  

Catalysts under pressure

Jeroen A. van Bokhoven

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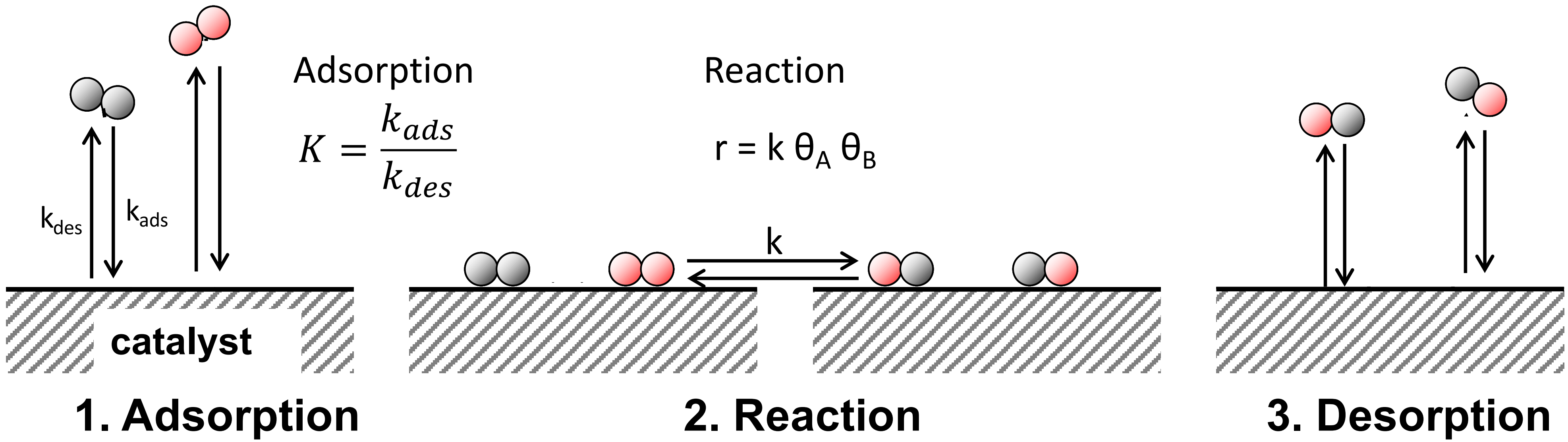
What does a catalyst do?

A catalyst breaks bonds ...

and makes bonds ...



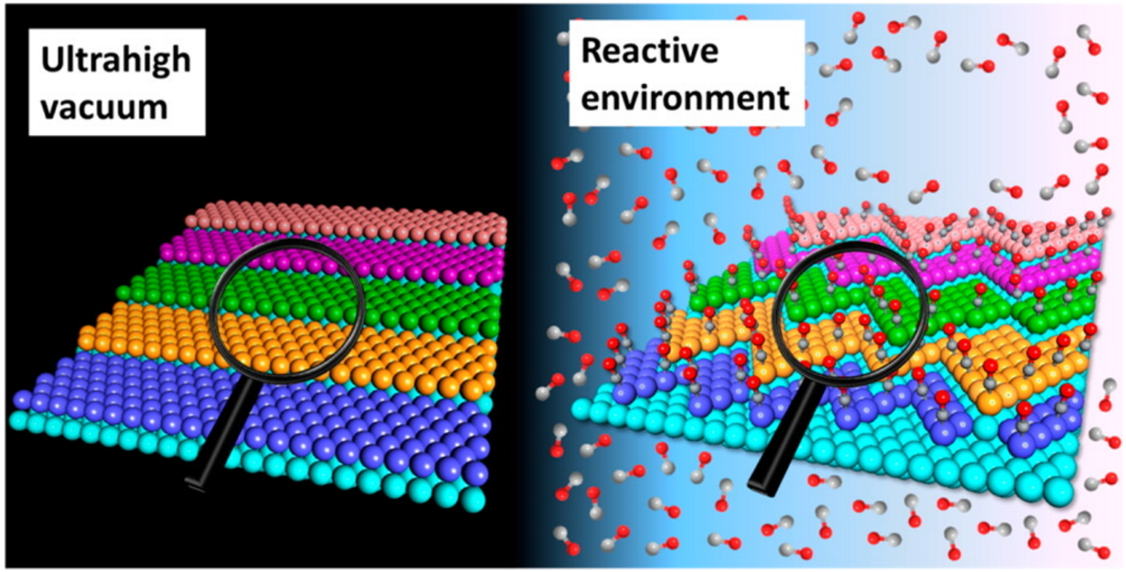
Catalysts often have multiple components

Industrial working conditions

Reaction	Conditions
Methanol synthesis $A * CO + B * CO_2 + C * H_2 \rightleftharpoons D* CH_3OH + B * H_2O$	250–300°C, 50–150 bar
Ammonia synthesis (Haber-Bosch) $1 * N_2 + 3 * H_2 \rightleftharpoons 2 * NH_3$	400–500°C, 150–300 bar
Fischer-Tropsch synthesis $A * CO + (2*A+1) H_2 \rightleftharpoons C_AH_{2A+2} + H_2O$	200–300°C, 10–25 bar
Water-Gas-Shift reaction (High temperature) $CO + H_2O \rightleftharpoons CO_2 + H_2$	350–550°C, 60–80 bar

In situ / operando spectroscopy

- Catalyst structure is a function of its environment
- Only structure measured under reaction conditions can give insight into activity
- Conversion changes the gas environment



Shiran Zhang *et al.* *Acc. Chem. Res.* 2013, 46, 1731-1739.

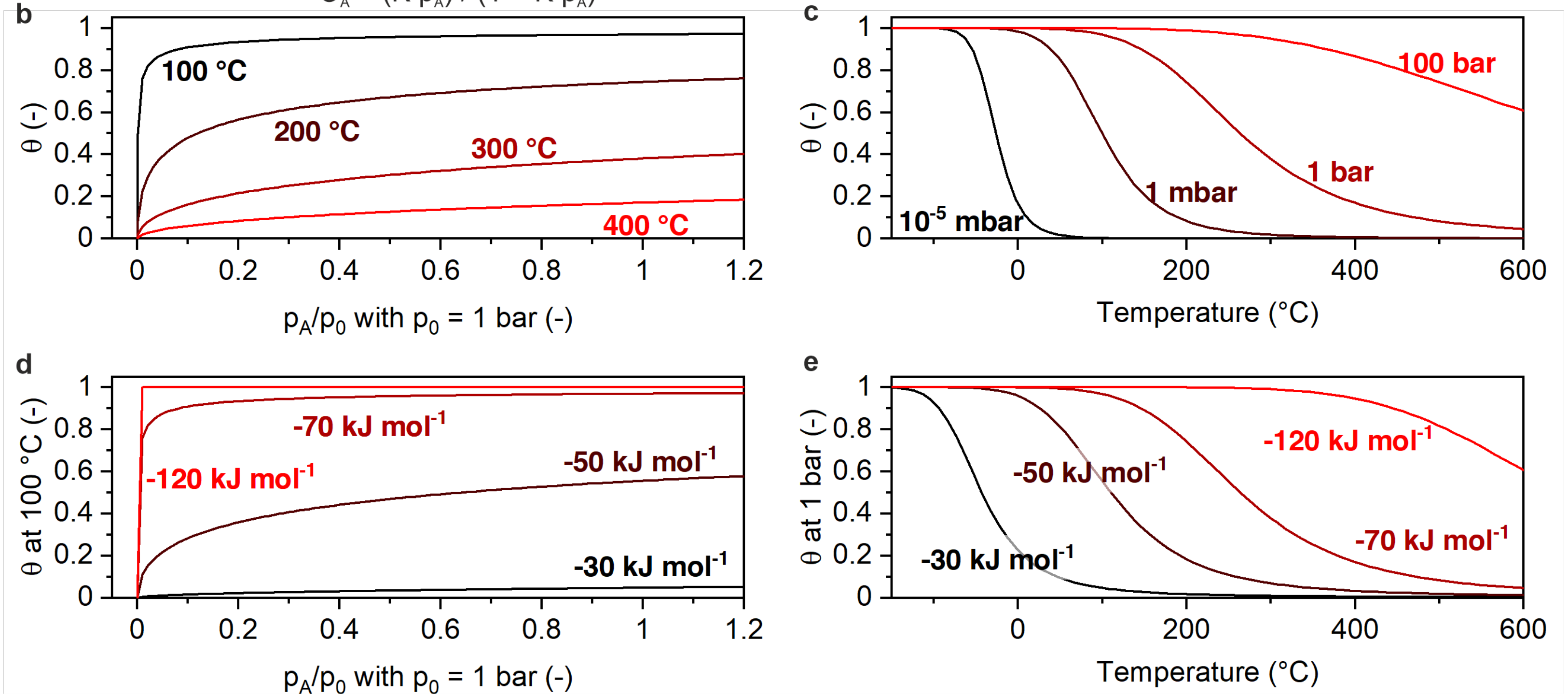
there are surprising few systematic studies

"Looking at catalysts under pressure"

How the surface looks like depends on conditions
adsorbates

surface coverage, H on Pt

$\Theta_A = (K\,p_A) / (1 + K\,p_A)$



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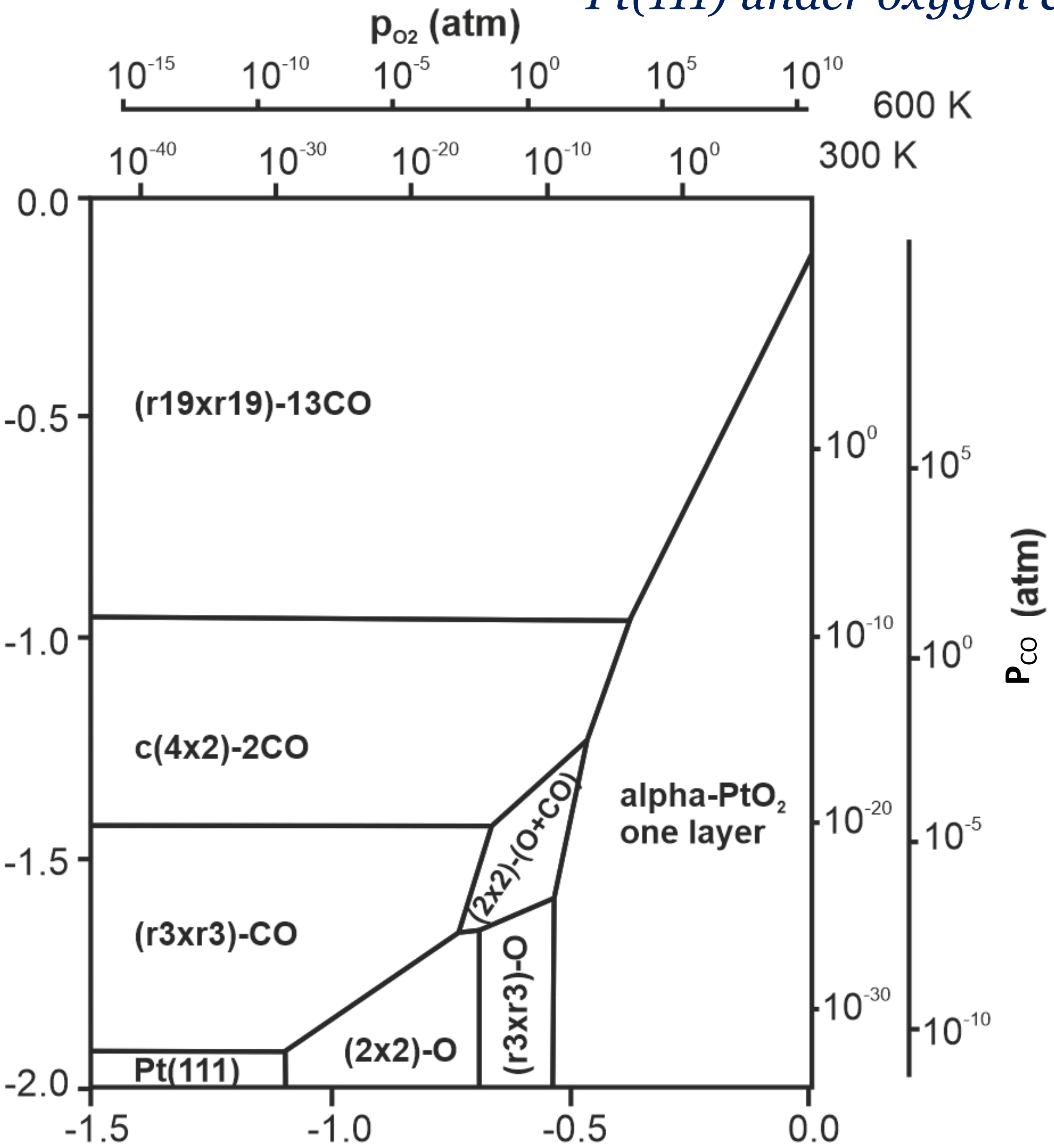
How the surface looks like depends on conditions

structure

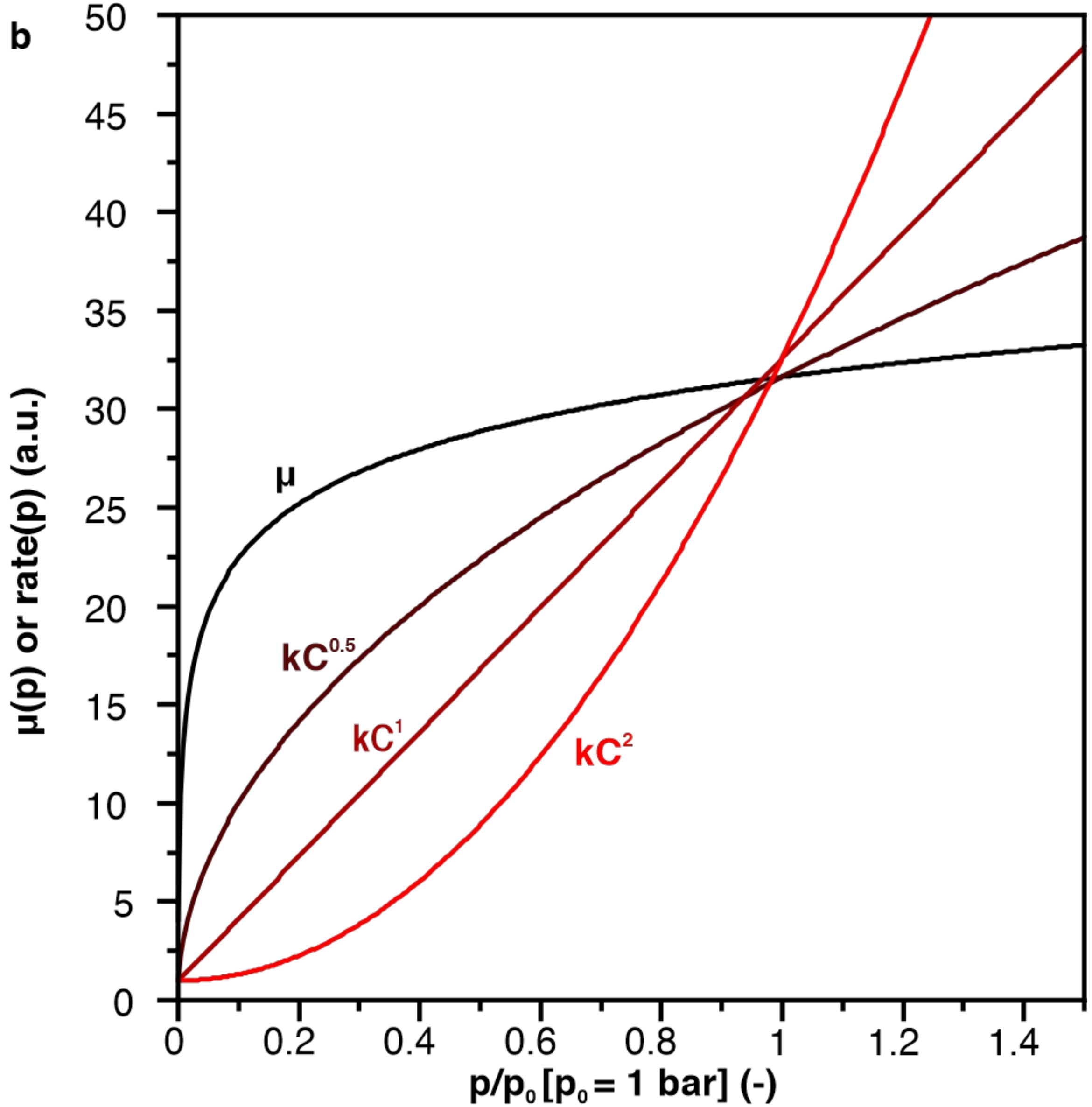
Pt(111) under oxygen & carbon monoxide



Pressure gap is a materials gap

Li & Hammer *Chem. Phys. Lett.* 409, 1–7 (2005)

The Pressure Gap *mechanism*



Arik Beck *in preparation*

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

Why study this?

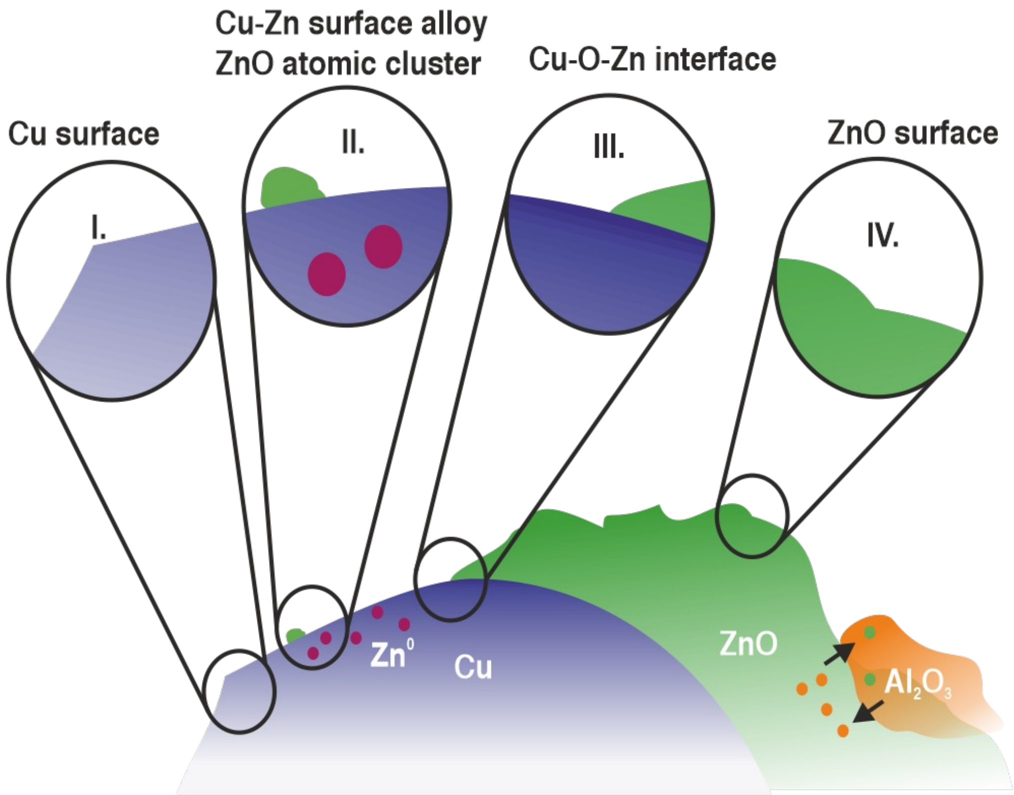
- environmental concern
- making chemicals / fuels from carbon dioxide
- scientific debate about the structure of the catalyst

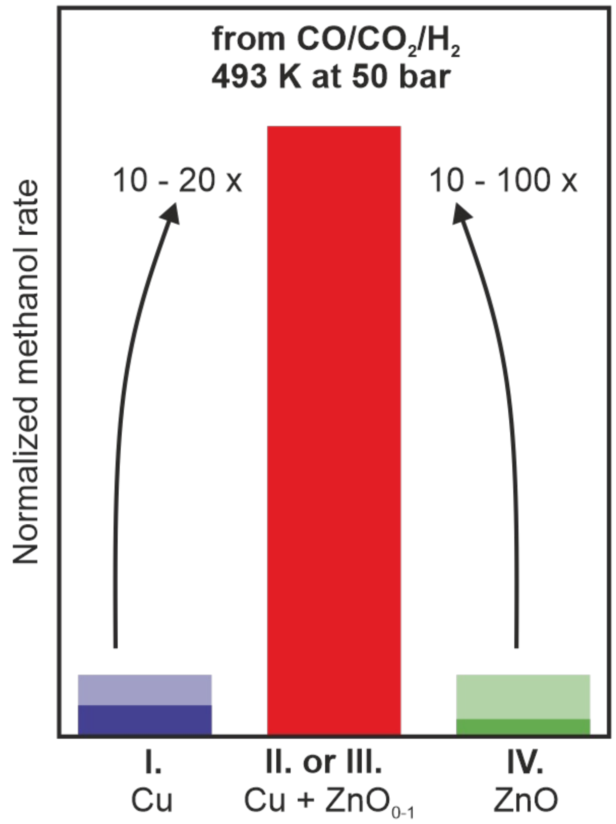
the big question:

Role of each component in multi-component catalysts

- *Cu/ZnO/Al_2O_3*
- *Pd/ZnO*

Active sites in $Cu/ZnO/Al_2O_3$





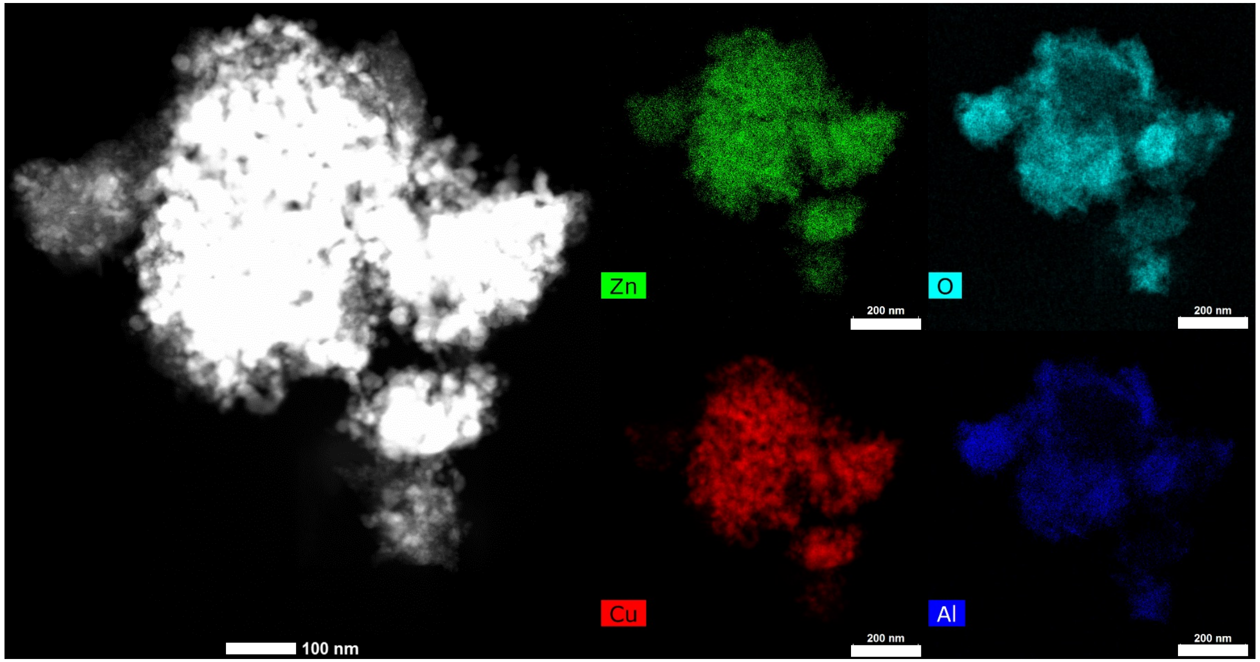
This talk

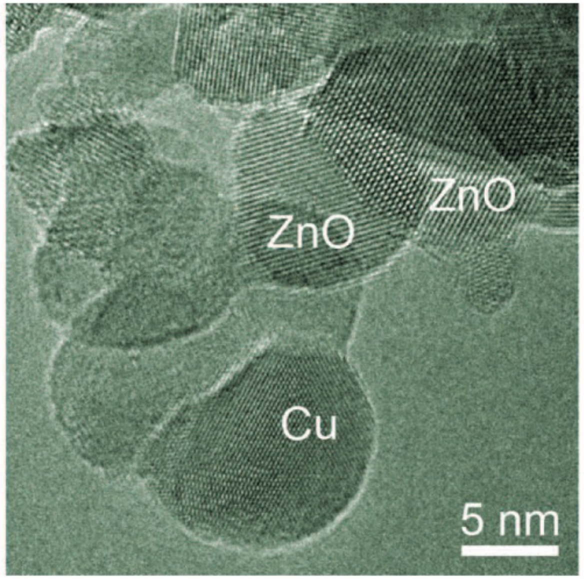
Part 1. *the pressure gap*: structure of multiple components in $Cu/ZnO/Al_2O_3$

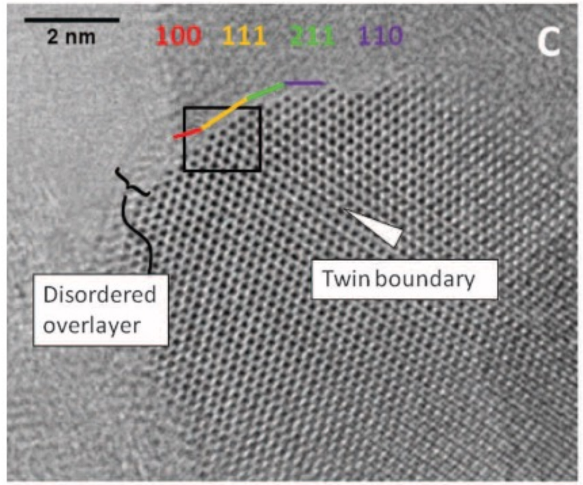
Part 2. methanol synthesis from carbon dioxide: multiple component catalyst

Copper-Zinc-Alumina (CZA)

The high pressure catalyst: Cu/Zn/Al_2O_3 catalyst for methanol synthesis, water-gas-shift







Kuld et al. *Science* 2016, 352, 969

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

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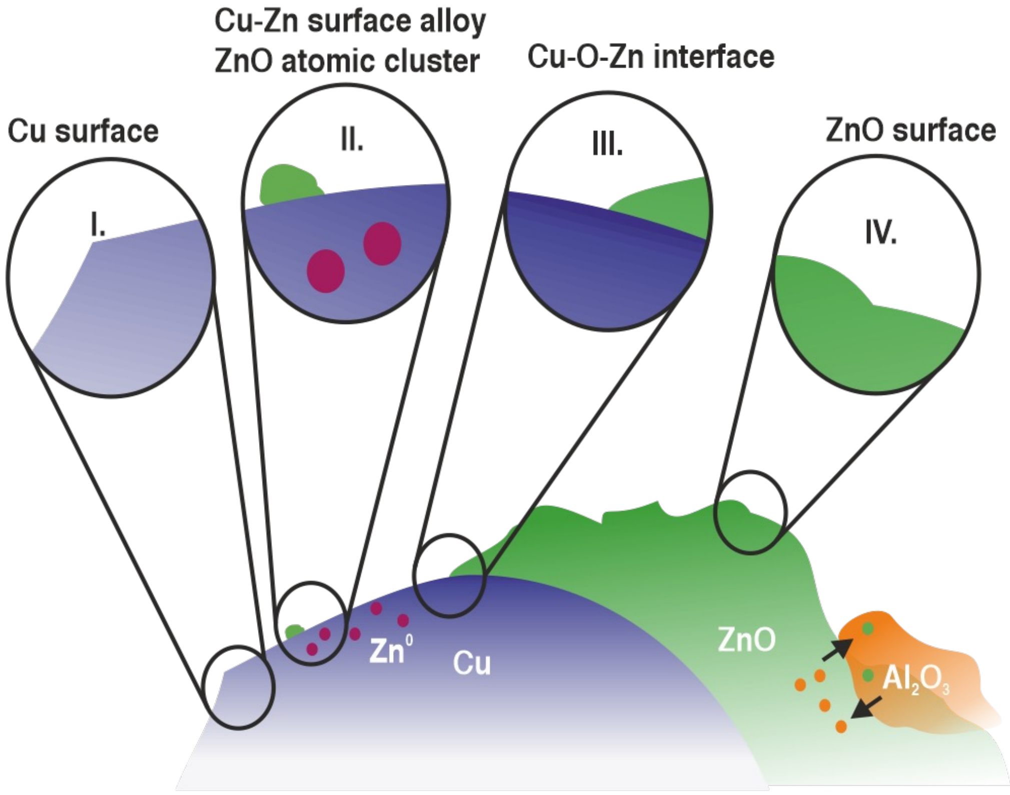
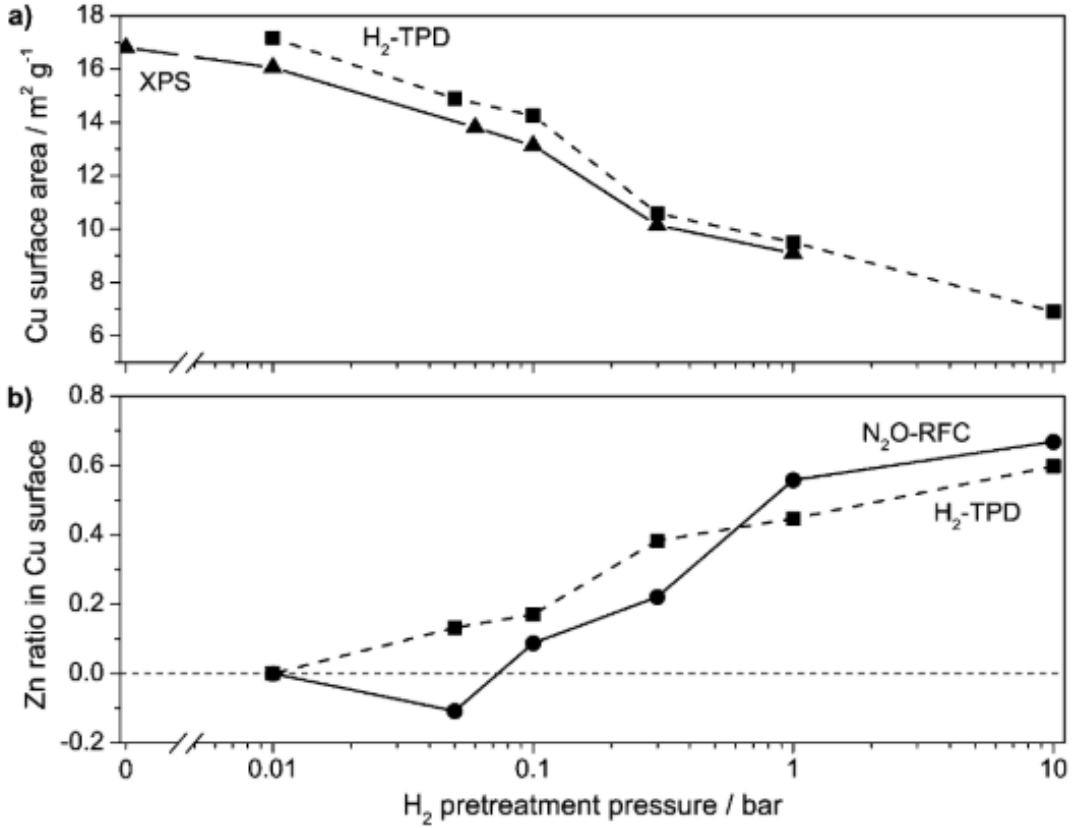
Arguments in the field

The synergism of copper-zinc is a prototype for multicomponent catalysts.
But it is poorly understood

1) Frei et al. *ACS Catalysis* 2019, 9, 5537-5544
2) Frei et al. *ChemCatChem* 2019, 11, 1587-1592
3) Kattel et al. *Science* 2017, 355, 1296-1299
4) Kuld et al. *Science* 2016, 352, 969-974
5) Van den Berg et al. *Nat. Comm.* 2016, 7, 13057
6) Lunkenbein et al. *Angew. Chem.* 2016, 55, 12708-12712
7) Kondrat et al. *Nature* 2016, 531, 83-87
8) Martin et al. *Angew. Chem.* 2016, 55, 11031-11036
9) Kuld et al. *Angew. Chem.* 2014, 53, 5941-5945
10) Fichtl et al. *Angew. Chem.* 2014, 53, 7043-7047
11) Kandemir et al. *Angew. Chem.* 2013, 52, 5166-5170
12) Zander et al. *Angew. Chem.* 2013, 52, 6536-6540
13) Prieto et al. *Nature Mat.* 2013, 12, 34-39
14) Behrens et al. *Science* 2012, 336, 893-897
15) Zabilskiy et al. *Nature Comm.* 2020, 11, 2409-2417



Pressure dependent zinc on copper surface coverage



16 h treatment at 200 °C at various hydrogen pressures leads to different surface coverages of zinc on copper

Kuld et al. ***Angew. Chem.*** **2014, 53, 5941-5945**

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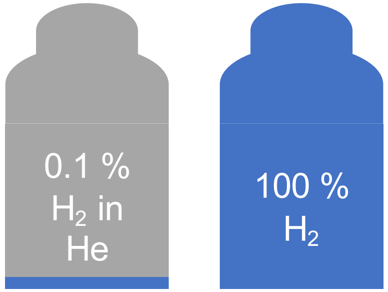
The pressure gap

Systematic study of structure of copper-zinc-alumina

Example for a pressure-bridging technique: X-ray absorption spectroscopy



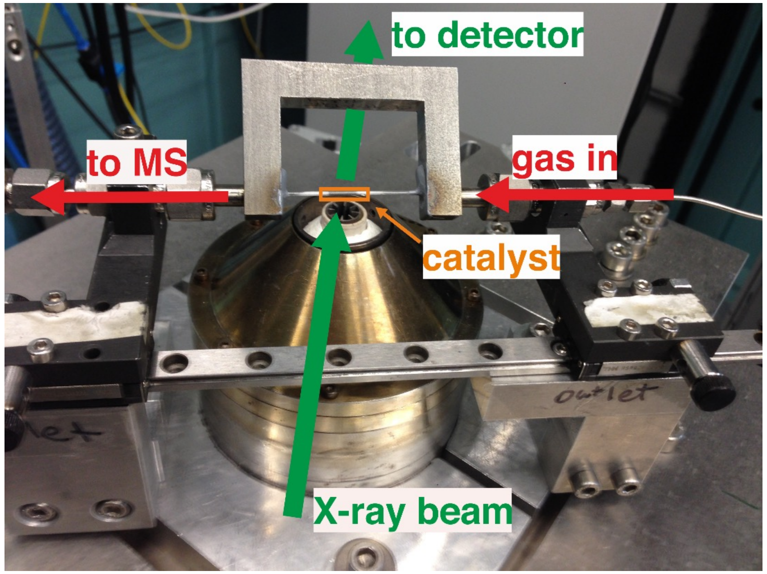
Do test at different partial pressures of H_2:

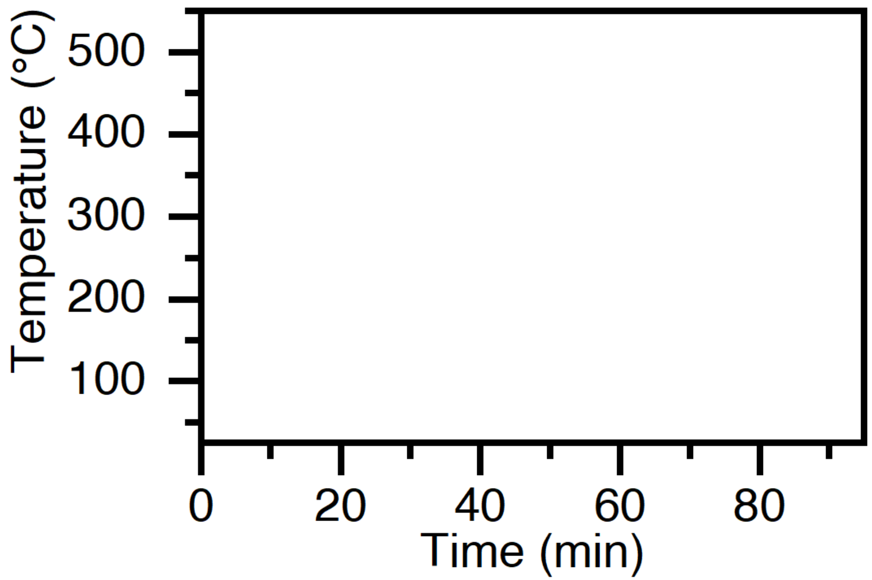
- 1 mbar
- 10 mbar
- 1000 mbar
- 1 bar
- 5 bar
- 10 bar

→ Bridge 4 orders of magnitude in partial pressure

SuperXAS - X10DA

Experimental set-up



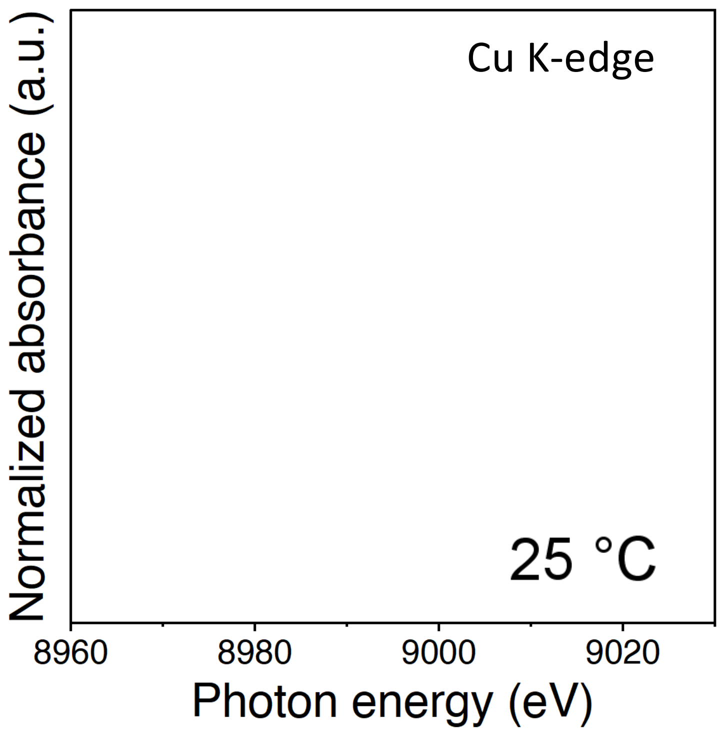


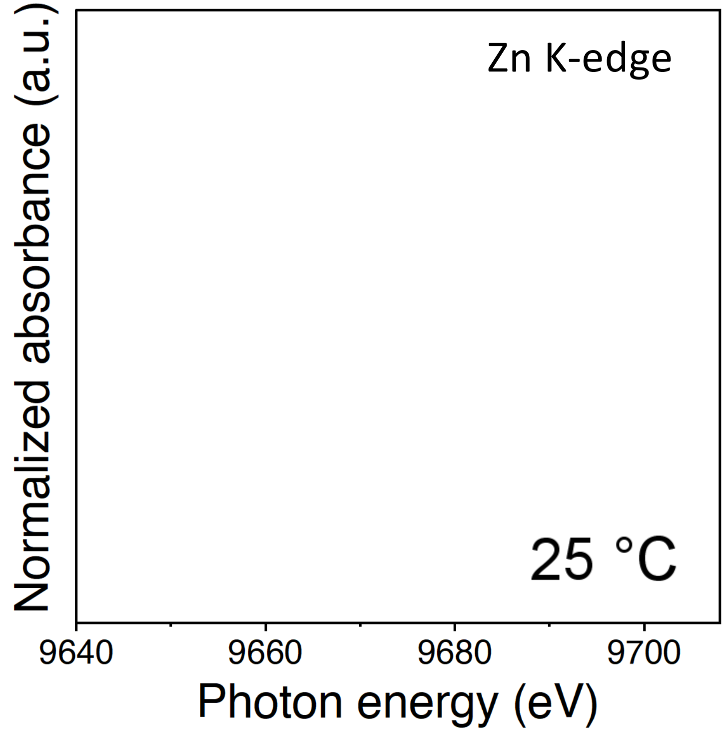
Temperature programmed reduction (TPR):

- 5 °C min^{-1}
- 1 mbar, 10 mbar, 100 mbar, 1 bar, 5 bar, 10 bar

Temperature programmed reduction

100 mbar H_2 (10% H_2/ He)

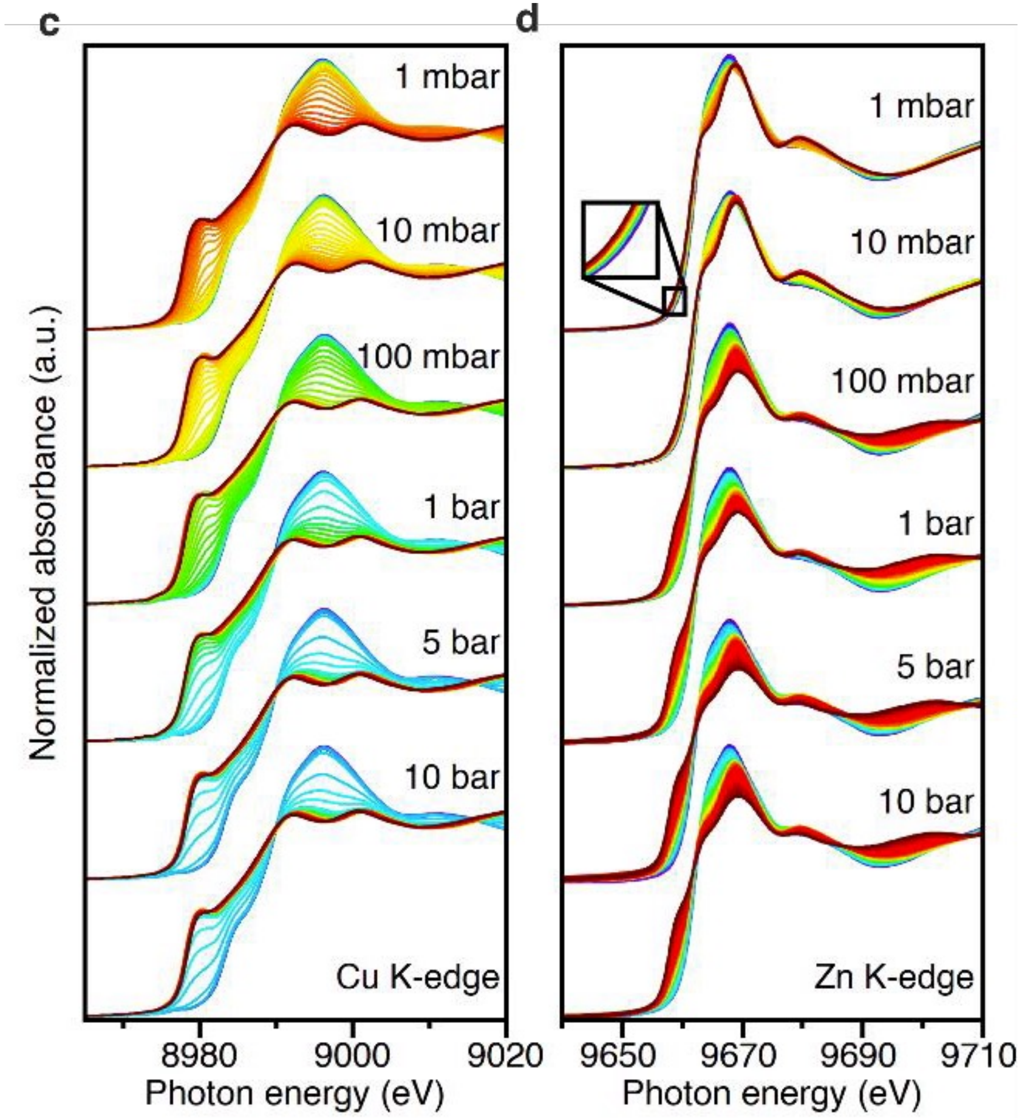


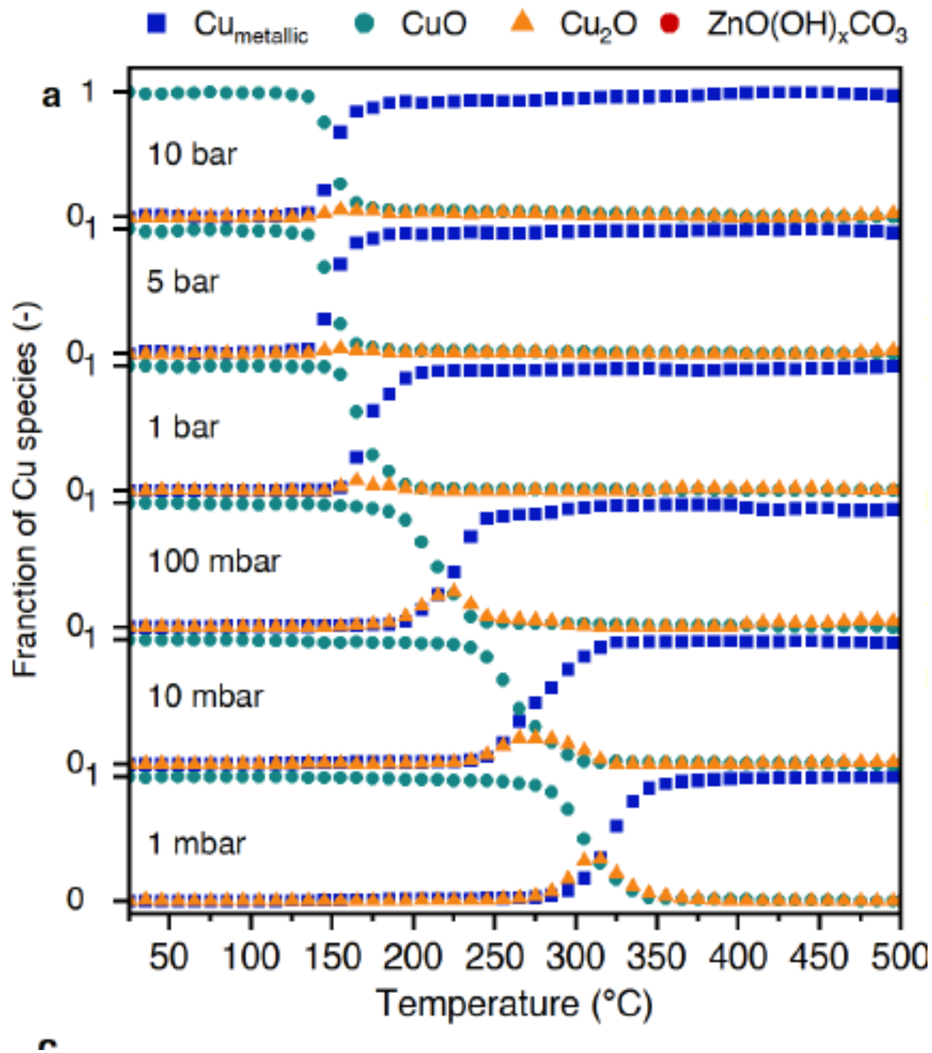


OK

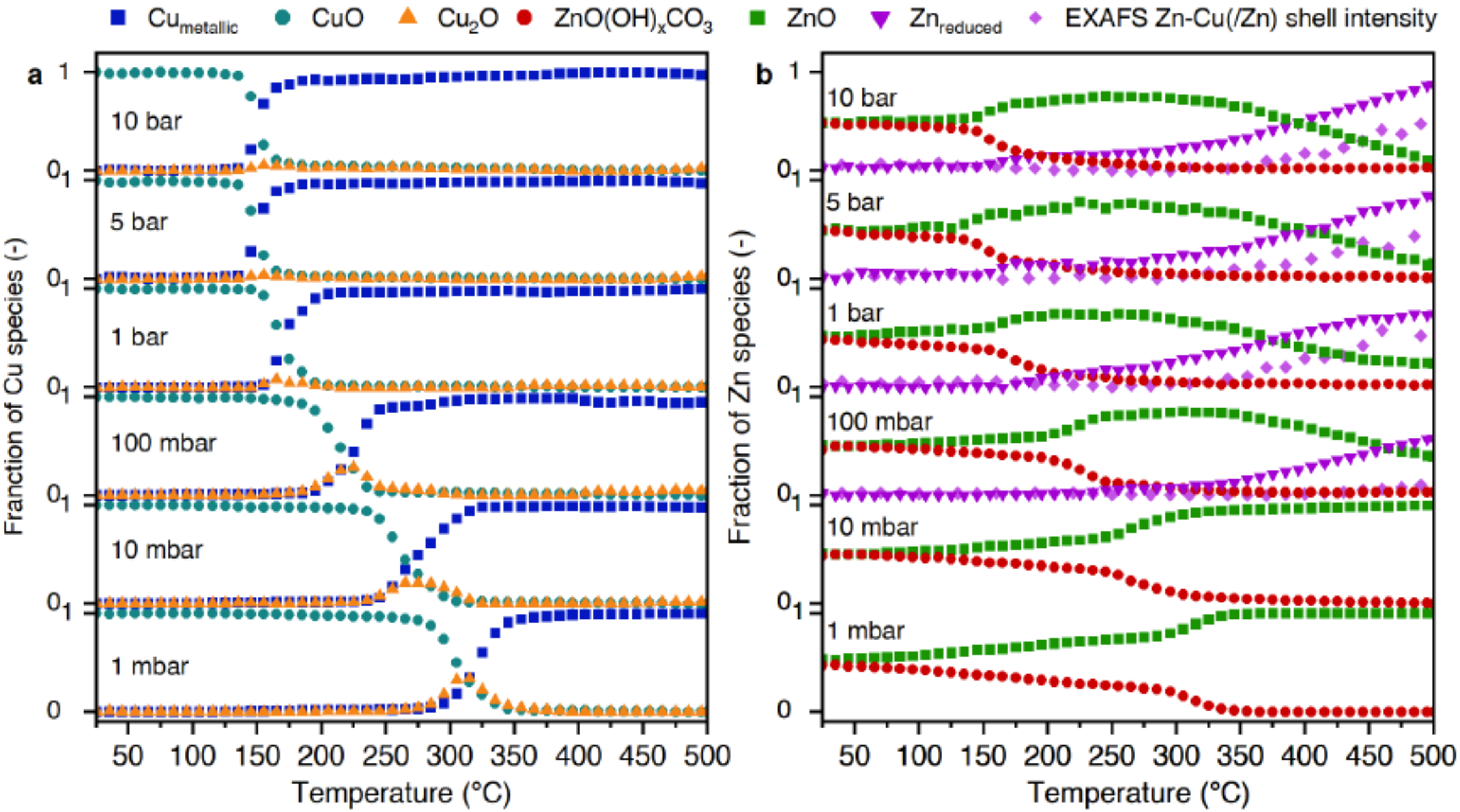
Temperature-programmed reduction

pressure dependence





Evolution of the catalyst formation under hydrogen



Reduction profile and speciation *strongly* pressure-dependent

Cu-Zn alloy at P>1 bar

So far, this is still trivial

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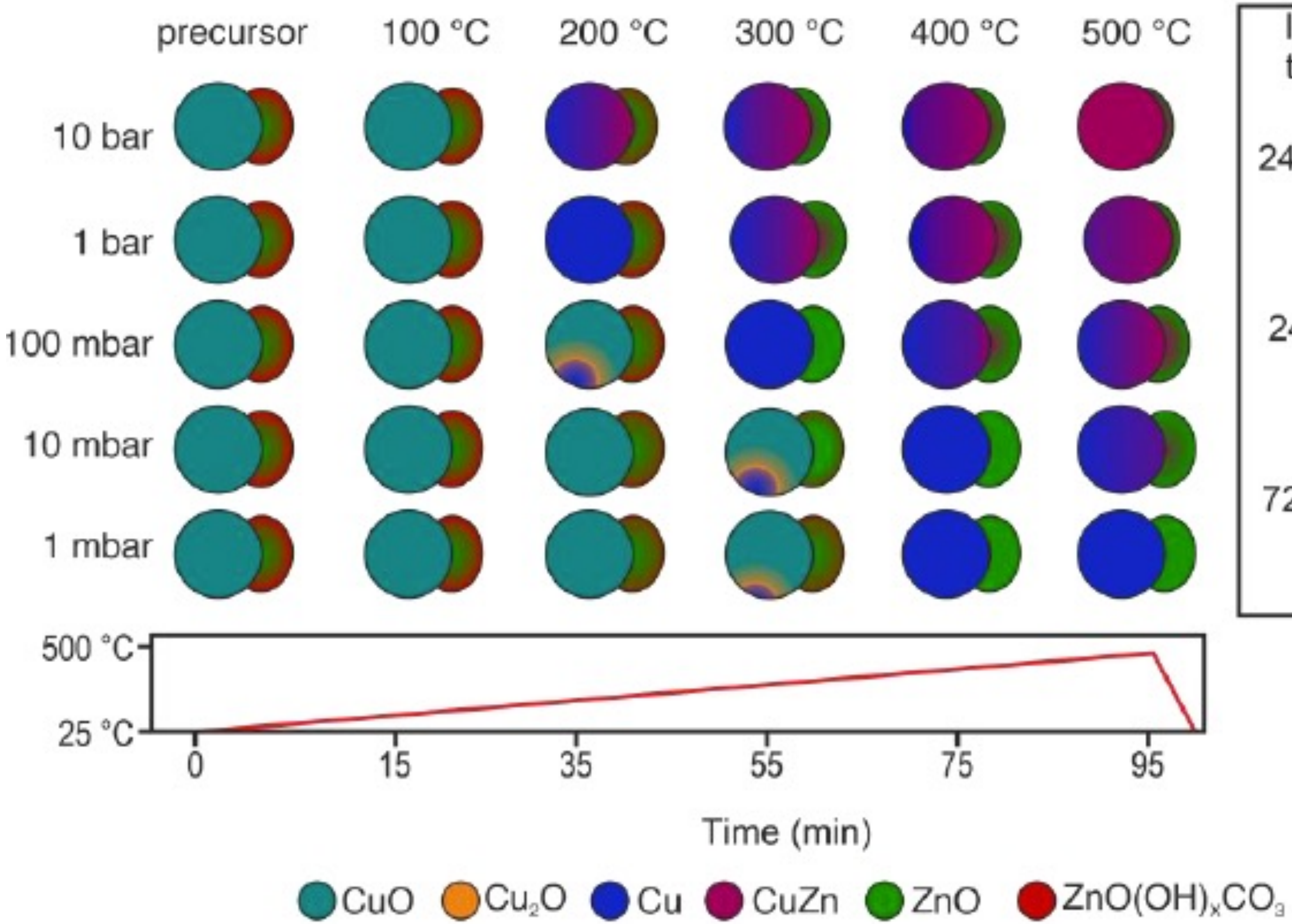

Different structures form under different pressure

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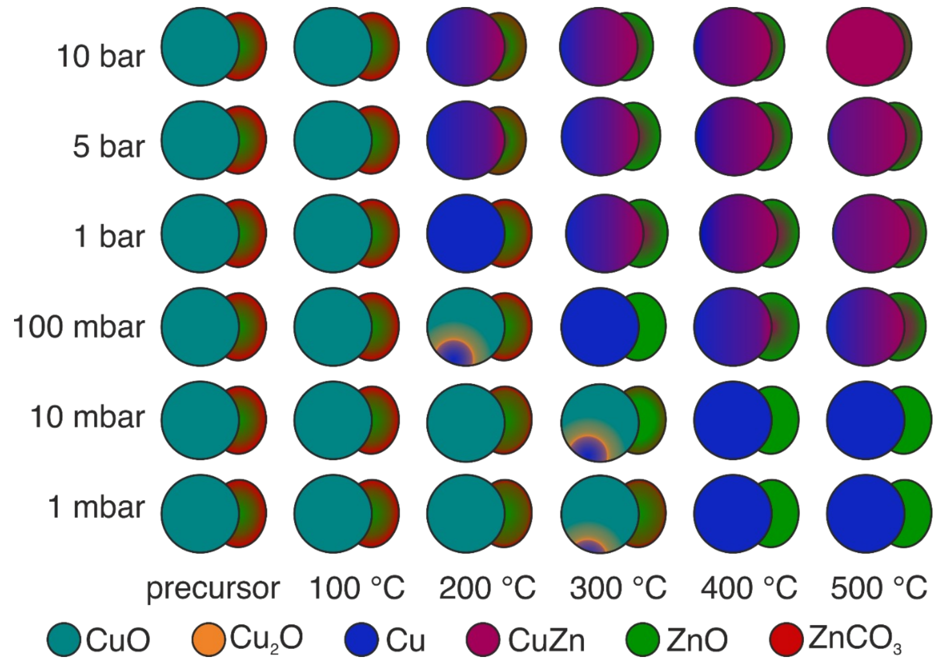
Conclusions part 1
the pressure gap is a materials gap

- The Cu-Zn-Al catalyst is sensitive to the hydrogen pressure *CuO reduction temperature changes by 40 °C per pressure decade*
- Cu(I) oxide is formed as short-lived intermediate at low hydrogen pressures (1-100 mbar).
- No copper-zinc (brass) alloy formation was detected at pressures below 100 mbar.
- There is a reduced form of ZnO_x prior to brass formation



Different pressures yield very different structures

Arik Beck, Maxim Zabilskiy et al. *Nature Catalysis* (2021)

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Carbon dioxide to chemicals and fuels

methanol synthesis

Materials synthesis and characterization go hand in hand

Lead author: Maxim Zabilskiy
Nature Comm. 11 (2020) 2409-2417

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

Why study this?

- environmental concern
- making chemicals / fuels from carbon dioxide
- scientific debate about the structure of the catalyst

the big question:

Role of each component in multi-component catalysts

- ➢ *$Cu/ZnO/Al_2O_3$*
- ➢ *Pd/ZnO*

Questions

- ➢ **role of zinc (oxide)?**
- ➢ **CuZn / PdZn ?**

Carbon dioxide hydrogenation to methanol:

$$CO_2 + 3H_2 = CH_3OH + H_2O$$

(Cu/ZnO/Al_2O_3 catalyst; P=15-50 bar; T=200-260 ºC)

$$CO_2 + H_2 = CO + H_2O$$

(side reaction)

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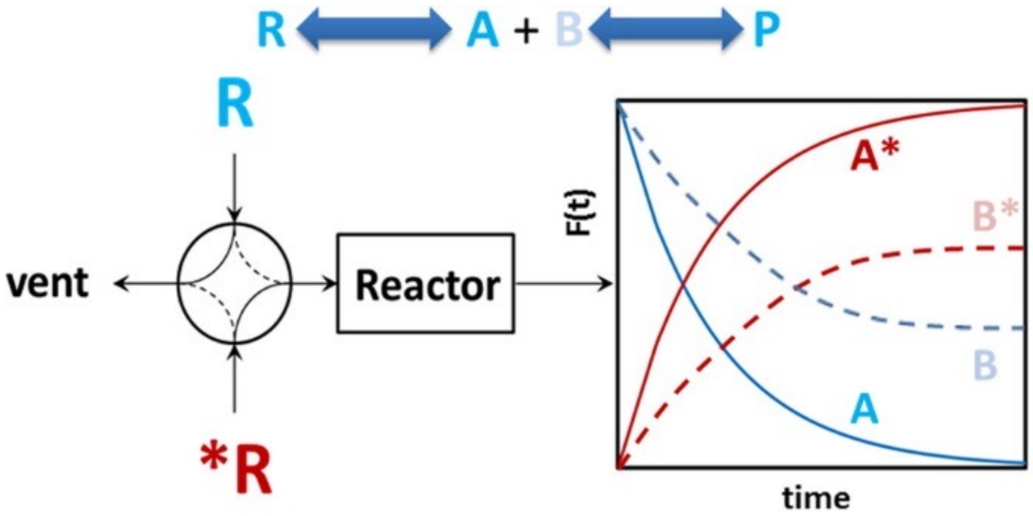
What are the reactive species at the surface?

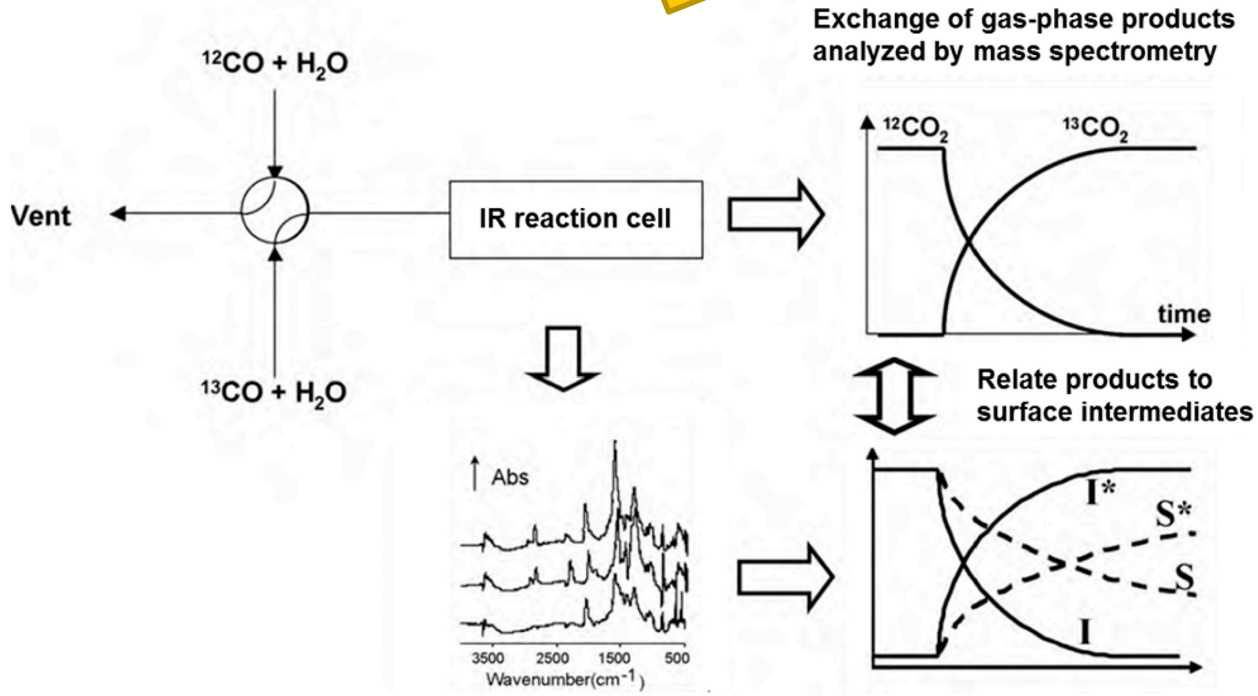
Combined SSITKA – FTIR

SSITKA -> SSITKA-FTIR



MS detects A and B as intermediates
IR elucidates spectator intermediates (B)

Kinetic analysis of surface species



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Operando SSITKA-FTIR

- **SSITKA/FTIR under high pressure!**

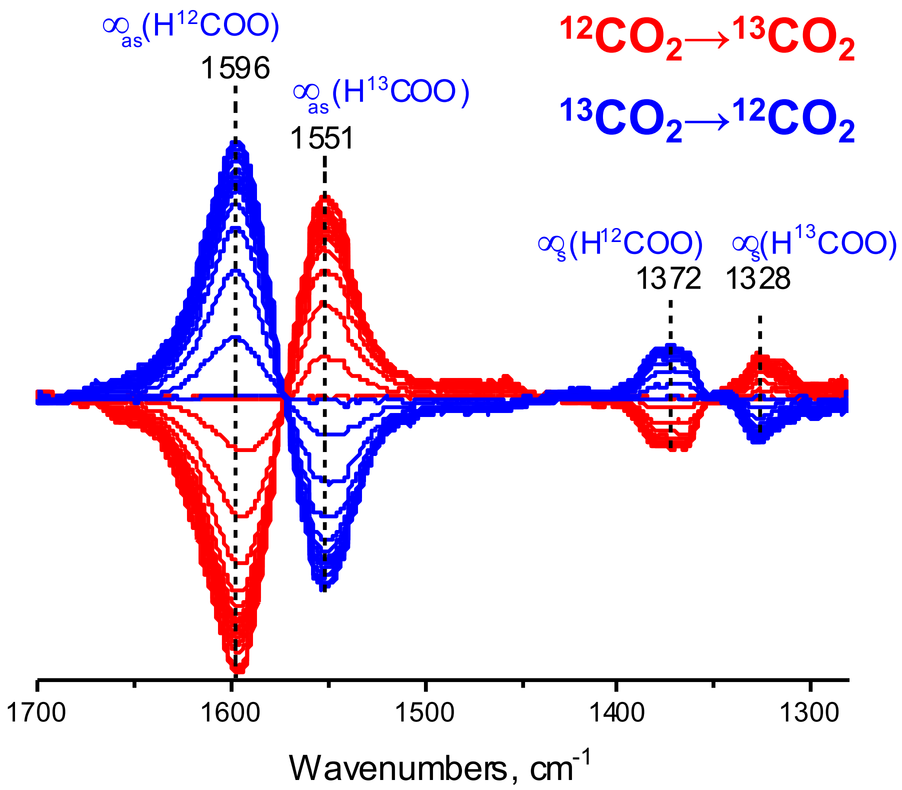
Catalyst:

- $CuO/ZnO/Al_2O_3$ (Alfa Aesar)

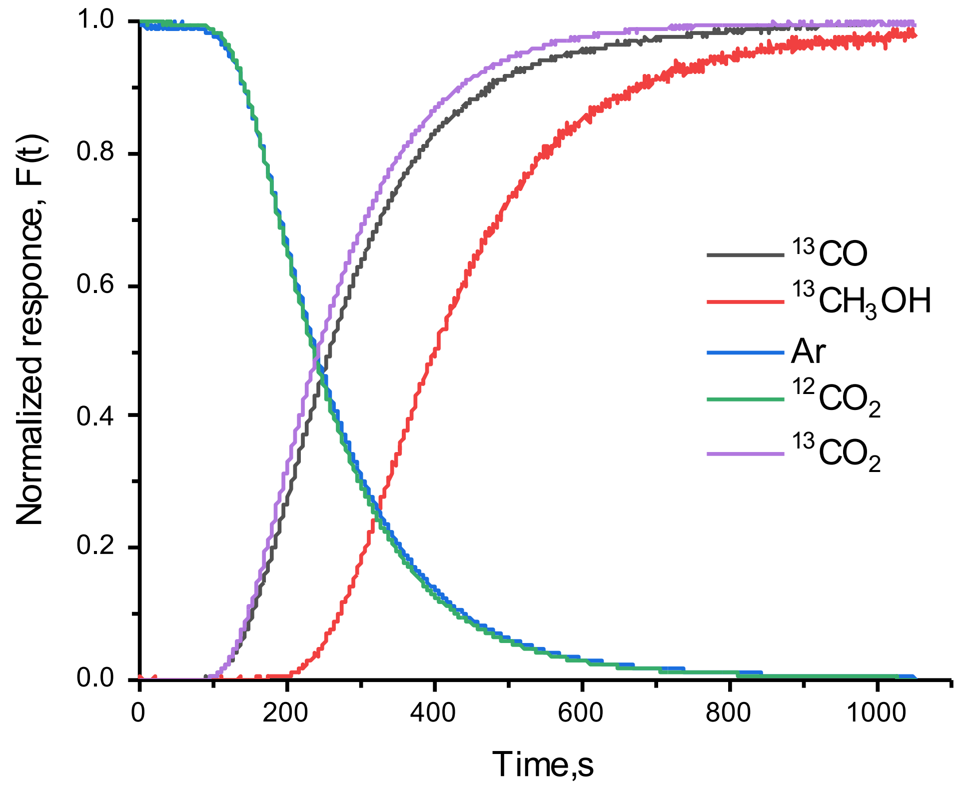
Experimental conditions:

- 15bars, 260 ° C;
- $H_2/CO_2 = 3$

FTIR-response after switches



MS-response following $^{12}CO_2/^{13}CO_2$ switch



Formates are primary products and undergo full interconversion during the isotope switch!

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Formate is a reactive intermediate

where is the formate?

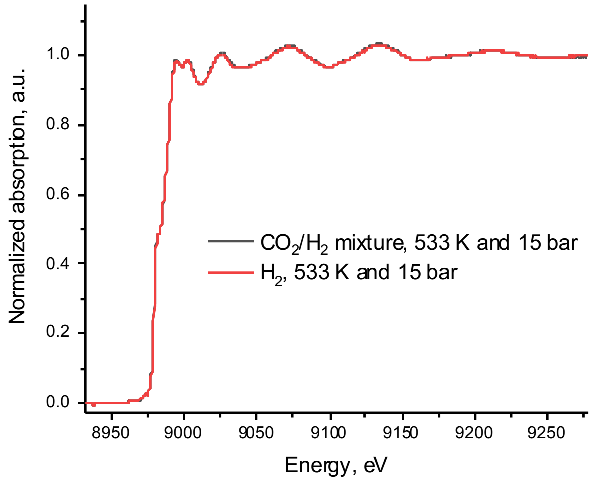
➔ *on copper, ZnO or alumina?*

Operando XAS

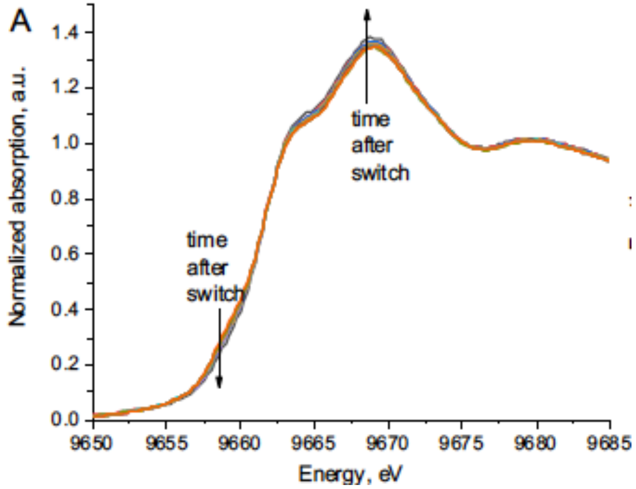
Experimental conditions:

- 15bars, 260 ° C; H_2/CO_2 = 3;
- Transient switch from hydrogen to CO_2/H_2 mixture

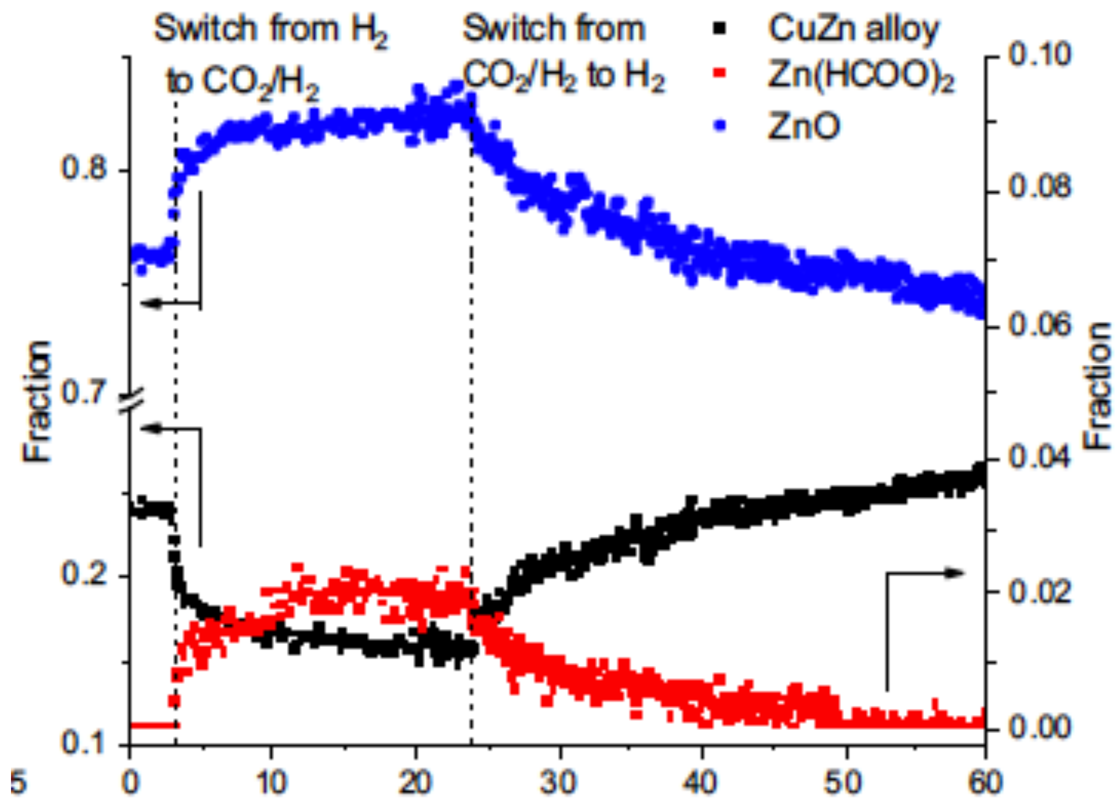
Cu K-edge XAS



Zn K-edge XANES



Zinc speciation



- Copper is always present in a metallic form
- Zinc is partially reduced after reduction
- *Zinc formate forms after exposure to carbon dioxide*

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Under reaction conditions

- CuZn de-alloys
- Formate is reactive intermediate
- Formate is associated with zinc

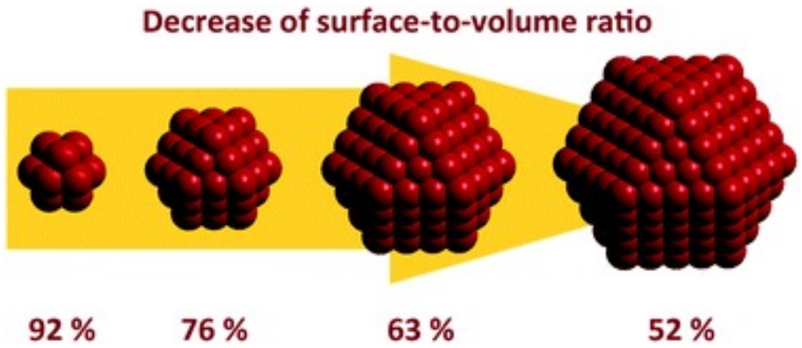
Zabilskiy M, Sushkevich VL, Palagin D, Newton MA, et al.

The unique interplay between copper and zinc during catalytic carbon dioxide hydrogenation to methanol

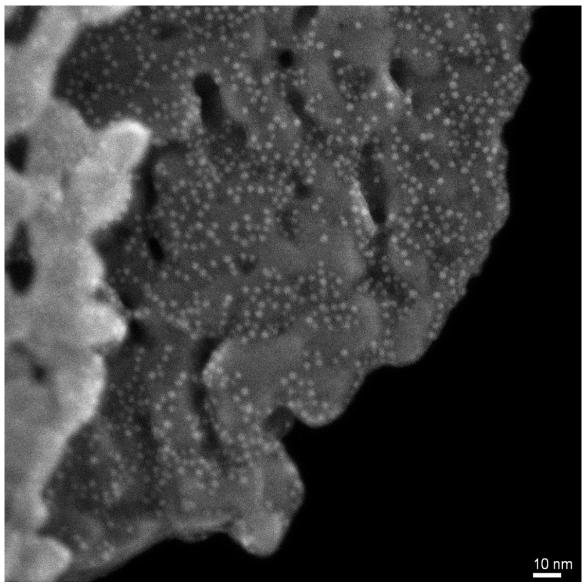
Nature Communications 11 (2020) 2409

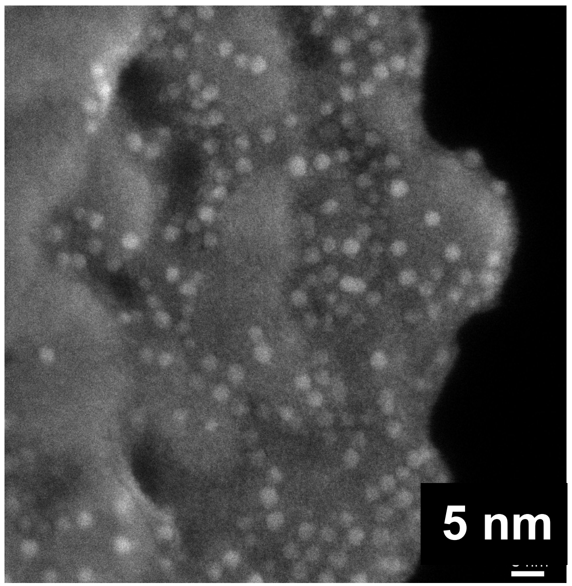
What about Pd/ZnO?

Synthesis of Pd/ZnO



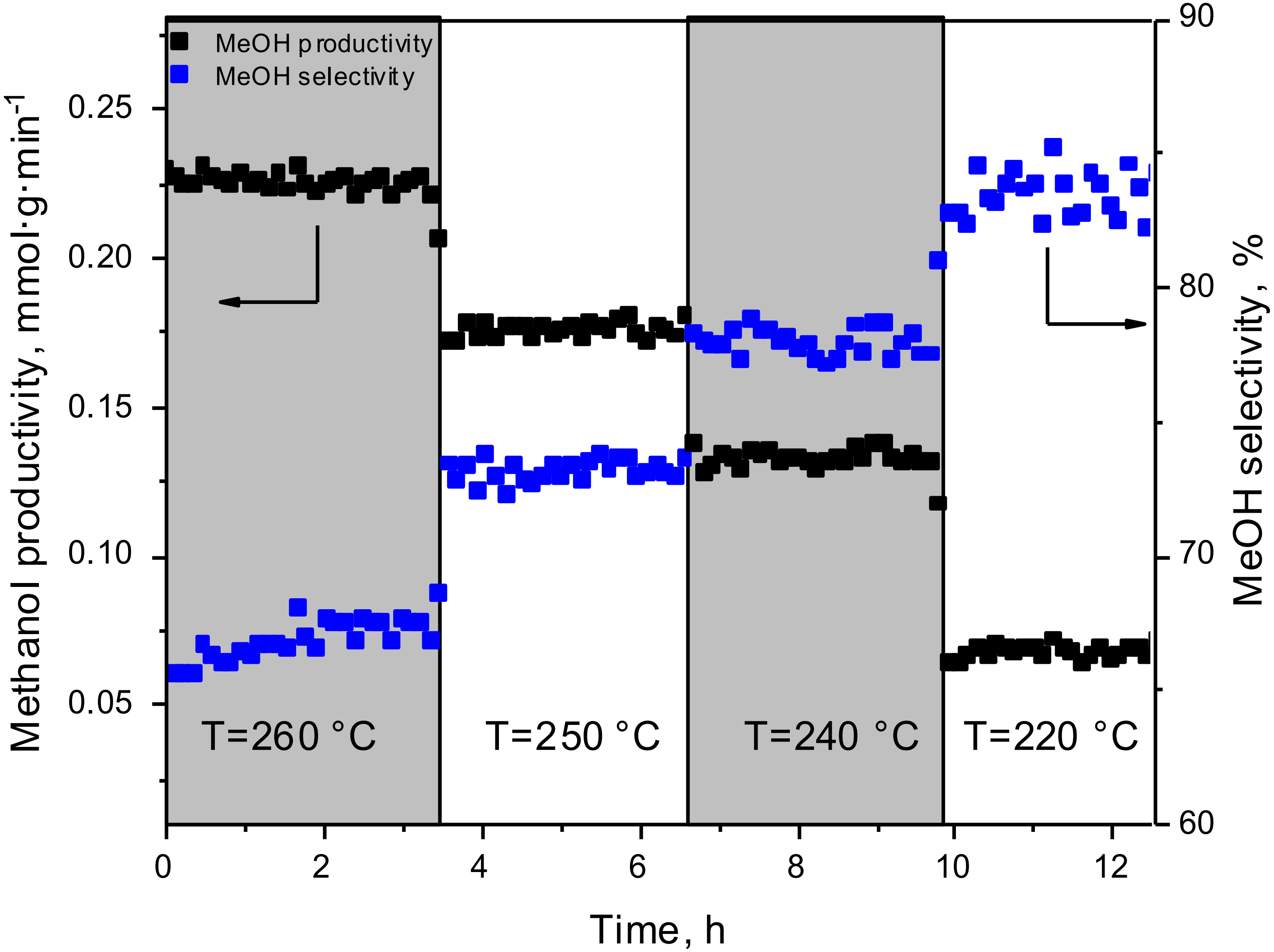
$$Pd(Acac)_2 + C_{17}H_{35}NH_2 + P(C_8H_{17})_3 \xrightarrow[\text{octadecene}]{250\,^\circ C} Pd$$





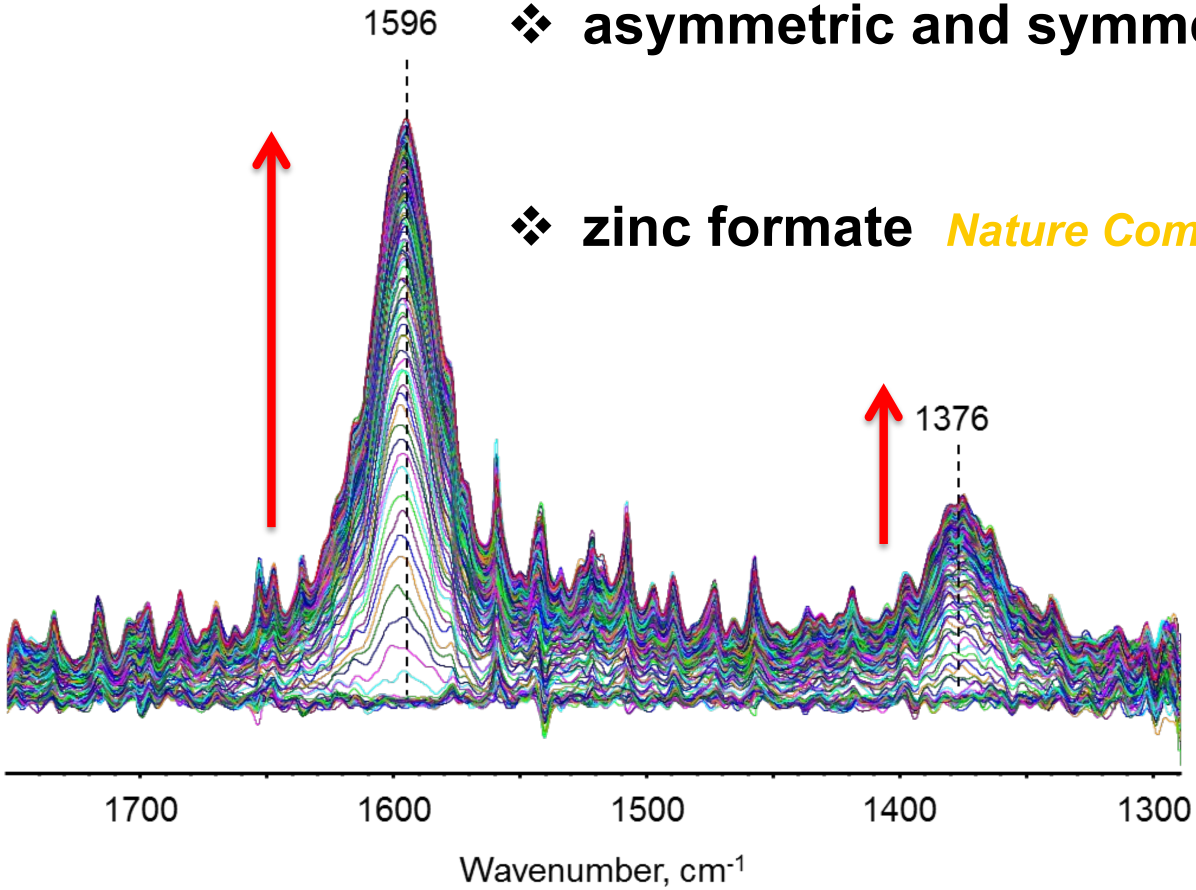
Catalytic carbon dioxide hydrogenation

Pd/ZnO is highly active and selective



50 bar, WHSV=120 $L \cdot g^{-1} \cdot h^{-1}$, $CO_2:H_2=1:3$

Switch from H2 to CO2/H2 mixture at 260° C and 15 bar



- ❖ **asymmetric and symmetric vibrations of formate**
- ❖ **zinc formate** *Nature Comm. 2020, 11, 2409*

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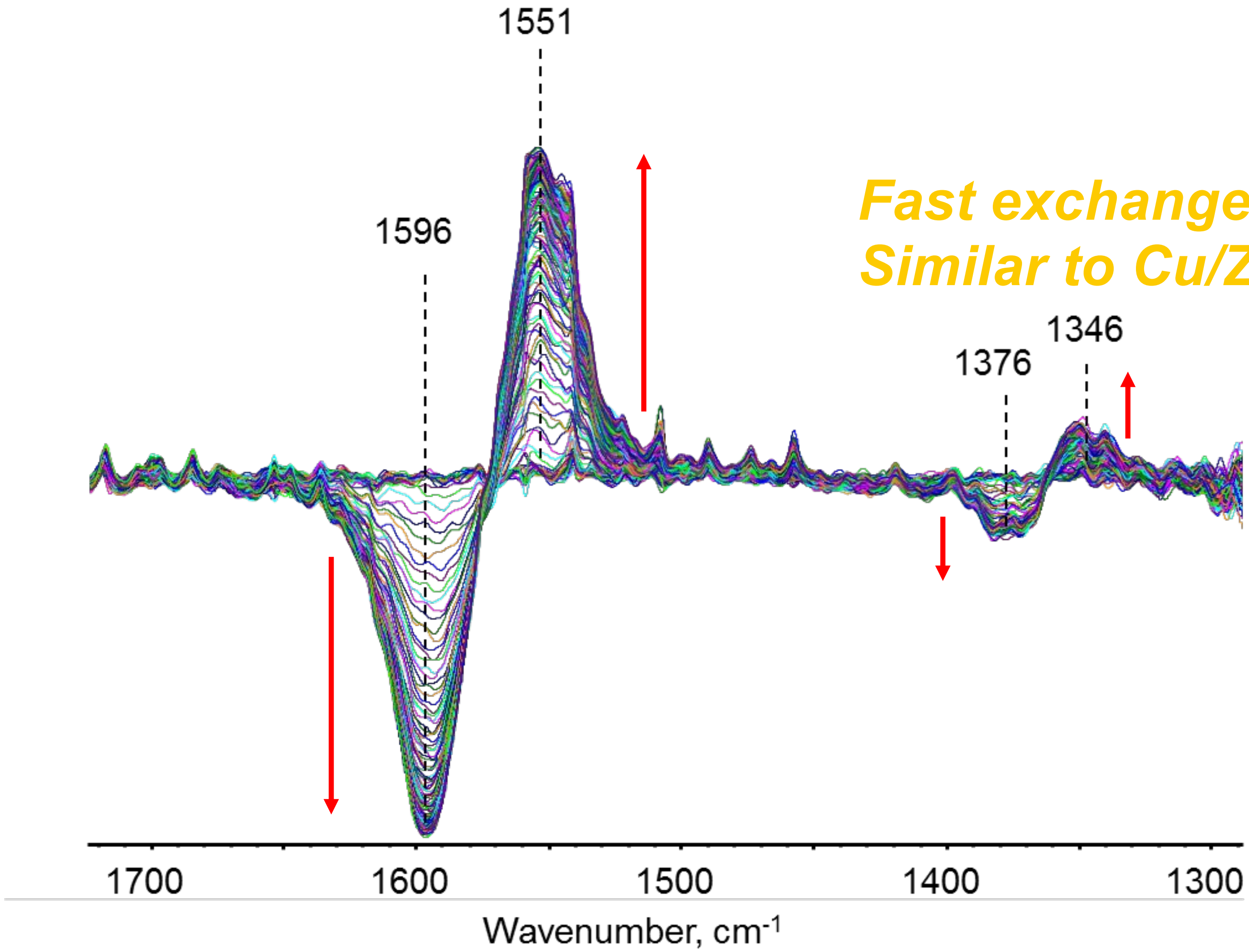
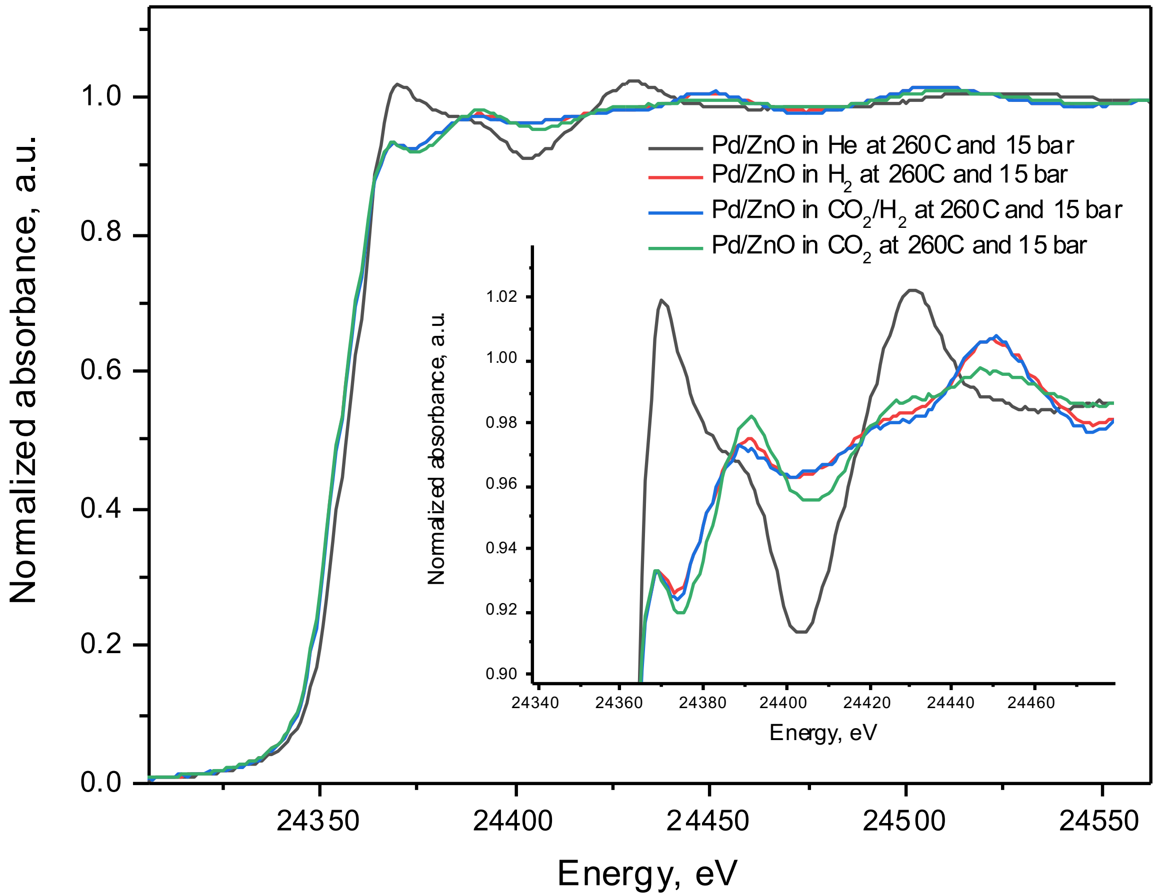
Isotope labeling experiment coupled with FTIR spectroscopy and MS analysis

Switch from a $^{12}CO_2/H_2$ to $^{13}CO_2/H_2$ at 260 ° C and 15 bar total pressure



Fast exchange of formates
Similar to $Cu/ZnO/Al_2O_3$

Operando XAS study of CO2 hydrogenation over Pd/ZnO catalyst

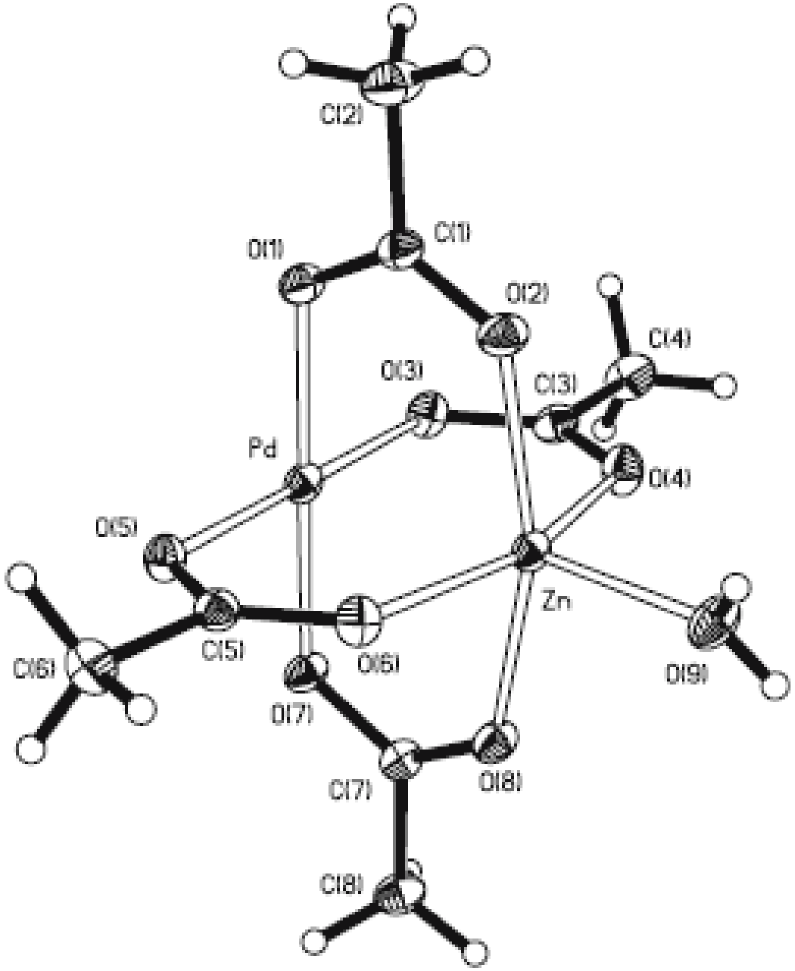


- **PdZn formation**
- **Alloy is stable during reaction**

PdZn on ZnO is the active material

Q. role of alloy vs zinc oxide

Supported PdZn catalysts



Decomposition of heterobimetallic $Pd^{II}Zn^{II}$ acetate bridge complex

$$PdZn \text{ (precursor)} \xrightarrow[150\text{-}250^{\circ}C]{5\text{-}10\%\ H_2/He} PdZn + 4\ CH_3COOH + H_2O$$

$PdZn/SiO_2$
$PdZn/Al_2O_3$
$PdZn/ZnO/SiO_2$

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Catalytic carbon dioxide hydrogenation

Catalyst	Carbon dioxide conversion, %	Methanol productivity, $g_{MeOH} \cdot kg_{cat}^{-1} \cdot hour^{-1}$	Methanol selectivity, %
PdZn/SiO_2	2.6	30	11.2
PdZn/Al_2O_3	4.4	27	6.0
PdZn/ZnO/SiO_2	3.6	184	49.8

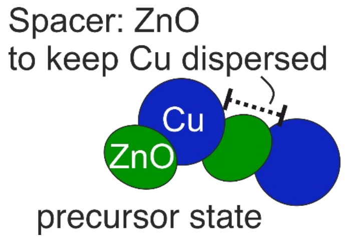
PdZn yields CO
PdZn/ZnO yields CH_3OH

Maxim Zabilskiy et al.
ACS Catalysis 10 (2020) 14240
ACIE 133 (2021) 17190

Catalytic experiments were performed at 260 ° C and 30 bar, catalyst mass: 100 mg, CO_2:H_2 ratio equals 1:3 and flowrate: 50 ml/min.

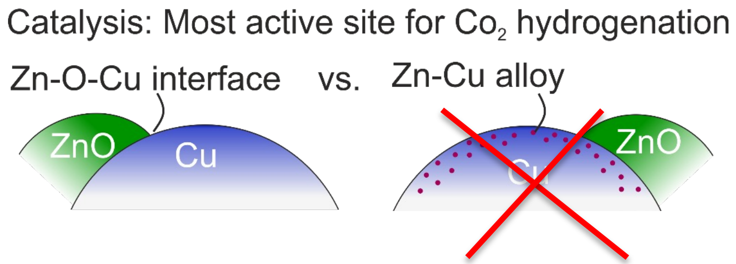
Take home message

Q. role of alloy vs zinc oxide



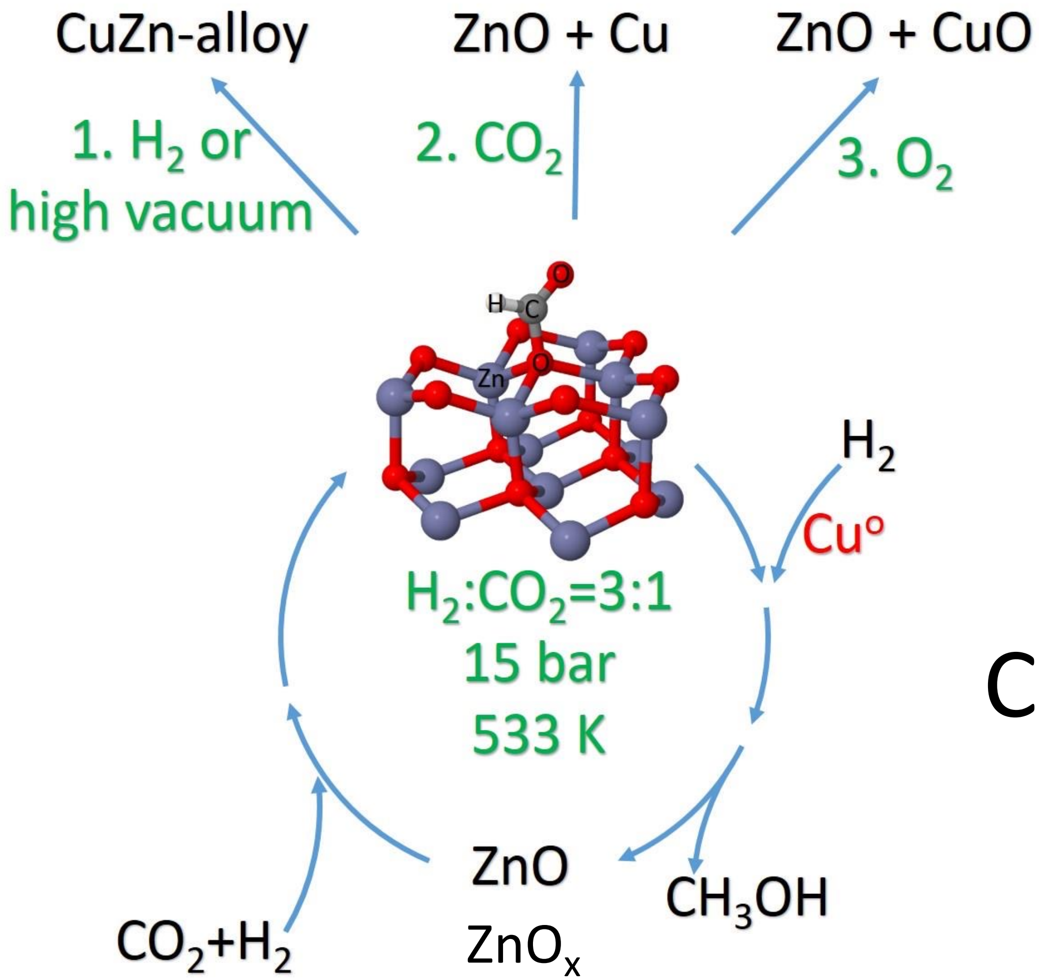
Alloy or not important?

- CuZn is unstable under reaction conditions
- PdZn is only selective in presence of zinc oxide



Zinc oxide induces selectivity to metanol

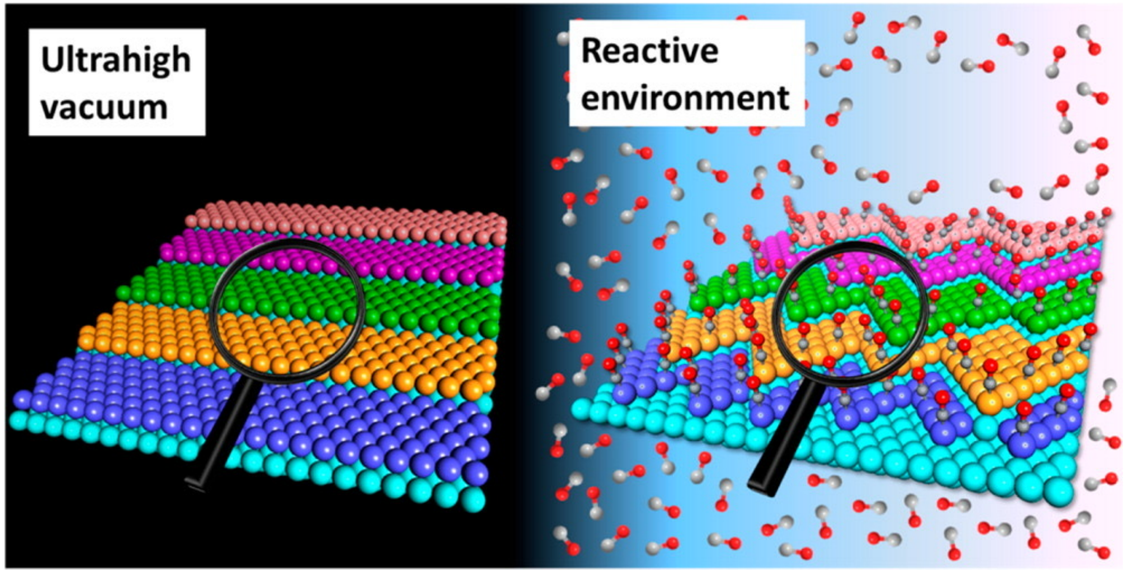
- stabilization of reactive intermediate (formate)


CuZn-alloy
ZnO + Cu
ZnO + CuO
1. H_2 or high vacuum
2. CO_2
3. O_2
H
C
O
Zn
H_2
Cu°
$H_2:CO_2=3:1$
15 bar
533 K
ZnO
ZnO_x
CH_3OH
CO_2+H_2

$Cu/ZnO/Al_2O_3$

In situ / operando spectroscopy

- Catalyst structure is a function of its environment
- Only structure measured under reaction conditions can give insight into activity
- Conversion changes the gas environment



Shiran Zhang *et al.* *Acc. Chem. Res.* 2013, 46, 1731-1739.

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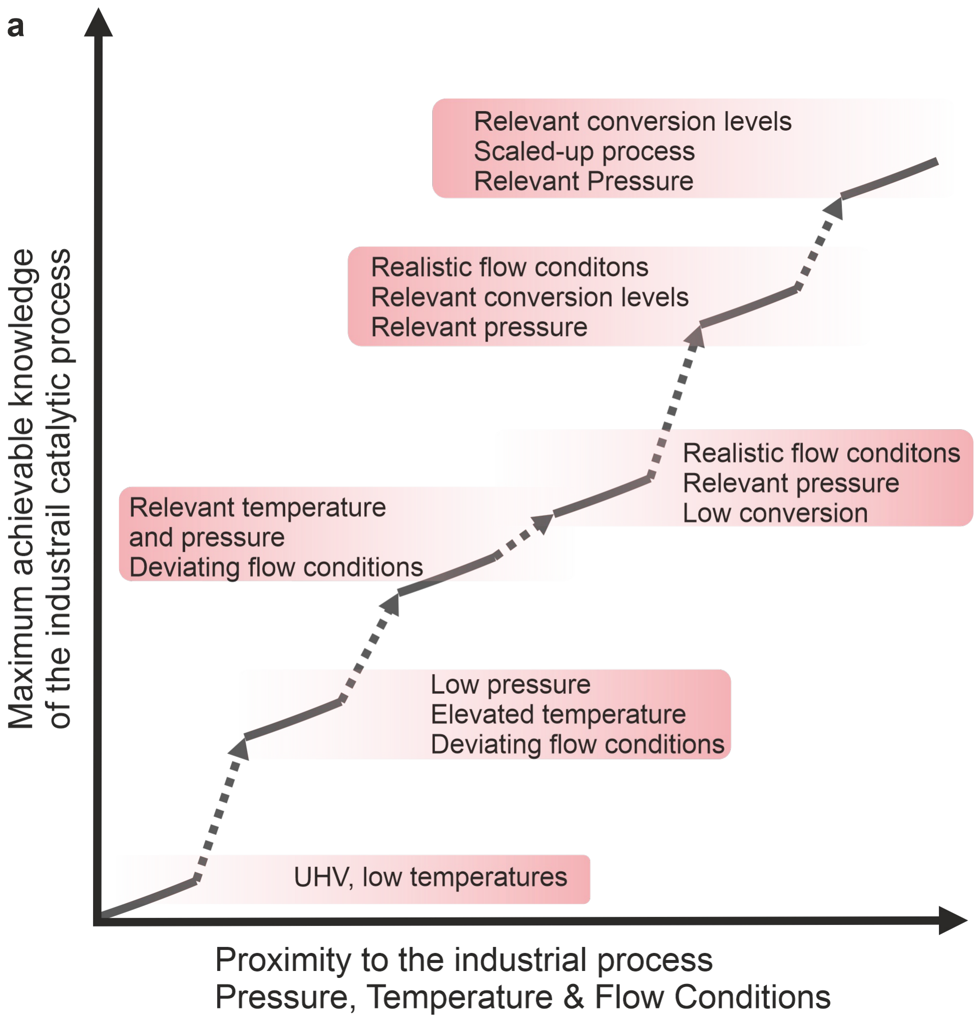

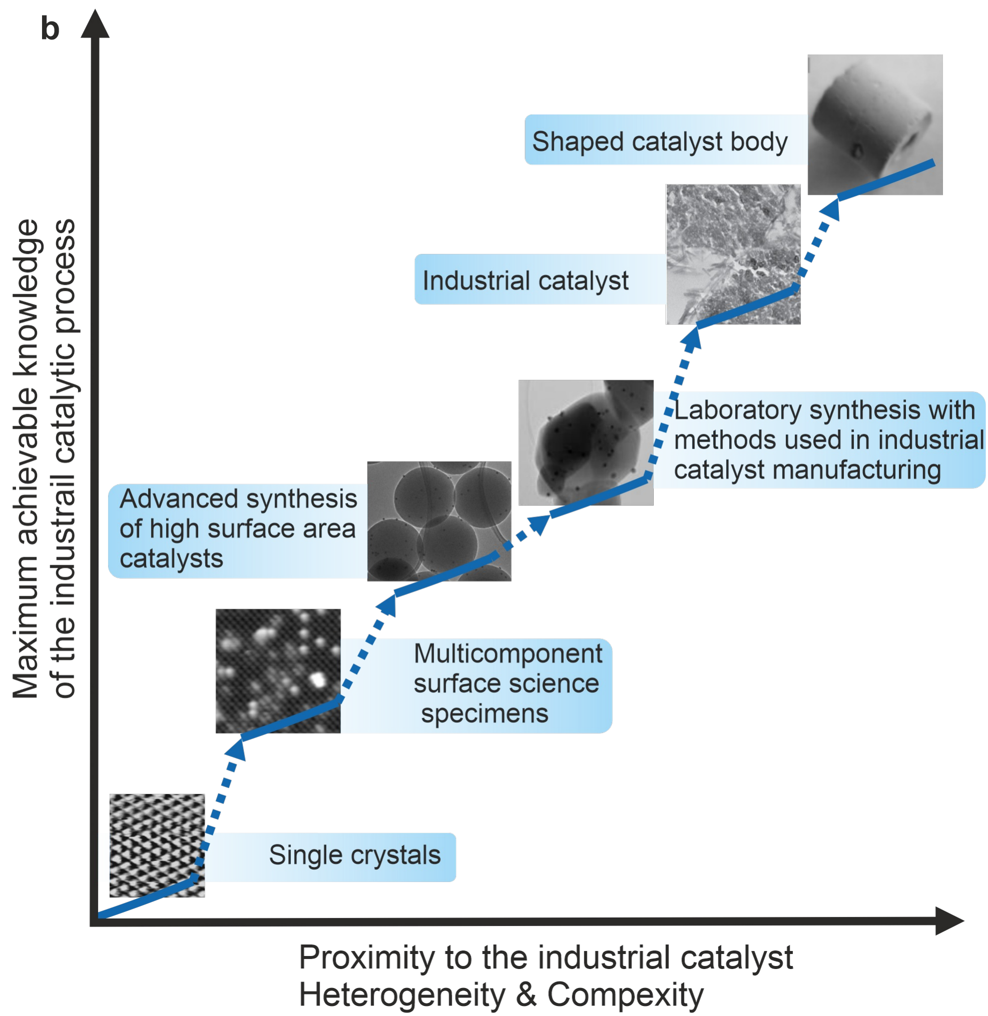

Be very careful with extrapolation of your results

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Acknowledgements

Maxim Zabilskiy
Arik Beck

Mark Newton
Vitaly Sushkevich
Dennis Palagin

Leon van de Water — *Johnson Matthey*
Gerhard Mestl — *Clariant*

Marc Willinger — *TUM*
Frank Krumeich
Maarten Nachtegaal
Olga Safonova

Funding

- *Swiss National Science Foundation*
- *ETHzurich*
- *Paul Scherrer Institute*

Beam lines

- SNBL at ESRF
- SuperXAS at SLS