations of chemical reaction pathways
- Very different reaction mechanisms, conditions, catalysts.

methanol synthesis



1.5 mbar H_2
220 °C

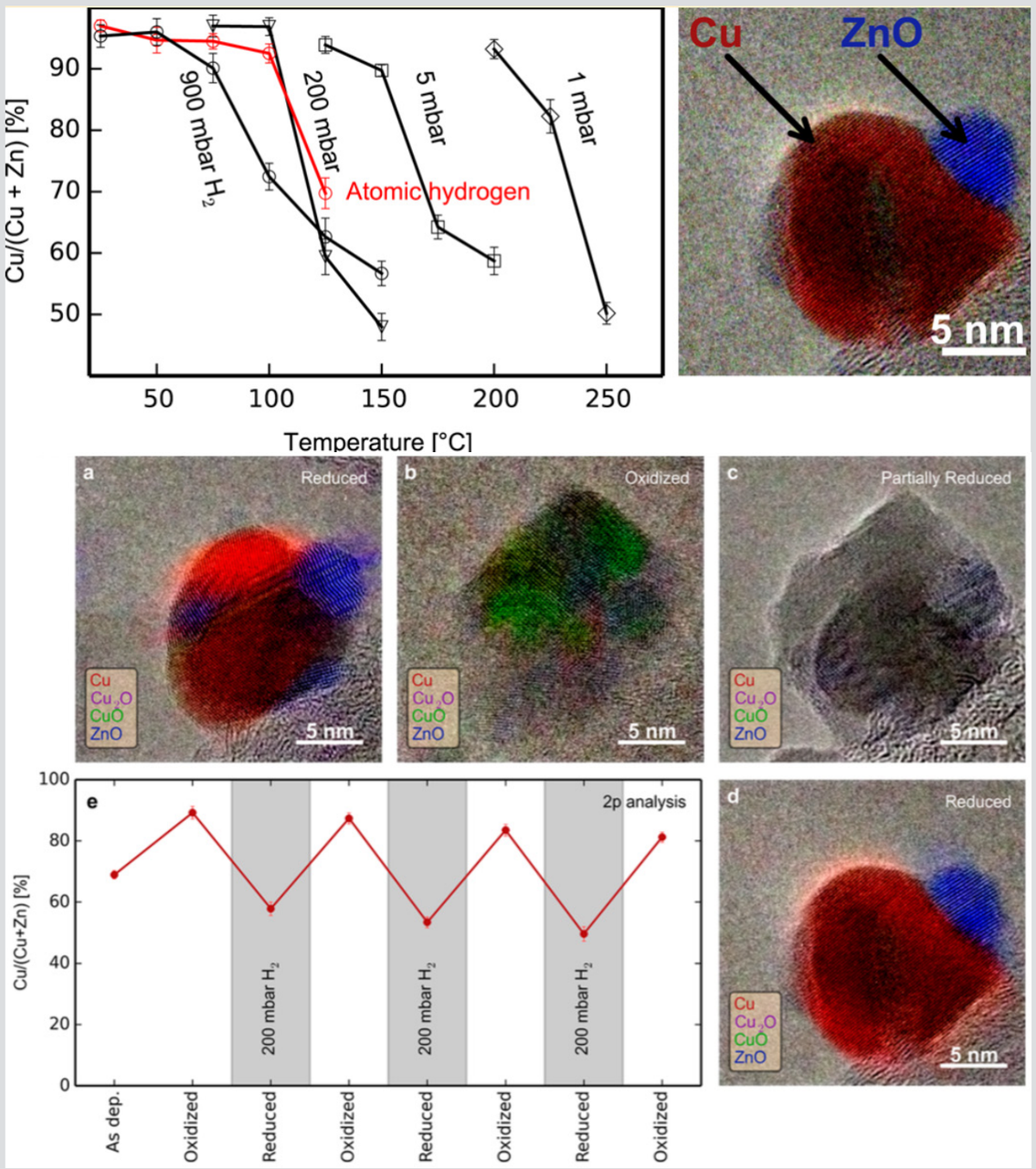
p_{tot} 1.5 mbar
H_2:H_2O = 3:1
220 °C

p_{tot} 5 mbar
H_2:CO = 20:1
220 °C

—> copper morphology changes

—> copper encapsulates and decapsulates ZnO reversibly

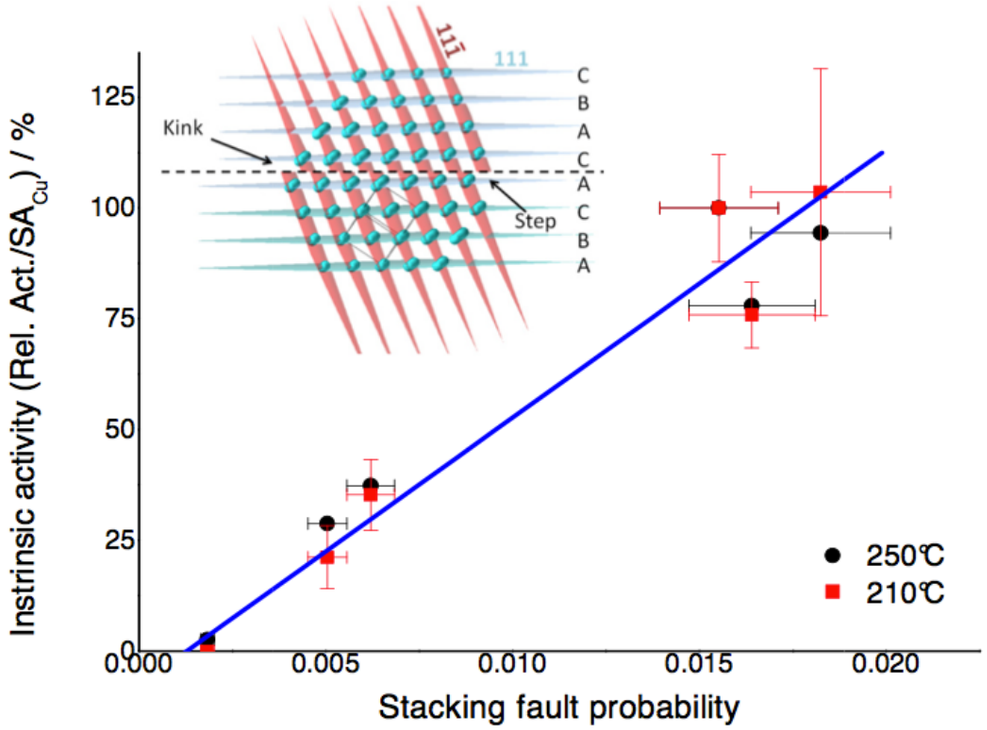
—> hydrogen is sufficient to reduce ZnO to metallic Zn on the surface

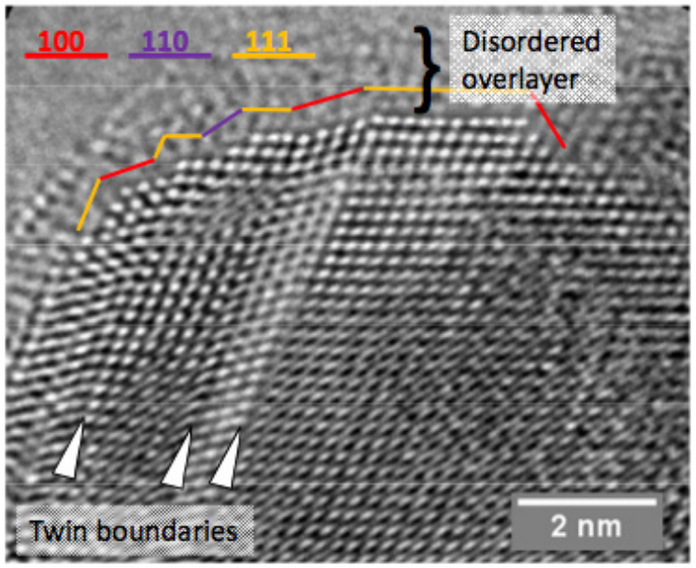


Hansen et al, *Science* **2002**, *295*, 2053.

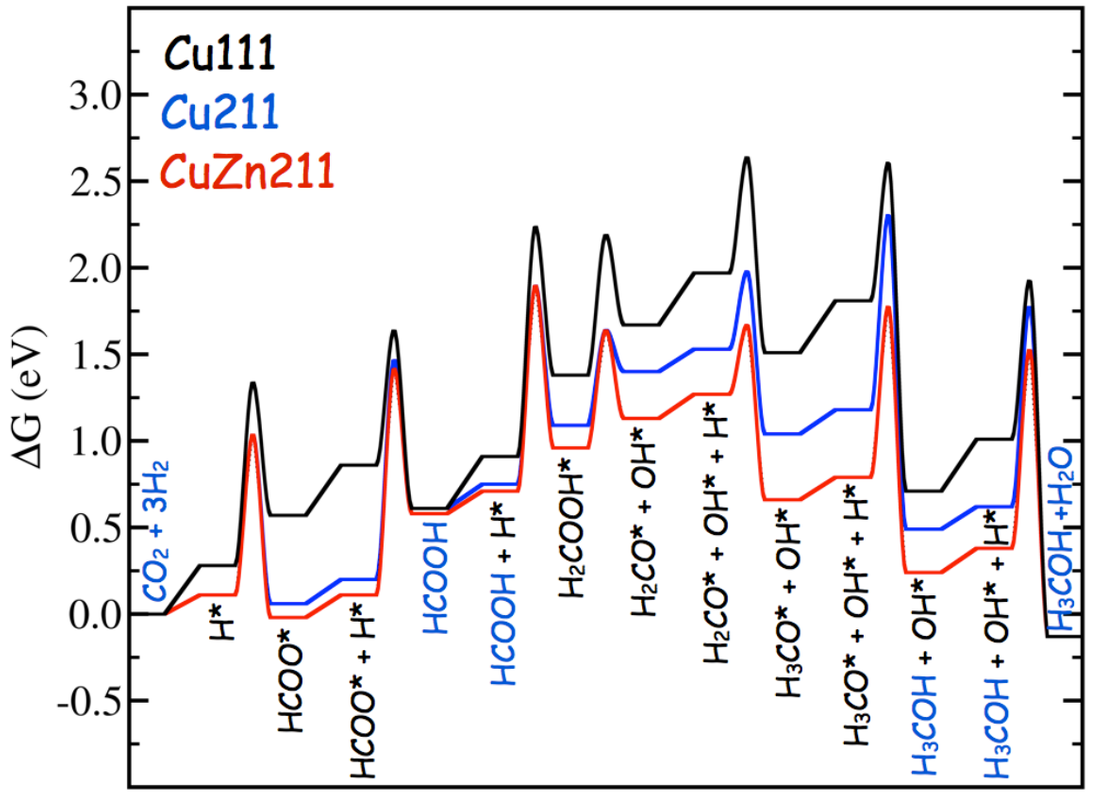
Holse et al, *J. Phys. Chem. C* **2015**, *119*, 2804.

the industrial $Cu/ZnO/Al_2O_3$ catalyst



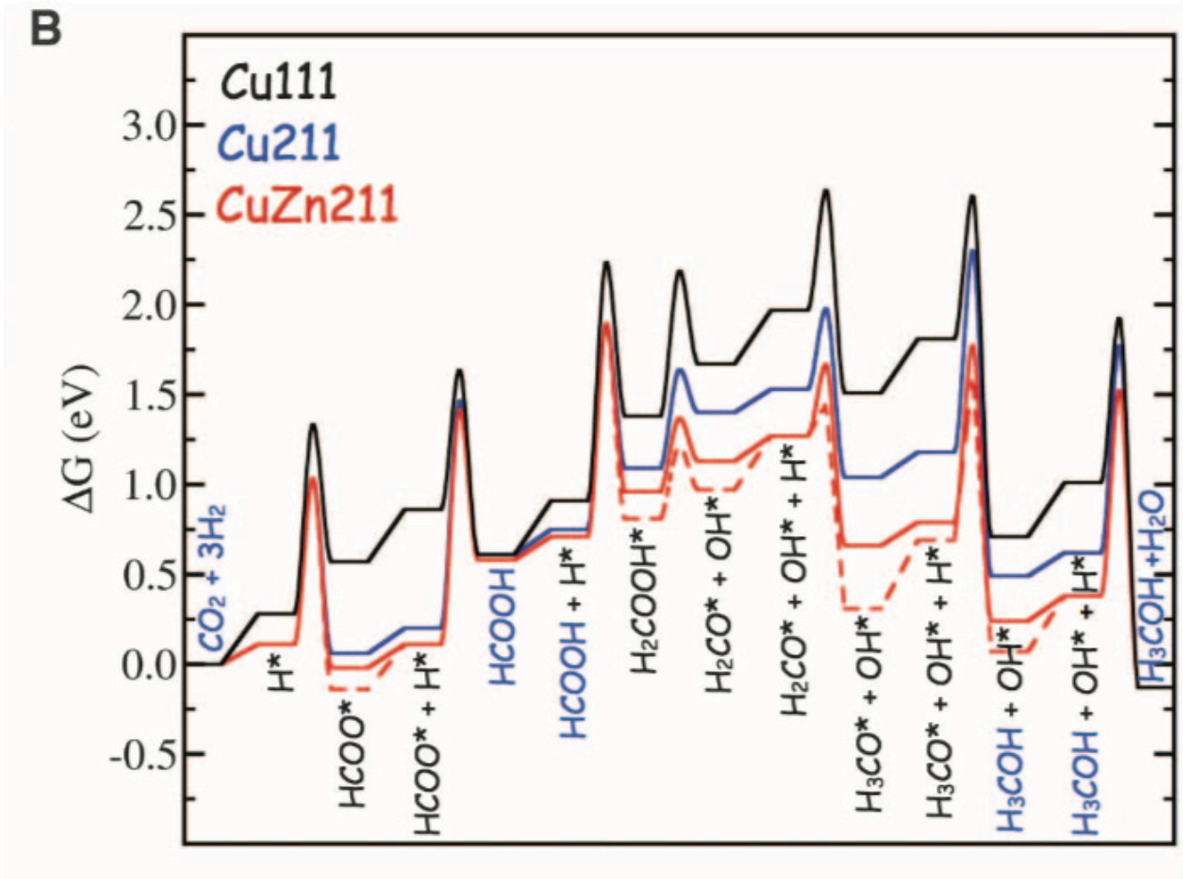


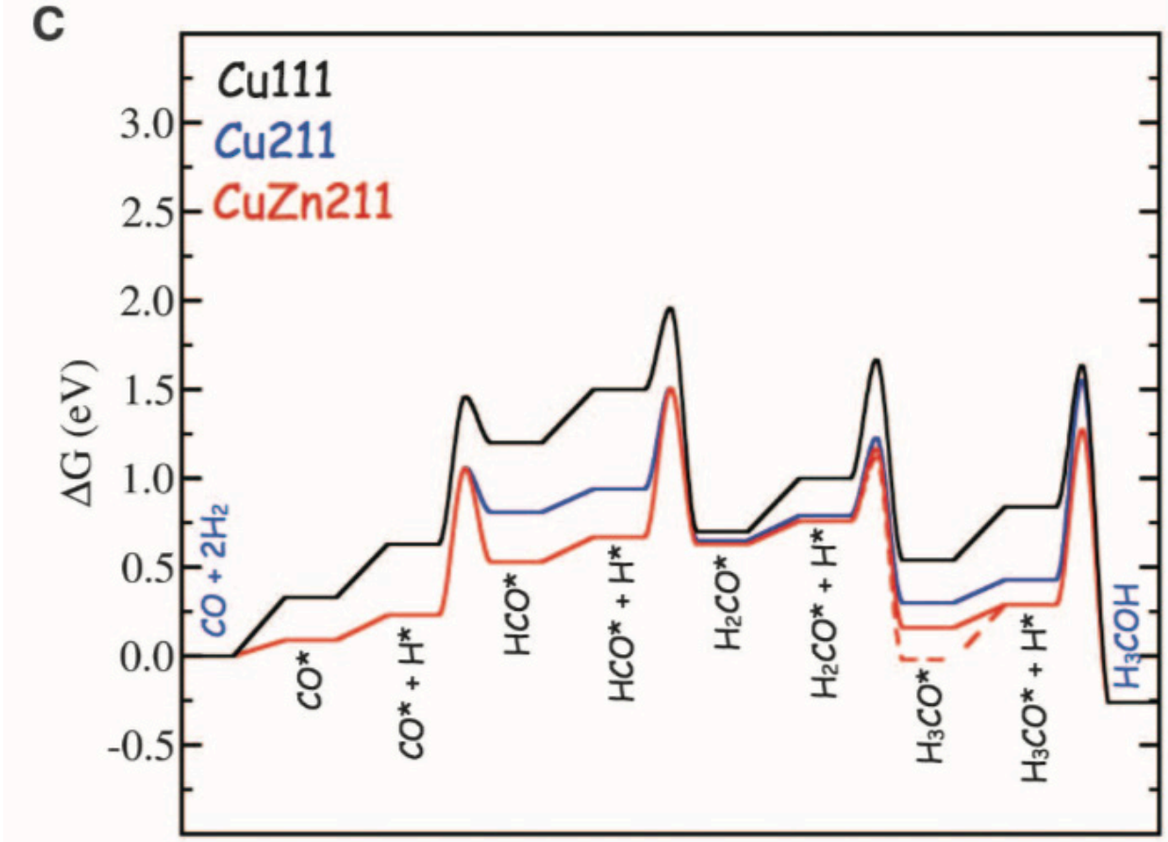
stacking faults —> surface defects
—> defects correlate well with activity



Behrens et al, Science 2012, 336, 893.

the industrial $Cu/ZnO/Al_2O_3$ catalyst

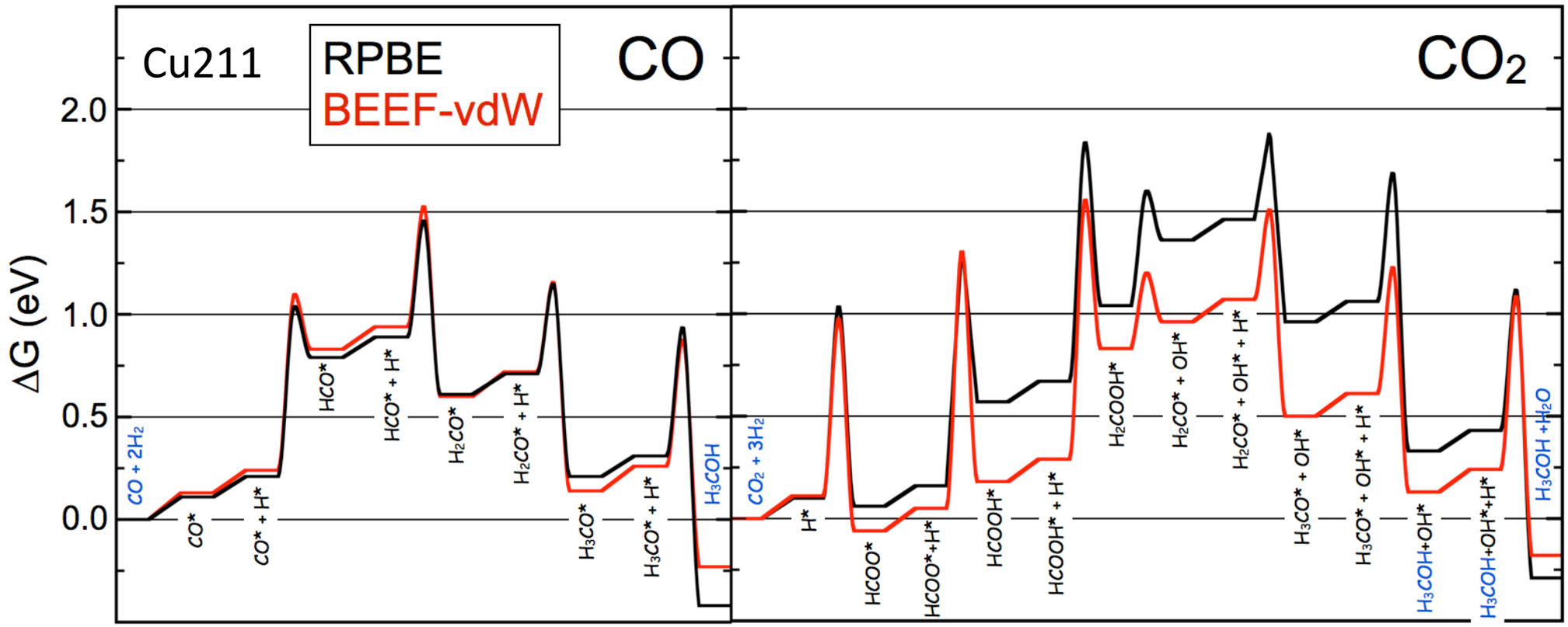




CO hydrogenation seems faster than CO_2 hydrogenation over copper —> contradicting experiments !!?

Behrens et al, *Science* **2012**, *336*, 893.

influence of vdW interactioons



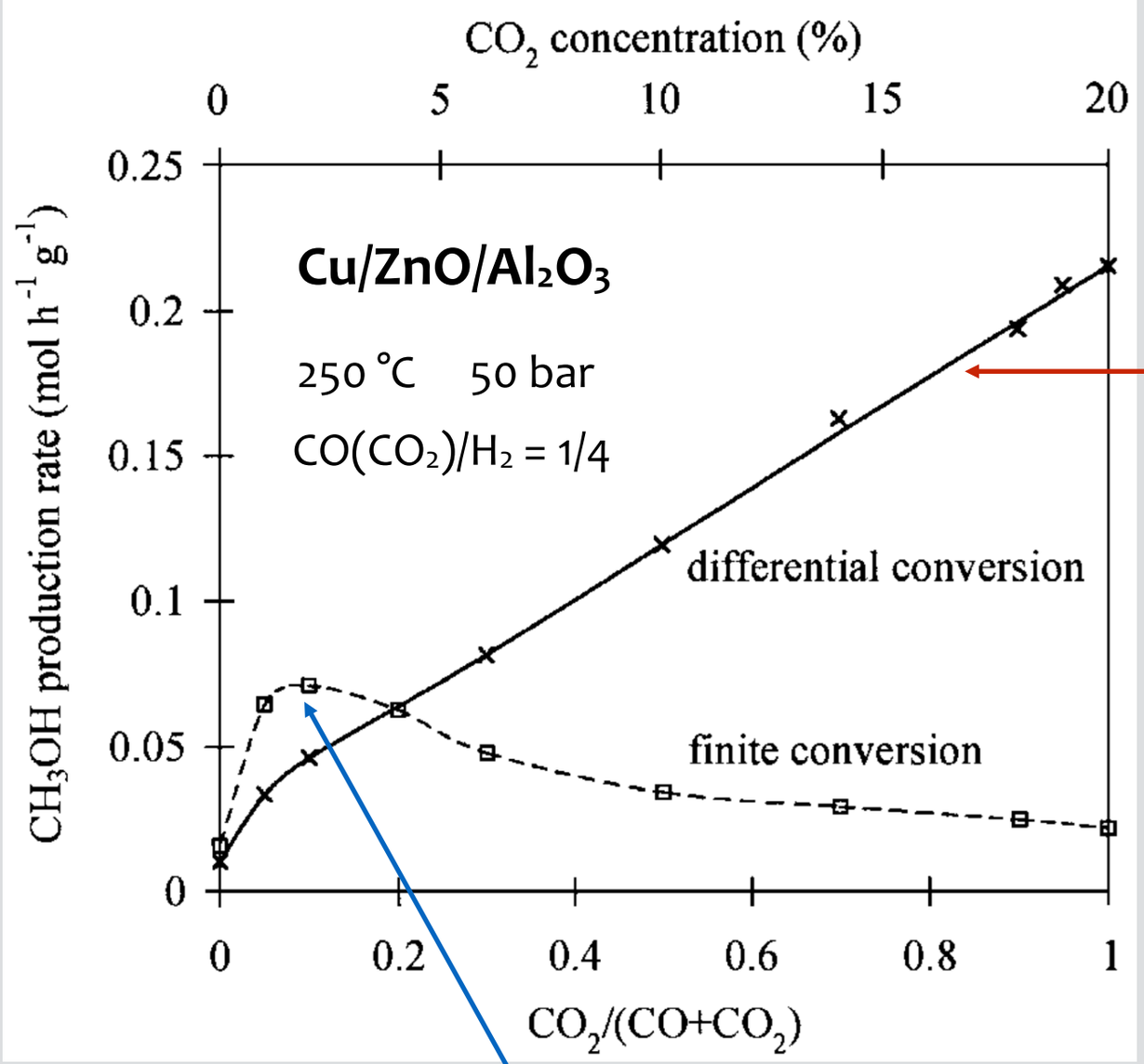
Large difference in CO_2 hydrogenation (up to 0.4 eV)

CO and CO2 hydrogenation on Cu(211) comparable —> CO still somewhat faster !?

—> BEEF-vdW able to describe CO and CO_2 hydrogenation !?

Studt et al, *Catal. Lett.* **2013**, *143*, 71.

influence of CO_2 differential vs integral conditions



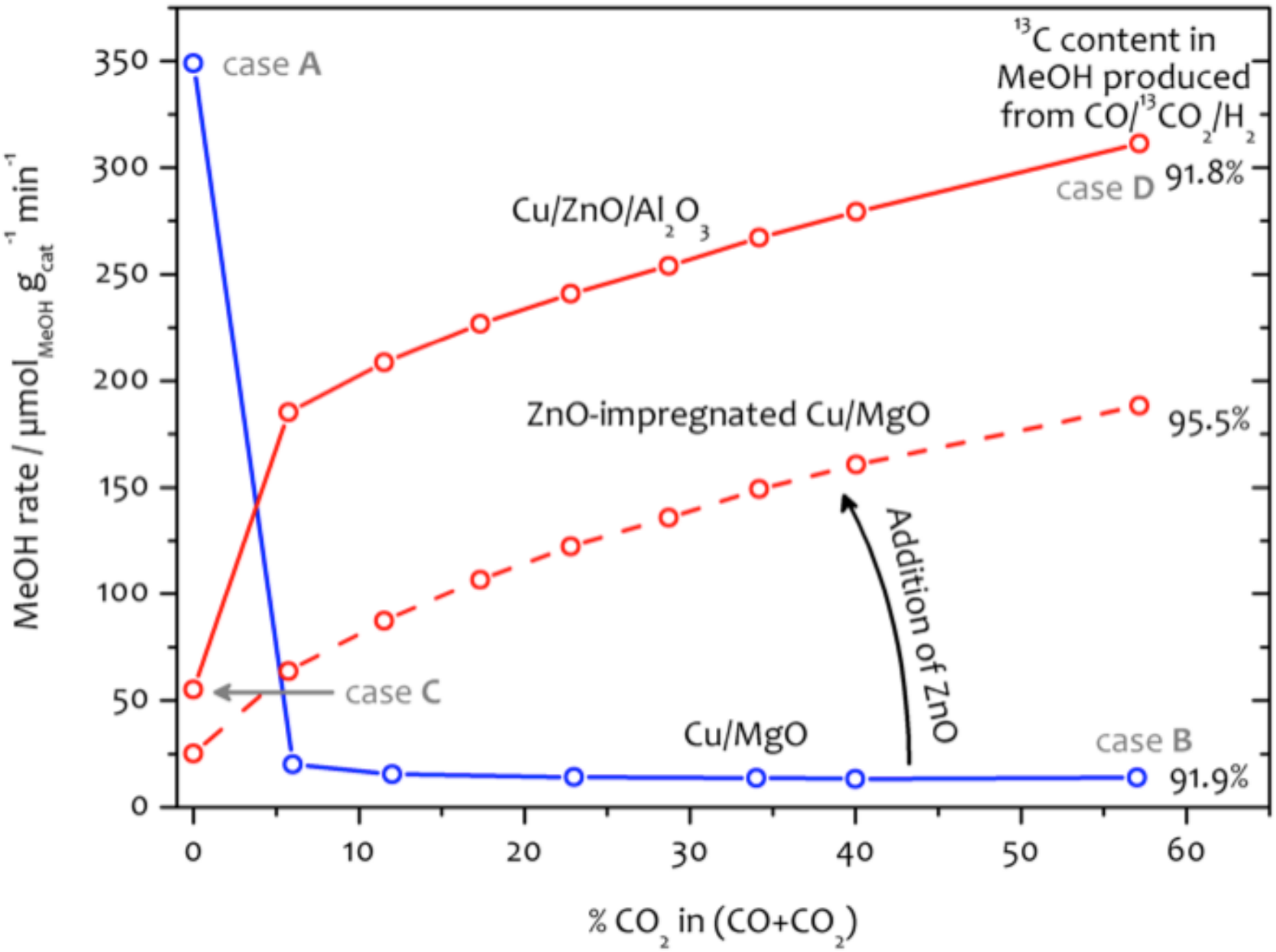
monotonically increasing

maximum at low CO_2 concentrations

Sahibzada, Metcalfe, Chadwick, *J. Catal.* **1998**, *174*, 111.

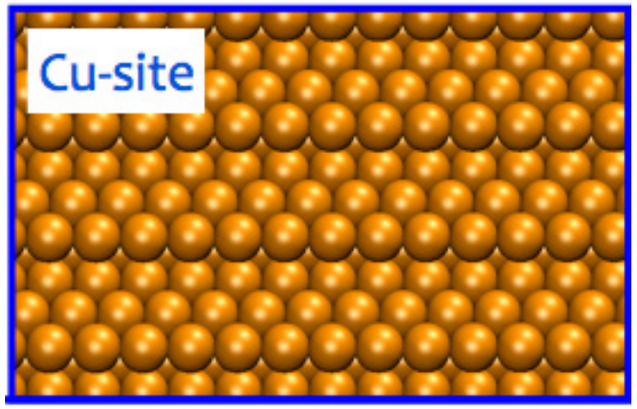
dependence of performance on catalyst and feed

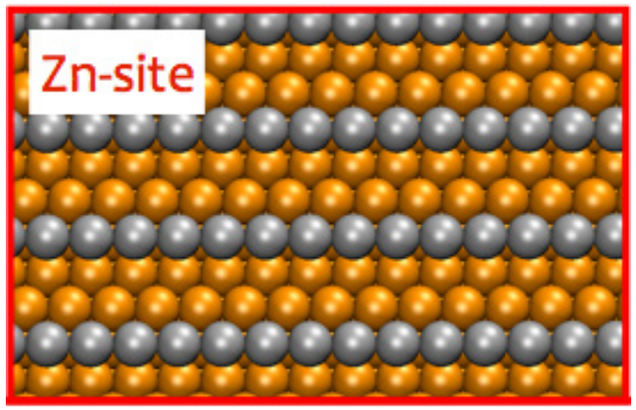
methanol synthesis under differential conditions

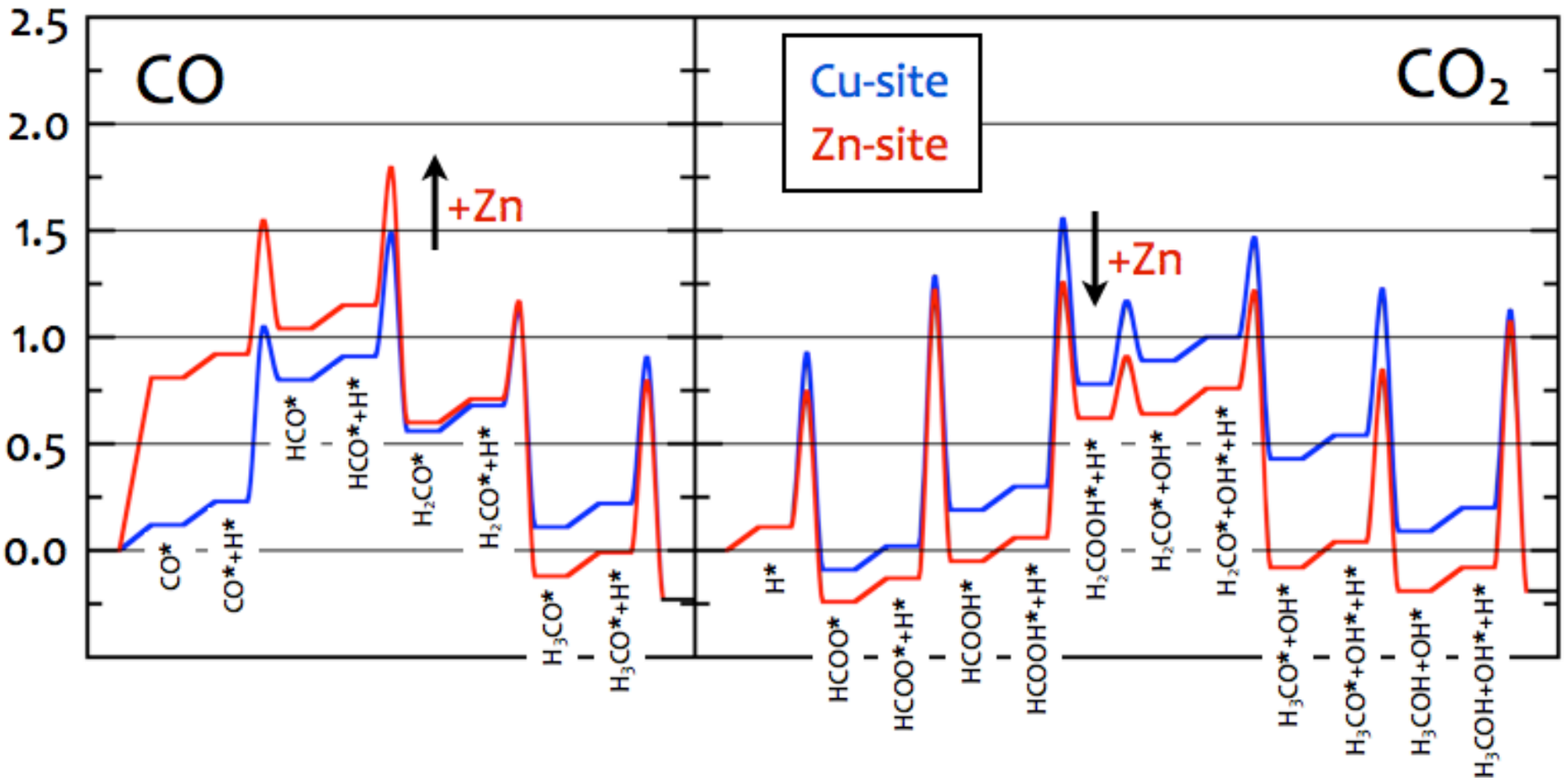


Studt, Behrens, Kunkes et al, *ChemCatChem* **2015**, *7*, 1105.

CO vs CO_2 hydrogenation

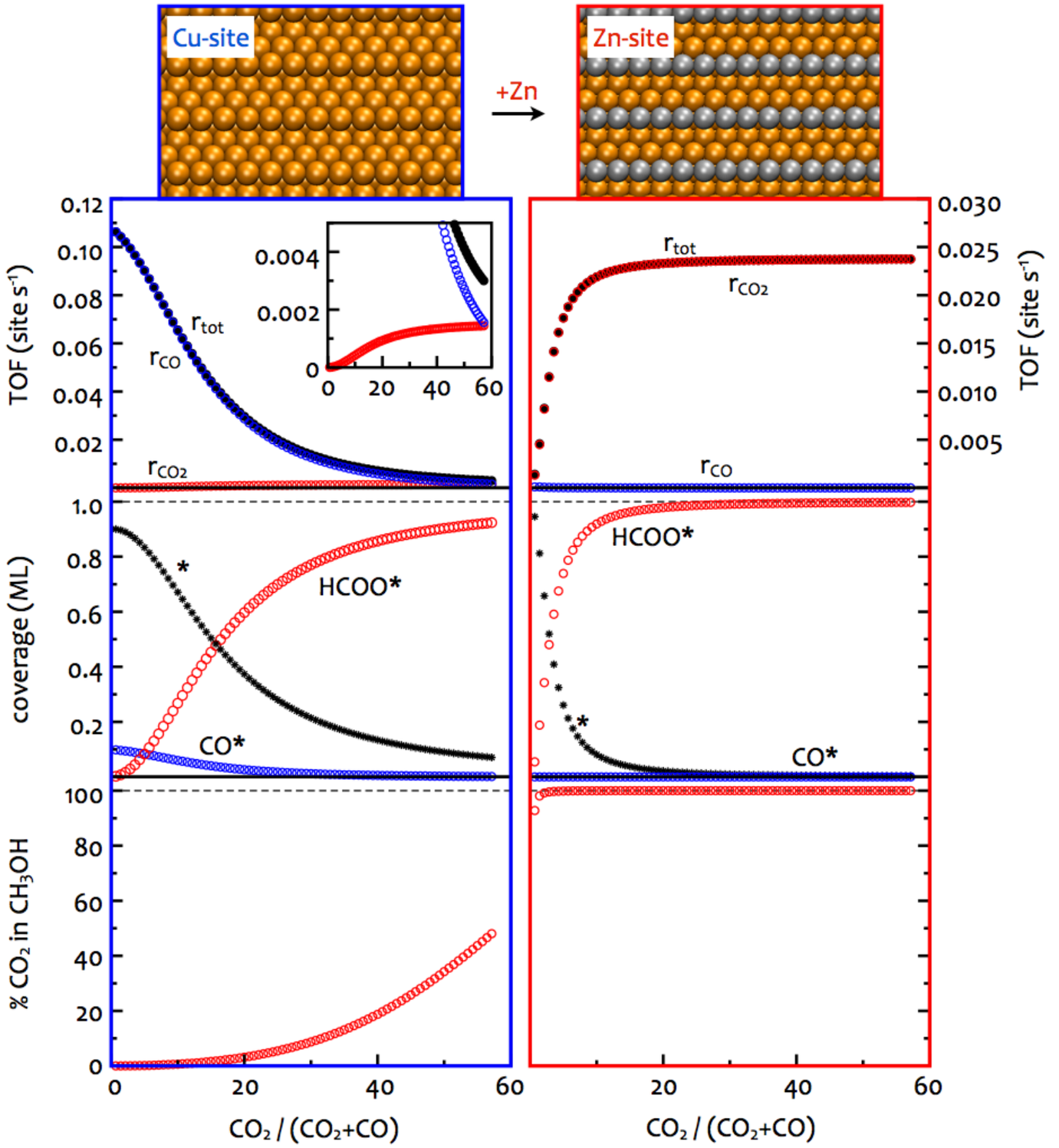






Studt, Behrens, Kunkes, Thomas, Zander, Tarasov, Schumann, Frei, Varley, Abild-Pedersen, Nørskov, Schlögl, *ChemCatChem* **2015**, *7*, 1105.

modeling CO and CO_2 hydrogenation



$H_2 + 2* \longrightarrow 2\,H*$

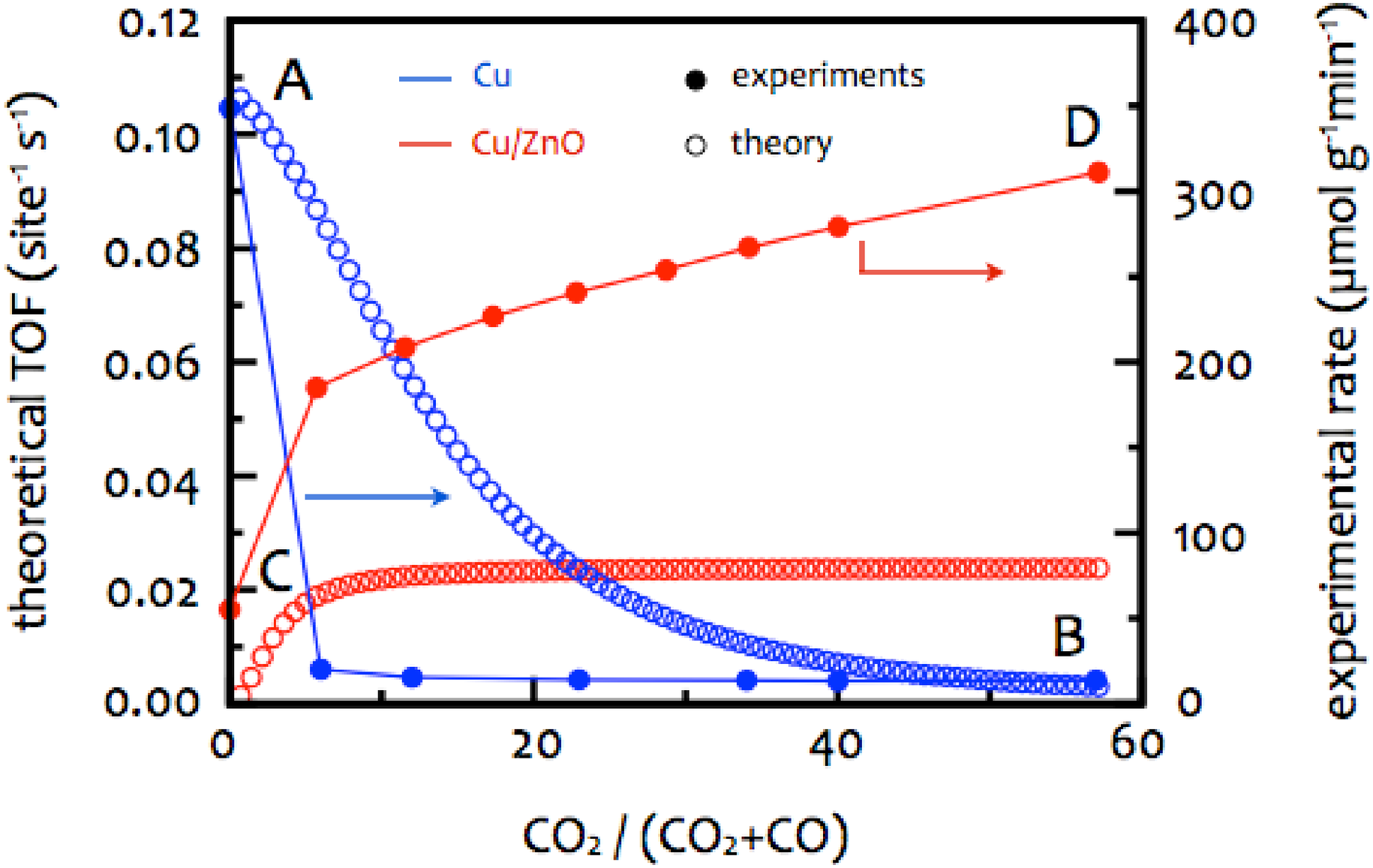
$CO_2 + H* \longrightarrow HCOO*$
$HCOO* + H* \longrightarrow HCOOH* + *$
$HCOOH* + H* \longrightarrow H_2COOH* + *$
$H_2COOH* + * \longrightarrow H_2CO* + OH*$

$CO + * \longrightarrow CO*$
$CO* + H* \longrightarrow HCO* + *$
$HCO* + H* \longrightarrow H_2CO* + *$

$H_2CO* + H* \longrightarrow H_3CO* + *$
$H_3CO* + H* \longrightarrow CH_3OH + 2*$

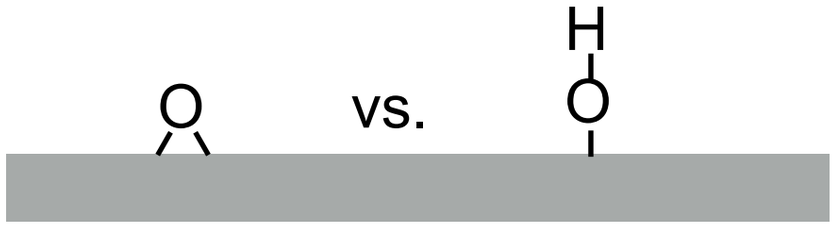
Studt, Behrens, Kunkes, Thomas, Zander, Tarasov, Schumann, Frei, Varley, Abild-Pedersen, Nørskov, Schlögl, *ChemCatChem* **2015**, *7*, 1105.

comparison experiment and theory

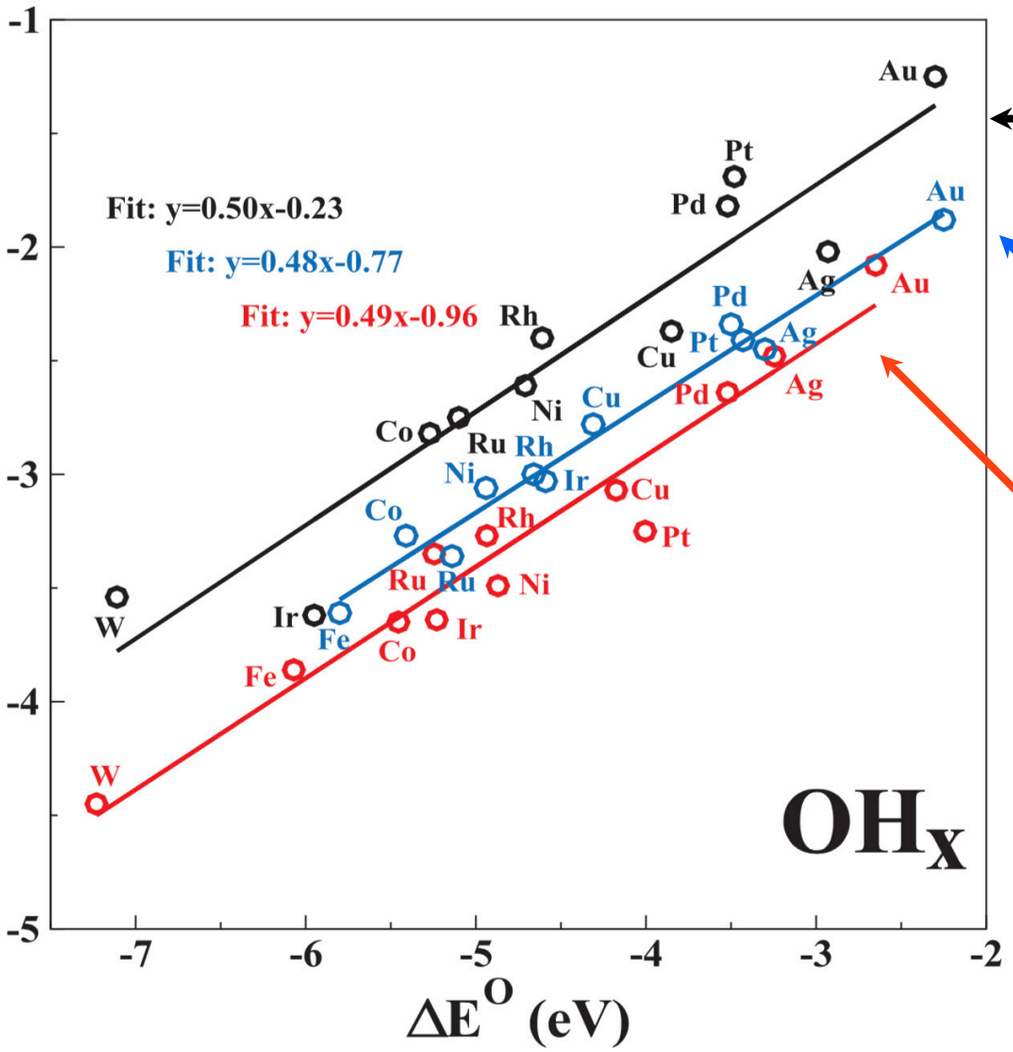


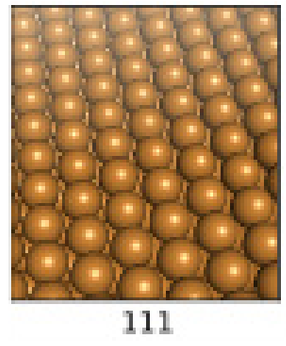
Studt, Behrens, Kunkes, Thomas, Zander, Tarasov, Schumann, Frei, Varley, Abild-Pedersen, Nørskov, Schlögl, ChemCatChem 2015, 7, 1105.

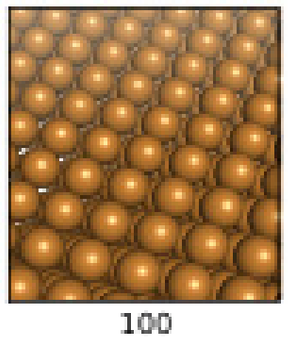
scaling relations for adsorption energies

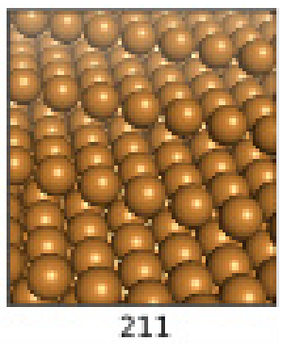


bond order conservation principle
O* two bonds, OH* one bond
—> slope equals 1/2





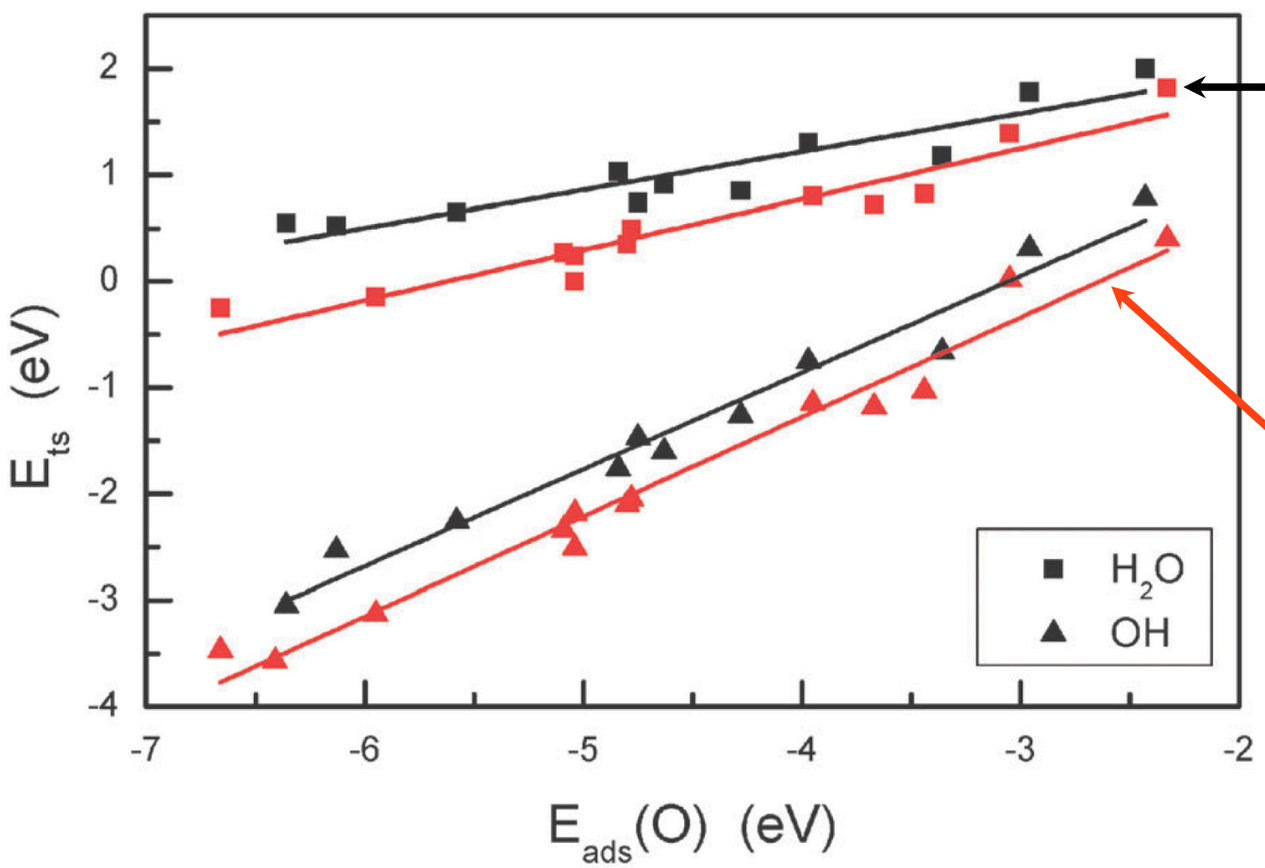


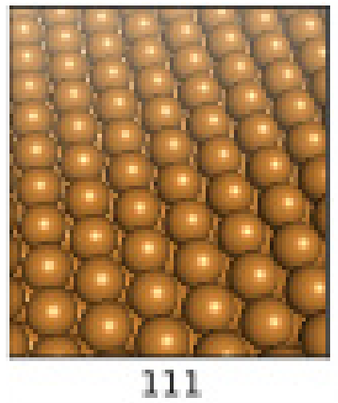


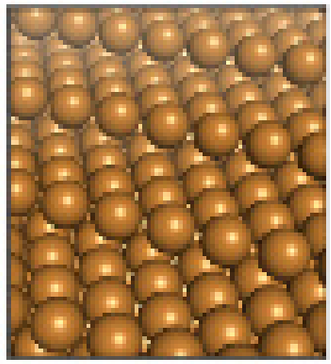
different intercepts
for different surfaces

Abild-Pedersen, Greeley, Studt, Rossmeisl, Munter, Moses, Skúlason, Bligaard, Nørskov, *Phys. Rev. Lett.* **2007**, *99*, 016105.

transition-state scaling relations




111


211

Wang et al, *Phys. Chem. Chem. Phys.* **2011**, *13*, 20760.

searching for new CO_2 hydrogenation catalysts

CO_2 + H* -> HCOO*
HCOO* + H* -> HCOOH* + *
HCOOH* + H* -> H_2COOH* + *
H_2COOH* + * -> H_2CO* + OH*
H_2CO* + H* -> H_3CO* + *
H_3CO* + H* -> CH_3OH + 2*

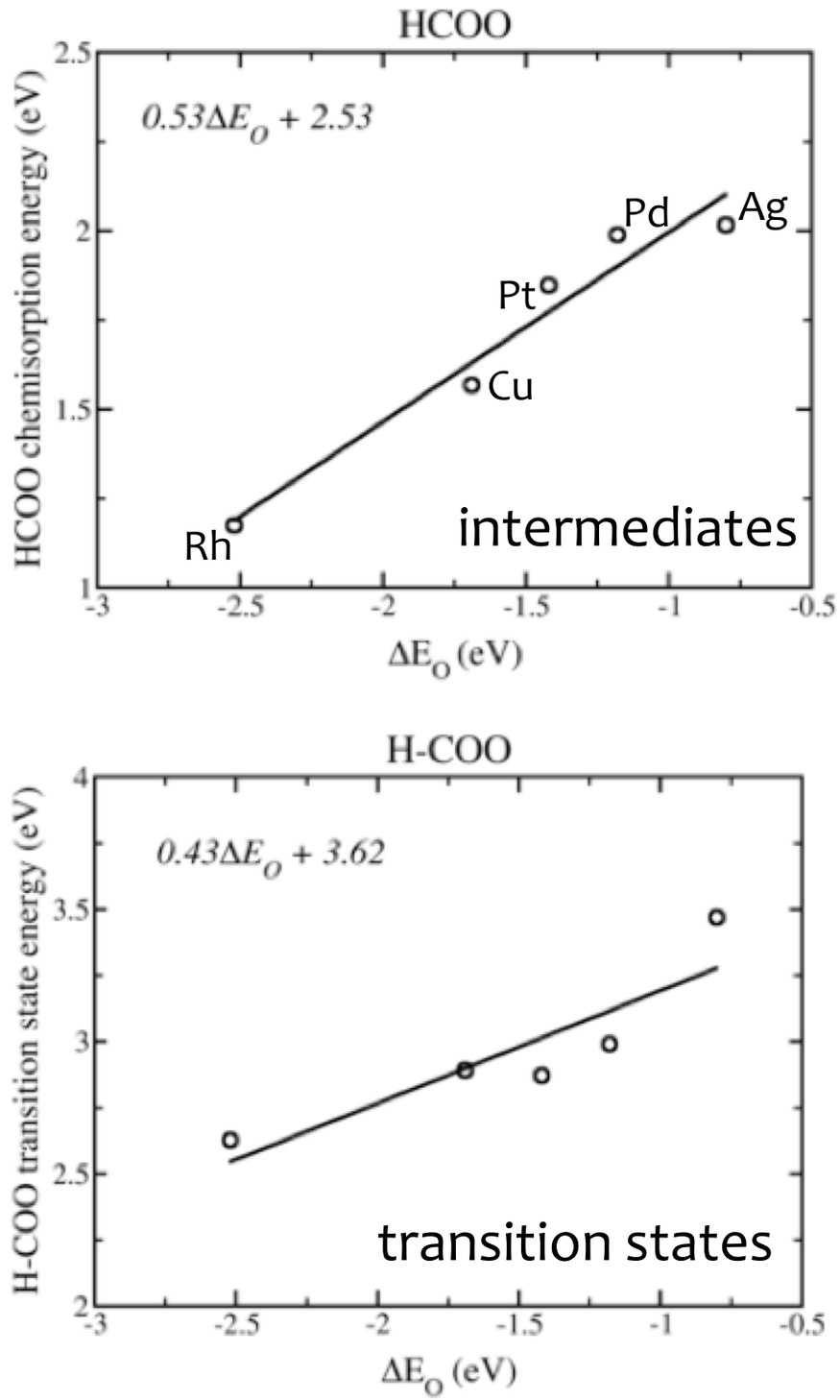
pathway identified for Cu(211)

all reaction intermediates bind through oxygen

calculate all intermediates on a range of surfaces (211)

express all energies in terms of ΔE_O

combine MM + Scaling —> R(ΔE_O)



Studt et al, *Nature Chem.* **2014**, 6, 320.

NiGa catalysts for CO_2 hydrogenation

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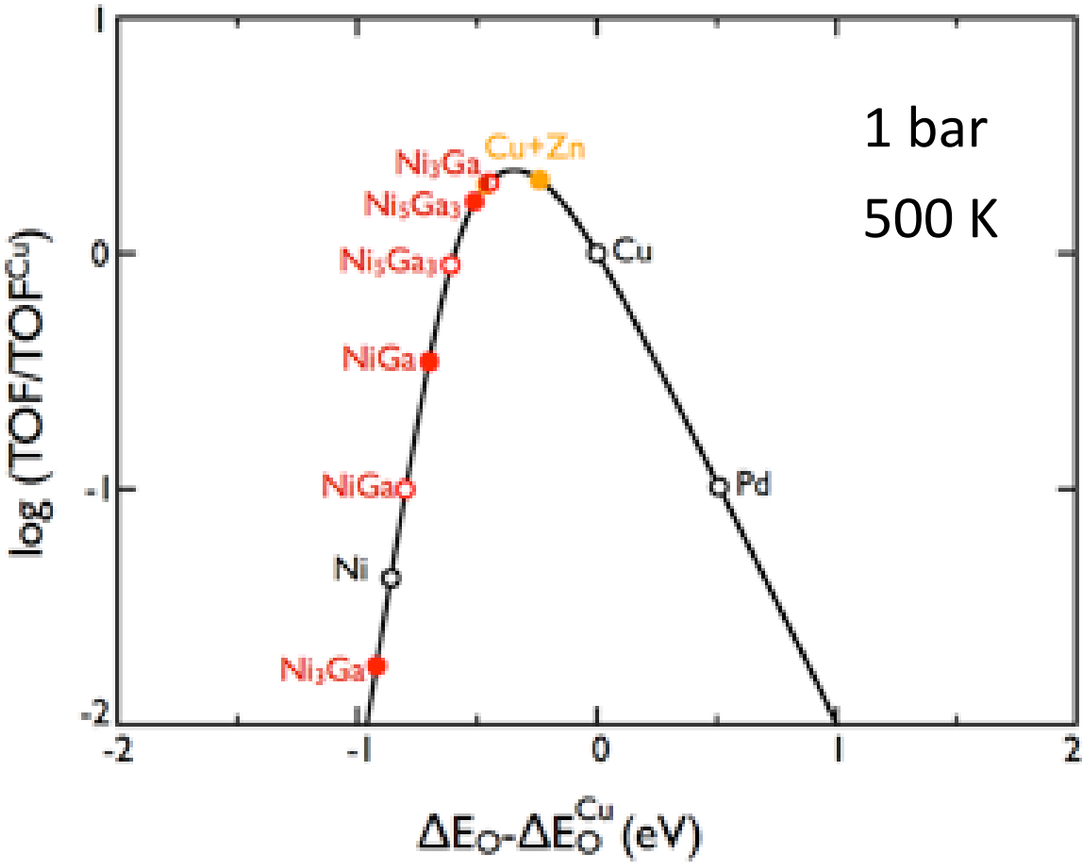
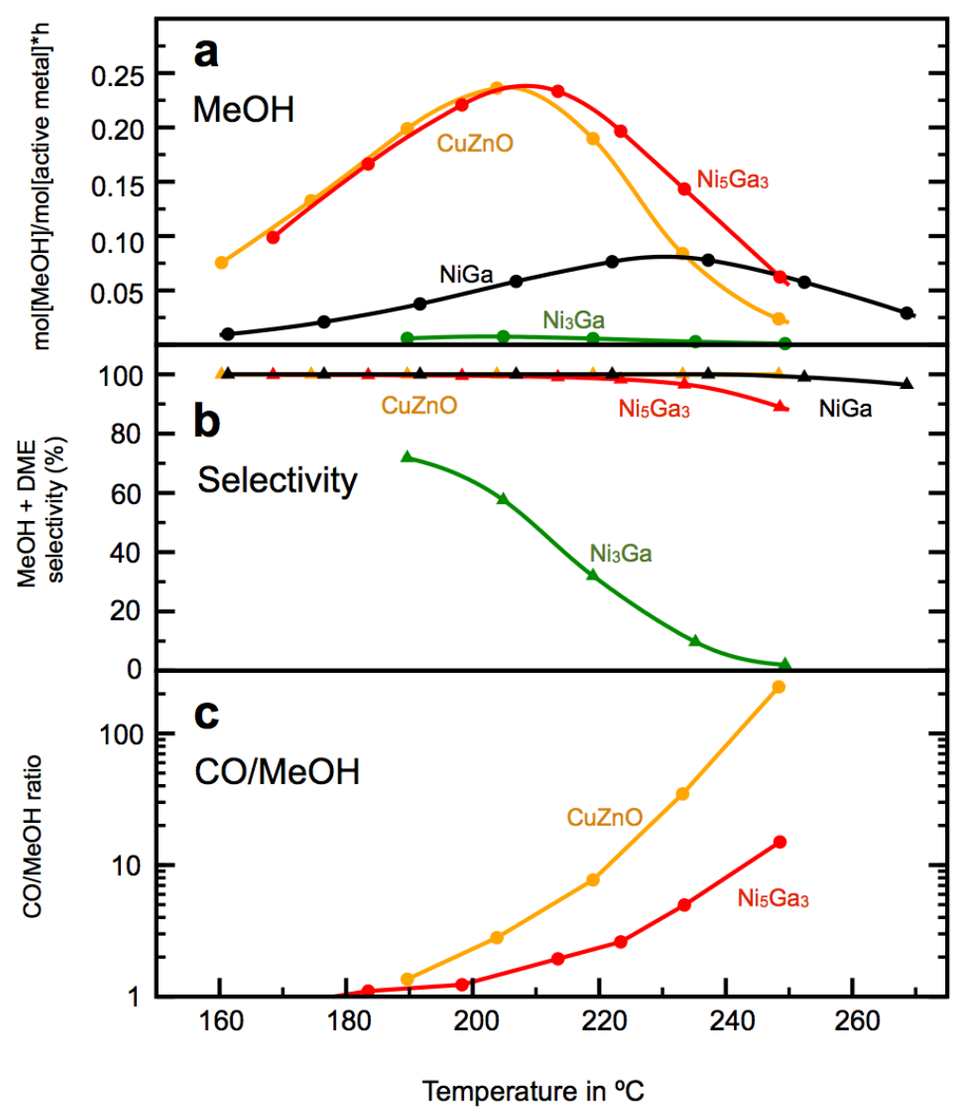
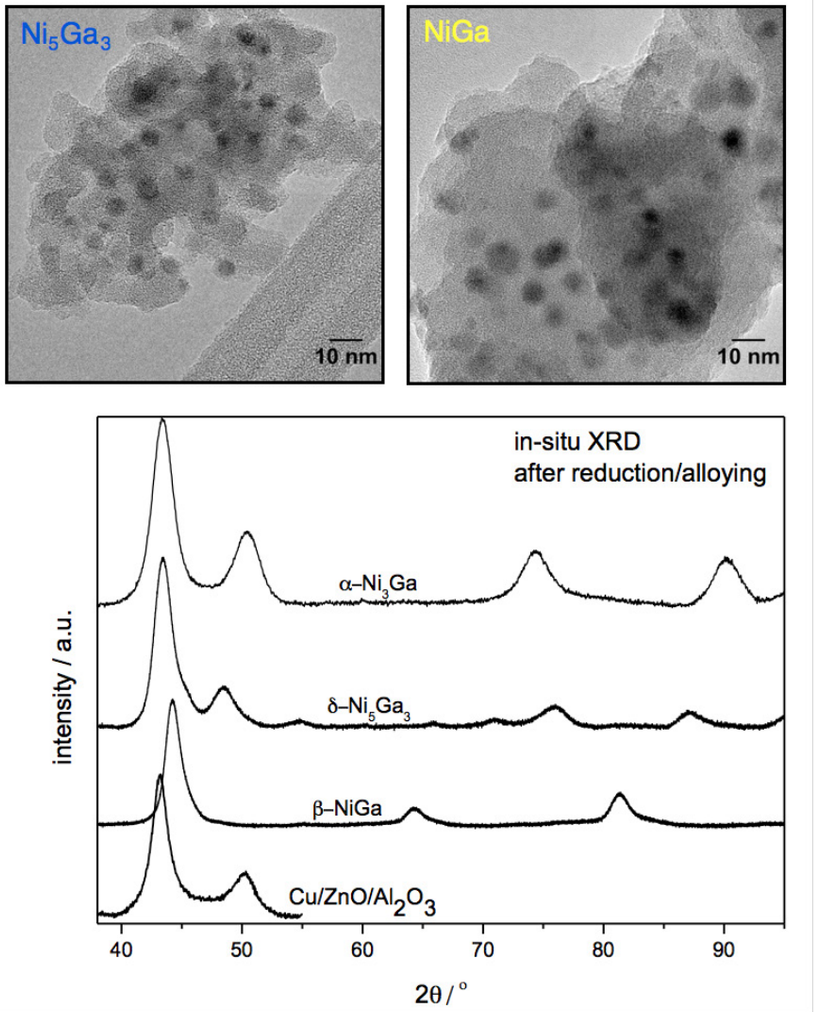
CO_2 reduction at ambient pressure

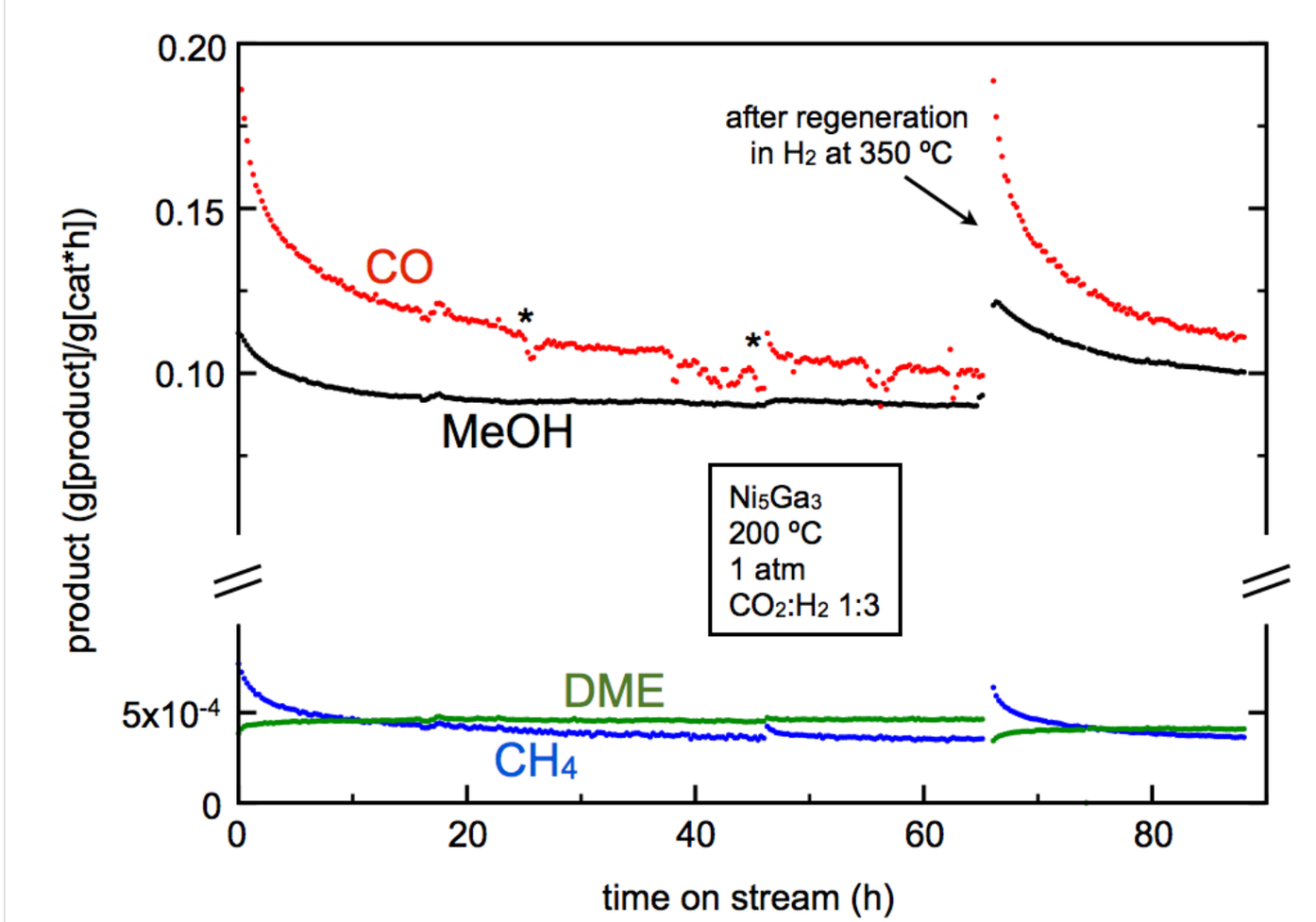




Studt et al, *Nature Chem.* **2014**, *6*, 320.

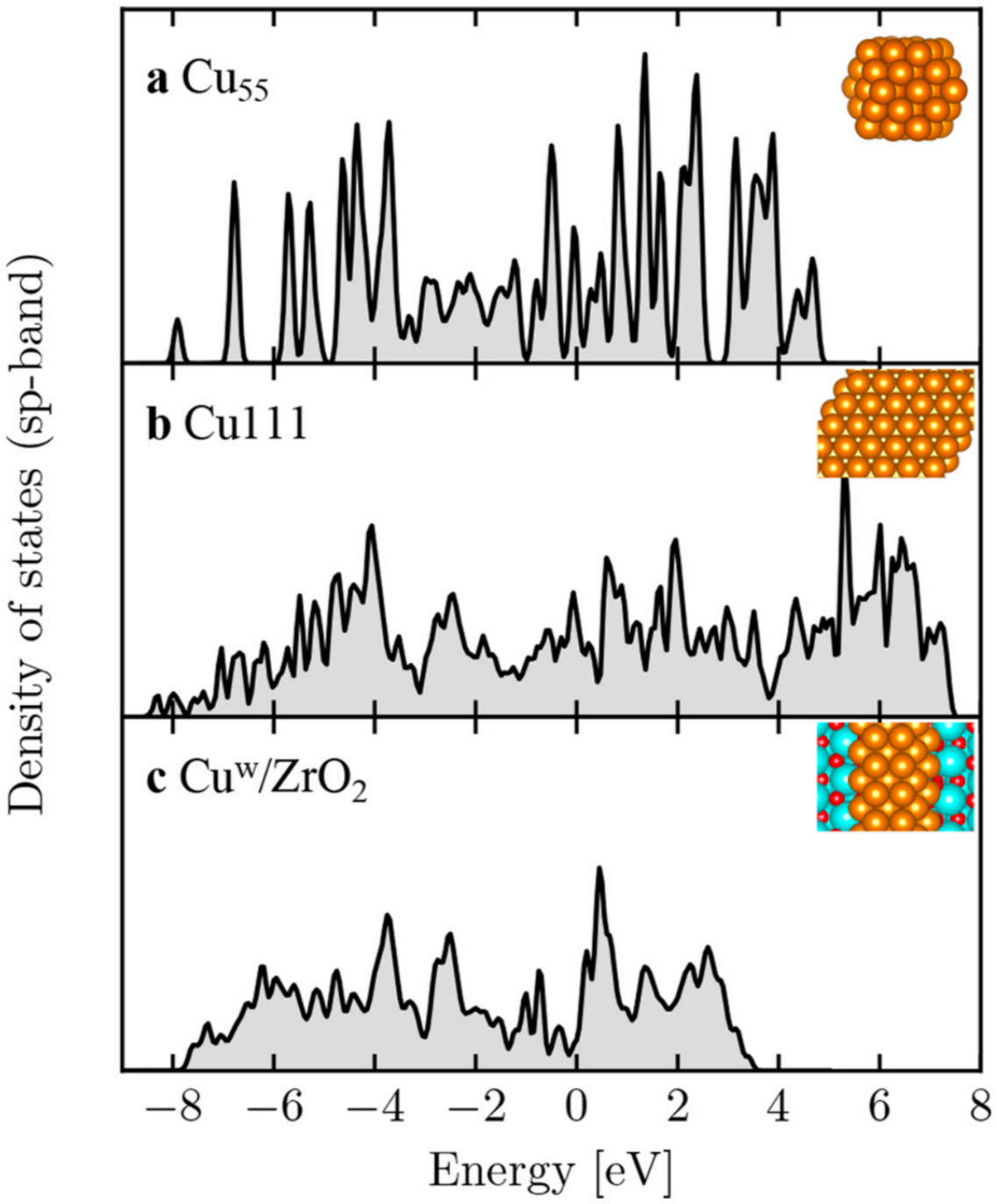
comparison experiment and theory





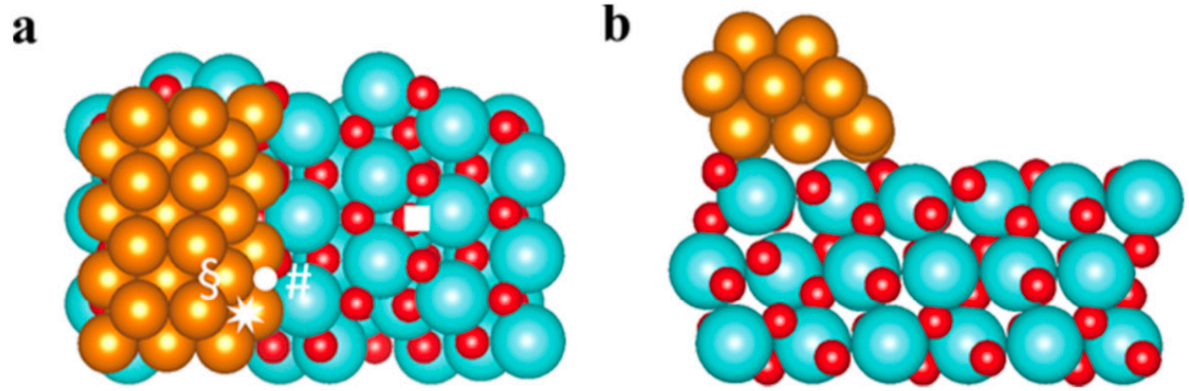
Studt et al, *Nature Chem.* **2014**, 6, 320.

The Cu/ZrO_2 system



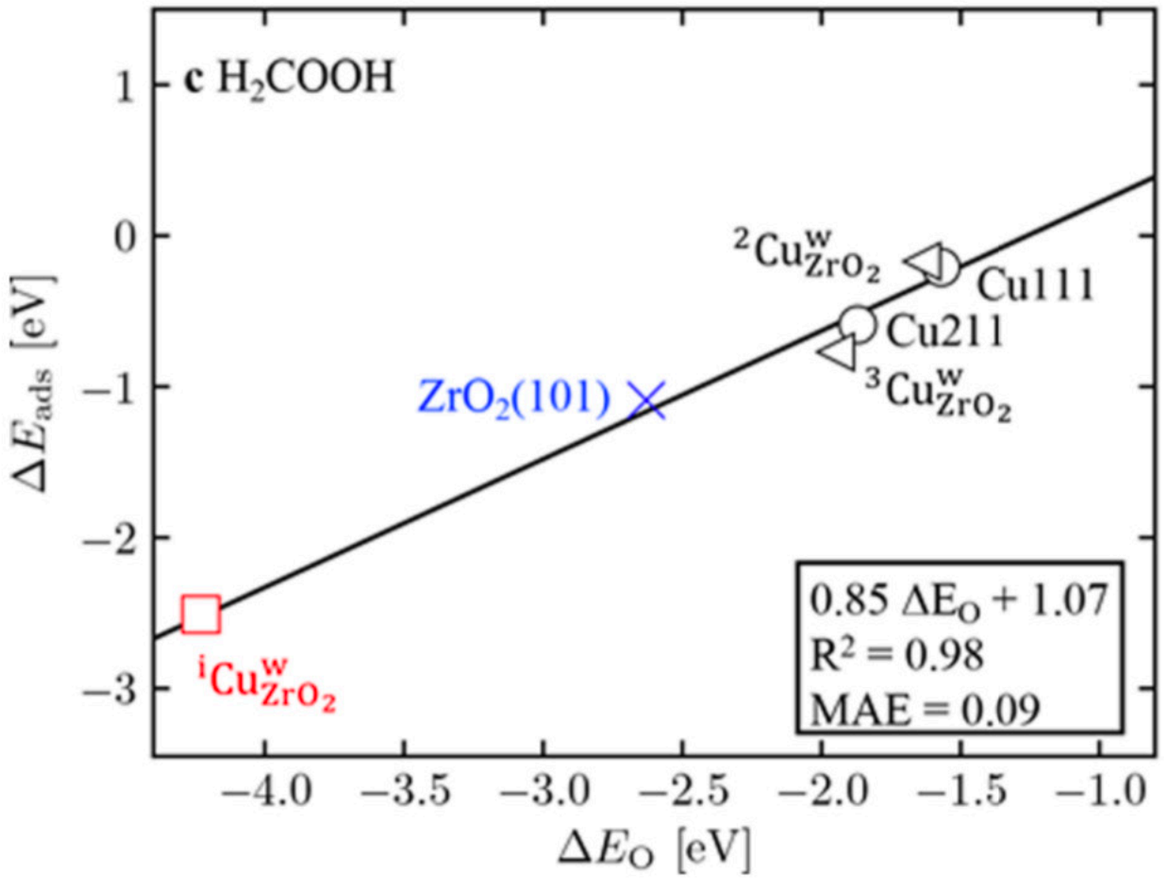
Small clusters do not represent electronic structure of metallic copper

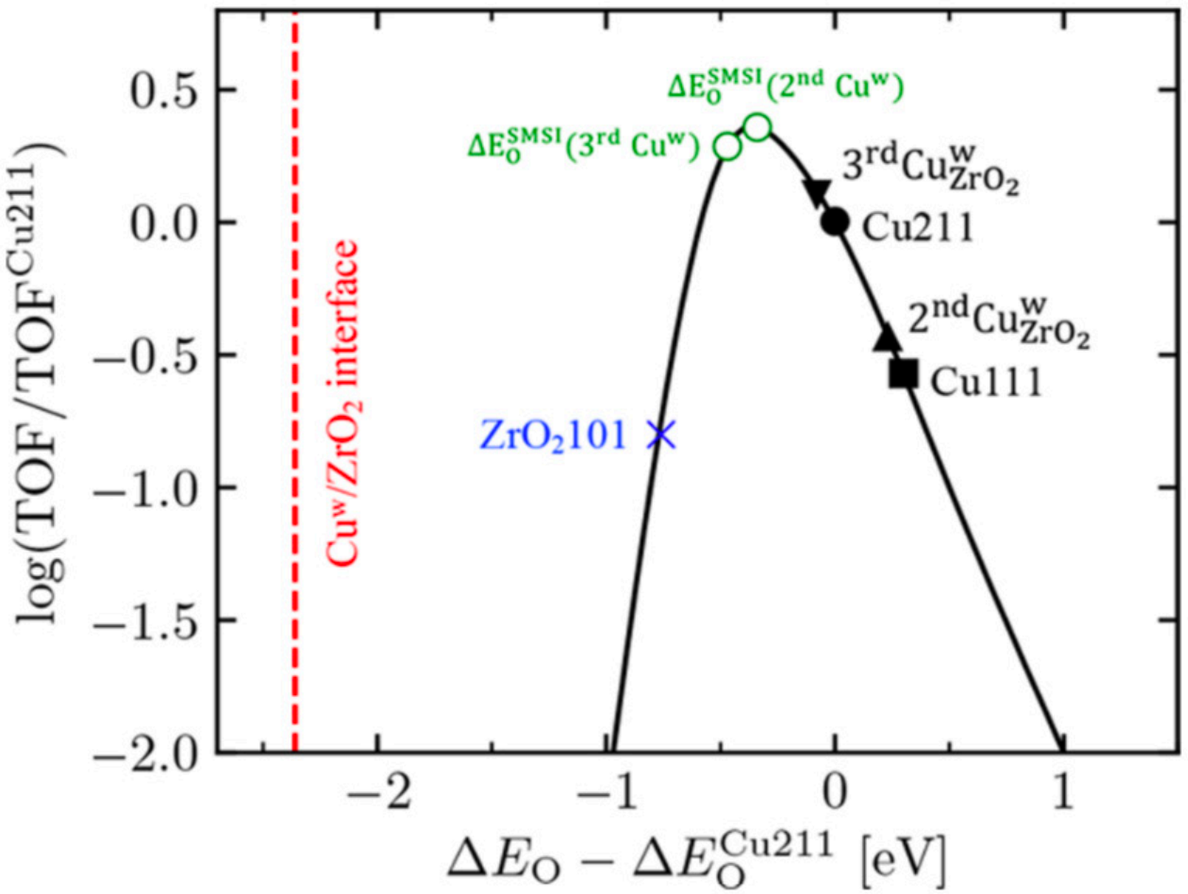
--> Supported nanowires may represent possible solution to study interface effects



Polierer et al, *J. Phys. Chem. C* **2019**, *123*, 26904.

The Cu/ZrO_2 system





Polierer et al, *J. Phys. Chem. C* **2019**, *123*, 26904.