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Membrane-assisted Ethylene Synthesis over Nanostructured Tandem Catalysts

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From Waste to Resource: Catalytic Strategies for CO_2 Valorization

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Fritz-Haber-Institut der Max-Planck-Gesellschaft
Berlin, Germany

International Workshop on Sustainable & Circular Technologies
Eindhoven Nov 2025

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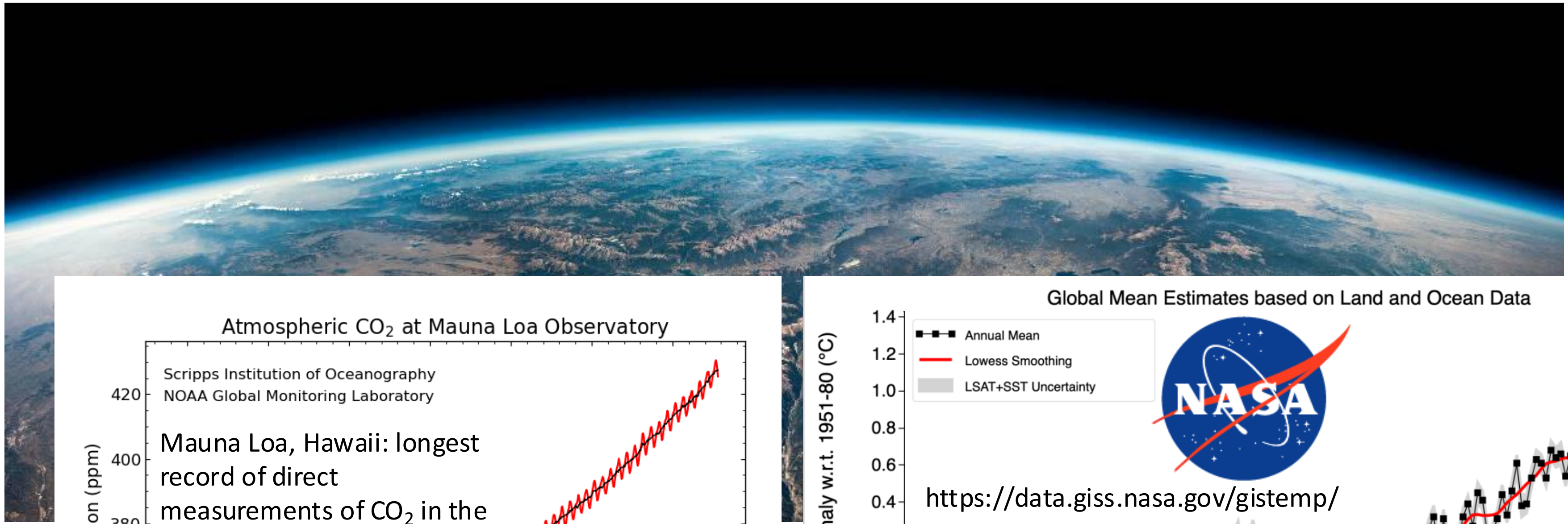
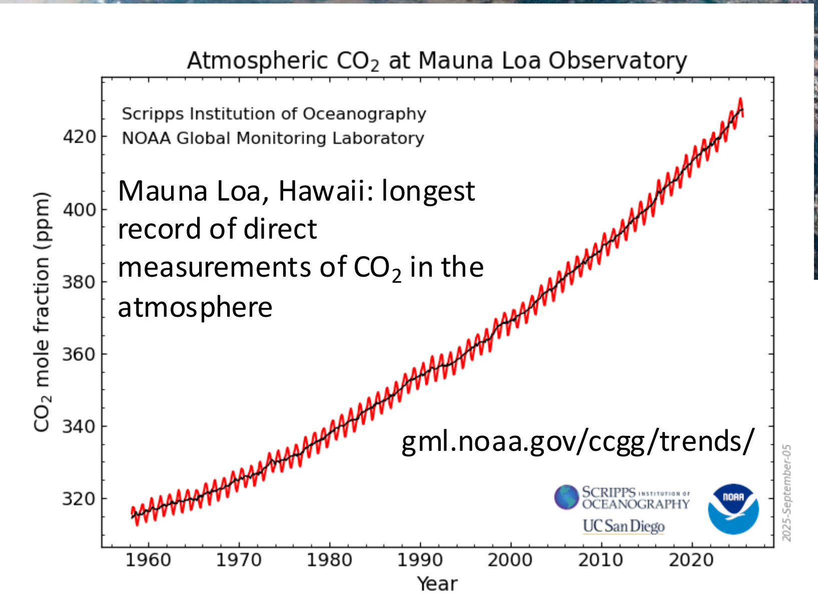
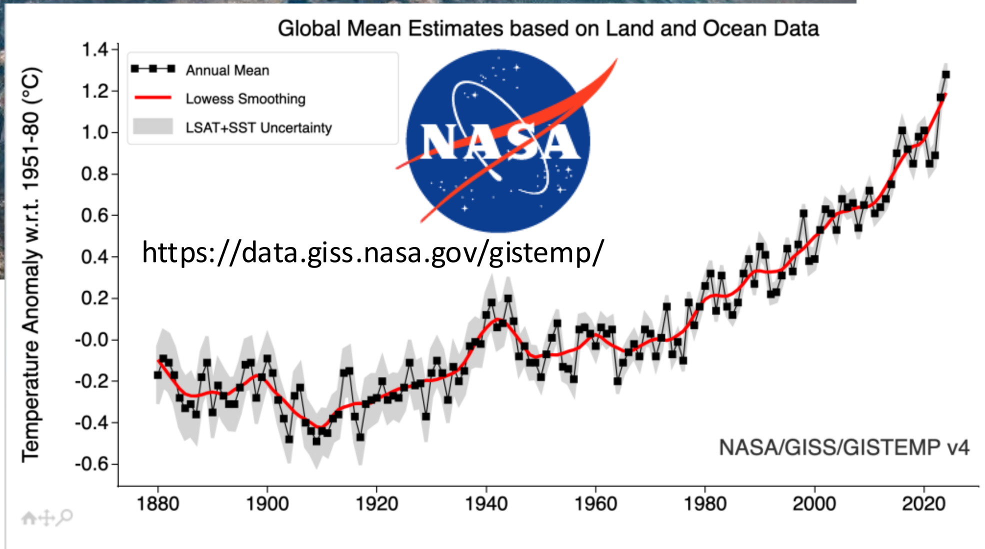
Global warming & greenhouse gases





C.D. Keeling, R.B. Bacastow, A.E. Bainbridge, C.A. Ekdahl, P.R. Guenther, and L.S. Waterman, (1976), *J. Geophys. Research,* vol. 94, 8549-8565



Land-ocean temperature index, 1880 to present, with base period 1951-1980. The solid black line is the global annual mean and the solid red line is the five-year lowess smooth. The gray shading represents the total (LSAT and SST) annual uncertainty at a 95% confidence interval and is available for download. [More information on the updated uncertainty model can be found here: Lenssen et al. (2019).]

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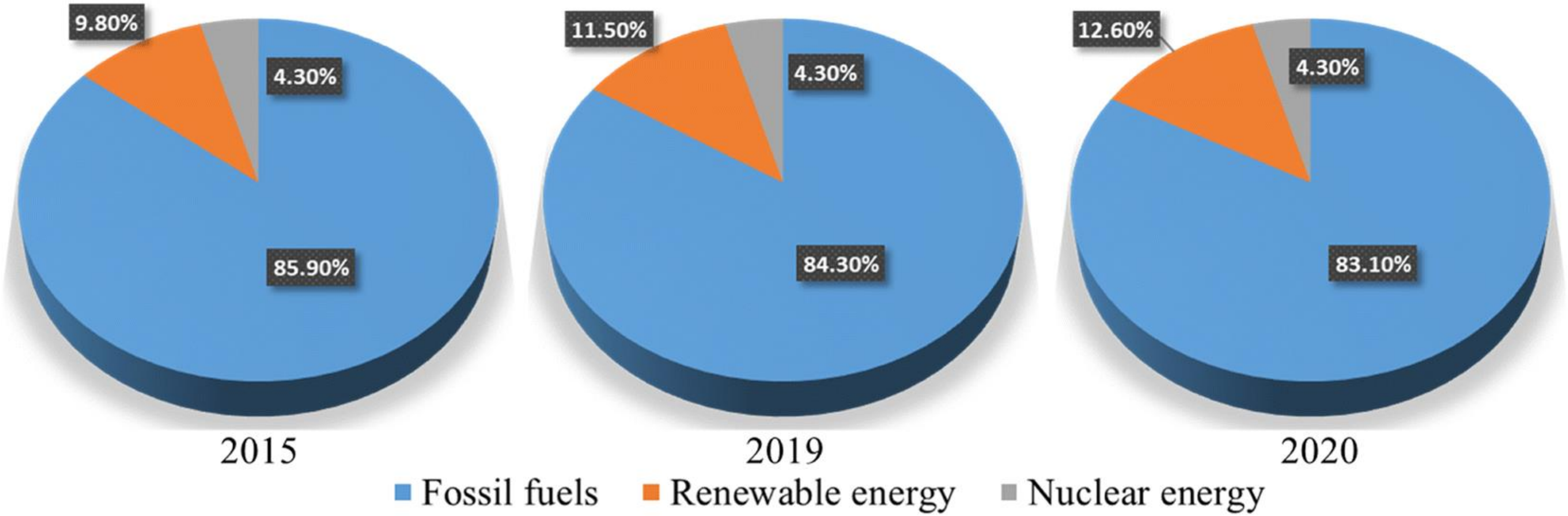
Slow transformation of the global economy

Proportion of different types of global primary energy consumption



Zhang, Y.; Zhao, S.; Li, L.; Feng, J.; Li, K.; Huang, Z.; Lin, H. Integrated CO2 capture and utilization: a review of the synergistic effects of dual function materials. *Catalysis Science & Technology* **2024**, *14* (4), 790-819, 10.1039/D3CY01289A. DOI: 10.1039/D3CY01289A.

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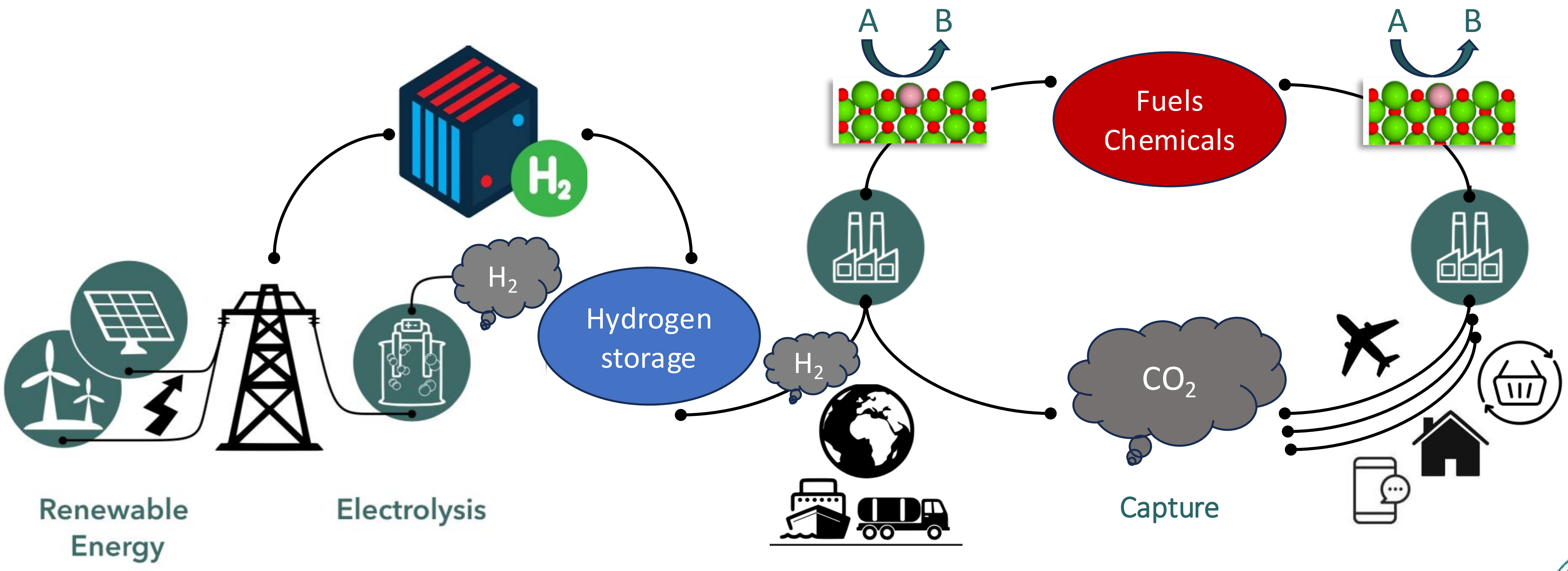
Catalysis as a key technology in a circular economy



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MEMCAT: Transformation of CO_2 to value-added products in tandem reactions

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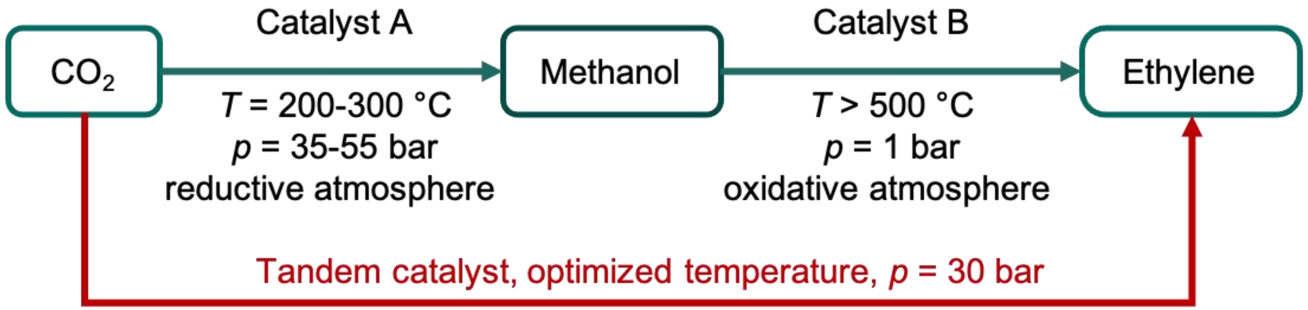
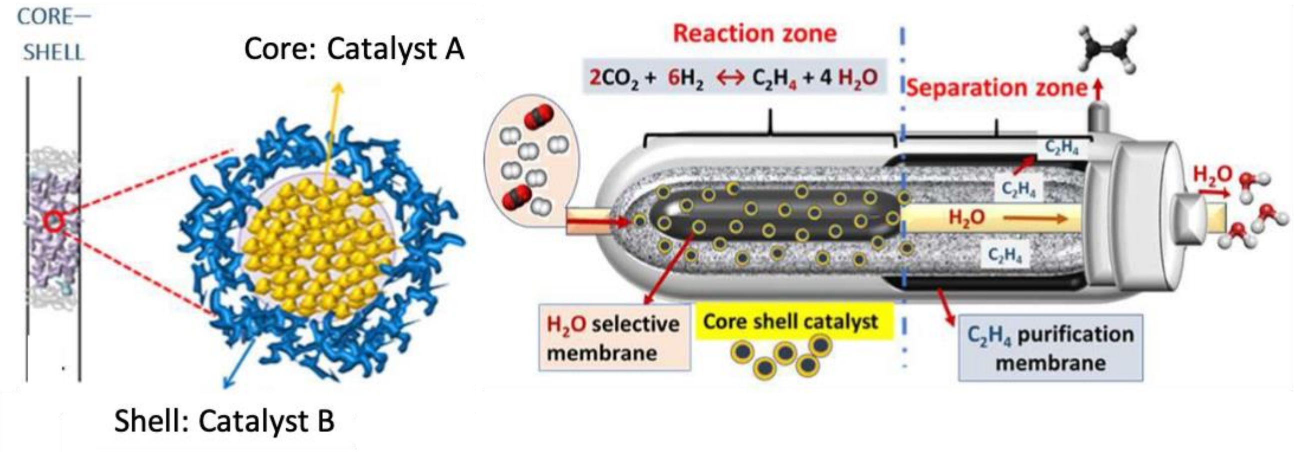
- Design of core-shell catalysts for one-step CO_2-to-ethylene conversion
- Optimization of process conditions
- Combination of catalyst and membrane technology to separate water (shift equilibrium) and ethylene (product purification)





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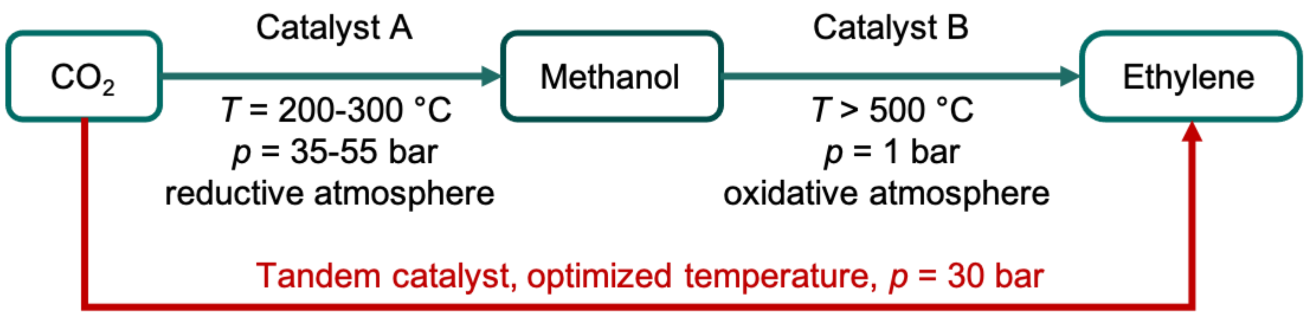
MEMCAT: Transformation of CO_2 to value-added products in tandem reactions

- Synthesis and testing of core-shell catalysts
- Optimization of process parameters
- Rational design of the catalysts using insights from spectroscopic characterization and theory



$Cu/ZnO/Al_2O_3$
ZnO/ZrO_2

- Analysis of surfaces and interfaces

US-Y
ZSM-5
SSZ-13
SAPOP-34

- Acidity characterization

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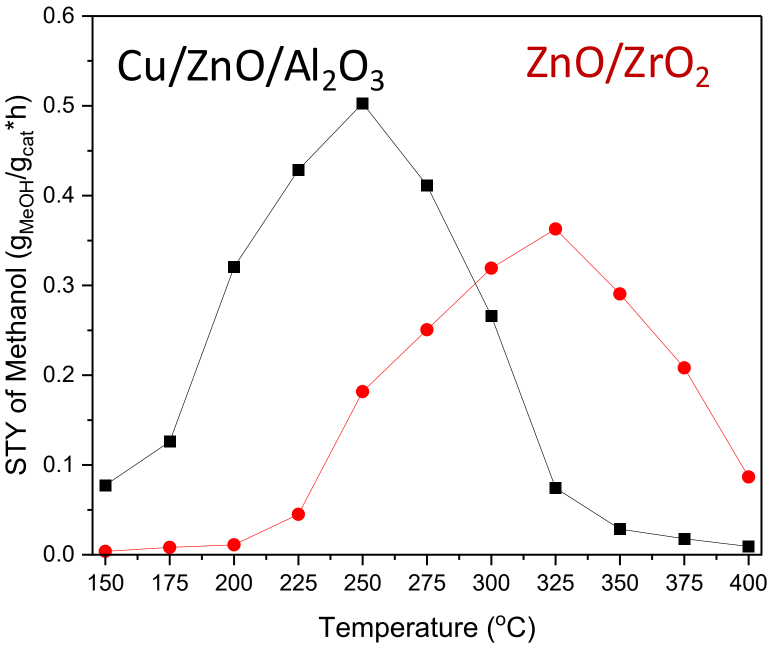
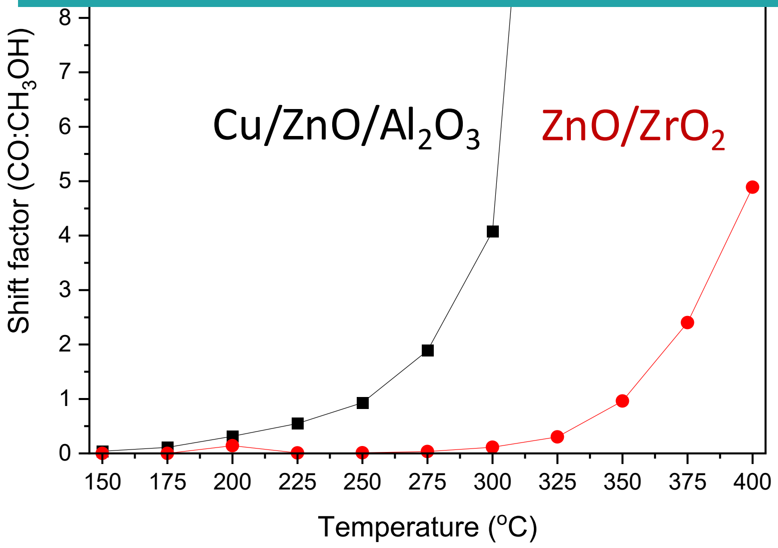
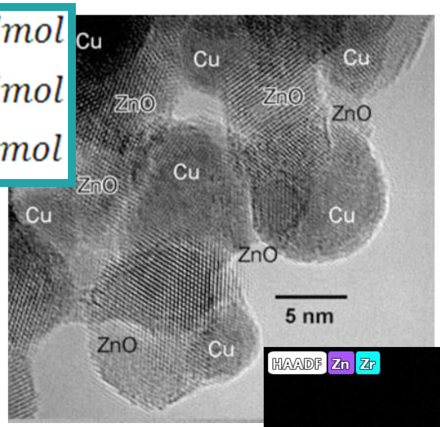
Methanol synthesis from CO_2

Cu/ZnO/Al_2O_3 is the industrial standard for methanol synthesis - Synergy between Cu and ZnO

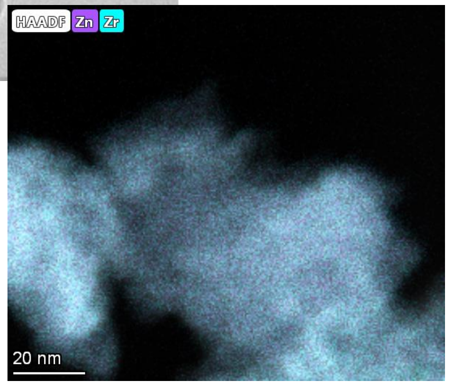
$$CO_2 + 3H_2 \rightleftarrows CH_3OH + H_2O \quad \Delta H_0 = -49.8\ kJ/mol$$
$$CO_2 + H_2 \rightleftarrows CO + H_2O \quad \Delta H_0 = +41.2\ kJ/mol$$
$$CO + 2H_2 \rightleftarrows CH_3OH \quad \Delta H_0 = -91.0\ kJ/mol$$







Angew. Chem. 2007, 119, 7465.



→ CO formation reduces the methanol yield at higher temperatures (favoured by thermodynamics)

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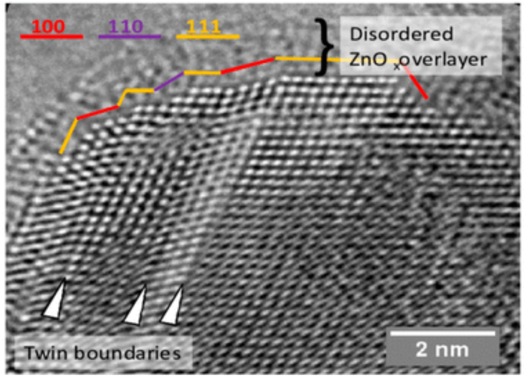
Reaction mechanism and active sites on $Cu/ZnO/Al_2O_3$

Science **2012**, *336* (6083), 893– 897

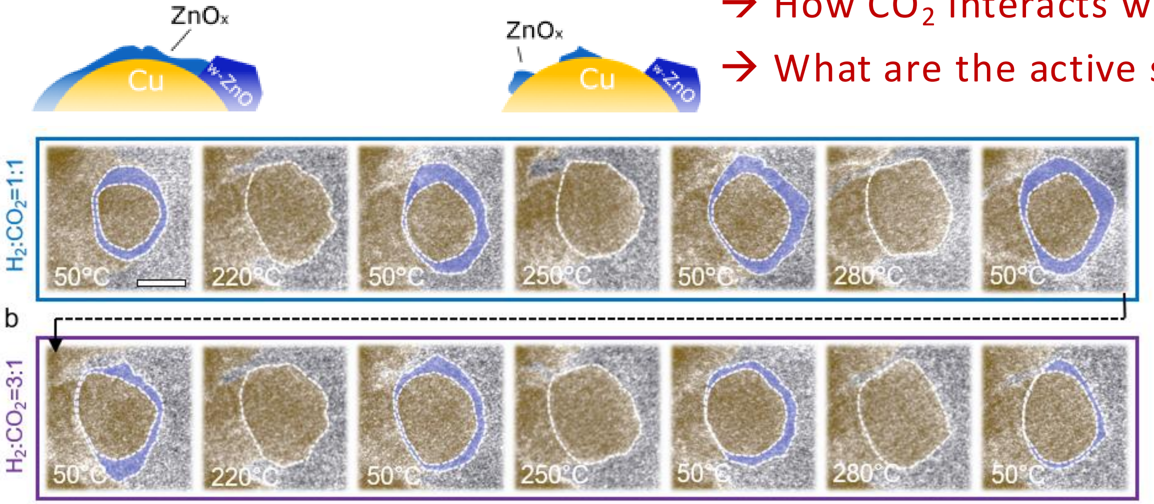


- Formate hydrogenation is the rate-determining step of methanol synthesis from CO_2
- Dynamic catalyst - structure continuously changes under reaction conditions
- Cu-ZnO interface determines performance

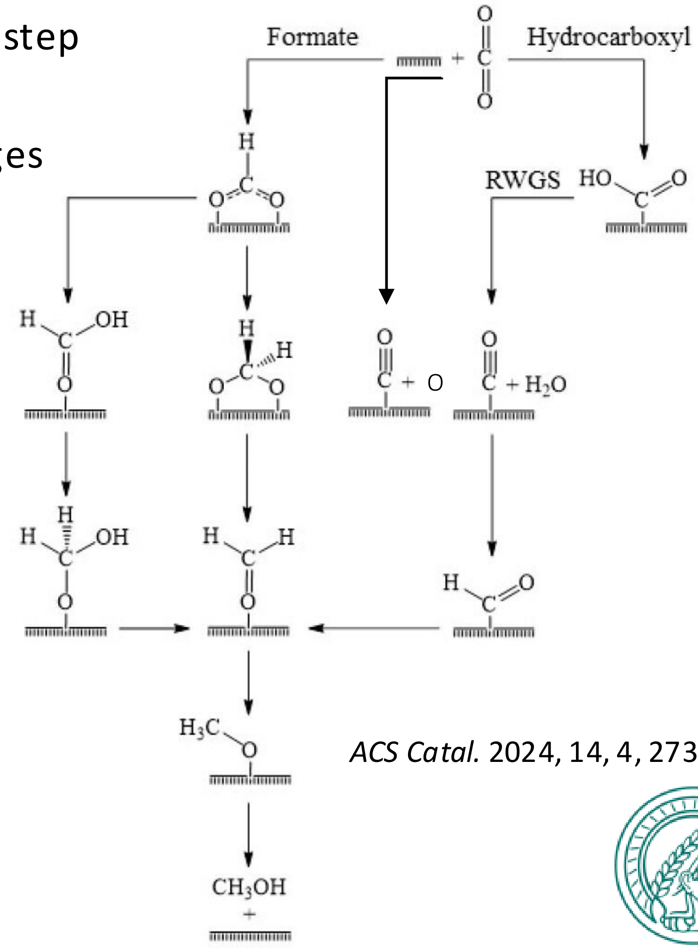
→ Kinetic control of selectivity

→ How CO_2 interacts with the surface

→ What are the active sites?



Boniface, Lunkenbein, under review.



ACS Catal. 2024, 14, 4, 2730–2745.

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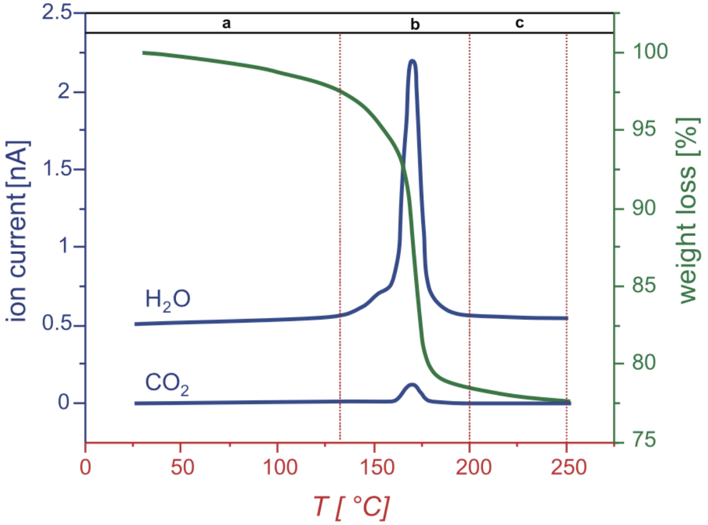
Reductive pretreatment

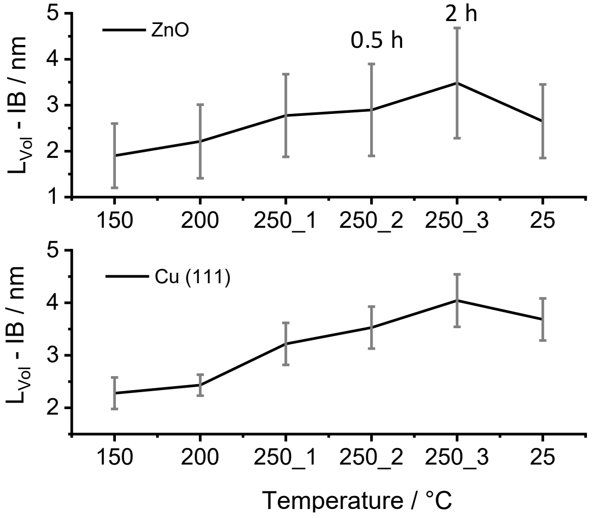
Restructuring of the ZnO phase and formation of the Cu-ZnO interface

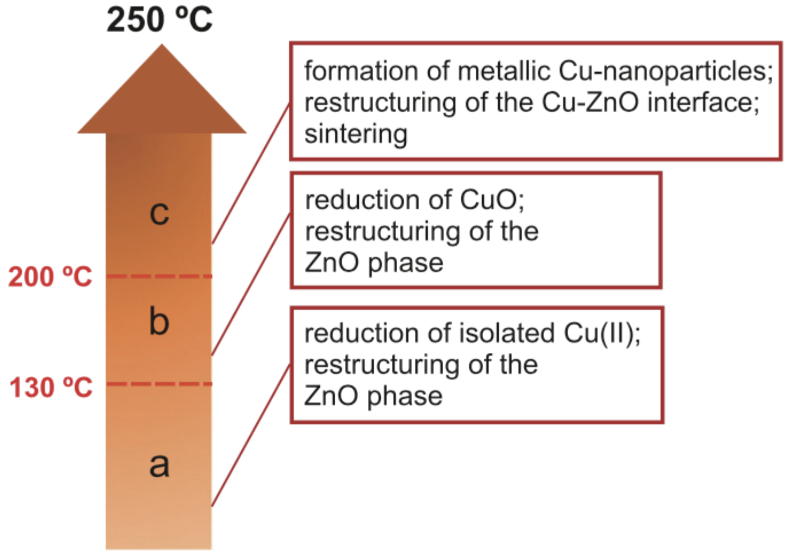
Temperature-programmed reduction



Angew. Chem. Int. Ed. **2025**, *64*, e202504280.

In-situ XRD





Angew. Chem. Int. Ed. **2025**, *64*, e202504280.

- Reduction is taking place between 130 °C and 200°C
- ZnO and Cu particles are sintering at 250°C

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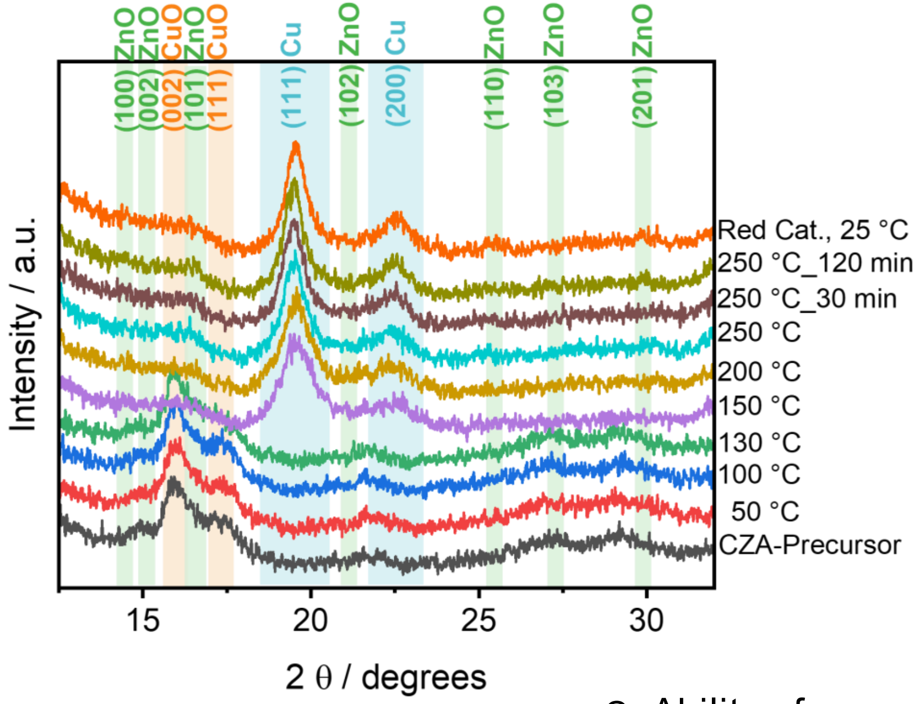
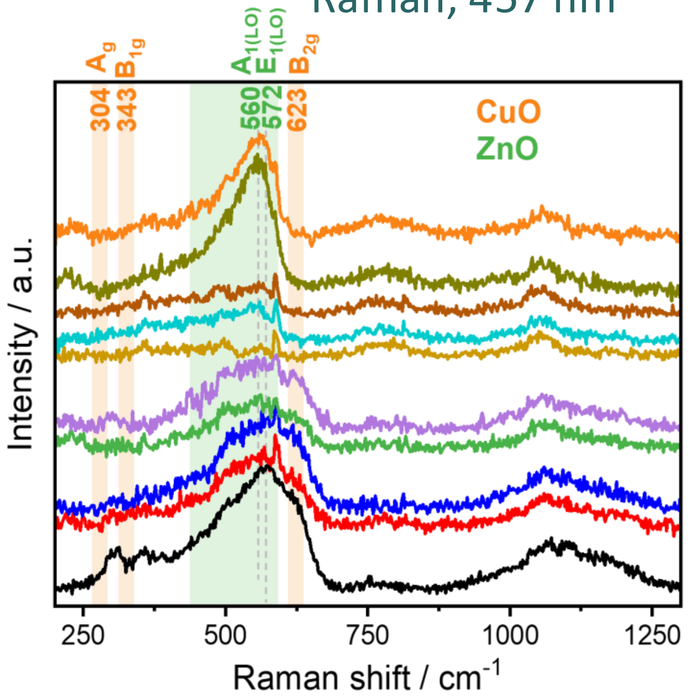
Reductive pretreatment

Restructuring of the ZnO phase and formation of the Cu-ZnO interface

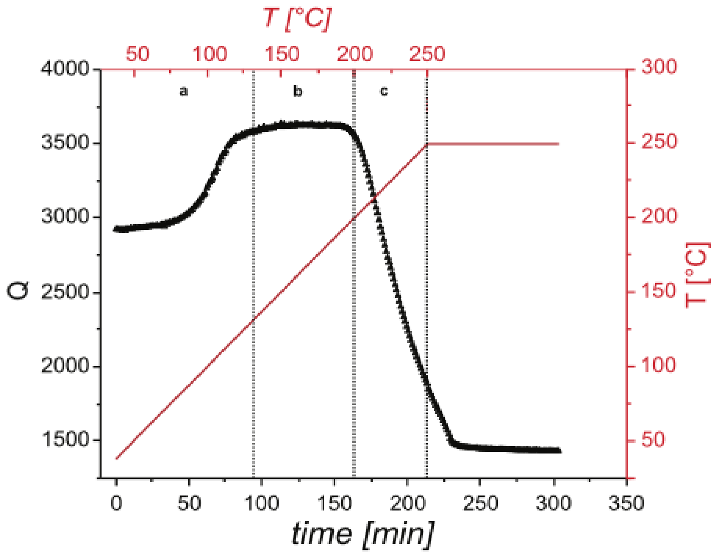
In-situ XRD



Raman, 457 nm



Microwave Cavity Perturbation Technique (MCPT)



- Q: Ability of a resonator to store energy → dielectric loss properties of a sample
- The evolution of the electronic properties of the catalyst requires at least 30 min at 250°C in H_2

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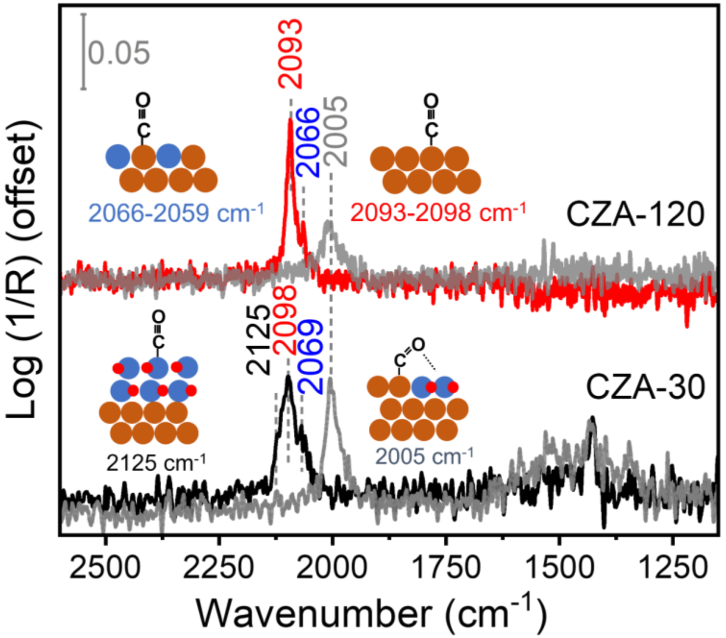
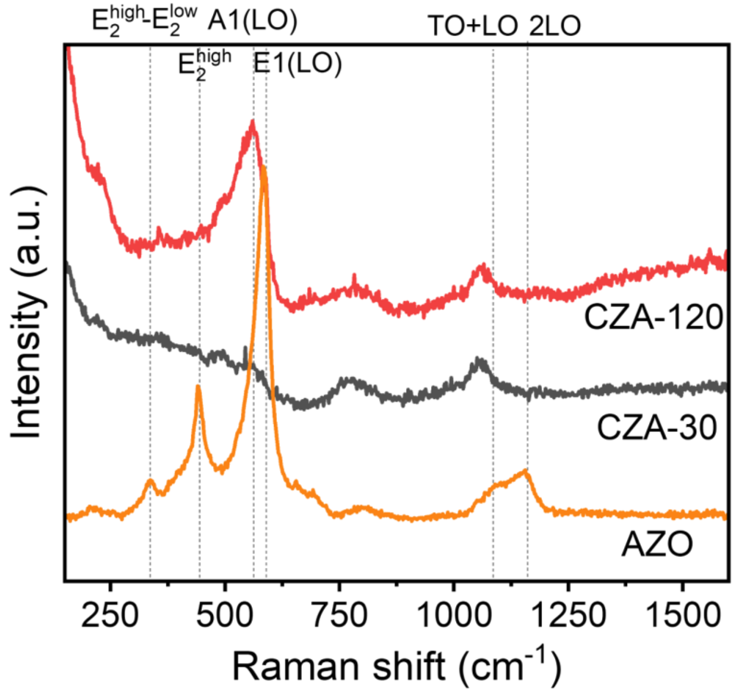
The reduced catalyst

From amorphous and graphite-like ZnO to more crystalline, wurzite-type ZnO

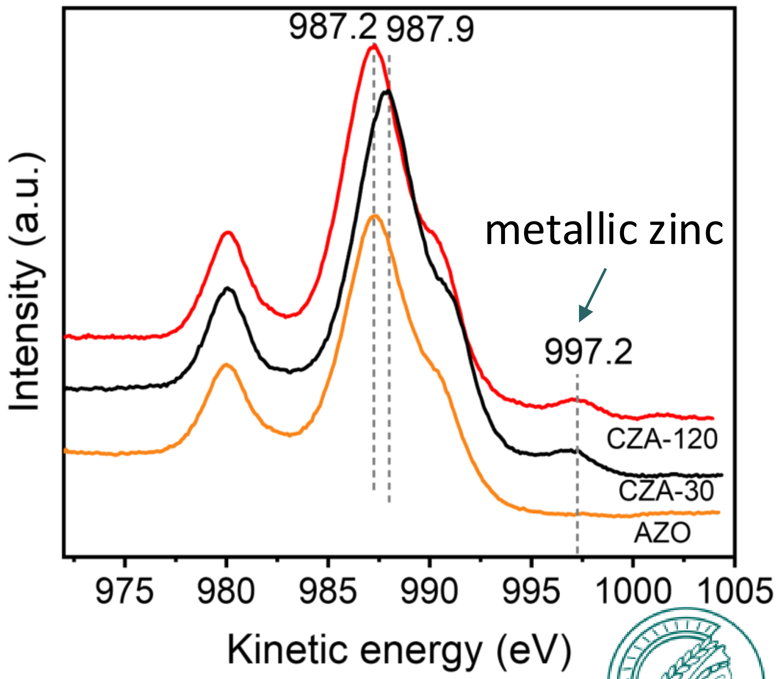
CO-DRIFTS



Raman, 457 nm



Auger Spectroscopy (Zn LMM)



- Defect structure of Al-doped ZnO is modified in the presence of Cu and the process depends on the reduction time
- The reduction time also determines the coverage of Cu with ZnO, i.e., the nature of the interface

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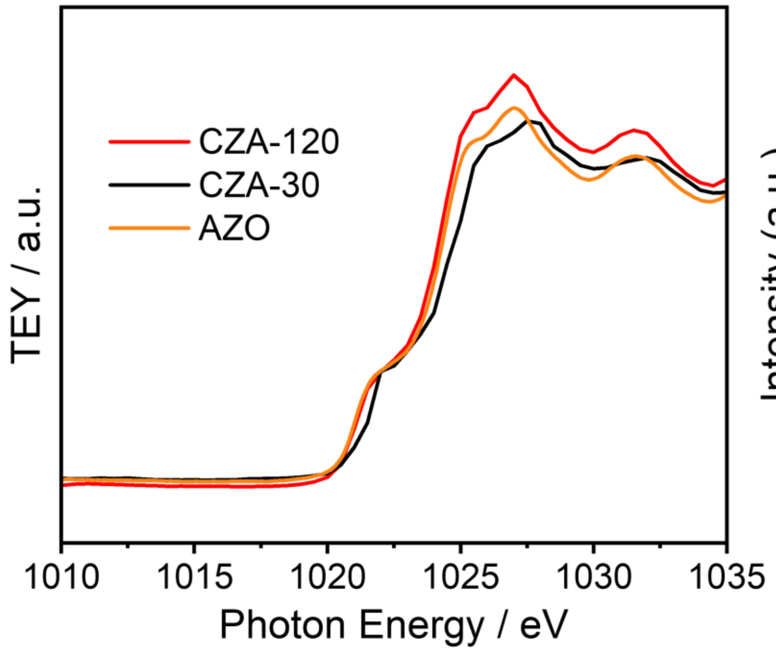
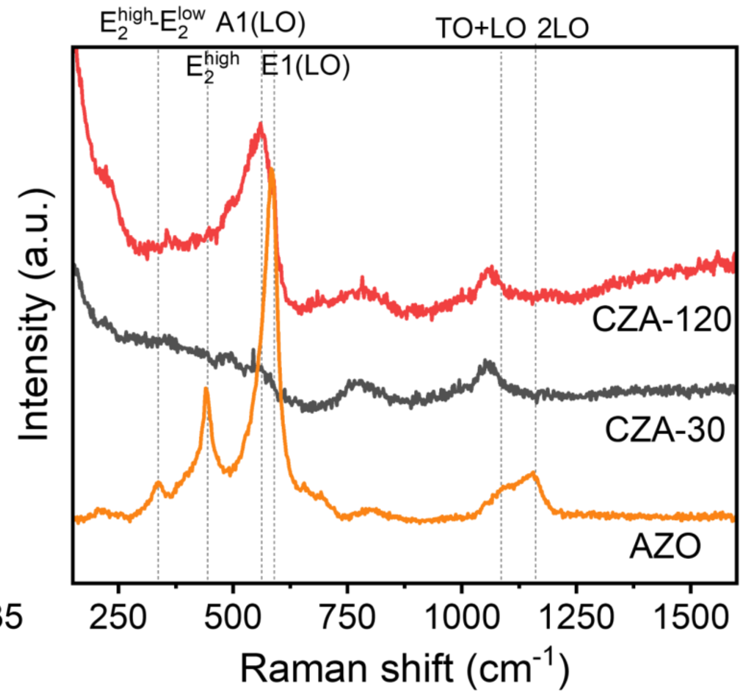
The reduced catalyst

Impact of Cu on the defect structure of ZnO

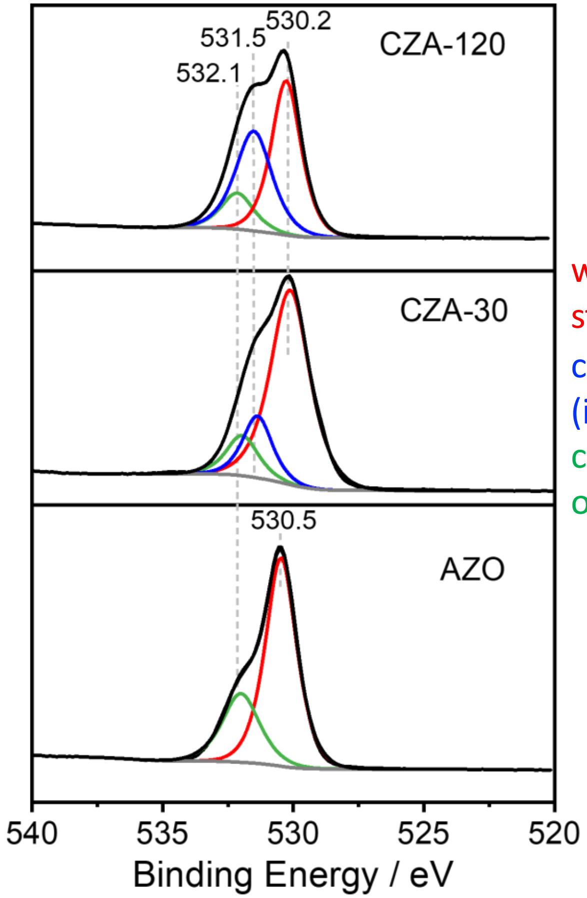
Zn L edge at 250 °C



Raman



XPS O 1s



wurzite structure
close to Zn (interstial)
close to an oxygen vacancy

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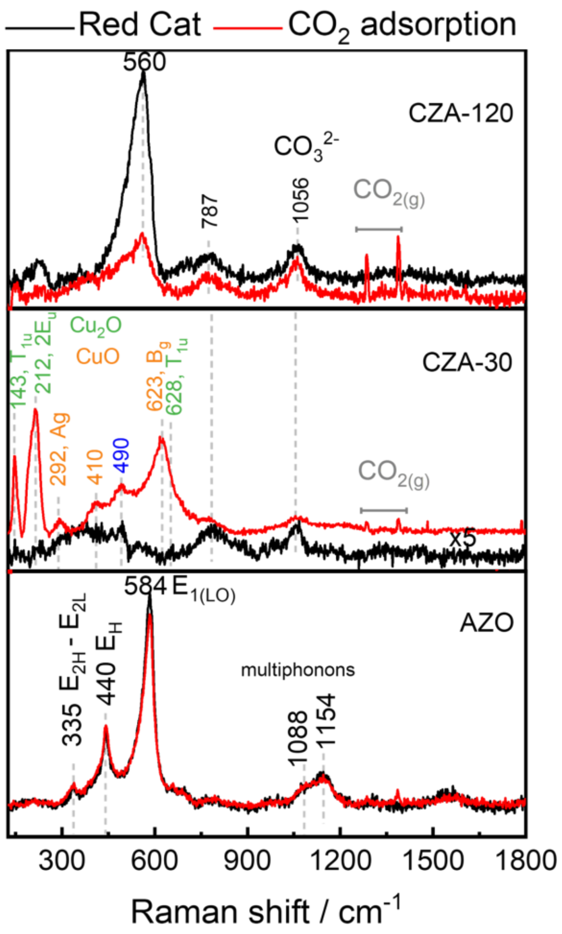
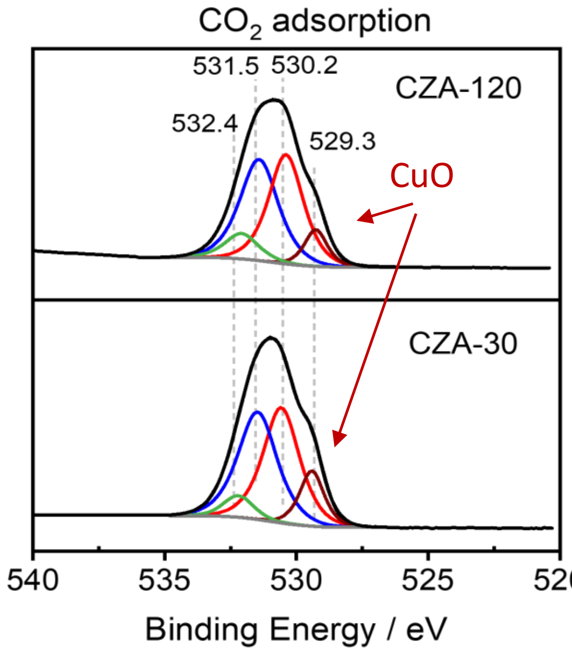
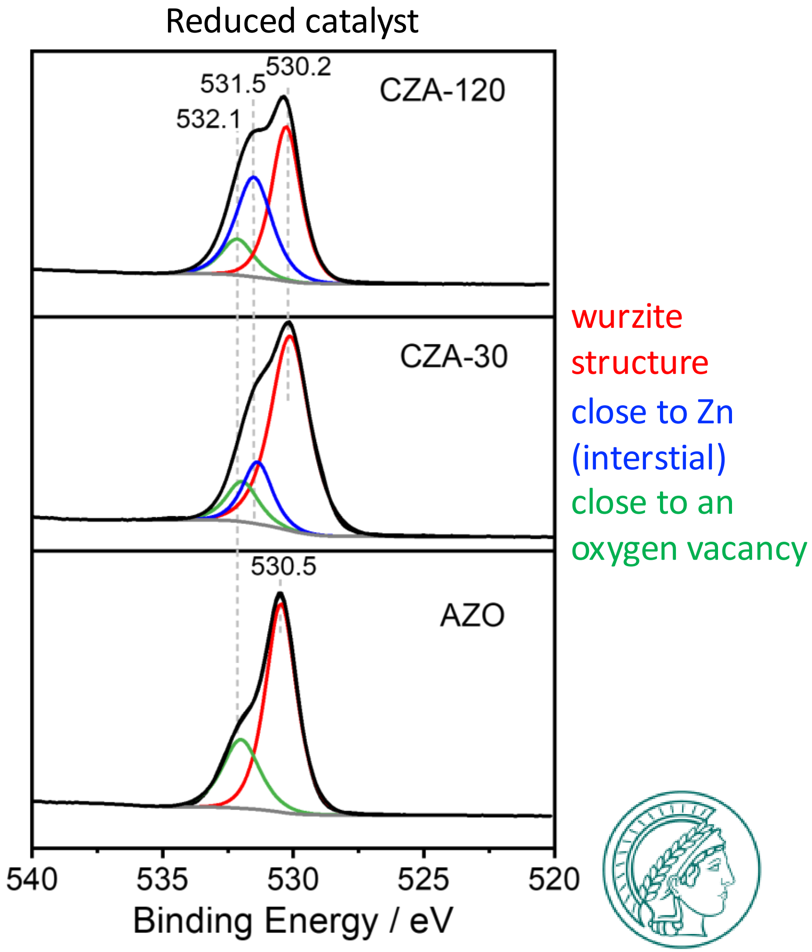
CO_2 adsorption at 300 K



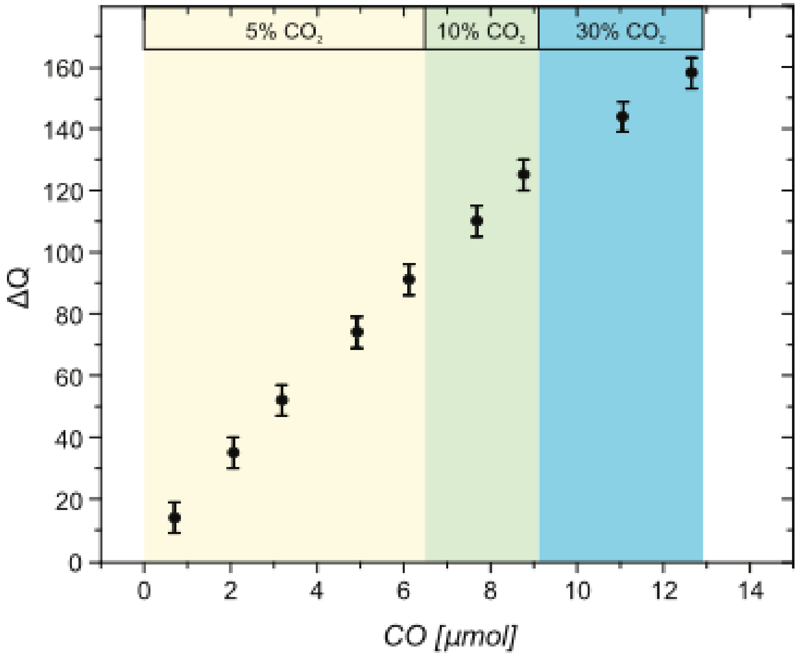




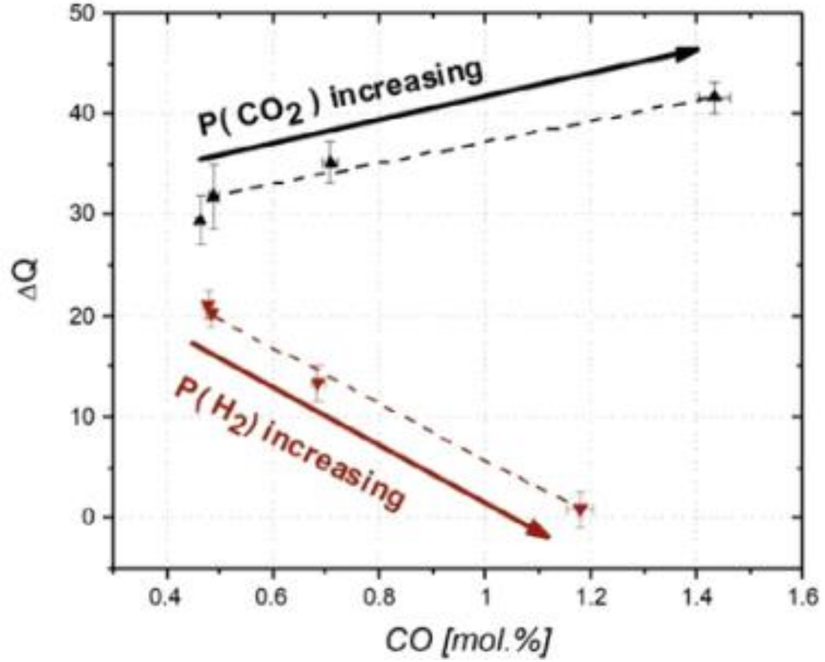
- Oxidation of Cu at room temperature
- Disappearance of the band due to defective ZnO
- No CO in the gas phase detectable

CO_2 adsorption and feed at 500 K

CO_2/N_2 flow



Feed, varying CO_2/H_2 ratios



Angew. Chem. Int. Ed. **2025**, *64*, e202504280.

- Changes in the dielectric losses observed as a function of the partial pressures of both reactant gases are linearly correlated with the yield of CO in the r-WGS reaction → transient uptake of oxygen (1 mol%) → redox mechanism
- The sites for hydrogen and carbon dioxide activation do not compete kinetically

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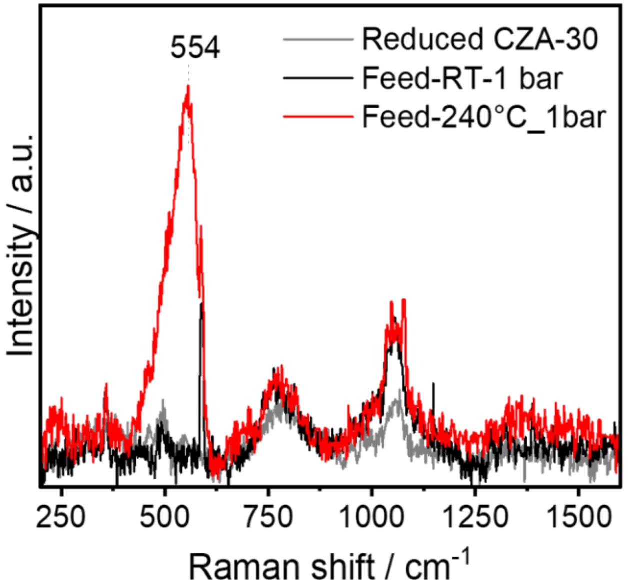
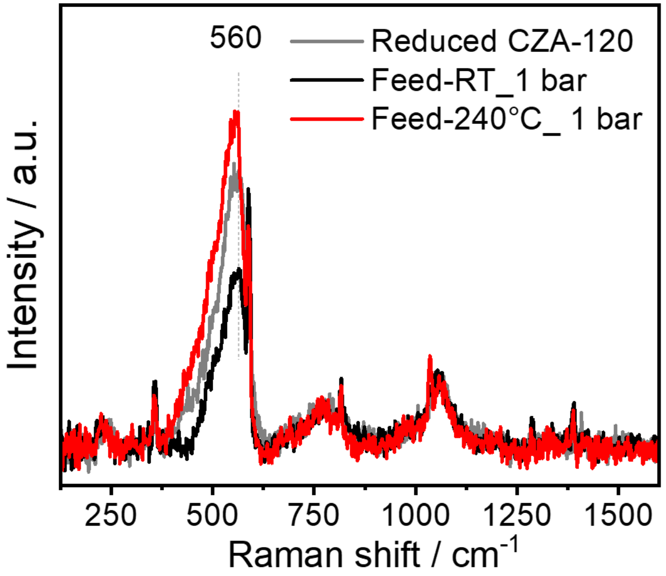
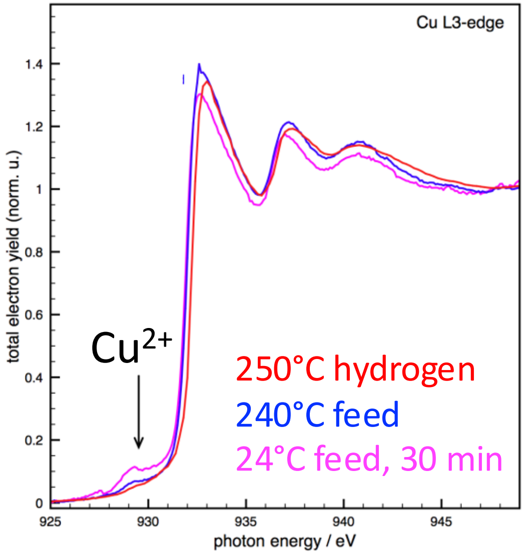
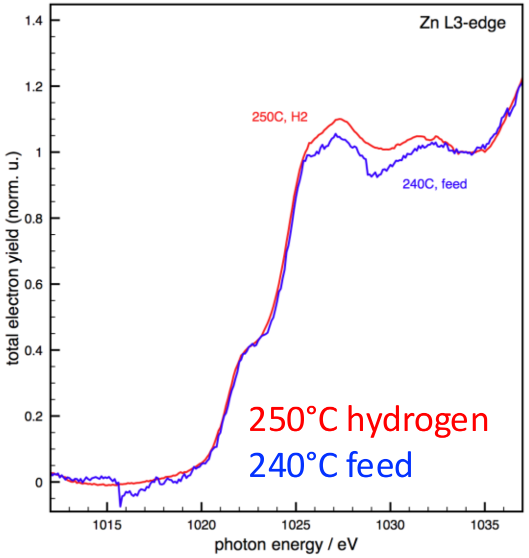
The working catalyst

Differences observed after different reduction treatments disappear









- Partial oxidation of Cu in the feed at 240°C, small O deficit
- Cu enrichment near the surface under reaction conditions
- Progressive crystallization of ZnO

Journal of Solid State Chemistry **2022**, *316*, 123567.

Cu/Zn ratio: 4 after reduction

3.5 in feed

M/O ratio: 0.98 in feed

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Conclusions and outlook

- Complex activation protocols are required to arrive at a high-performance $Cu/Zn/Al_2O_3$ catalyst as chemical transformation is necessary but not sufficient to establish a functional system
- The differences after different reductive treatments are balanced out under reaction conditions
- The r-WGS reaction on $Cu/Zn/Al_2O_3$ proceeds according to the redox mechanism
- The amount of oxygen, which can be stored in a reduced ZnO:Al sample by reaction with CO_2, is considerably smaller than for the CZA catalyst,* suggesting either a direct contribution of the Cu particles to CO_2 reduction or the role of Cu particles in promoting ZnO as a catalyst for r-WGS reaction
- The influence of Cu on the nanostructure of ZnO is being further investigated through systematic Raman experiments in which the chemical potential is varied (temperature, water vapour); The results are compared with the insights from modelling (University of Jyväskylä)

J. Phys. Chem. C*, **2025, *129*, 18841–18854.

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Membrane-assisted Ethylene Synthesis over Nanostructured Tandem Catalysts

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M6 Consortium Meeting
Eindhoven, 2024-11-20

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