



# Membrane-assisted Ethylene Synthesis over Nanostructured Tandem Catalysts



## Identification of Active Sites for CO<sub>2</sub> conversion on ZnO/Cu(III) Catalysts

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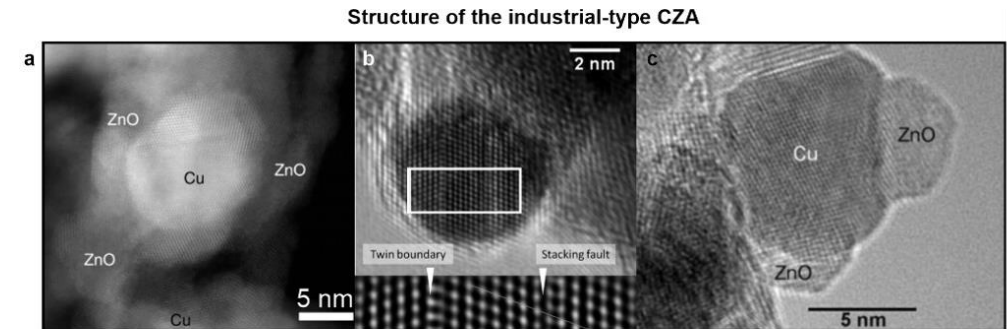
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UNIVERSITY OF JYVÄSKYLÄ

## Methanol synthesis on Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> (CZA) catalyst

- ❖ Methanol synthesis over Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> has been used industrially for decades, with CO<sub>2</sub> hydrogenation playing a central role.
- ❖ Al<sub>2</sub>O<sub>3</sub> acts as support while Cu-ZnO interface constitutes primary active sites
- ❖ CZA simultaneously catalysis,
  - ❖  $\text{CO}_2 + \text{H}_2 \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$   $\Delta H = -49.5 \text{ kJ/mol}$  (main reaction)
  - ❖  $\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$   $\Delta H = 41.5 \text{ kJ/mol}$  (side reaction)
- ❖ Under reaction conditions, the catalyst is structurally dynamic
  - ❖ Cu NPs exhibit a high number of extended defects like stacking faults (b)
  - ❖ Partial encapsulation of Cu by ZnO
  - ❖ The defects propagate to the surface (and to the interface with ZnO)
- ❖ Due to complex and inhomogeneous structure of the CZA, the nature of active sites and phases remains unresolved.



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DOI: 10.1002/anie.201209539

DOI: 10.1002/ange.200702600

## Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> (CZA) catalyst: Active Sites

- ❖ In situ and operando techniques allow identification of active sites under working conditions.
- ❖ Role of active sites over Cu-ZnO catalysts
  - ❖ **ZnO<sub>x</sub> (reduced ZnO)** is believed to provide active sites for CO<sub>2</sub> adsorption.
  - ❖ **Metallic Cu<sup>0</sup>** promotes H<sub>2</sub> dissociation and hydrogen spillover.
  - ❖ **Cu<sup>+</sup> species** might stabilize CO intermediates and the monodentate formate species.
  - ❖ Different activate sites on CZA have been attributed to different reaction steps
- ❖ **Consensus from activation studies:**
  - ❖ Cu<sup>0</sup> particles decorated with oxygen-deficient ZnO<sub>x</sub> overlayers are considered the most relevant interfacial active sites.
  - ❖ The roles of Cu<sup>+</sup> and Cu-Zn alloys remain debated and appear to be highly pretreatment-dependent.

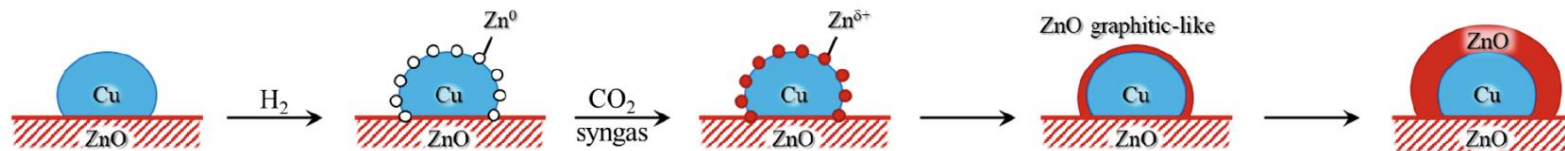
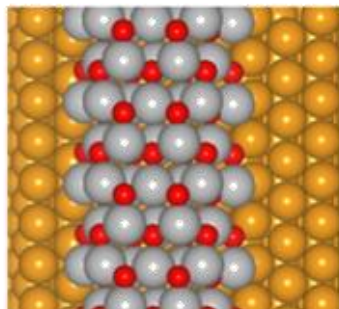


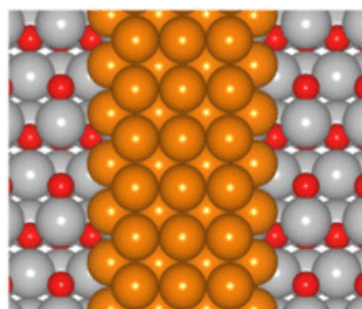
Fig. Schematic evolution of active sites in Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> industrial catalyst under working conditions. (ACS Catal. 2024,14,2730–2745)

“CZA contains multiple phases, different particle morphology & various Cu/Zn interfaces  
possessing a challenge to modelling”

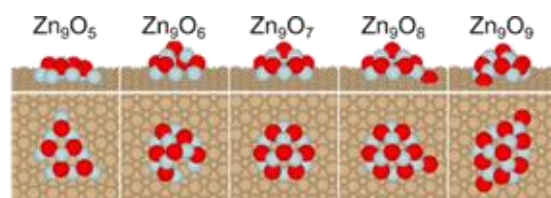
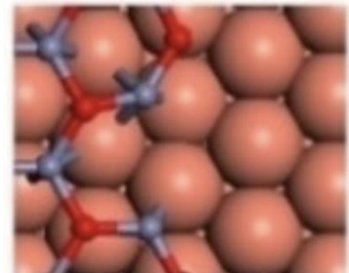
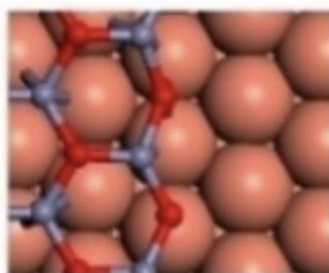
## Computational Model Catalysts



ZnO nanorod/Cu(111)[1]



Cu nanorod/Zn(10-10)[1]

ZnO<sub>x-1</sub> clusters/Cu(111) [2]

- Most computational studies on CO<sub>2</sub>/CO hydrogenation have focused on CuZn(211) surfaces
- Nanorod models (both ZnO@Cu or Cu@ZnO) have also been used
- ZnO<sub>x</sub> models have been lacking
  - Oxygen-deficient nanoclusters by Reichenbach *et al.*
  - Small *ad hoc* nanorod models
- ❖ The **atomic-level structure** of the active Cu–ZnO (or inverse) interface remains unresolved.
- ❖ **Dynamic structural changes** under working conditions are difficult to capture experimentally and are often oversimplified in theoretical models.
- ❖ **Complexity of the interface** must be incorporated into theoretical models to obtain relevant and realistic results.

[1] Chowdhury, *et al.*, *The Journal of Physical Chemistry C* 129.12 (2025): 5860-5867.

[2] Xinyu Liu, *et al.*, *Angew. Chem. Int. Ed.* 2022, 61, e202202330.

[3] Reichenbach, Thomas, *et al.*, *The Journal of Physical Chemistry C* 123.51 (2019): 30903-30916.

Oxide clusters on a metal support are often referred to as “inverse catalysts”.

# Modelling of CZA Catalyst

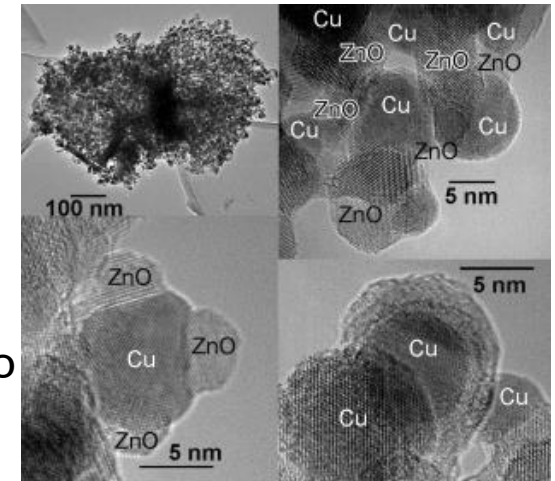
**Our goal:** Build realistic models for CZA interfaces based on the experimental information; employ density functional theory (DFT) to investigate CO<sub>2</sub>-to-MeOH conversion and identify rate controlling descriptors of the reaction.

## ❖ Research focus:

- ❖ Identify active sites for reactants (such as CO, CO<sub>2</sub> and H<sub>2</sub>)
- ❖ Thermodynamics & Kinetics of hydrogenation
- ❖ Calculate vibrational frequency and compare with experimental DRIFTS results to validate models

## Building Computational Catalyst model:

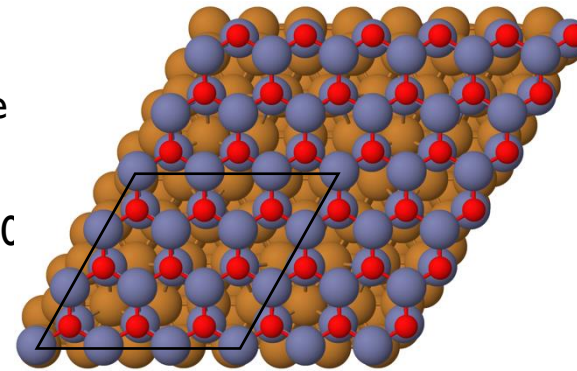
- ❖ model 1: Graphitic-like bilayer ZnO on Cu(111)
- ❖ model 2: Submonolayer ZnO motifs/Cu(111)
- ❖ model 3: ZnO<sub>x</sub> nanorod on Cu(111)



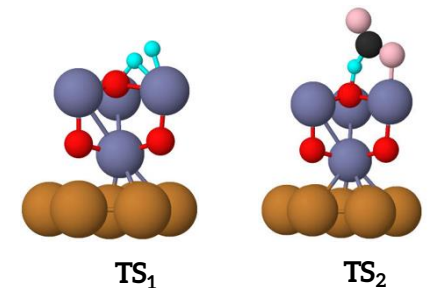
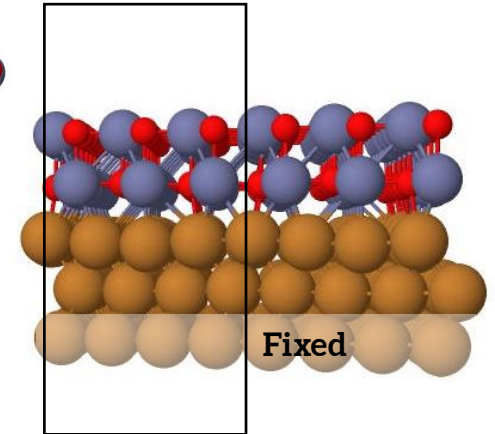
Microstructural features revealed with TEM and high-resolution TEM [*Angew. Chem. Int. Ed.* 2007, 46, 7324–7327].

## Model I: Graphitic like bilayer-ZnO/Cu(111)

- ❖ Graphitic-like B-ZnO has been observed to grow on Cu nanoparticles.
- ❖ A bilayer (BL) model[1] was chosen, with surface or ZnO—Cu-interface
- ❖ Stoichiometric model: periodic (3 × 3) ZnO-bilayer/(4 × 4) Cu(111)
  - ❖ Selection of this model limit the strain released on ZnO around -2.0
- ❖ **DFT results:**
  - ❖ DFT-method: BEEF-vdW + U (U = 3.4 eV)
  - ❖ CO<sub>2</sub>, CO and H<sub>2</sub> only weakly physisorb onto the bilayer
  - ❖ Activation energies for H<sub>2</sub> dissociation ( $\Delta E_a = 87$  kJ/mol) and CO<sub>2</sub> hydrogenation ( $\Delta E_a = 198$  kJ/mol) are inaccessible at process conditions.
  - ❖ **The stoichiometric bilayer model was deemed inactive**
  - ❖ The interface oxygen vacancy performed similarly to the ideal bilayer
  - ❖ The surface oxygen vacancy inhibits H<sub>2</sub> dissociation ( $\Delta E_a = 125$  kJ/mol), but promotes CO<sub>2</sub> hydrogenation ( $\Delta E_a = 52$  kJ/mol)
  - ❖ However, surface oxygen vacancies are likely depleted after CO<sub>2</sub> hydrogenation or if the OH<sup>-</sup> is present.



Top view

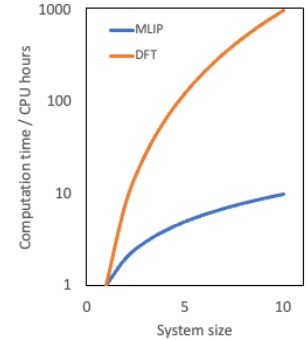
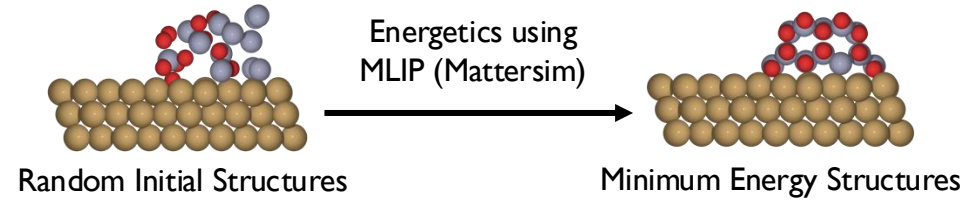
TS<sub>1</sub>TS<sub>2</sub>

# Computational Strategy

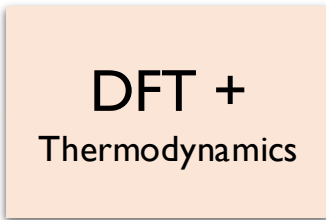
## Structure Exploration



Global search of ZnO/Cu(III) vast configurational space using a genetic algorithm accelerated by machine-learned potentials

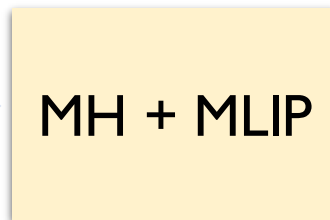


### Validation

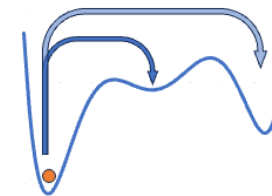


Accurate energetics and stability of candidate structures under realistic conditions

### Reactivity



Sampling of active sites for adsorbates over candidate structures



### Validation

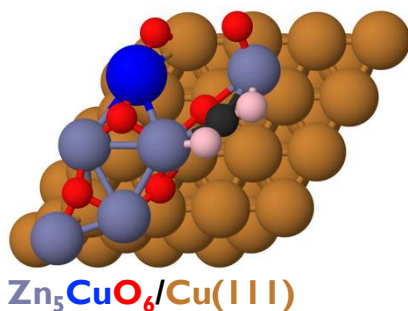
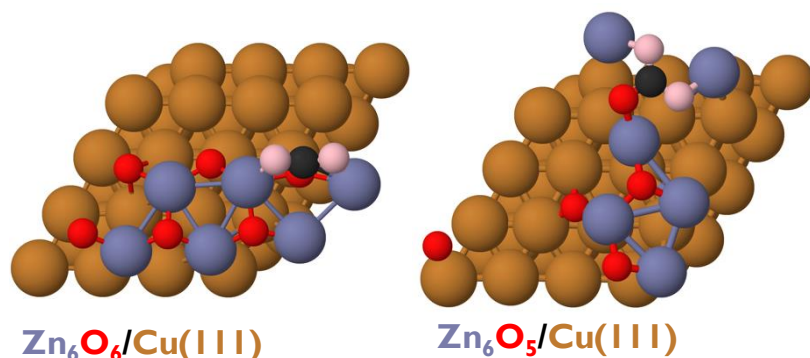
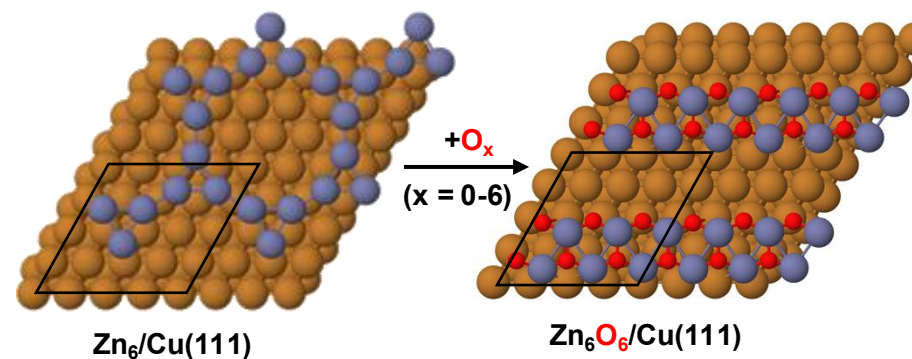


DFT verification of adsorption energetics

[1] Yang, Han, et al. "Mattersim: A deep learning atomistic model across elements, temperatures and pressures." *arXiv preprint arXiv:2405.04967* (2024).

## Model 2: Submonolayer $\text{ZnO}_x$ film/Cu(111)

- ❖ Submonolayer  $\text{ZnO}_x$  motifs/Cu(111) (GA + ML Generated)
- ❖ Minimum energy structures for  $\text{ZnO}_x$  layers with different composition can be generated
- ❖  $\text{ZnO}_x$  structures with vacancies and interfacial sites



### $\text{CO}_2$ activation

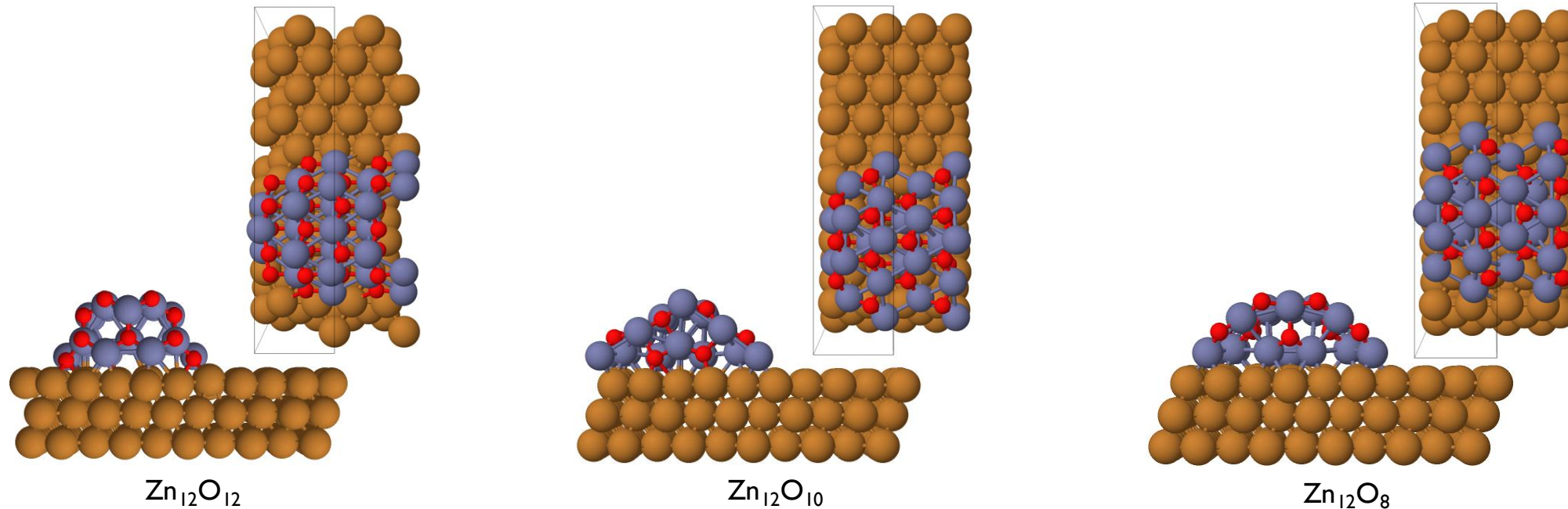
- ❖  $\text{CO}_2$  binds weakly at **Zn–O–Zn bridge sites** in a tridentate configuration, with an adsorption energy of approximately  $-50 \text{ kJ mol}^{-1}$ .
- ❖ At the **oxygen-vacancy site**,  $\text{CO}_2$  exhibits **strong chemisorption** with an adsorption energy of about  $-160 \text{ kJ mol}^{-1}$ .

**Role of  $\text{Cu}^{+6}$ :** A single Zn atom was replaced by Cu to evaluate its effect on  $\text{CO}_2$  binding.

- ❖  $\text{CO}_2$  preferentially adsorbs at **Zn–O–Zn sites with approximately  $-70 \text{ kJ/mol}$  energy** rather than at the **Cu–O–Zn site**.

## Model 3: $\text{ZnO}_x$ nanorod on $\text{Cu}(111)$

- ❖  $\text{ZnO}$  nanorods on  $\text{Cu}$  surface can be used as models for nanoparticle interfaces
- ❖  $\text{ZnO}$  nanorod structures with varying oxygen ( $x = 0-12$ ) content to find a representative structure at process conditions
- ❖  $\text{ZnO}$  nanorods with different  $\text{Zn}:\text{O}$  ratios are sampled using ML-accelerated genetic algorithm



## Model 3: *Ab initio* Thermodynamics

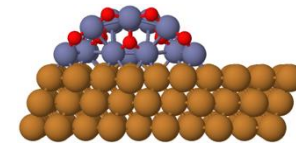
- ❖ Evaluate the most stable nanorod structure at process conditions

$$\Delta G = G(\text{Zn}_y\text{O}_x/\text{Cu}(111)) - G(\text{Zn}_y/\text{Cu}(111)) - x\mu_{\text{O}}$$

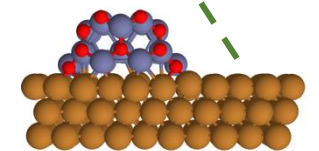
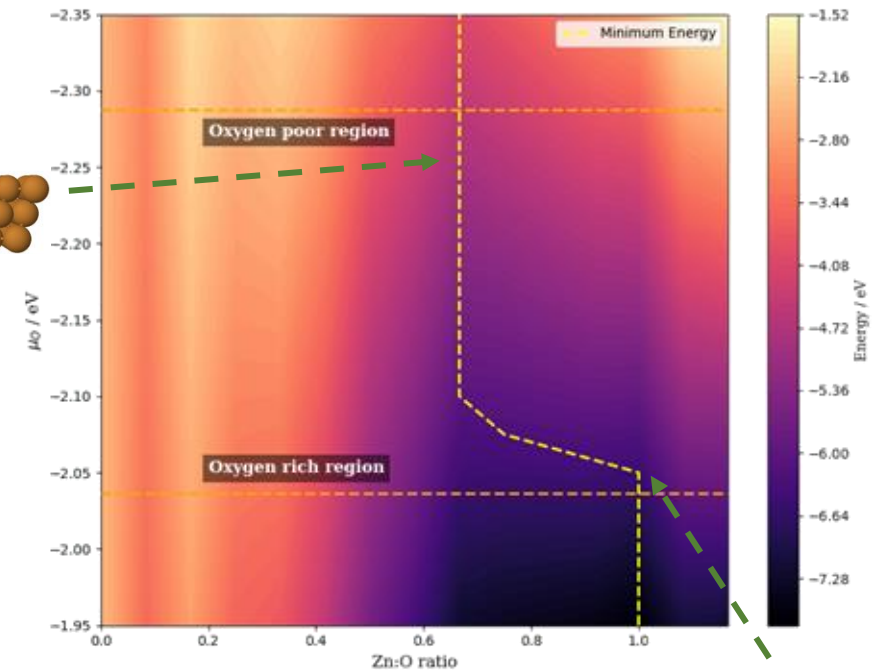
- ❖ ZnO in equilibrium with  $\text{CO}_2 / \text{CO}$  and  $\text{H}_2\text{O} / \text{H}_2$  reservoir
- ❖ We include ZPE into the slab energies, free energies for the gas-phase species,

$$\begin{aligned} \mu_{\text{O}}(T, p_{\text{O}_2}) &= \frac{1}{2}E_{\text{O}_2} + \Delta\mu_{\text{O}}(T, p_{\text{O}_2}) \\ &= \max\{(\mu_{\text{CO}_2}(T, P_{\text{CO}_2}) - \mu_{\text{CO}}(T, P_{\text{CO}}), (\mu_{\text{H}_2\text{O}}(T, P_{\text{H}_2\text{O}}) \\ &\quad - \mu_{\text{H}_2}(T, P_{\text{H}_2})\} \\ -2.29 \text{ eV} &< \Delta\mu_{\text{O}}(T, P_{\text{O}_2}) < -2.04 \text{ eV} \end{aligned}$$

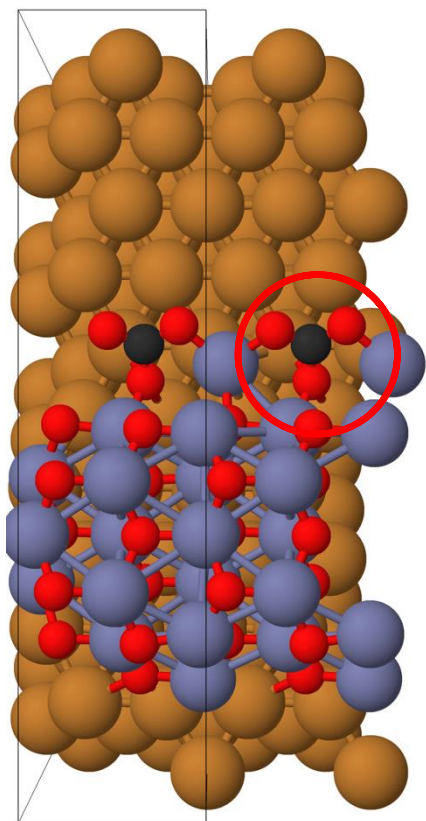
- ❖ Two distinct minima on the free energy surface depending on the chemical potential of oxygen
- ❖  $\mu_{\text{min}}$  corresponds to oxygen poor atmosphere,  $\mu_{\text{max}}$  to oxygen rich



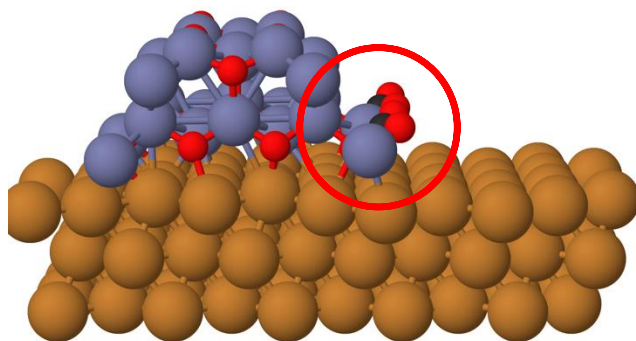
### Free Energy Surface Profile



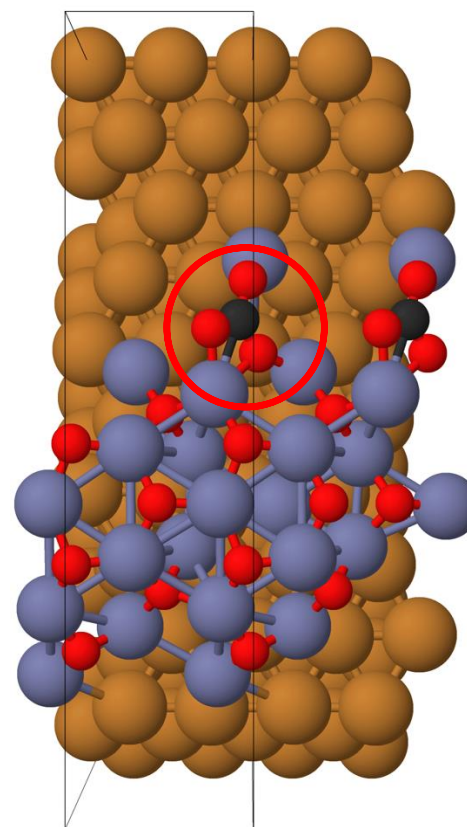
## Model 3: ZnO/Cu interface – CO<sub>2</sub>



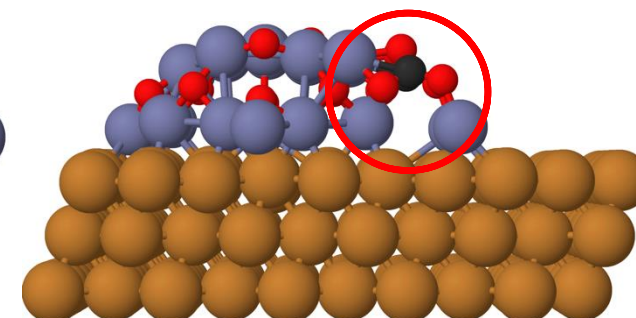
Zn<sub>12</sub>O<sub>12</sub>



$$\Delta E_{\text{ads}} = -43 \text{ kJ/mol}$$



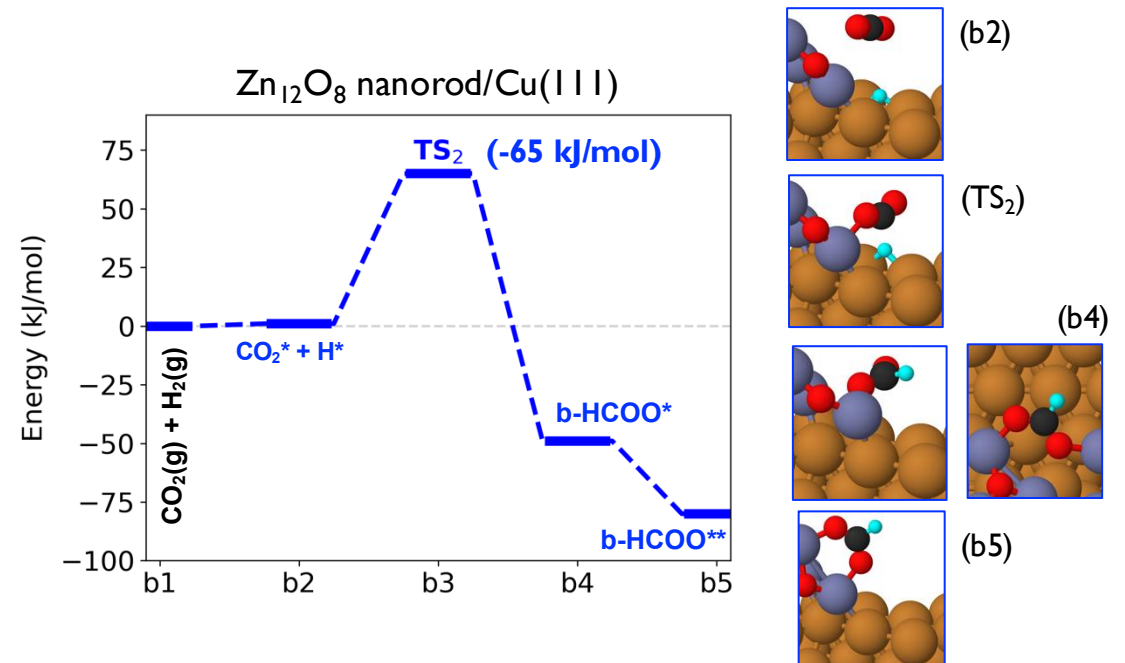
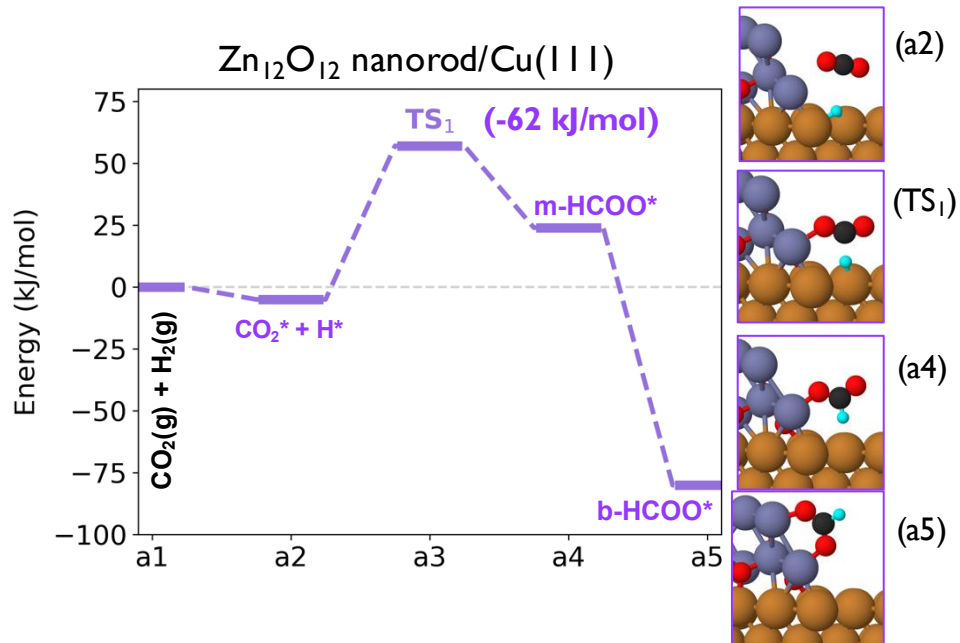
Zn<sub>12</sub>O<sub>8</sub>



$$\Delta E_{\text{ads}} = -33 \text{ kJ/mol}$$

## Model 3: DFT derived PES for CO<sub>2</sub> hydrogenation

- ❖ Eley–Rideal mechanism: linearly adsorbed CO<sub>2</sub> reacts directly with pre-adsorbed surface H to form HCOO\* (formate intermediate)
- ❖ Elementary step: CO<sub>2</sub>\* + H\* → HCOO\*
- ❖ Compare stoichiometric vs reduced systems PES results



- ❖ Activation barrier ( $\Delta E_a$ ) for m-HCOO formation is almost identical in both systems
- ❖ Reaction is endothermic on the stoichiometric system (+29 kJ/mol) but strongly exothermic on the reduced system (-50 kJ/mol), indicating enhanced thermodynamic favorability



## Summary

- ❖ We leverage machine learning and genetic algorithm to generate  $\text{ZnO}_x$ —Cu interface structures
- ❖  $\text{ZnO}_x$  nanorods are used to model the nanoparticle interface
- ❖ The stability of the nanorods are evaluated using *ab initio* thermodynamics
- ❖ Adsorption of reactants can be accelerated using minima hopping with machine learning
- ❖ Foundation MLIPs are versatile tools to accelerate computational workflow
- ❖  $\text{CO}_2$  to methanol conversion will be carried out on reduced and stoichiometric ZnO nanorods
- ❖ Other modifications
  - ❖ Cationic Cu atoms on nanorod
  - ❖ CuZn alloy formation at nanorod edge



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- ❖ At JYU: Prof. Karoliina Honkala, Dr. Timo Weckman, Dr. Minttu Smith
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- ❖ Computer time: CSC – IT Center for Science



# Membrane-assisted Ethylene Synthesis over Nanostructured Tandem Catalysts



**Thank you for your attention**

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