



Membrane-assisted Ethylene Synthesis over Nanostructured Tandem Catalysts



Modelling CO_2 catalytic conversion to valuable products

Karoliina Honkala

Department of Chemistry, Nanoscience Center

University of Jyväskylä, Finland

karoliina.honkala@jyu.fi

“Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the EU or EIC and SMEs Executive Agency (EISMEA). Neither the European Union nor the granting authority can be held responsible for them”.

Disclosure or reproduction without prior permission of MEMCAT project is prohibited.

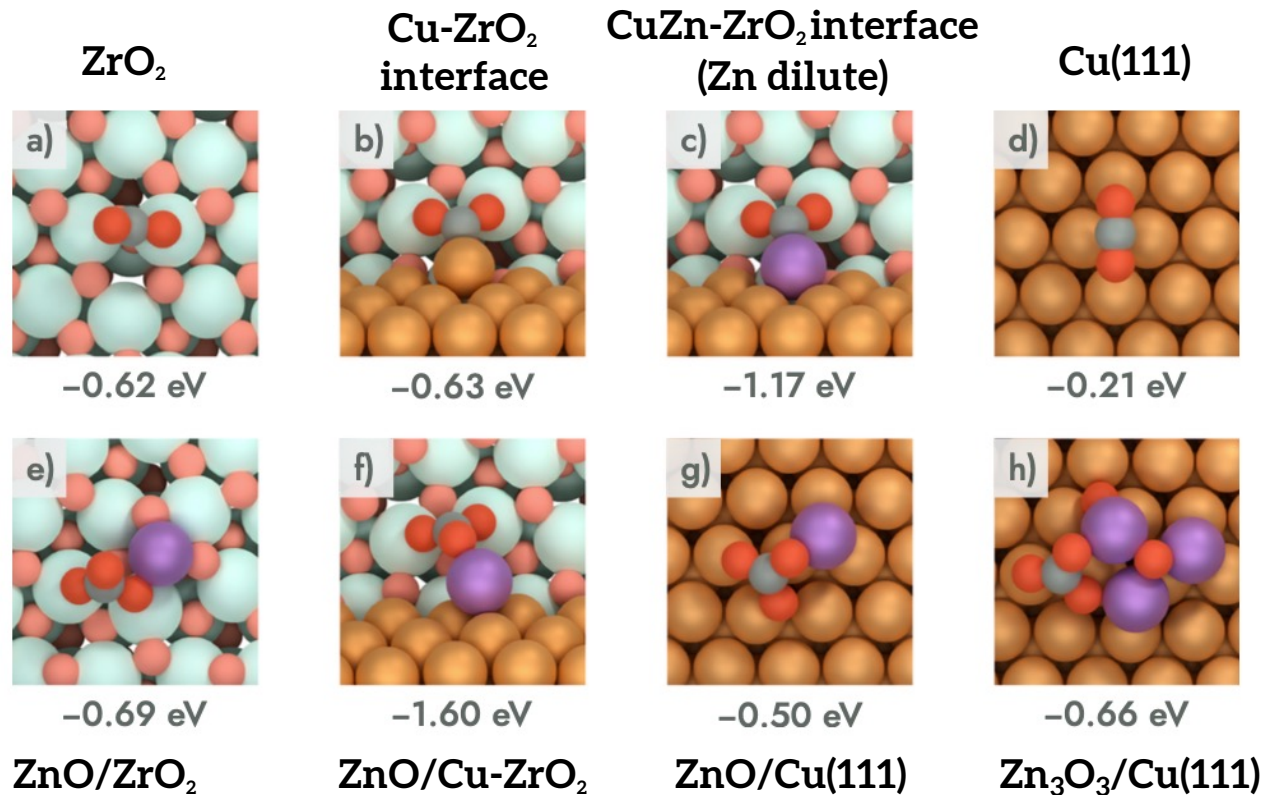


Modelling of Active sites for CO₂ Hydrogenation to Methanol via DFT

- ❖ **Multi-component catalyst systems:**
 - Metals, oxides, promoters, and interfaces—each offer different potential active sites.
- ❖ **Dynamic behaviour:**
 - Catalyst structure changes with temperature, pressure, and gas composition (e.g., restructuring, alloying, oxidation/reduction).
- ❖ **Competitive reaction pathways:**
 - Formate route, RWGS route, and CO hydrogenation can occur simultaneously on different sites.
- ❖ **Complexity of surface structure:**
 - Steps, vacancies, grain boundaries, and amorphous regions are difficult to include in simplified computational models.



Diverse active sites and CO₂ adsorption and activation



CO₂ geometries and adsorption energies (E_{ads}) at several sites relevant to the Cu/ZnO/ZrO₂ system.

Lempelto, A. (2024). Computational modelling of carbon dioxide reduction to methanol on heterogeneous zirconia-supported copper catalysts.

- ❖ CO₂ binds moderately at the Cu-ZrO₂ interface, adopting a bidentate configuration (b)
- ❖ Introducing Zn at the interface enhances the CO₂ adsorption strength (c).
- ❖ CO₂ adsorption at the the ZnO/Cu-ZrO₂ interface (f) is the strongest (-1.6 eV) among other examined cases.
- ❖ CO₂ preferentially adopts trigonal, carbonate-like form over systems shown in panel (e-h)
- ❖ Across ZrO₂, ZnO/ZrO₂, ZnO/Cu(111) and Cu-ZrO₂ structures, CO₂ adsorption energies remains consistent (-0.5 eV to -0.7 eV)





Cu/ZnO/Al₂O₃ (CZA) catalyst

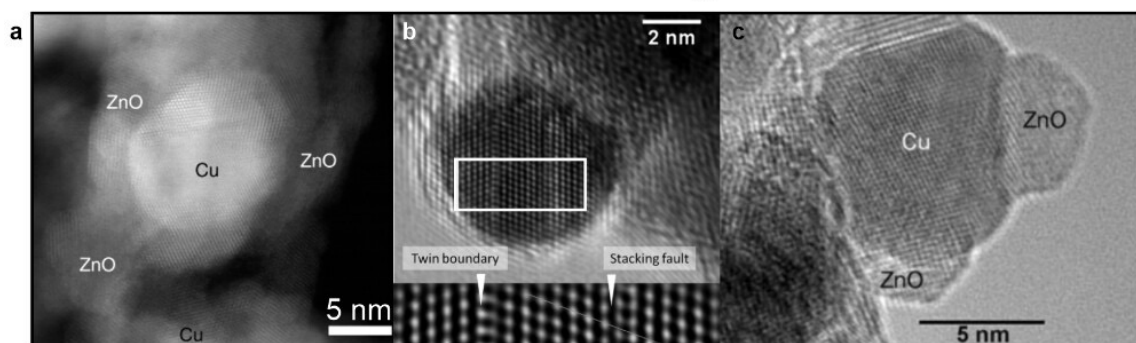
- ❖ CZA is the industrial preferred catalyst for methanol synthesis from syngas, since its development in the 1960s.
- ❖ Al₂O₃ acts as support while Cu-ZnO interface constitutes primary active sites
- ❖ CZA simultaneously catalyses,
 - ❖ $\text{CO}_2 + \text{H}_2 \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$ $\Delta H = -49.5 \text{ kJ/mol}$ (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)
- ❖ **Challenges:**
 - ❖ Opposing temperature effects of exothermic methanol synthesis and endothermic RWGS inherently limit CO₂ conversion and methanol selectivity.
 - ❖ CO₂ conversion remains low (<20%) because CO₂ is highly stable and difficult to activate



Cu/ZnO/Al₂O₃ (CZA) catalyst

- ❖ The nanostructure of high-performance CZA is very complex & inhomogeneous¹
- ❖ CZA contains multiple phases, different particle morphology & various Cu/Zn interfaces **possessing a challenge to modelling**

Structure of the industrial-type CZA



DOI: 10.1038/s41467-020-15445-z

DOI: 10.1002/anie.201209539

DOI: 10.1002/ange.200702600

- Cu NPs exhibit a high number of extended defects like stacking faults (b)
- ZnO nanoparticles act as spacer of the Cu nanoparticles
- Partial encapsulation of Cu by ZnO
- Cu nanoparticles are characterized by strain and defects
- The defects propagate to the surface (and to the interface with ZnO)

[1] Beck, A.; The Enigma of Methanol Synthesis by Cu/ZnO/Al₂O₃-Based Catalysts. *Chemical Reviews* 2024, 124 (8), 4543-4678.

[2] Ruland, H.; CO₂ Hydrogenation with Cu/ZnO/Al₂O₃: A Benchmark Study. *ChemCatChem* 2020, 12 (12), 3216-3222.

Cu/ZnO/Al₂O₃ (CZA) catalyst: Active sites

- ❖ In situ and operando techniques allow precise identification of active sites under working conditions.
- ❖ Role of active components over CZA catalysts
 - ❖ ZnO_x (reduced ZnO) is believed to provide active sites for CO₂ adsorption.
 - ❖ Metallic Cu⁰ promotes H₂ dissociation and hydrogen spillover.
 - ❖ Cu⁺ species stabilize CO intermediates and the monodentate formate species.
- ❖ **Consensus from activation studies:**
 - ❖ Cu⁰ particles decorated with oxygen-deficient ZnO_x overlayers are considered the most relevant interfacial active sites.
 - ❖ The roles of Cu⁺ and Cu-Zn alloys remain debated and appear to be highly pretreatment-dependent.

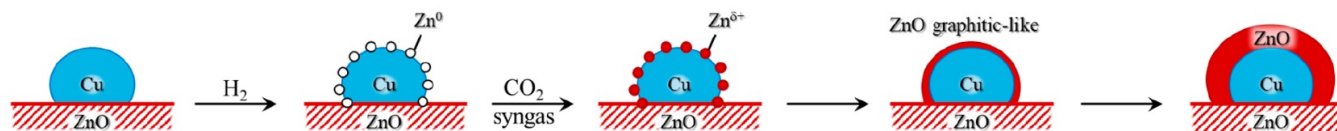
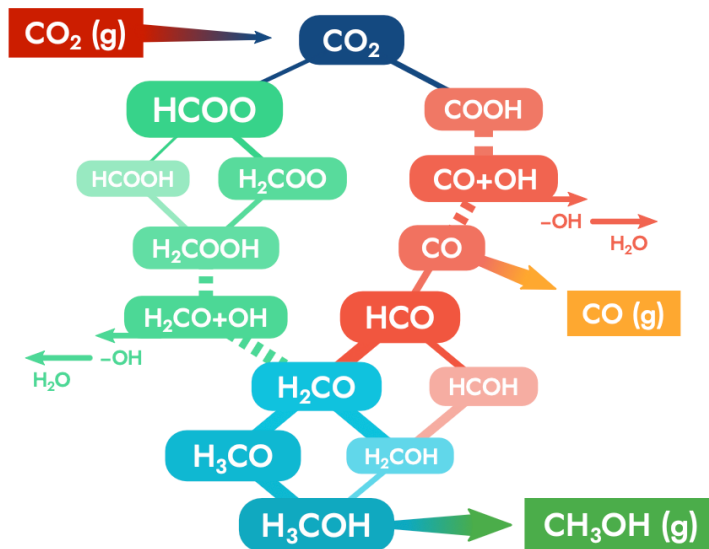


Fig. Schematic evolution of active sites in Cu/ZnO/Al₂O₃ industrial catalyst under working conditions. (ACS Catal. 2024,14,2730–2745)

Reaction mechanism for CO₂ hydrogenation to methanol



Theoretical reaction network for carbon dioxide conversion to methanol.

CO₂ adsorption:

- ❖ CO₂ adsorbs and activates at the Cu-ZnO interface

Hydrogenation pathway:

- ❖ The CO₂ hydrogenation through formate and methoxy intermediate is called **formate pathway**, where hydrogen atoms are sequentially added to form methanol.
- ❖ The **reverse water-gas shift** pathway through CO formation and hydrogenation to form methanol.

Product formation:

- ❖ Methanol desorption from the catalyst surface and water byproduct (require careful management to prevent deactivation)

Lempelto, A. (2024). Computational modelling of carbon dioxide reduction to methanol on heterogeneous zirconia-supported copper catalysts.

Disclosure or reproduction without prior permission of MEMCAT project is prohibited.



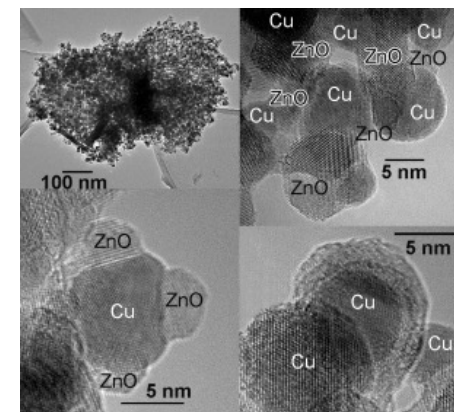
Modelling of CZA Catalyst

Our goal: Build realistic models for CZA interfaces based on the experimental information; employ density functional theory (DFT) to investigate CO₂-to-MeOH conversion and identify rate controlling descriptors of the reaction.

The ZnO–Cu interface is proposed to be active but **the precise nature of active sites remains difficult to identify.**

Scientific Challenges :

- ❖ 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.
- ❖ **Research focus:**
 - ❖ Identify active sites for reactants (such as CO, CO₂ and H₂)
 - ❖ Thermodynamics & Kinetics of hydrogenation
 - ❖ Calculate vibrational frequency and compare with experimental DRIFTS results to validate models



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



✦ Experimental input crucial

✦ **Dynamic structure** is often oversimplified in theoretical models

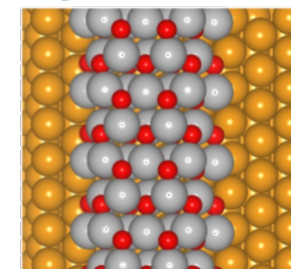
❖ The **atomic-level structure** of the active Cu-ZnO interface is unresolved.

Building Computational Catalyst model:

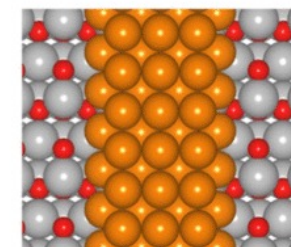
- ❖ Catalyst model 1: Graphitic-like bilayer ZnO on Cu(111)
- ❖ Catalyst model 2: Periodic ZnO/Cu systems generated using genetic algorithm (GA) and machine learning (ML)
- ❖ Catalyst model 3: ZnO_x nanorod on Cu(111)

Develop insight on:

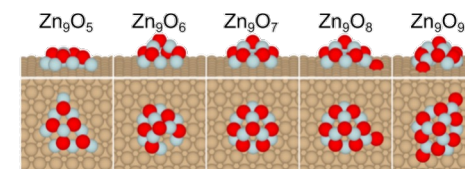
- ❖ Active sites for reactants (such as CO, CO₂ and H₂)
- ❖ Kinetics of hydrogenation (CO₂ to formate)
- ❖ Compare with experimental results (e.g. vibrational modes of absorbates)



ZnO nanorod/Cu(111)[1]



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



ZnO_{x-1} clusters/Cu(111) [2]

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

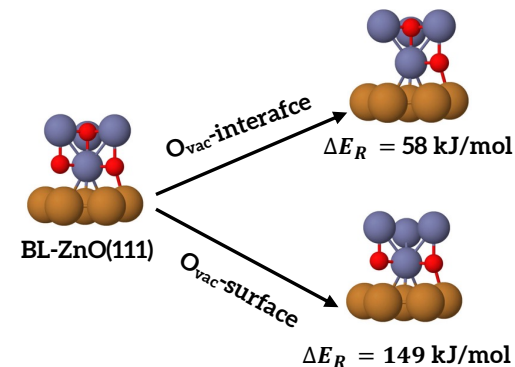
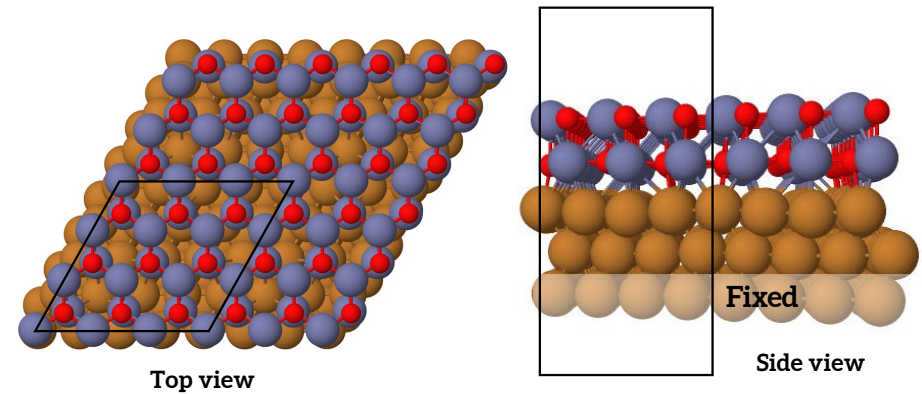
[2] Reichenbach, Thomas, et al., *The Journal of Physical Chemistry C* 123.51 (2019): 30903-30916.

Disclosure or reproduction without prior permission of MEMCAT project is prohibited.



Graphitic like bilayer-ZnO/Cu(111) surface

- ❖ Graphitic-like ZnO has been observed to grow on Cu nanoparticles.
- ❖ A bilayer (BL) model[1] was chosen, with surface or ZnO–Cu-interface oxygen vacancies.
- ❖ Stoichiometric model: periodic (3 x 3) ZnO-bilayer/(4 x 4) Cu(111)
 - ❖ Selection of this model limit the strain released on ZnO around -2.0 %
- ❖ Reduced ZnO-bilayer/Cu(111) models
 - ❖ O-vacancy introduced at the surface and interface
 - ❖ $\Delta E_R = E_{(Ovac-sur)} - E_{(stochiometric-sur)} + (E_{H_2O} - E_{H_2})$
 - ❖ O-vacancy creation is more favourable at the interface compared to the surface



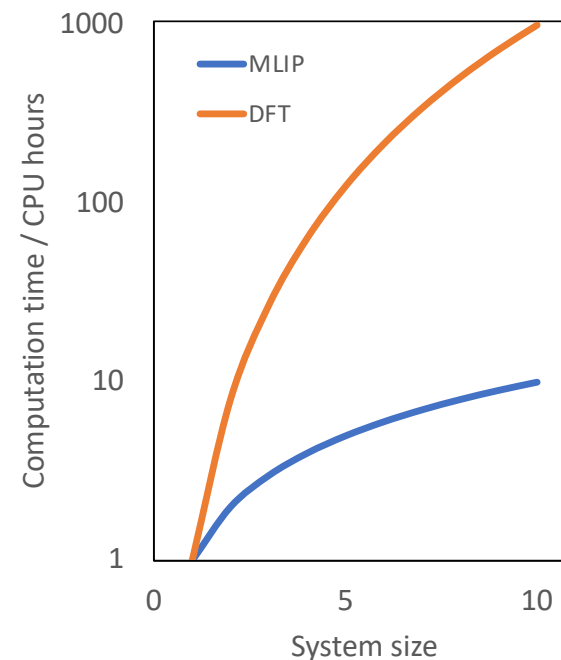
[1] Thang, Ho Viet, and Gianfranco Pacchioni., *Jour. of Phys. Chem. C*122.36 (2018): 20880-20887.



Computational tools



- ❖ Density functional theory (DFT) is used to study atomic and electronic structure of matter
 - ❖ Quantum mechanical modelling method
 - ❖ Accurate, even for large extended systems
 - ❖ Scaling with system size is a limiting factor
- ❖ Machine learning interatomic potential (MLIP)
 - ❖ Interatomic interactions are trained by machine learning[1]
 - ❖ Fast and relatively accurate
 - ❖ Accuracy/versatility depends on training data
 - ❖ Can be extended to very large systems
- ✚ We use ML to accelerate sampling of the vast configurational space
 - ❖ Investigate ZnO_x nanorods by varying oxygen content
 - ❖ Study reactant adsorption using minima hopping (MH)



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

Disclosure or reproduction without prior permission of MEMCAT project is prohibited.

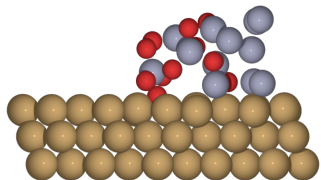




Computational workflow



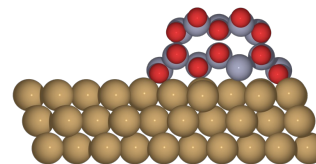
Random initial structures



Genetic algorithm

Energetics using ML-
potential (MatterSim)

Minimum energy structures



GA-ML

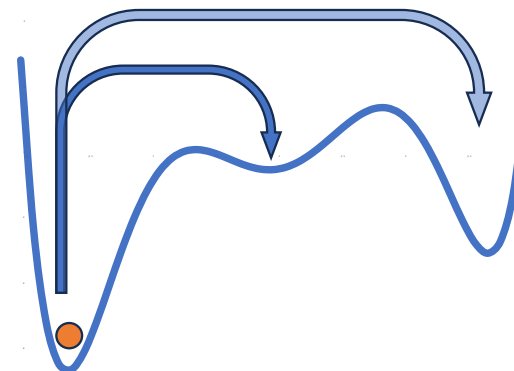
- Machine learning accelerated genetic algorithm (GA)
- Sample vast configurational and chemical space

MH-ML

- Use minima hopping (MH) to sample adsorbate interaction on candidate structures

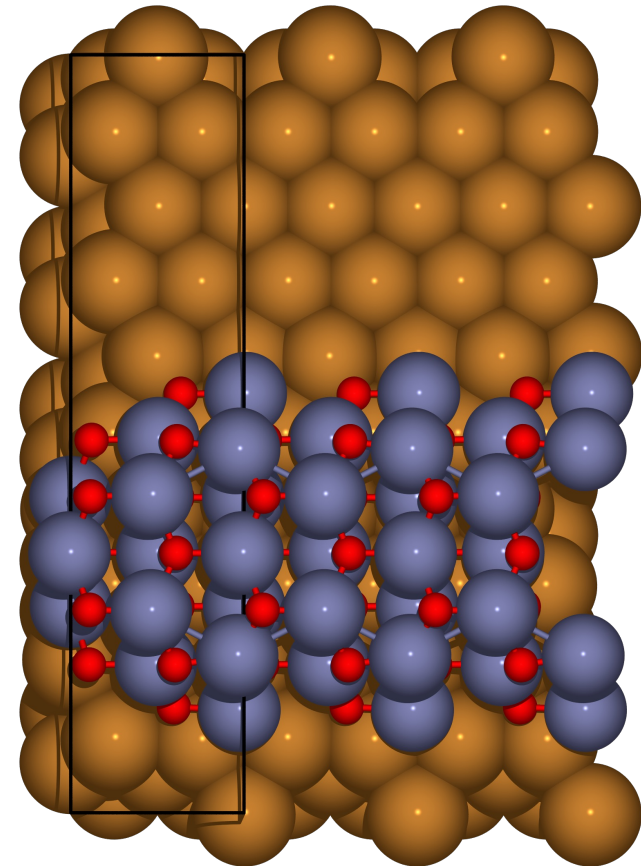
DFT

- Verify all end points using DFT



Crystalline ZnO nanorods

- ❖ ZnO nanorods on Cu surface can be used as models for nanoparticle interfaces
- ❖ We can generate nanorod structures with different Zn:O ratios to find a representative structure at process conditions
- ❖ ZnO nanorods with different Zn:O ratios are sampled using ML-accelerated genetic algorithm
- ❖ The stability of the nanorods can be evaluated using *ab initio* thermodynamics

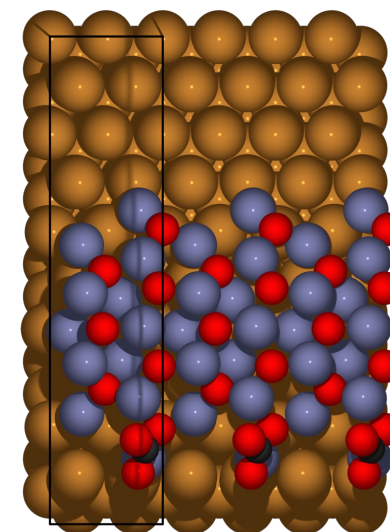




Summary



- ❖ We leverage machine learning and genetic algorithm to generate non-ideal ZnO–Cu interface structures
- ❖ ZnO 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





Acknowledgements



- ❖ At JYU: Dr Bhumi Baryana and Dr Timo Weckman
- ❖ At FHI: Dr Mino Borreli and Dr Annette Truschke
- ❖ Funding: MemCat project
- ❖ Computer time: CSC – IT Center for Science





Membrane-assisted Ethylene Synthesis over Nanostructured Tandem Catalysts



Thank you for your attention

“Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the EU or EIC and SMEs Executive Agency (EISMEA). Neither the European Union nor the granting authority can be held responsible for them”.

