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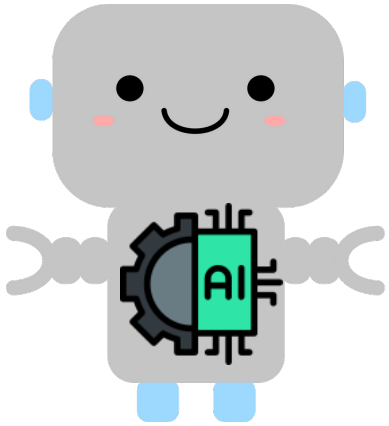
Bridging Experiment and Theory through Multi-Scale Simulations and Machine Learning Force Fields

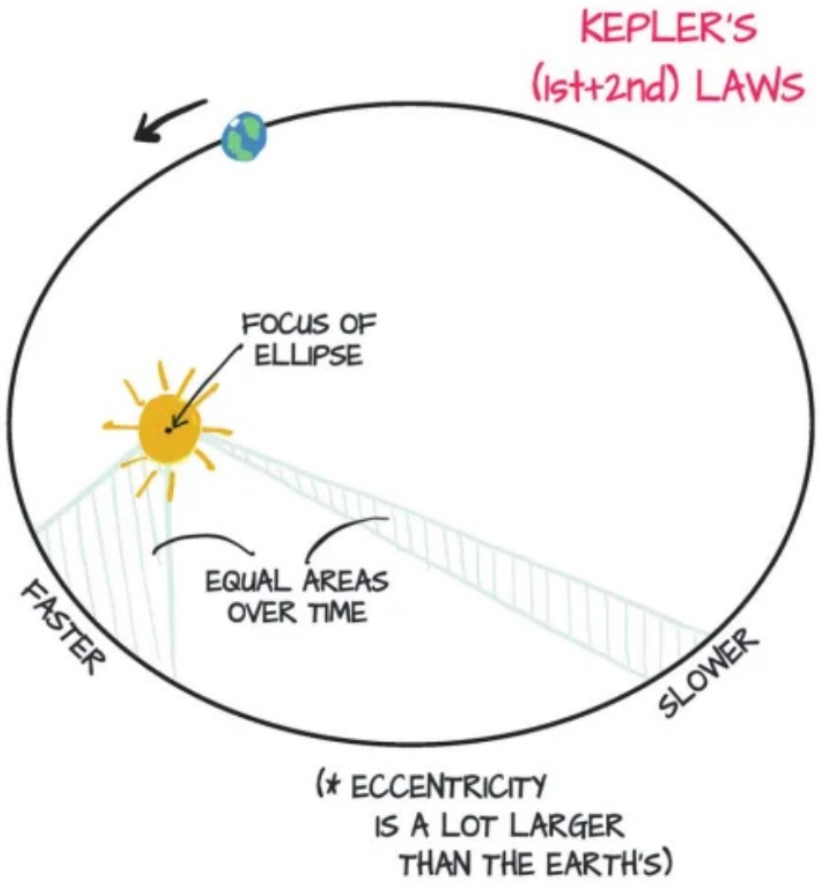
Harry H. Halim

Assistant Professor in Morikawa Laboratory

Graduate School of Engineering, The University of Osaka



Great discovery happens when theories meet observations



Statue of Tycho Brahe and Johannes Kepler
Prague, Czech

“Have you compared it with experiments?”

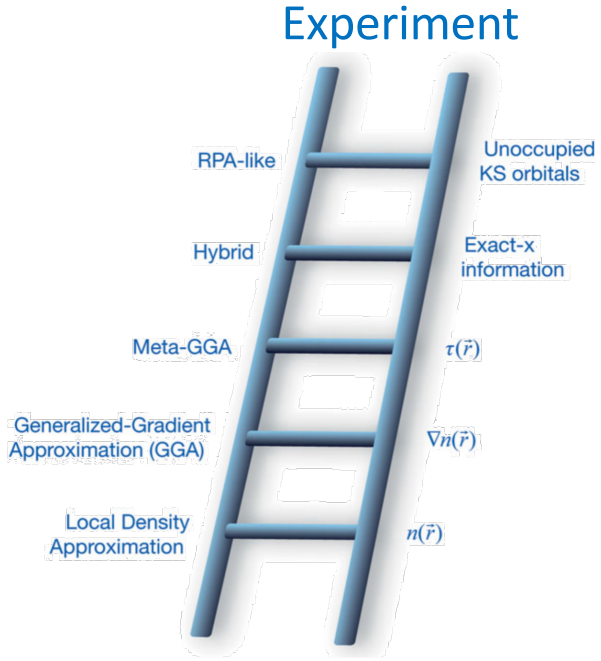
Morikawa Group

Computational Physics Area,
Department of Precision Engineering,
Graduate School of Engineering, Osaka University

What is the most frequent question asked by Morikawa-sensei?

Have You Compared It With Experiment ?

- Important question, because…
  - Understanding limitations and assumptions
  - Avoid misinterpretation of the results
  - Validation of theoretical models
- Yet it is difficult, because…
  - The reality at the nanoscale is rarely simple
  - Good modeling needs prior knowledge
  - Functionals & method limitations



“Have you compared it with calculations?”

❑ *Operando* techniques for atomic-scale studies of surface catalysis.

Shi, X., et al., JACS Au 2021, 1, 2100−2120

- Infrared (IR) spectroscopy
- Raman spectroscopy
- X-ray diffraction (XRD)
- X-ray photoelectron spectroscopy (XPS)
- X-ray emission spectroscopy (XES)
- Atomic force microscopy (AFM)
- Nuclear magnetic resonance (NMR) spectroscopy
- Electron paramagnetic resonance (EPR) spectroscopy
- Scanning/transmission electron microscopes (S/TEM)
- Scanning electrochemical microscopy (SECM)
- Differential electrochemical mass spectrometry (DEMS)
- Electrochemical quartz crystal microbalance (EQCM)
- X-ray absorption near edge structure (XANES) spectroscopy
- Extended X-ray absorption fine structure (EXAFS) spectroscopy

❑ Challenges in the experiment techniques

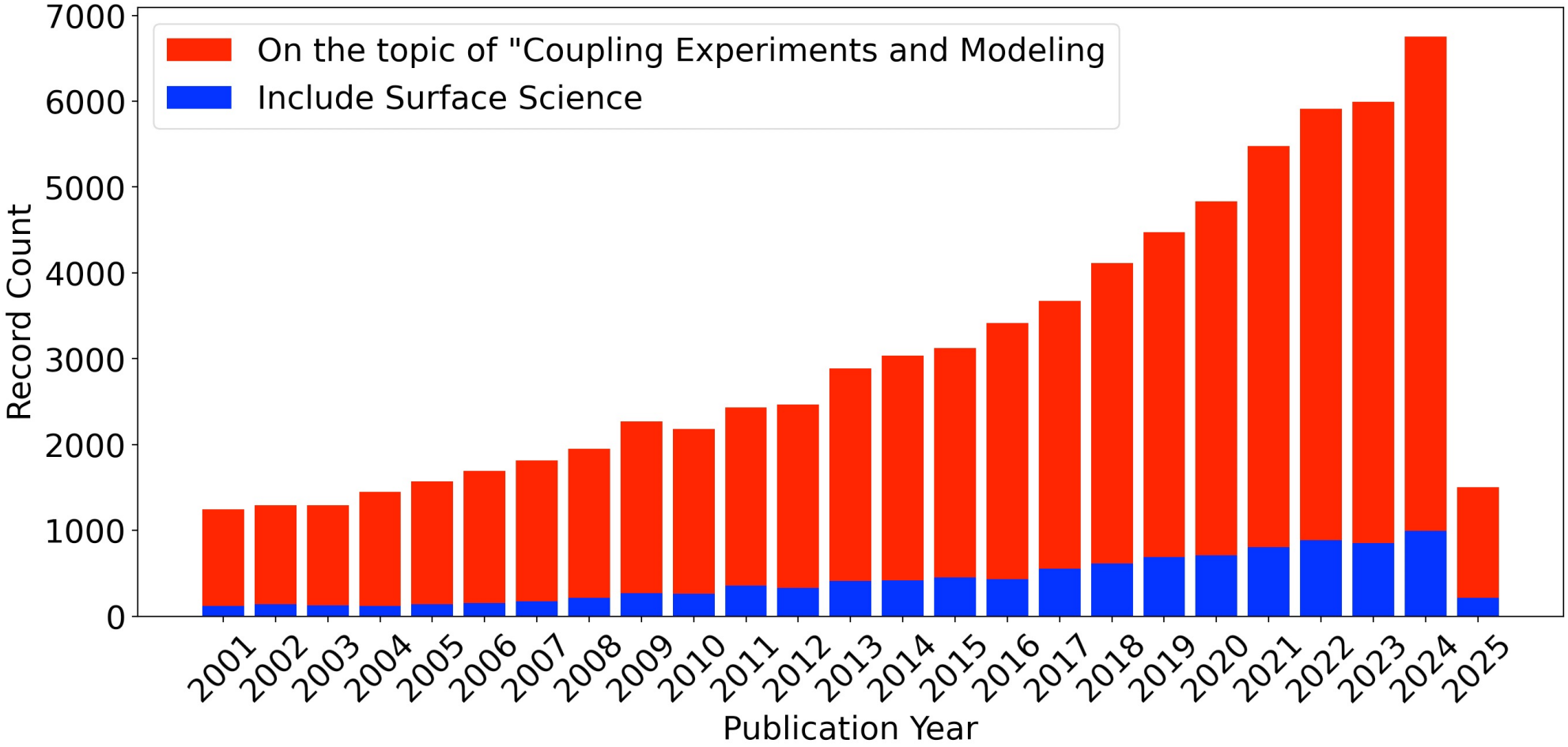
Limitations at high pressure (**pressure gap**)	Non-equilibrium reaction dynamics	Surface dynamics at realistic conditions	Complexity of the systems (**materials gap**)

Experiment and modeling can inform and enhance one another

Coupling Experiments and modeling

Publication Trend Related to Experiments and Modeling

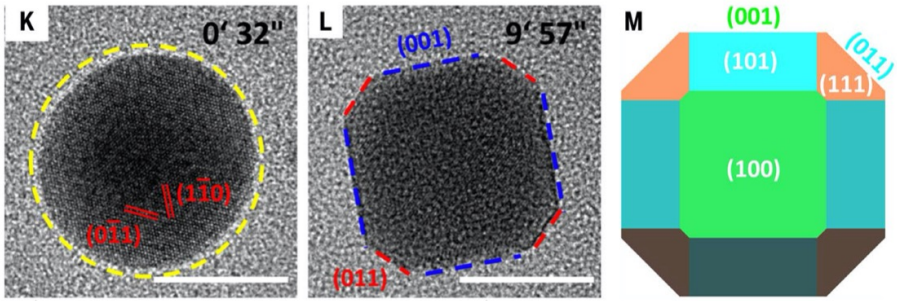
Data from https://www.webofscience.com/



Surface restructuring at realistic condition

Pressure-driven

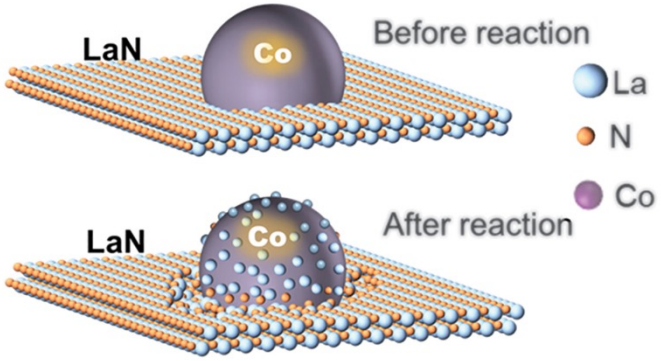
Hydrogen-induced surface faceting of PdCu nanoparticles



Y. Jiang et al., Angew. Chem. Int. Ed. 55, 12427–12430 (2016).

Support metal interaction-driven

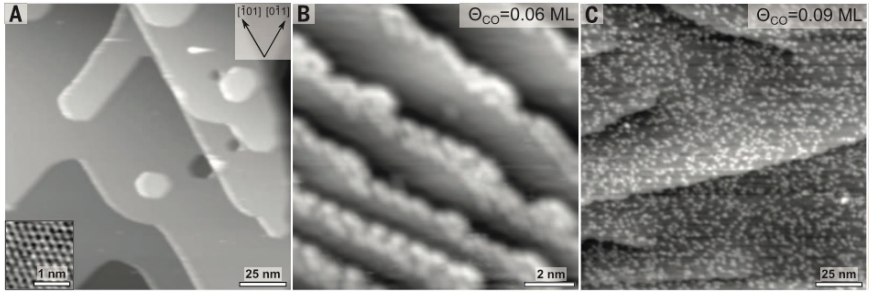
Oxygen-driven core-shell formation of Pt_3Co



K. Zhang et al., Science 383, 1357–1363 (2024).

Gas environment-driven

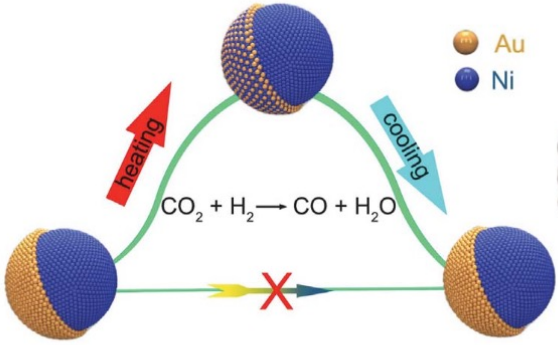
CO-induced formation of active nanocluster on Cu(111) surface



B. Eren et al., Science 351, 475–478 (2016).

Catalytic reaction-driven

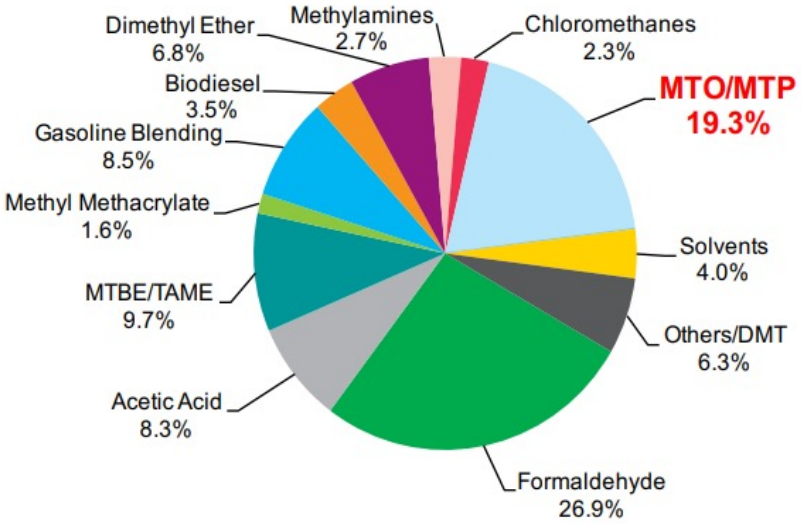
CO_2 Hydrogenation-driven *loss* of core-shell structure of Ni-Au



X. Zhang et al., Nat. Catal. 3, 411–417 (2020).

Introduction

The Importance of Methanol



Demand = 95.2 Million Metric Tons

✓ Valuable chemical ✓ Green energy source

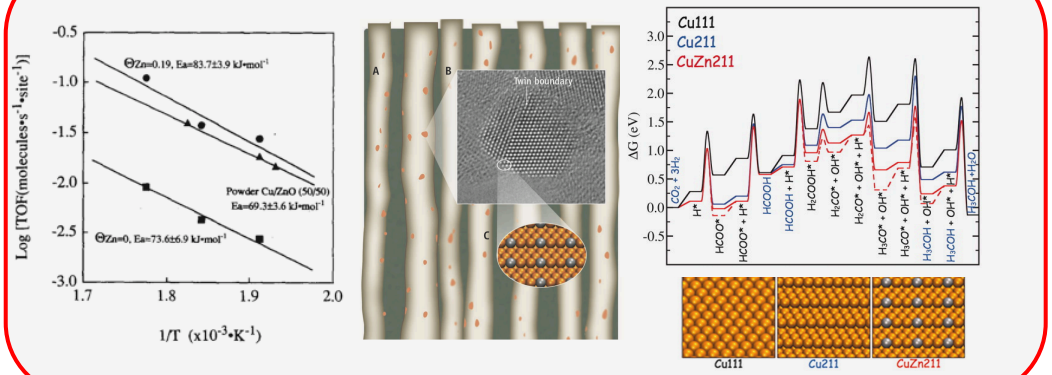
Methanol Synthesis

Synthetic Gas (CO / CO_2 / H_2) $\xrightarrow[200^oC - 300^oC]{Cu/ZnO/Al_2O_3}$ Methanol

The active site of **$Cu/ZnO/Al_2O_3$** is still under controversy.

The Controversy on the Active Sites

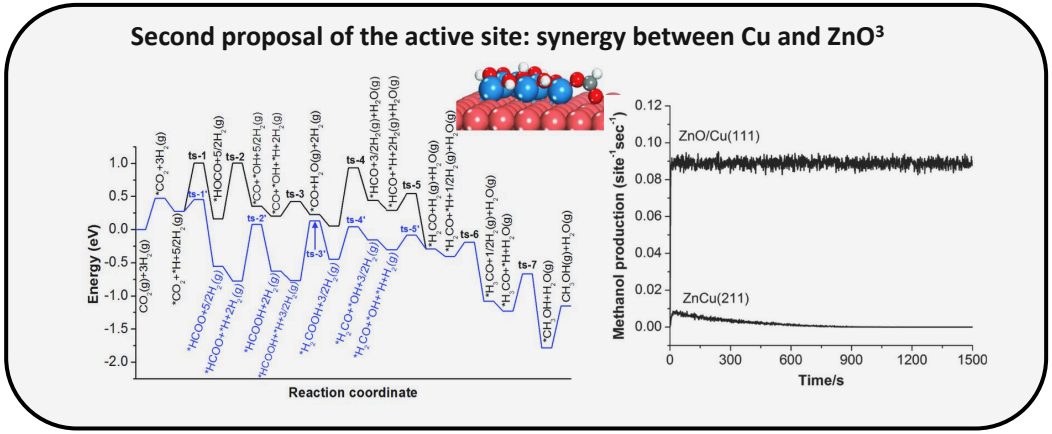
First proposal of the active site: metallic Cu-Zn in the shape of stacking faults[1,2]



[1]Nakamura et al., *Surface Science*, 383(2):285-298, 1997.

[2]Behrens et al., *Science*, 336(6083): 893-897,2012.

Second proposal of the active site: synergy between Cu and ZnO[3]

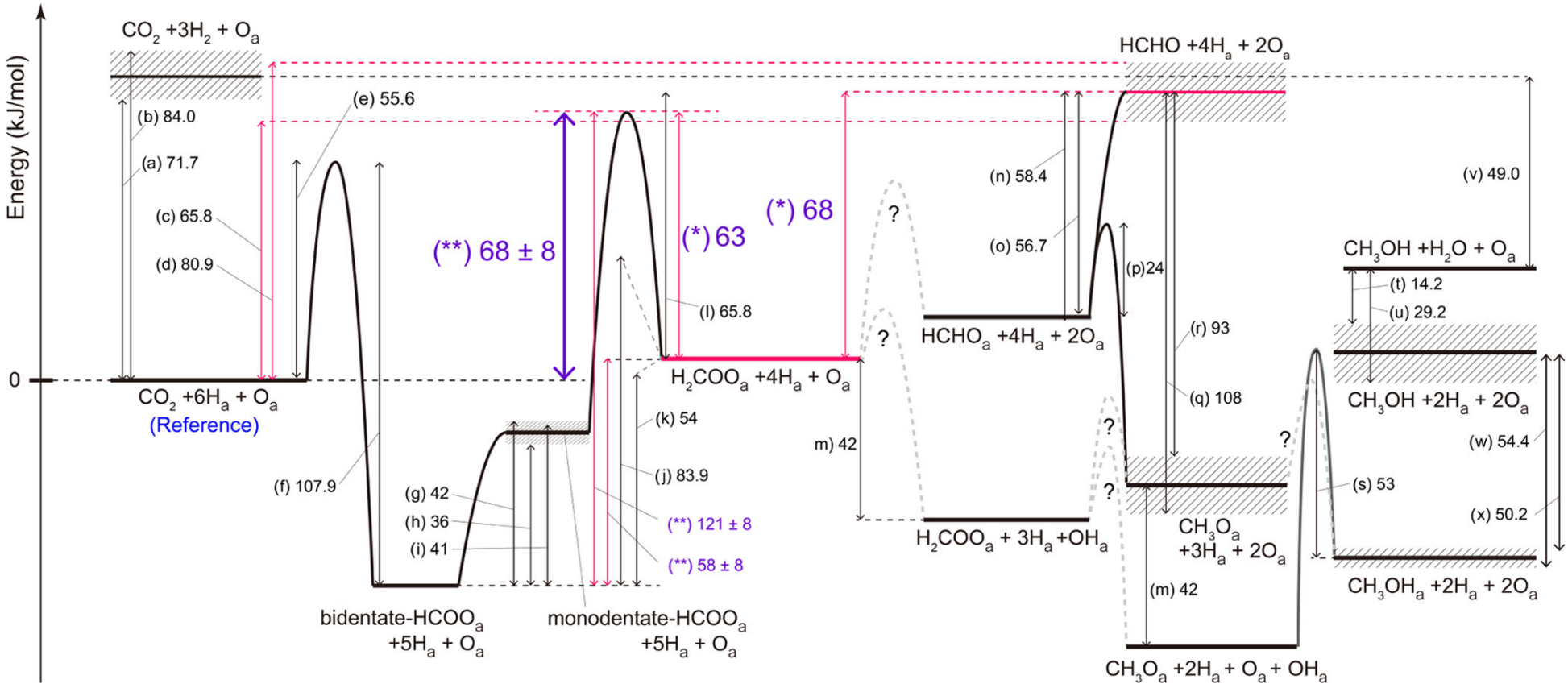


[3]Kattel et al., *Science*, 355(6331): 1296-1299,2017.

The challenge lies in the **intractable non-equilibrium states** of methanol synthesis

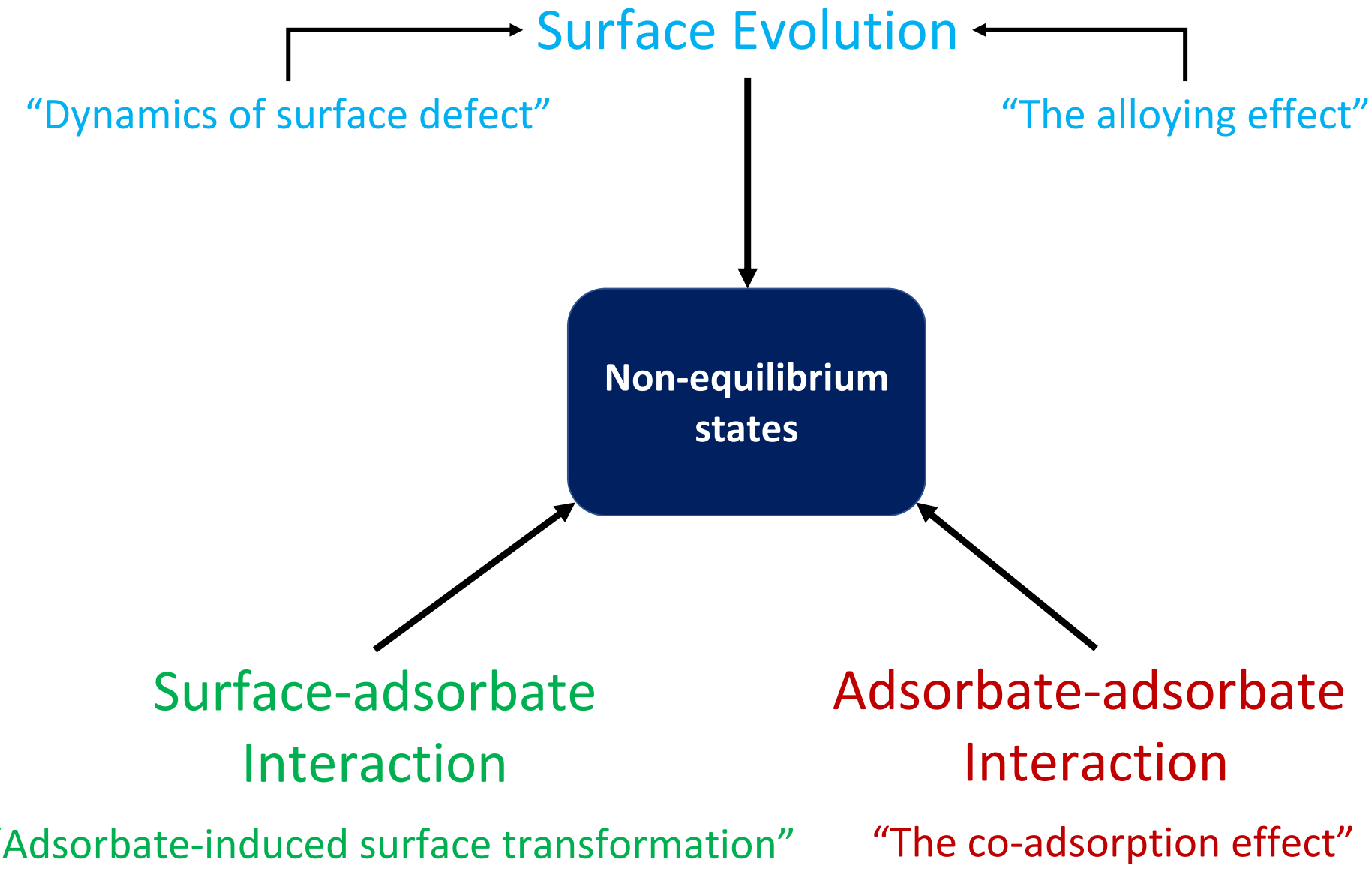
Energy Diagram of methanol synthesis from CO_2 and H_2 on Cu surfaces

Takeyasu, K. *et al., J. Am. Chem. Soc.* 2022, 144, 27, 12158–12166



Methanol synthesis has **complex reaction pathway** even on Cu surface

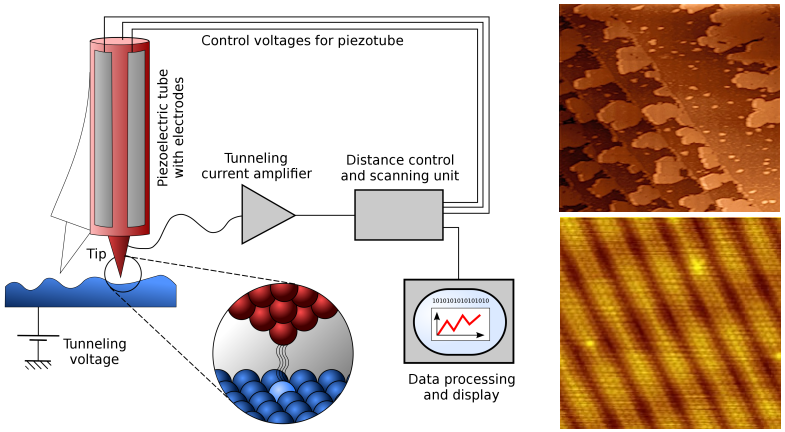
Introduction



Introduction

Experimental Approach

➢ **Scanning Tunneling Microscope (STM)**

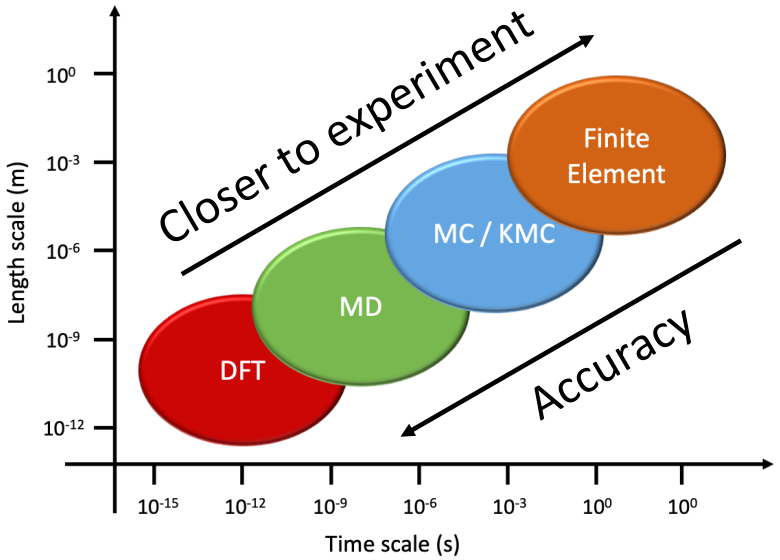


https://en.wikipedia.org/wiki/Scanning_tunneling_microscope

Experiment has difficulty to capture atomistic events

Computational Approach

➢ **Single-scale simulations**



There is a trade-off between scale and accuracy

Multi-scale Simulation

Machine Learning Molecular Dynamics

DFT Calculation → "Bridge" → Molecular simulation

Machine learning force-field — Molecular Dynamics

✓ Accurate for general chemical species

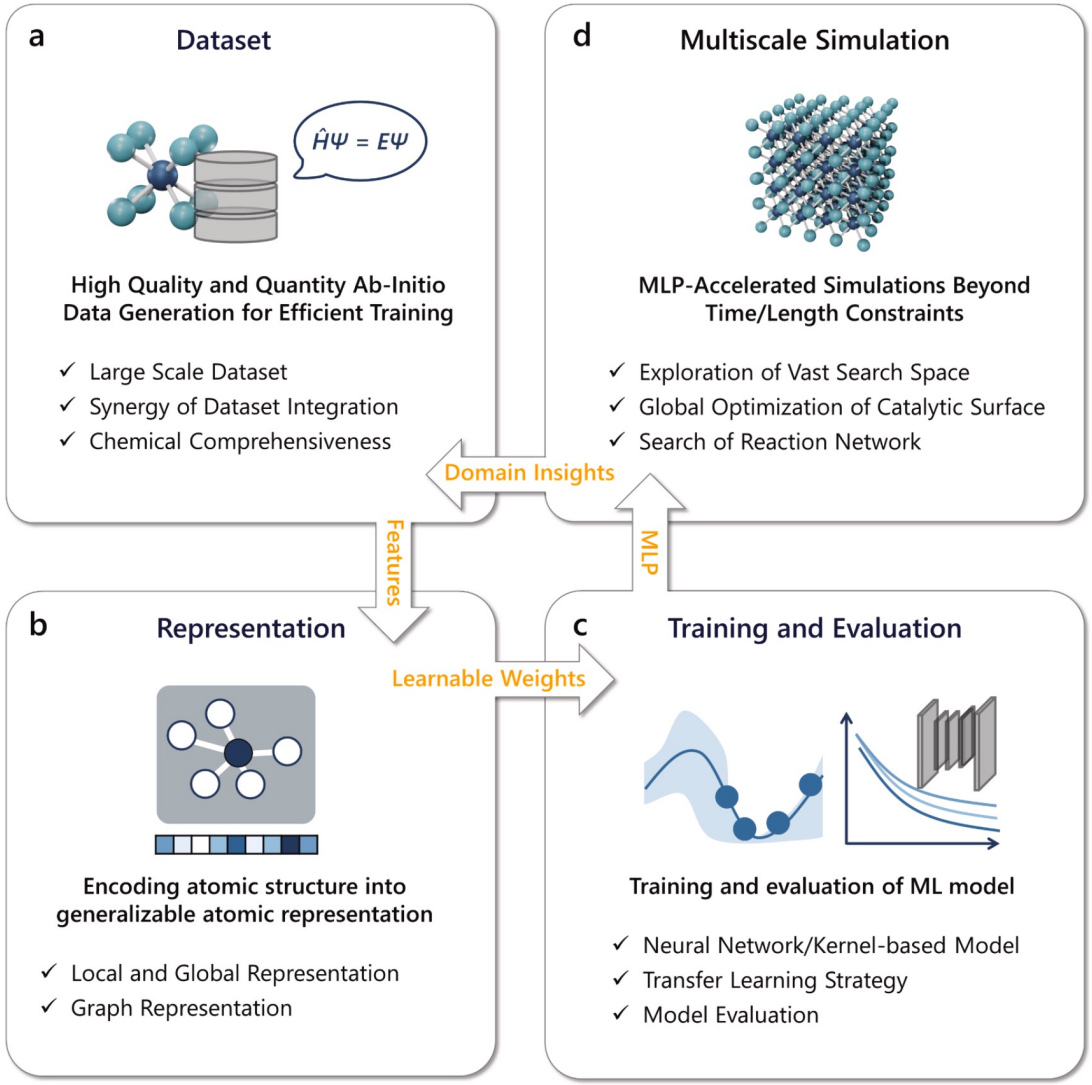
✓ Feasible for large system and long time scale

Machine Learning force-field/potential

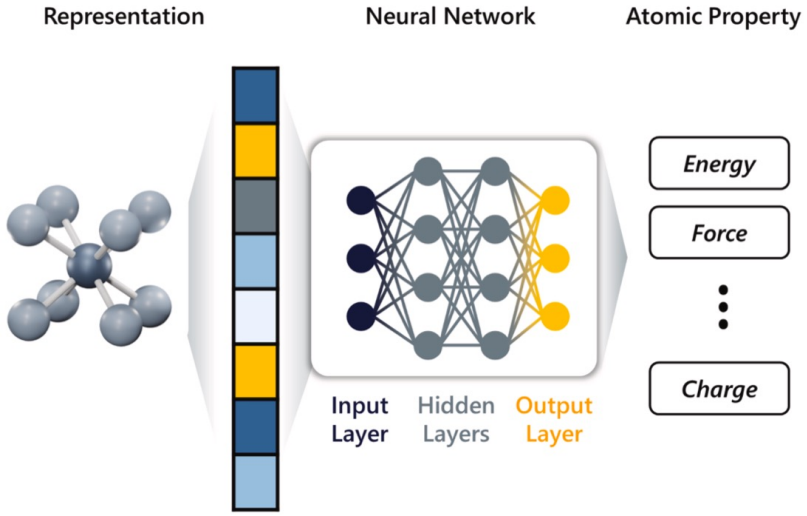
Rise of machine learning potentials in heterogenous catalysis

S. Choung et al. Chemical Engineering Journal 494 (2024) 152757

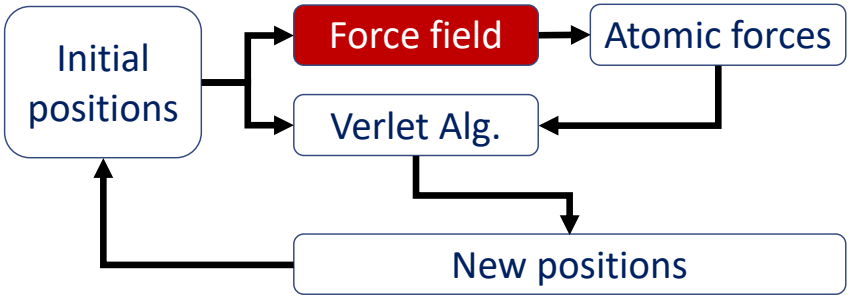
❑ Workflow



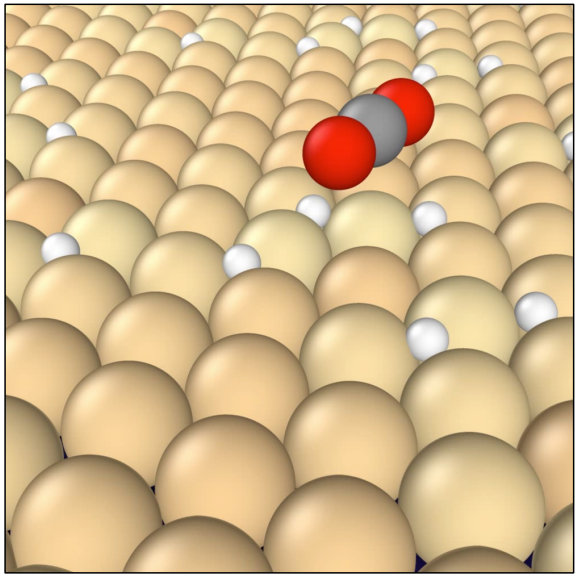
❑ How MLFF works

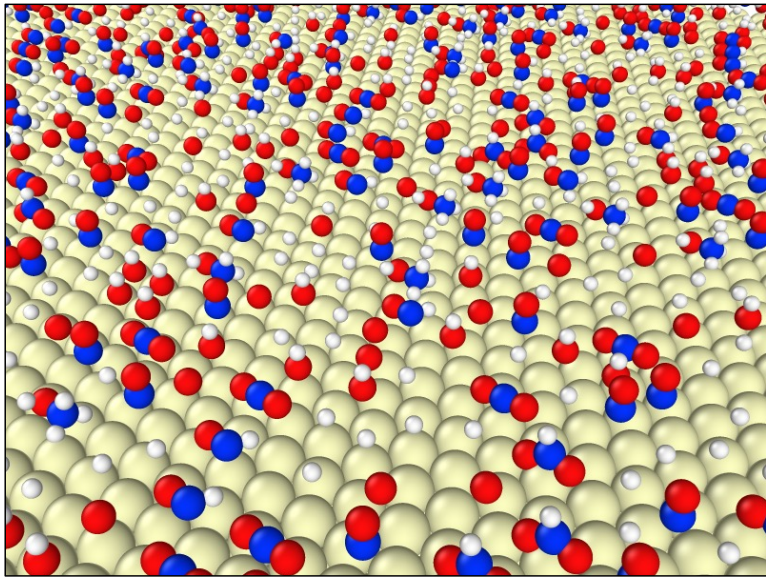


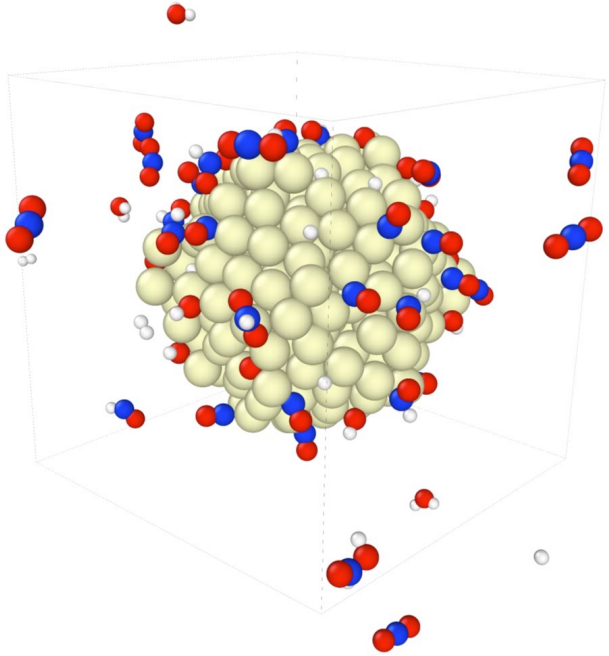
❑ How MLFF is applied



The Digital Twin of methanol synthesis on Cu surface and nanoparticle







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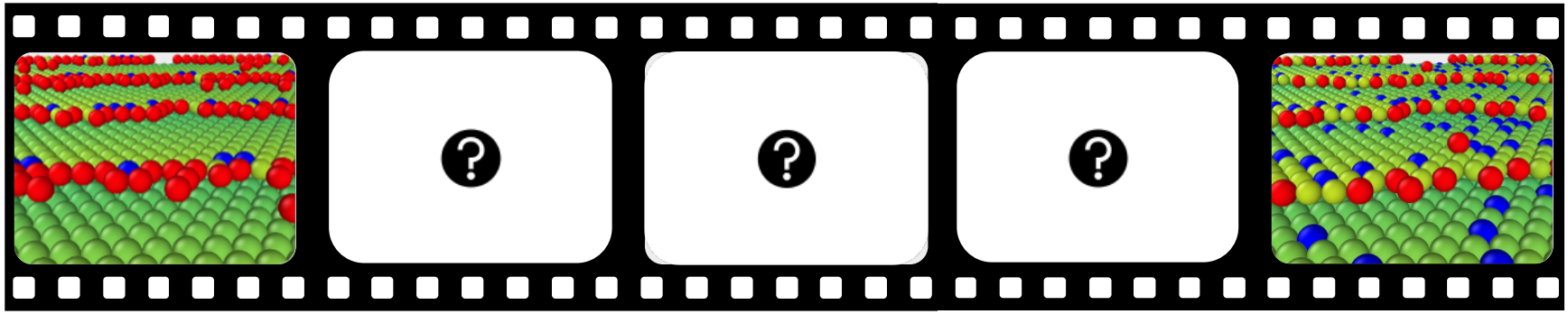
The Elucidation of Cu-Zn Surface Alloying on Cu(997) by Machine-Learning Molecular Dynamics

Harry H. Halim and Yoshitada Morikawa

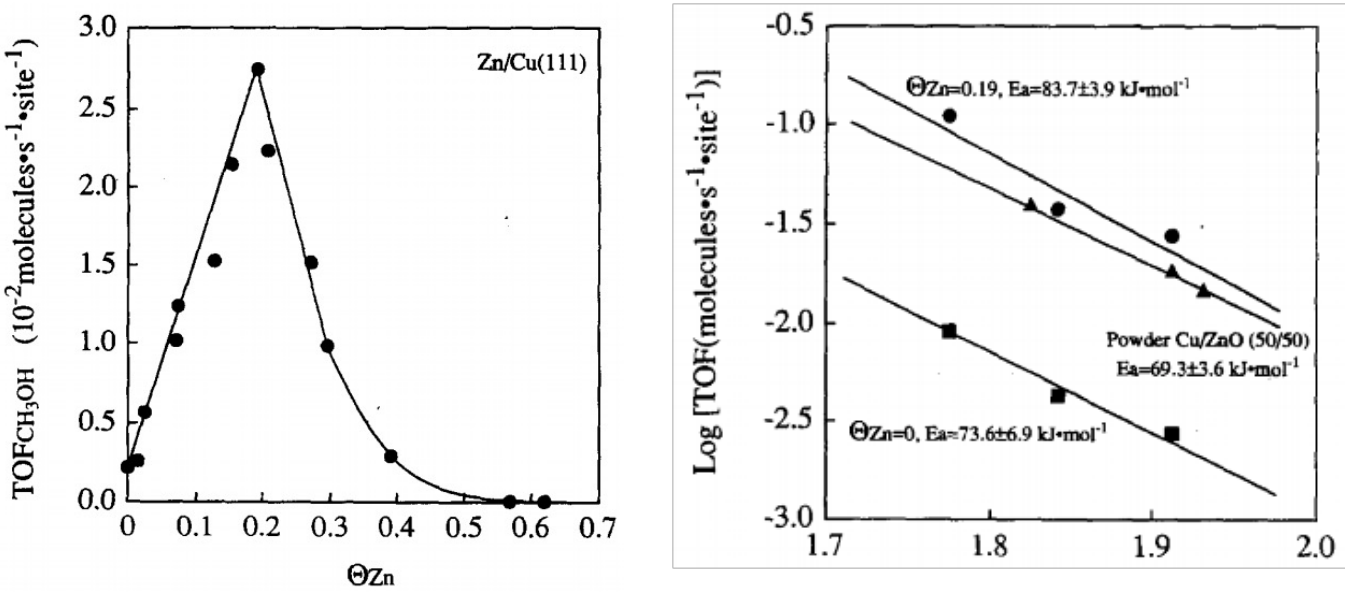
ACS Phys. Chem. Au, 5, 430-447 (2022).

Graduate School of Engineering
Osaka University

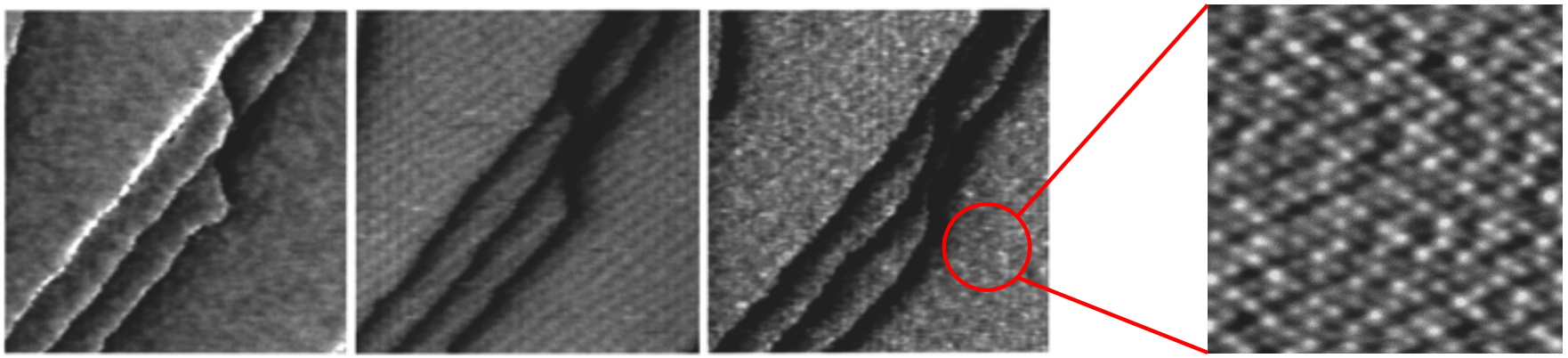


Promotional effect by Cu-Zn alloy

Fujitani, T., et al., *Surface Science*. **1997**, *121,122, 583-586*.



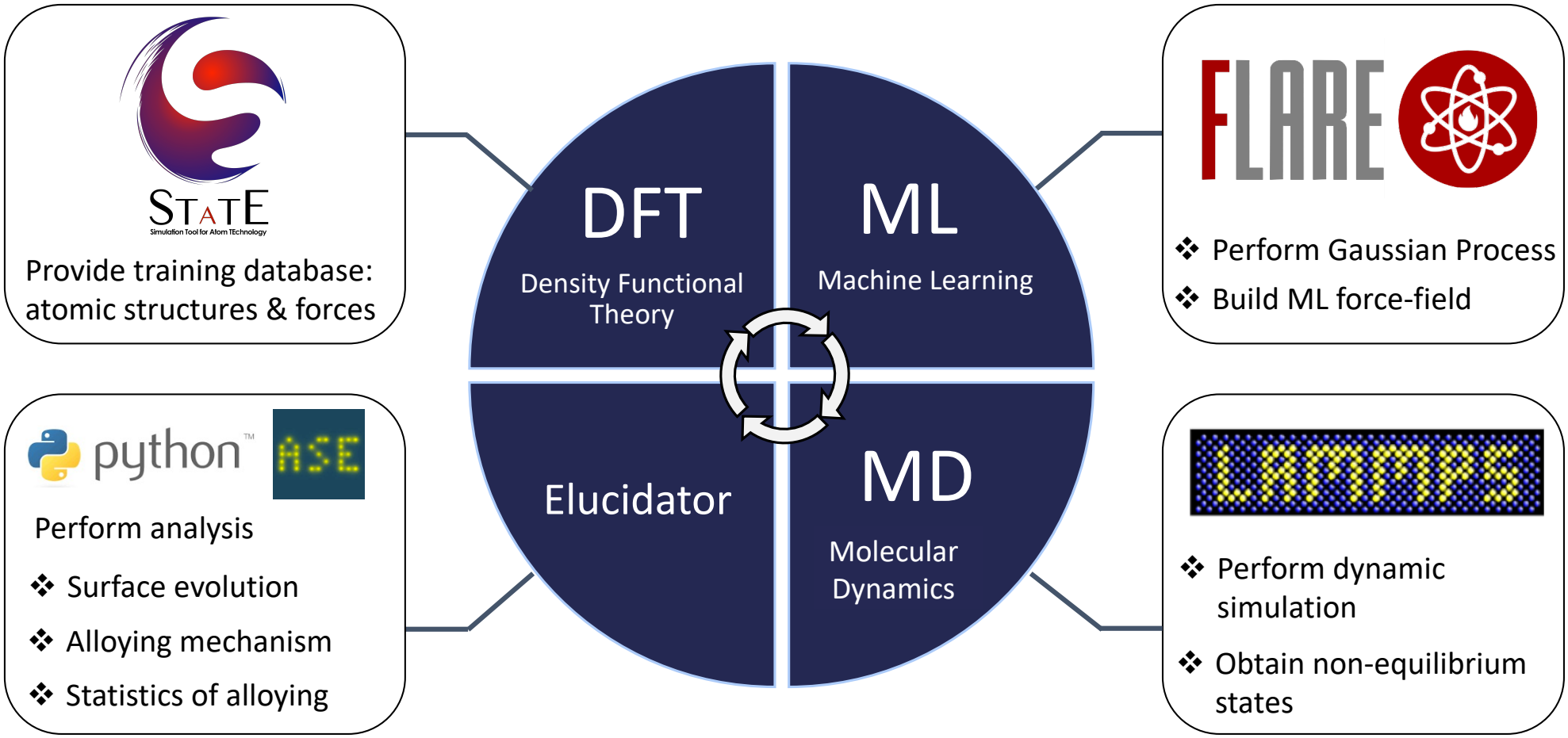
Formation of Cu-Zn surface alloy on Cu(111)



Sano, et.al. *J. Phys. Chem. B,* (2002),106, 31,7627-7633

Methodology

Machine Learning Molecular Dynamics



[STATE] Morikawa. Y., et.al, Appl. Sur. Sci **169-170**, 11 (2001).

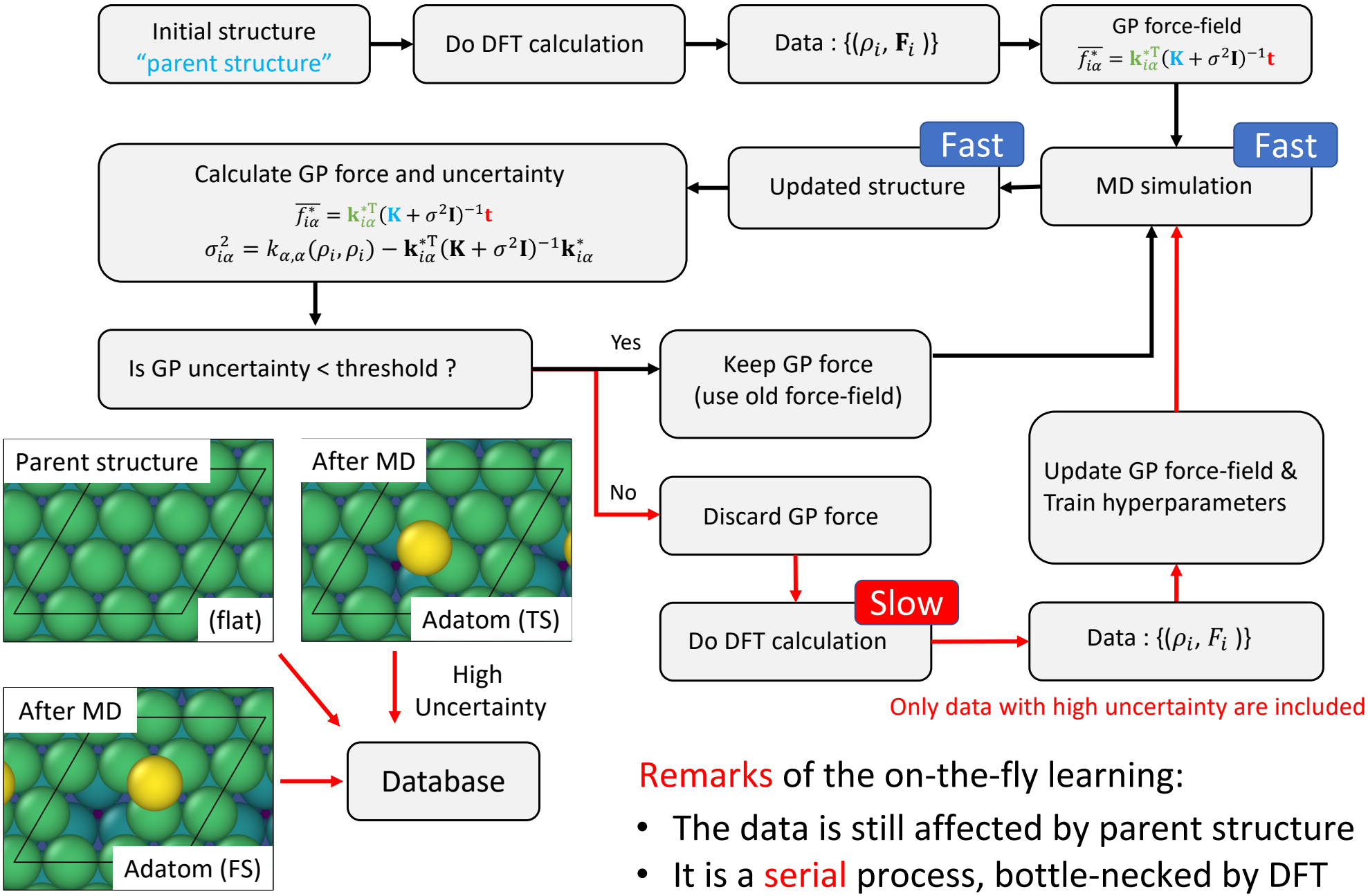
[Elucidator] https://github.com/hhlim12 (under development)

[FLARE] Vandermause. J., et.al, npj Comput Mater 6, 20 (2020).

[LAMMPS] Thompson, A.P., *et al.,* Comp Phys Comm, **271** (2022) 10817.

Active and On-the-fly Learning

Vandermause. J., et.al, npj Comput Mater 6, 20 (2020).



Only data with high uncertainty are included

Remarks of the on-the-fly learning:

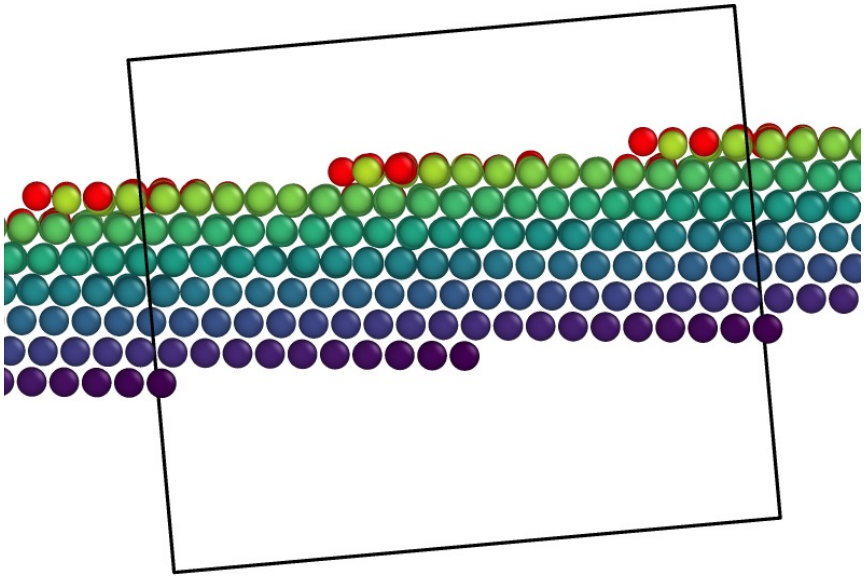
- The data is still affected by parent structure
- It is a serial process, bottle-necked by DFT

MD Preparations

Definitions used in surface model (Cu(997) – Zn alloy)

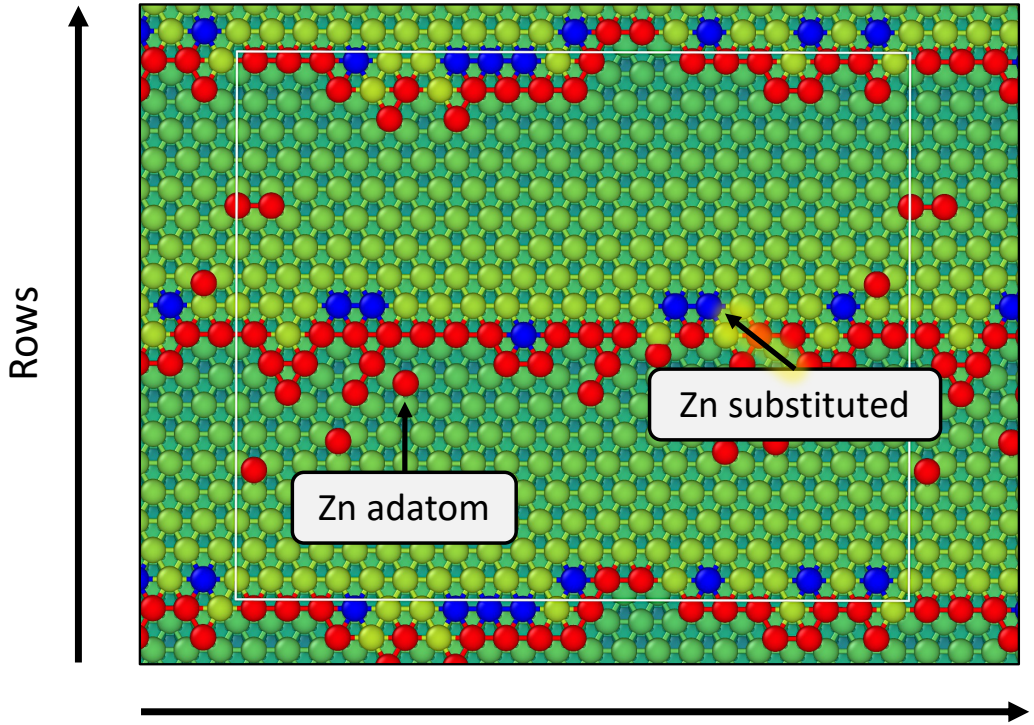
Cu $Zn^{(ad)}$ $Zn^{(sub)}$

Side View



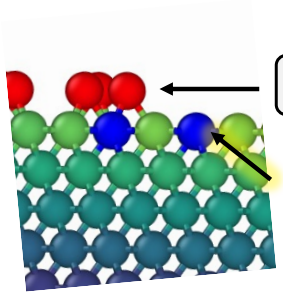
20 rows x 20 columns = 400 atoms / layer

Top View



Terrace

Step edge



Zn adatom — Coordination number < 9

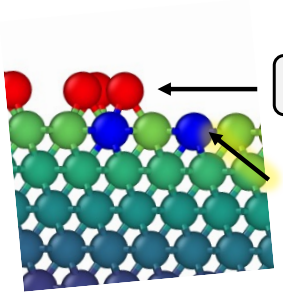
Zn substituted — Coordination number ≥ 9

Results and Discussion

Evolution of Zn Atoms on Cu(997) at 700 K

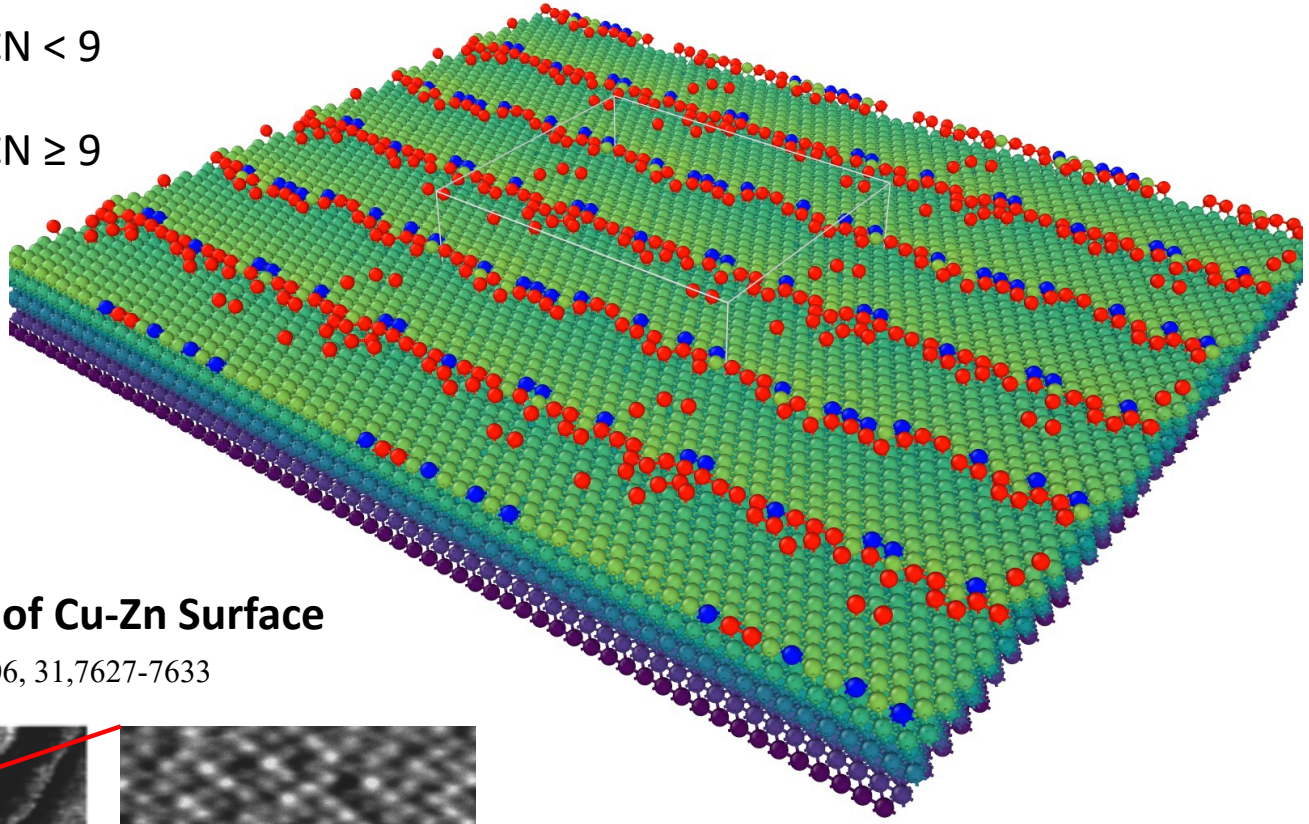
Cu $Zn^{(ad)}$ $Zn^{(sub)}$

MLMD Observation on Formation of Cu-Zn Surface



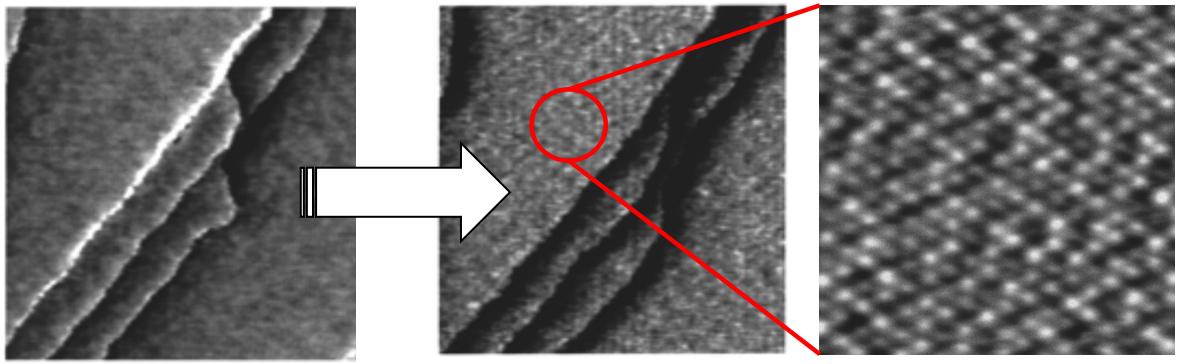
Zn adatom CN < 9

Zn substituted CN ≥ 9



STM Observation on Formation of Cu-Zn Surface

Sano, et.al. *J. Phys. Chem. B,* (2002),106, 31,7627-7633

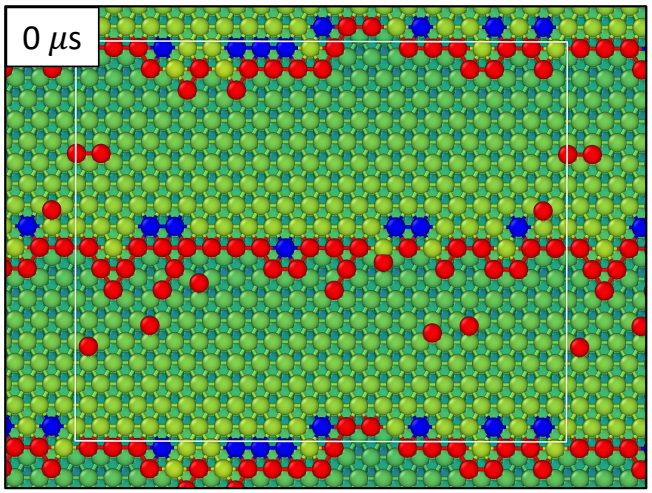


The MLMD and STM show Zn alloyed from the **step edge** to **middle terrace**.

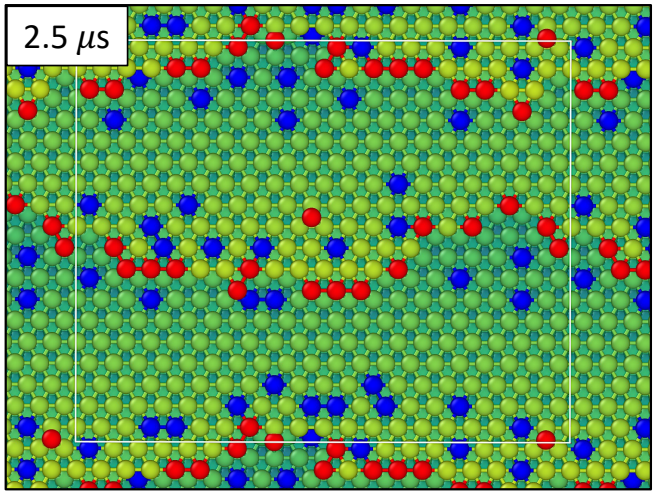
Results and Discussion

Evolution of Zn Atoms on Cu(997) at 700 K $\Delta t = 5\ fs$

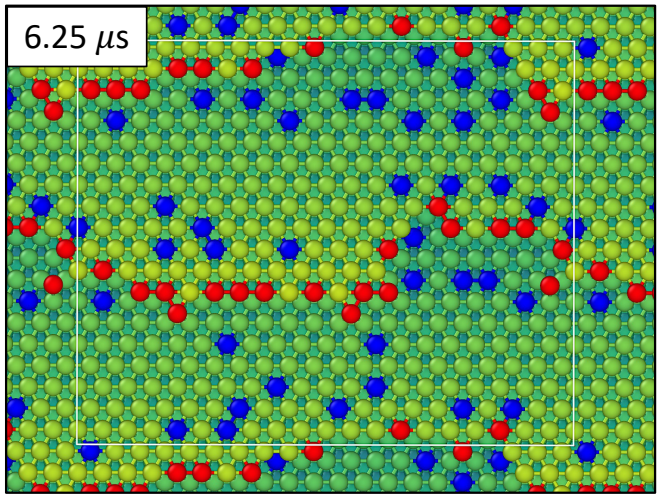
Cu $Zn^{(ad)}$ $Zn^{(sub)}$



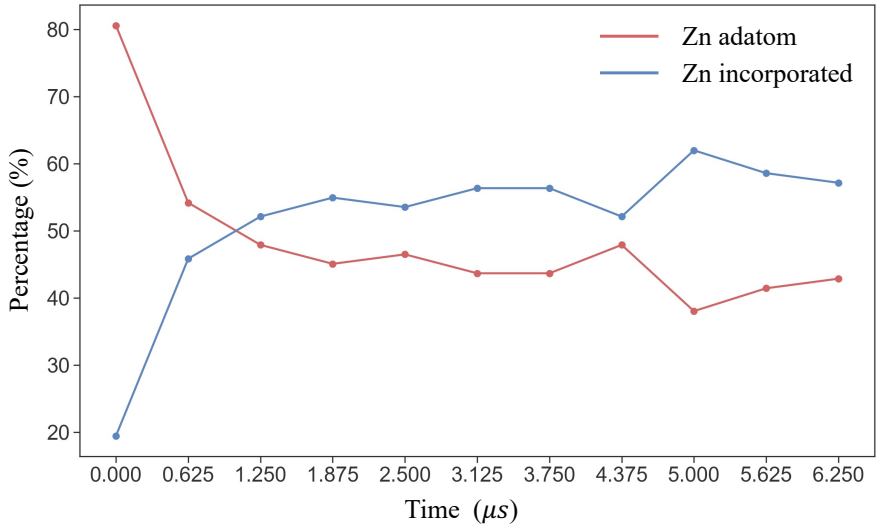
Initially most of the Zn attach to the step edge

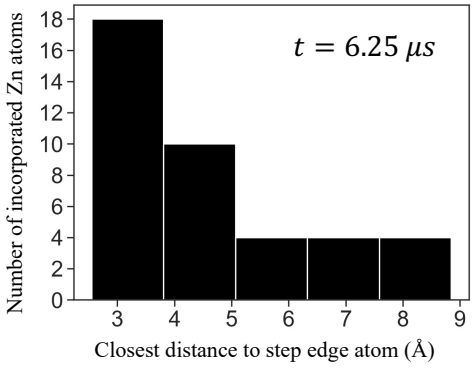


Zn incorporate the upper and lower terrace

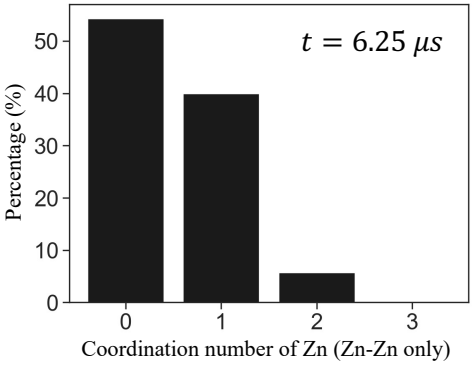


Some Zn atoms are incorporated at middle terrace





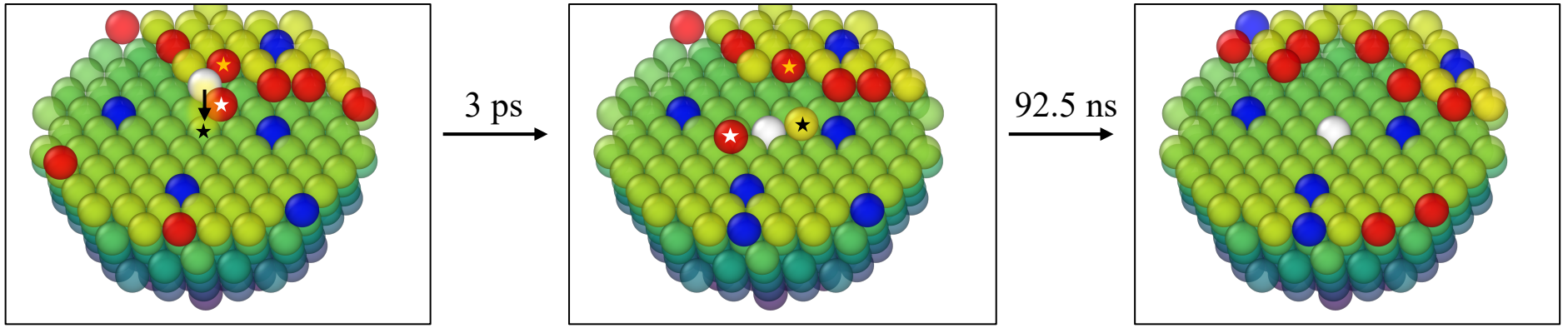
Zn mostly incorporate region near step edge.

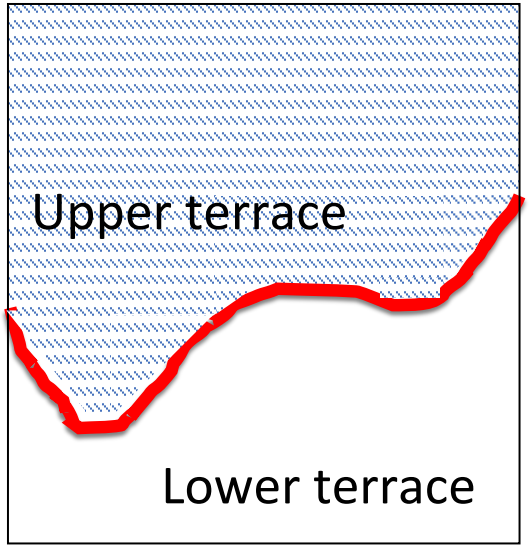


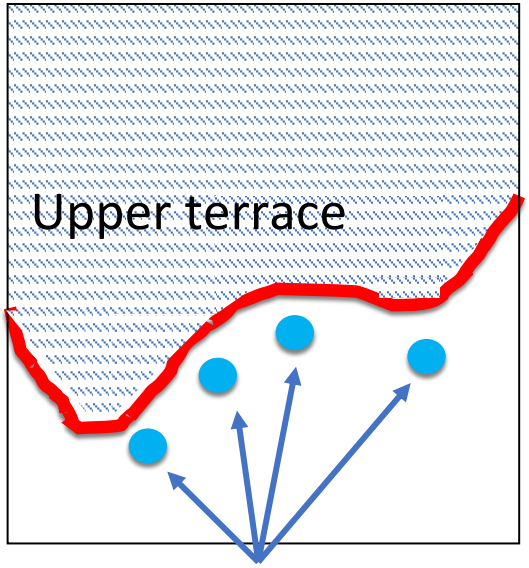
No significant Zn-Zn interaction in the alloy.

Dominant alloying mechanisms at **Middle terrace**

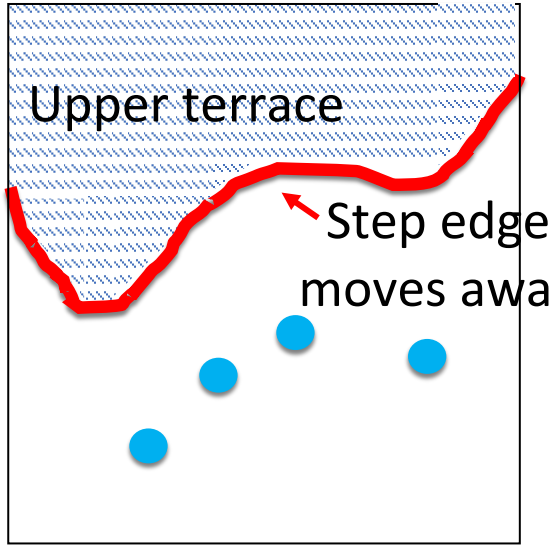
Wave deposition







Alloying takes place at lower terrace



Steps help transporting Zn atoms to middle terrace

Atomic-Scale Site Characterization of Cu–Zn Exchange on Cu(111)

M. Mammen, S. Jensen, M. Andersen, and J. V. Lauritsen*

Cite This: *J. Phys. Chem. C* 2023, 127, 3268–3275 Read Online

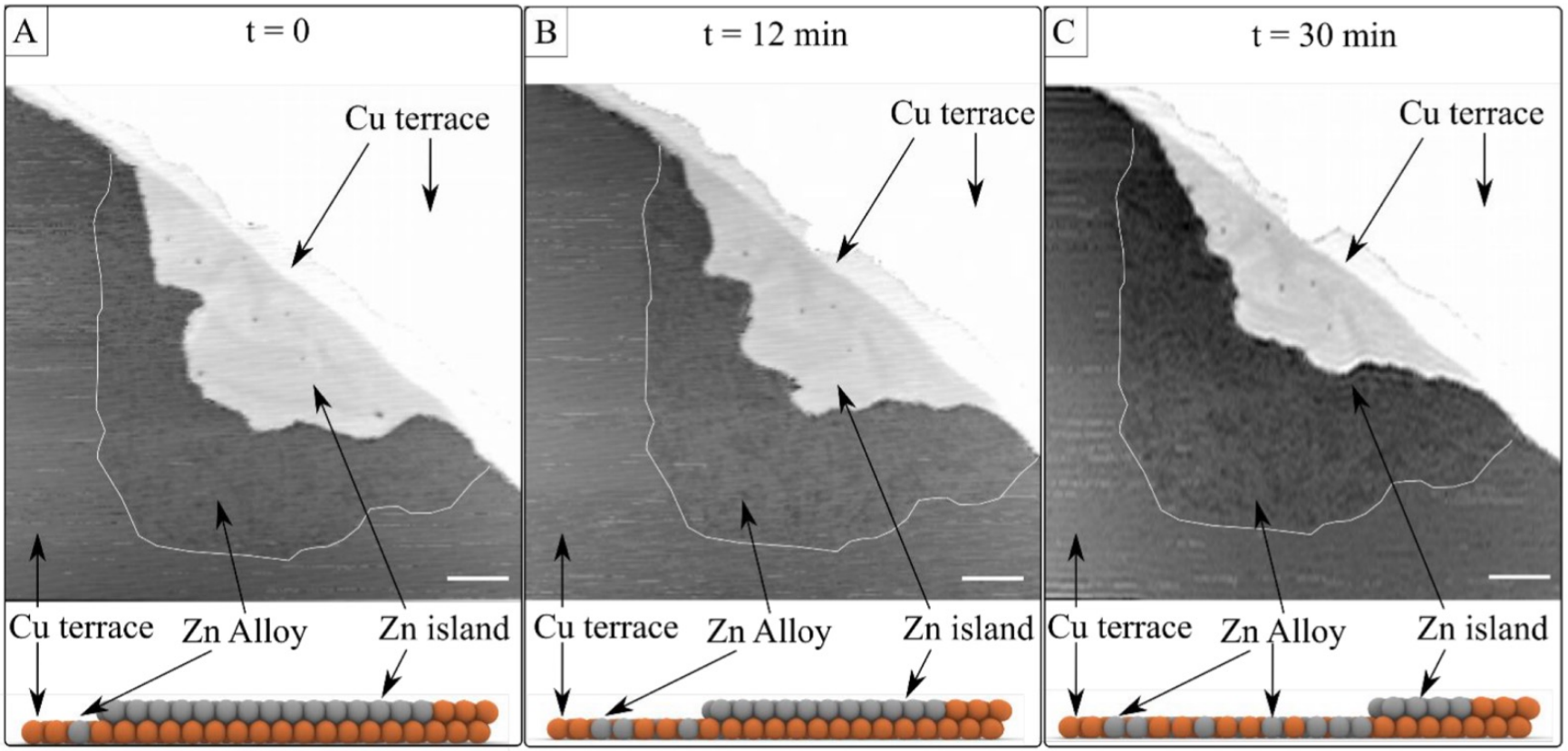


Figure 1. (A–C) Consecutive STM images of the Cu(111) after deposition of 0.2 ML Zn at room temperature. Irregular-shaped Zn islands form on the Cu terrace often extending from the step edges and with a lower-contrast perimeter surrounding the islands outlined by the white line. The island contracts over time, leading to the formation of a large darkened area reflecting the incorporation of Zn atoms into the Cu lattice. The ball models illustrate the dynamic degradation and substitution. Orange: Cu, Gray: Zn.. Scale bar: 10 nm. I_t = 0.27 nA, V_t = 1250 mV.

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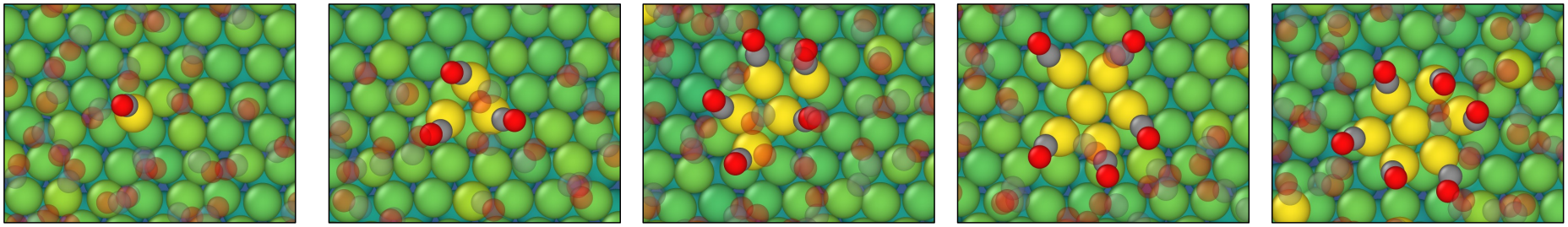
Machine Learning Molecular Dynamics Simulation of CO-driven Formation of Cu Clusters on Cu(111)

Harry H. Halim, Ryo Ueda, and Yoshitada Morikawa

Graduate School of Engineering
Osaka University

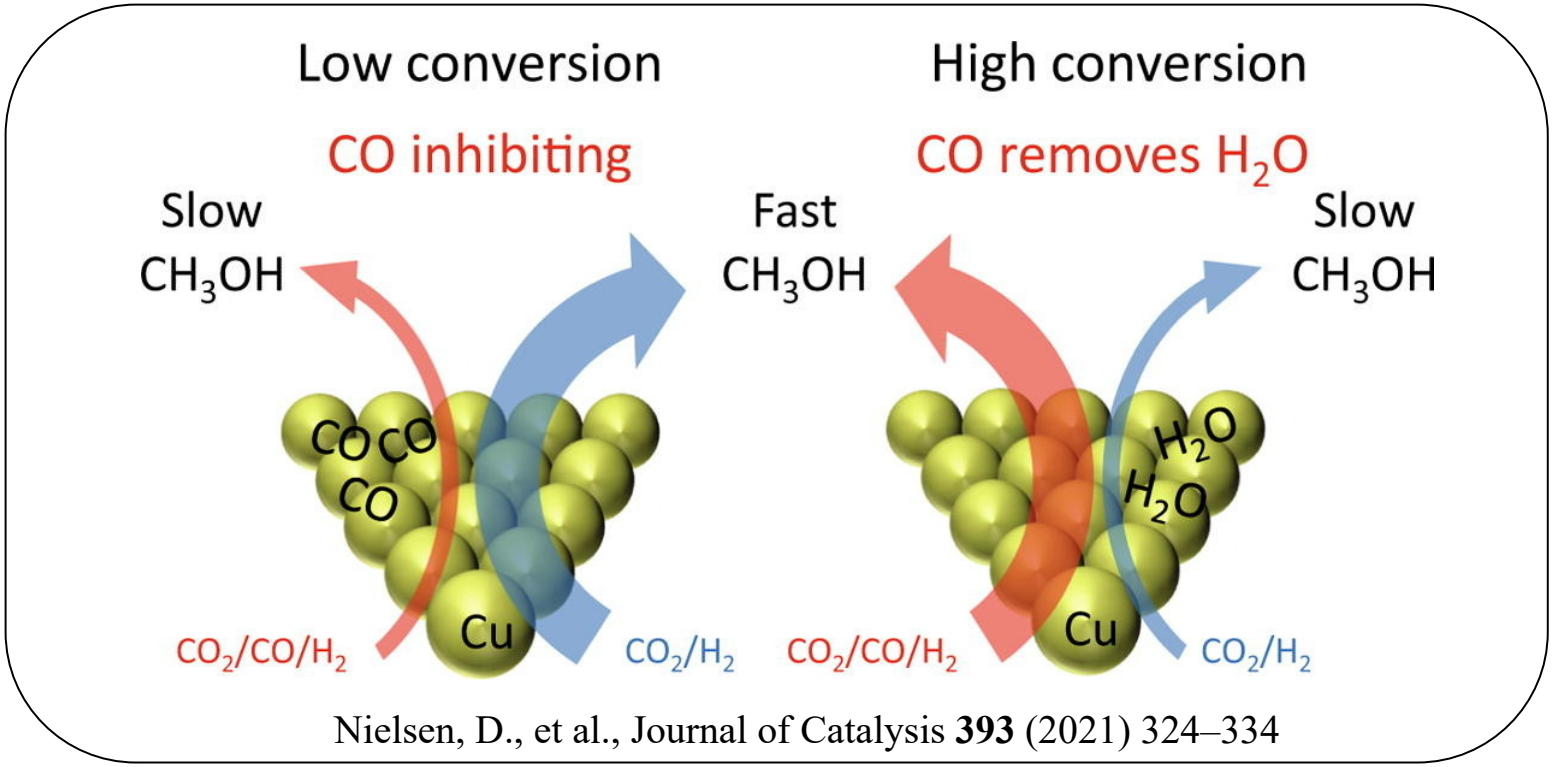


Halim., H. H., Ueda, R., and Morikawa, Y. *J. Physics: Condensed Matter* 35 (49), 495001, 2023.

The role of CO in methanol synthesis

Synthetic Gas
(**CO** / CO_2 / H_2)

$\xrightarrow[200^oC - 300^oC]{Cu/ZnO/Al_2O_3}$ Methanol + Water

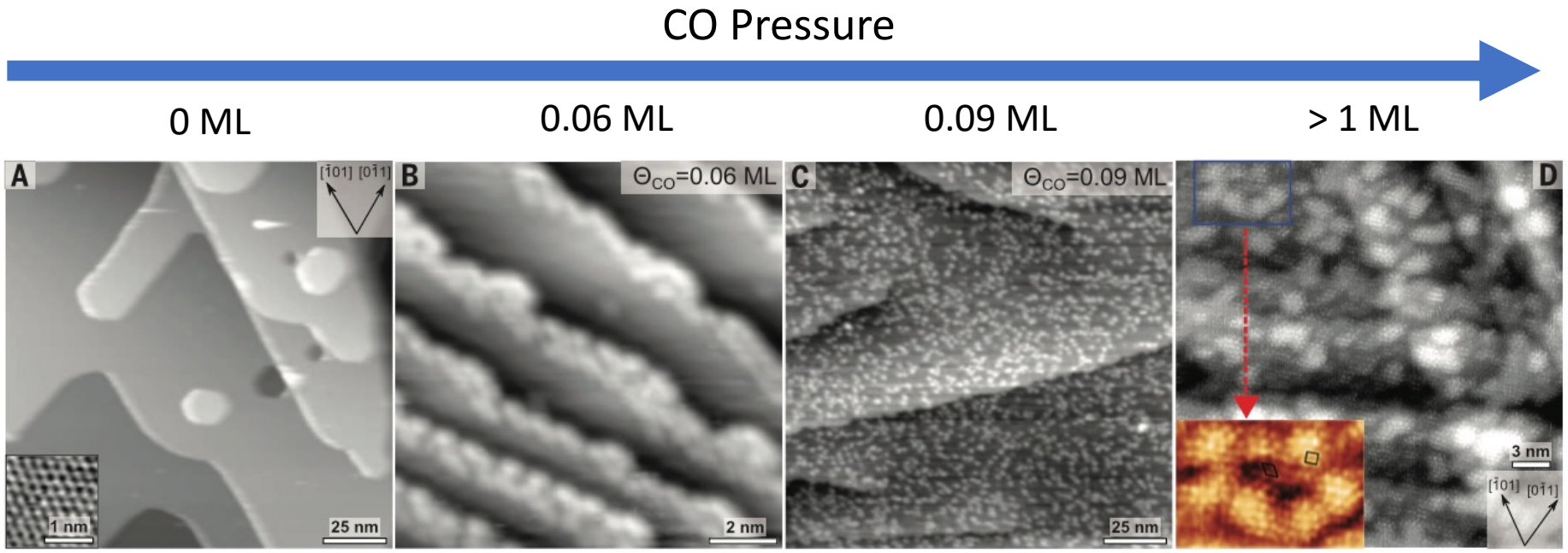


Nielsen, D., et al., Journal of Catalysis **393** (2021) 324–334

- ❖ CO becomes **inhibitor** during **low conversion** of methanol synthesis
- ❖ CO becomes **promoter** during **high conversion** of methanol synthesis

CO-induced formation of Cu clusters on Cu surfaces

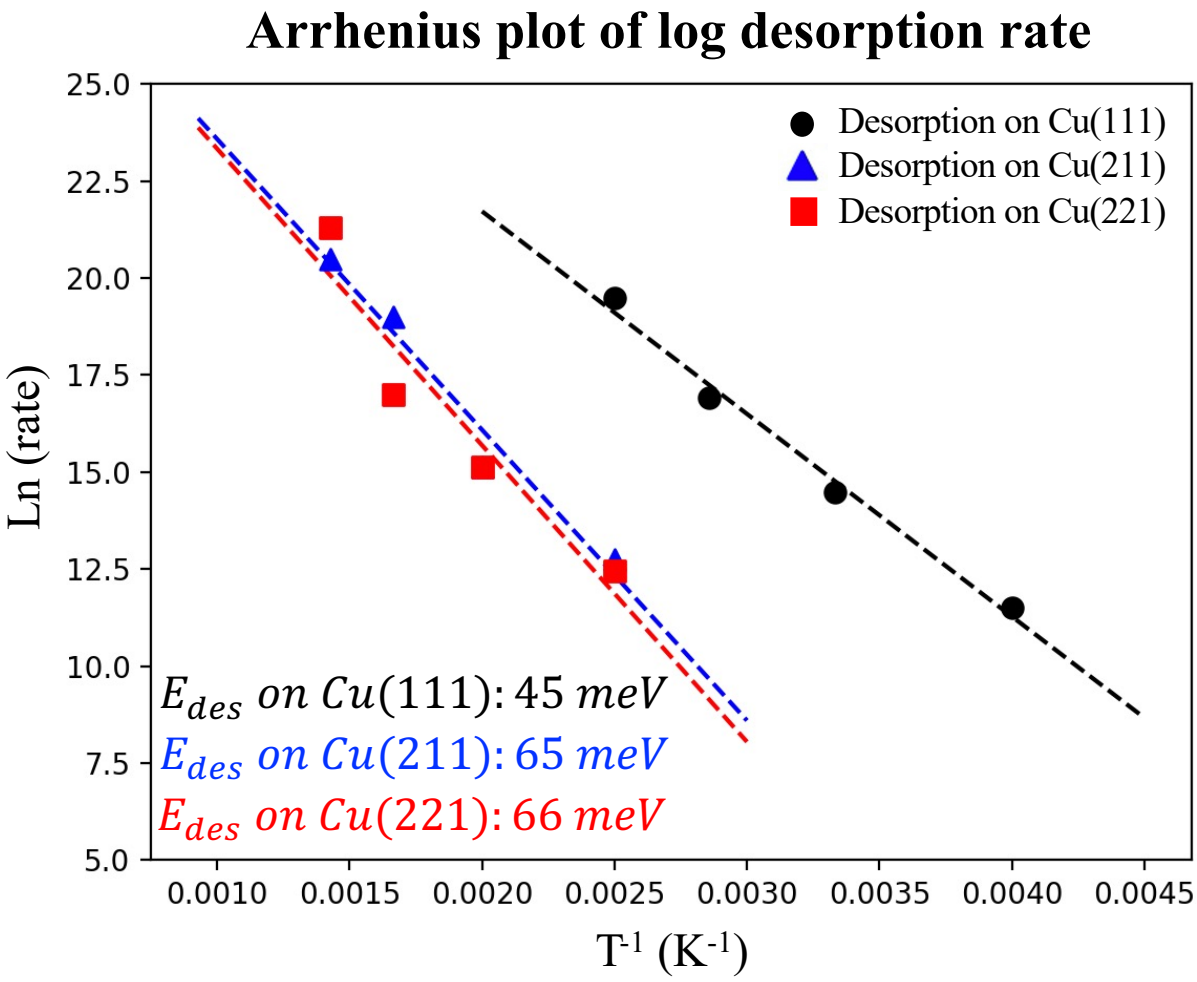
Eren, B. *et al.*, Science, **351** (2016), 475-478.



- Cu stepped surface **transforms** into **Cu clusters** when **exposed to CO**
- Cu clusters are **active for water dissociation** in WGS reaction
- CO might **affect the catalysis** by transforming the Cu surface

Methodology
Validation of ML model (desorption energy)

The **desorption rate** and **desorption energy** can be measured from MLMD.



Arrhenius equation

$$\ln(rate) = \ln \nu - \frac{E_{des}}{RT}$$

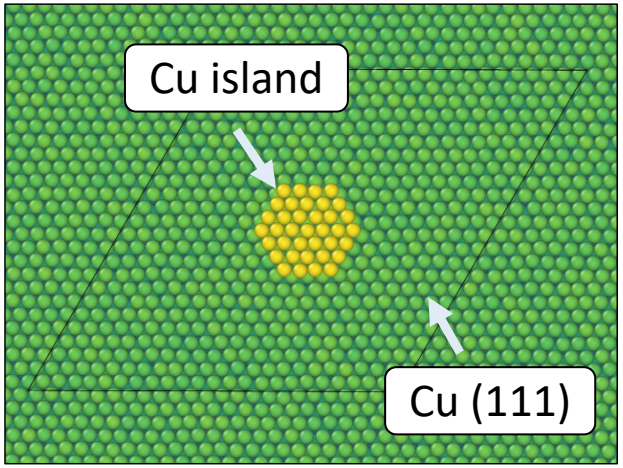
Surface	Desorption Energy (eV)	
	Exp.[1]	MLMD
Cu(111)	0.49	0.45
Cu(221)	0.60	0.66
Cu(211)	0.61	0.65

[1]Vollmer, S. *Catal. Lett. 2001, 77(1), 97-101.*

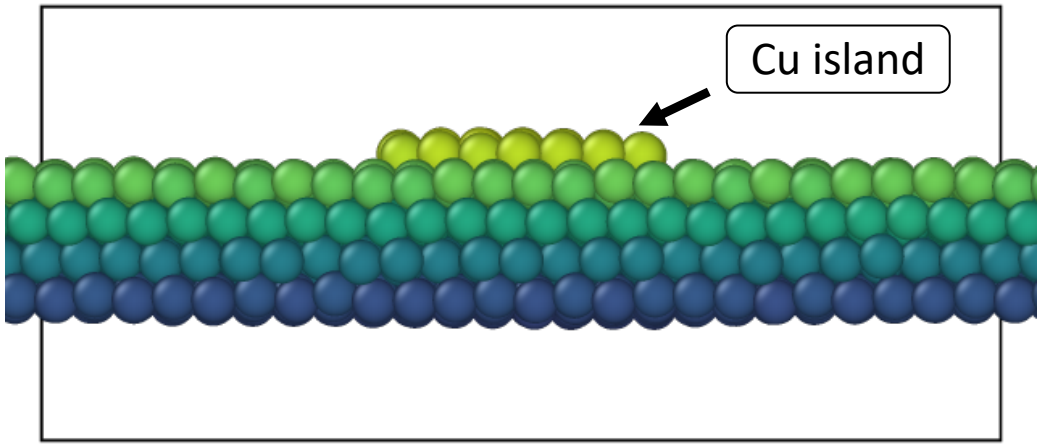
MLMD can well reproduce the desorption energy of CO on Cu surfaces

Methodology
Initial structures in MD simulation

Cu-island is deposited on Cu(111) (2341 atoms / unit cell)

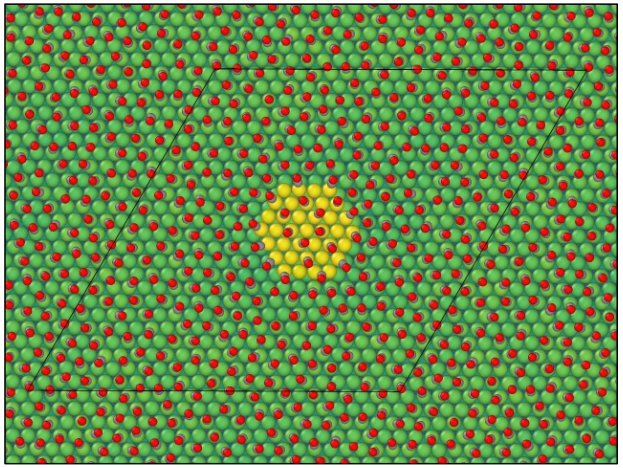


Top view

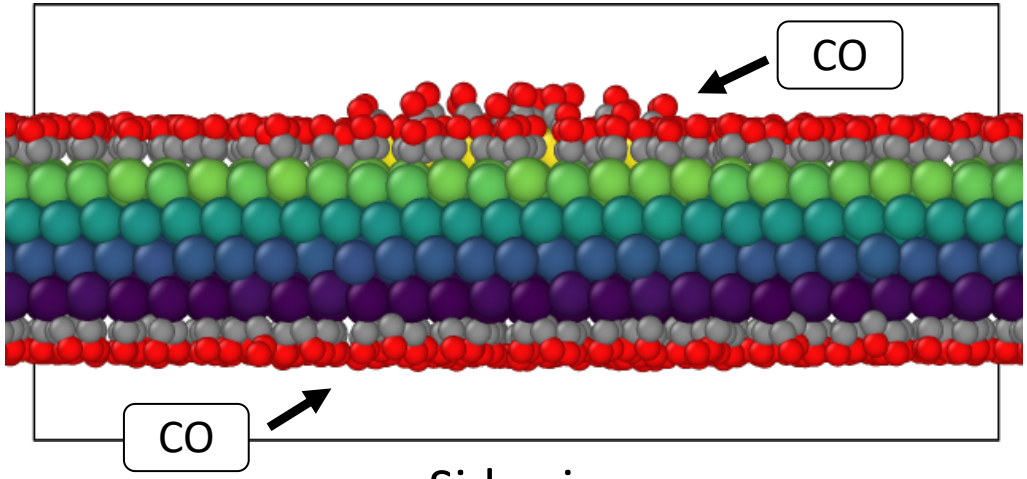


Side view

CO ($\theta = 0.5$) and Cu-island is deposited on Cu(111) (3485 atoms / unit cell)

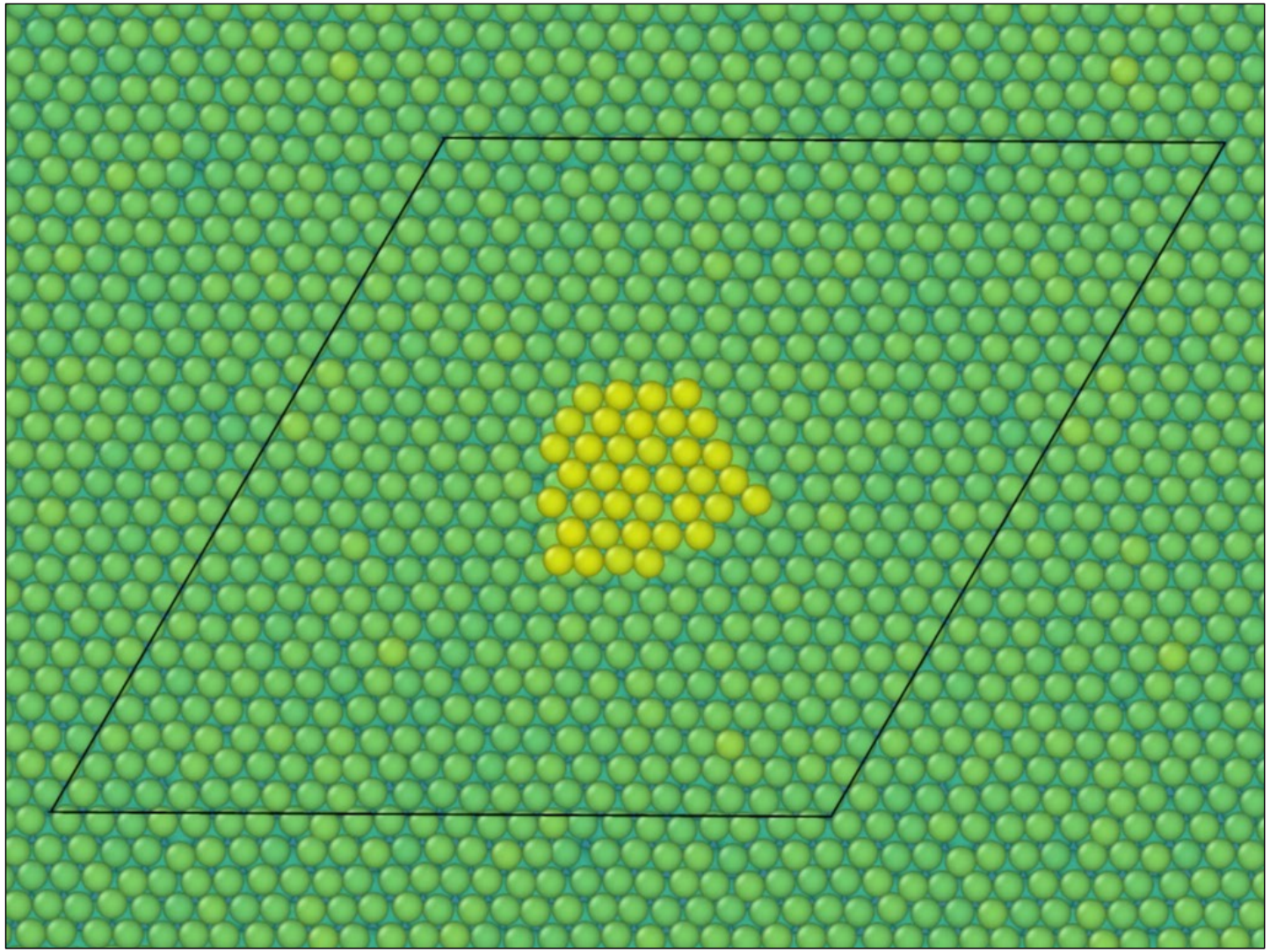


Top view



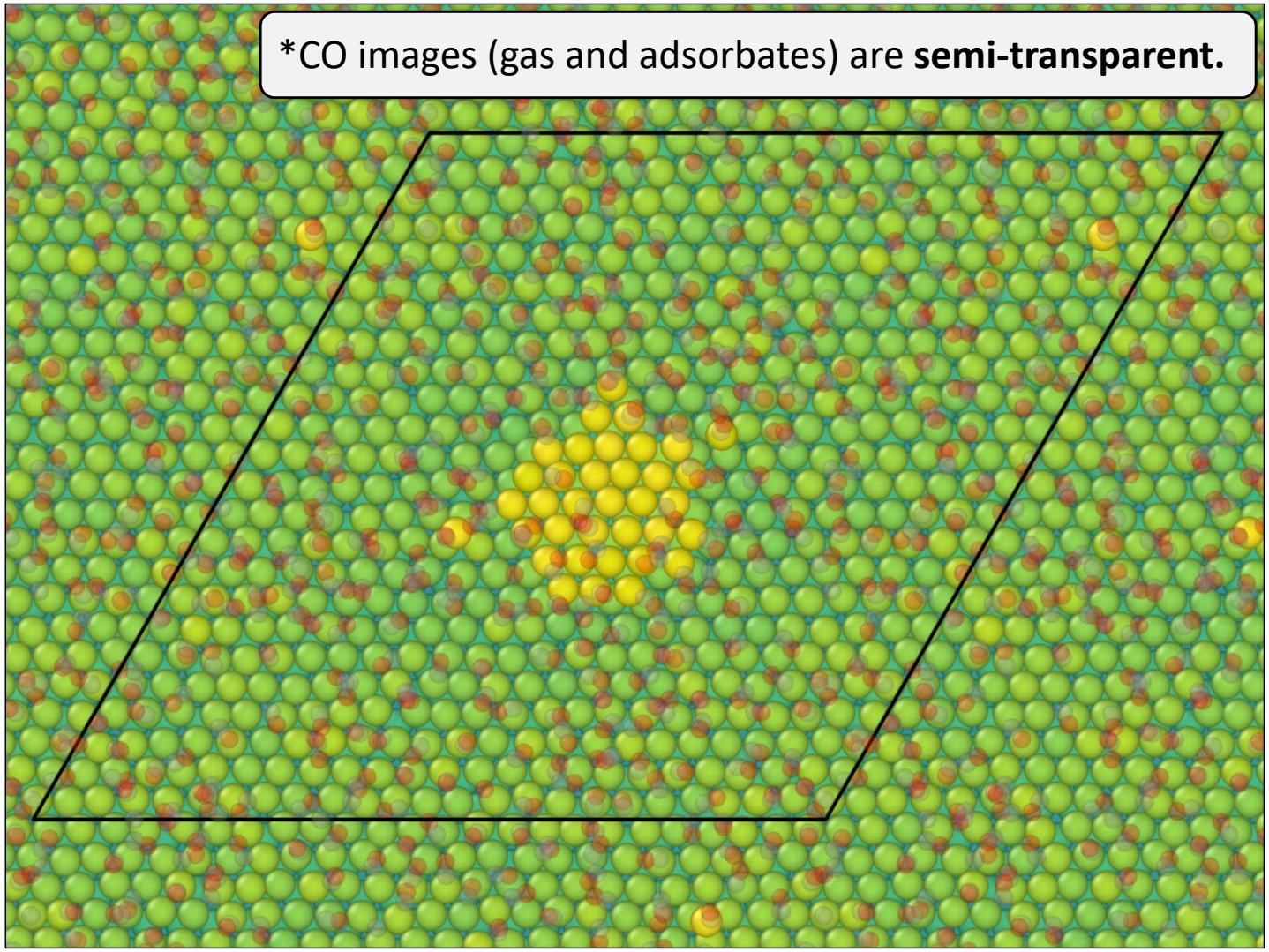
Side view

Results and discussion
Evolution of surface without CO (T = 550 K)



Without CO exposure, **no cluster** formation is observed even at 550 K

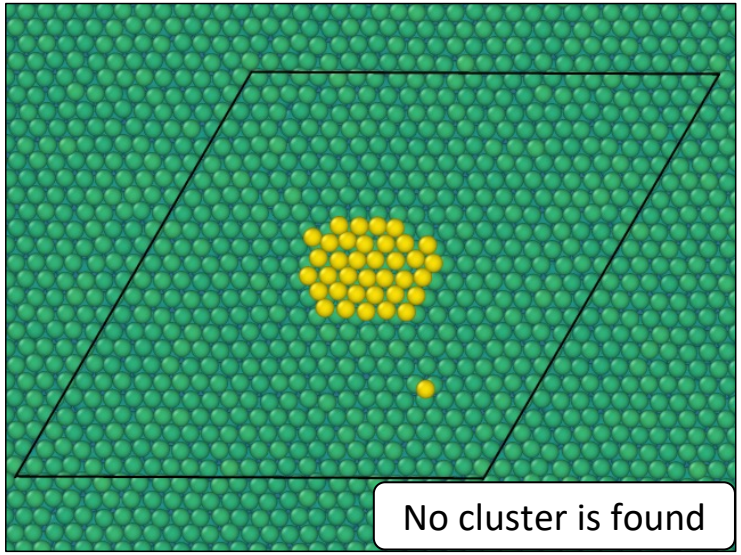
Results and discussion
Evolution of surface with CO (T = 550 K)



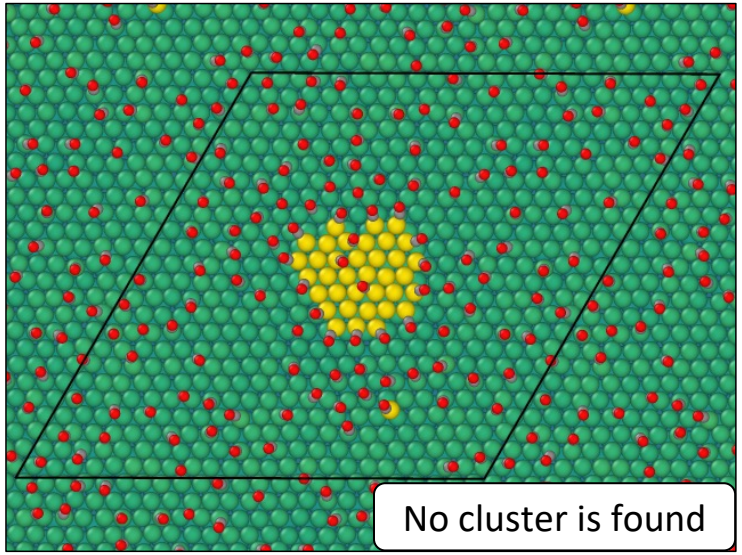
With CO exposure, **nanoclusters is formed** within tens of ns.

Results and Discussion
Evolution of Cu Surface at different temperatures

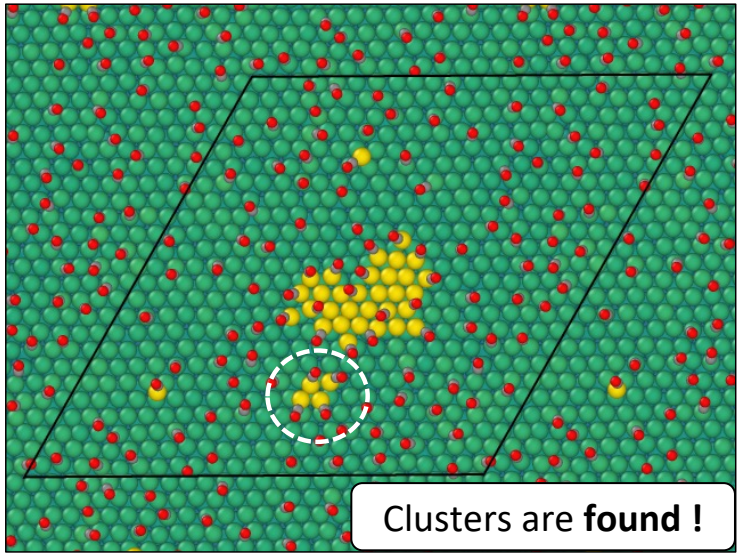
Cu only (550 K)



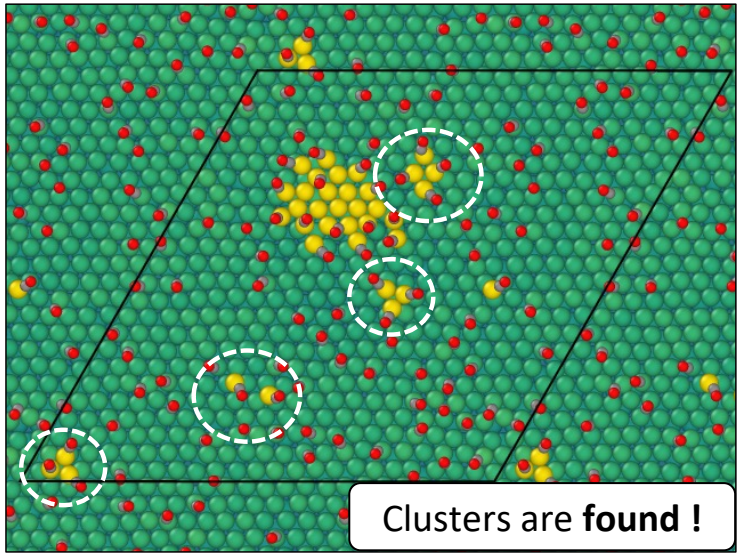
Cu + CO (350 K)

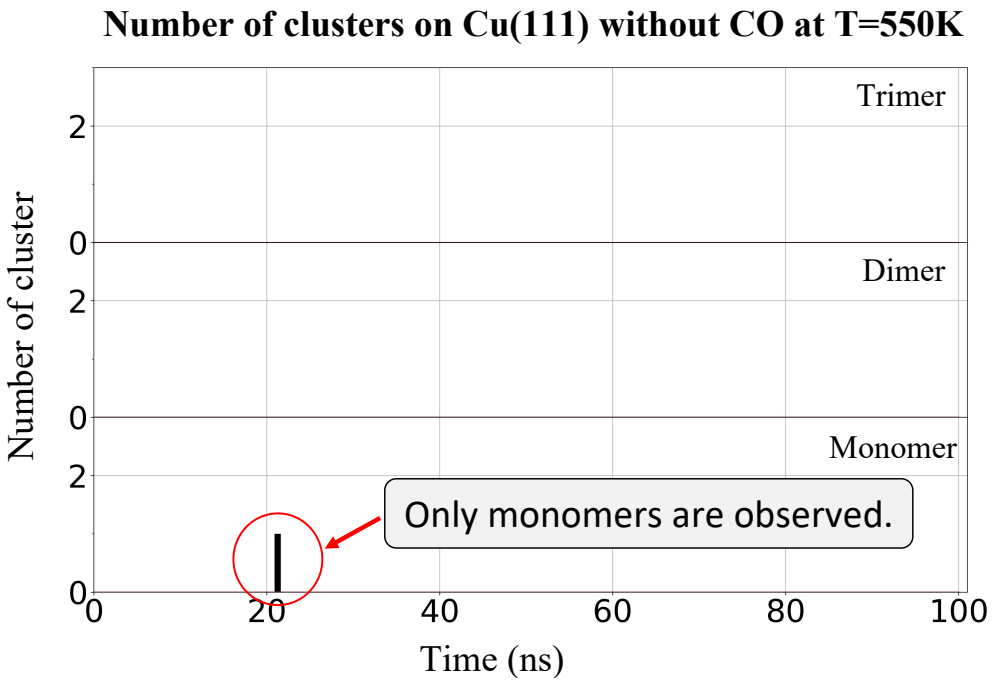


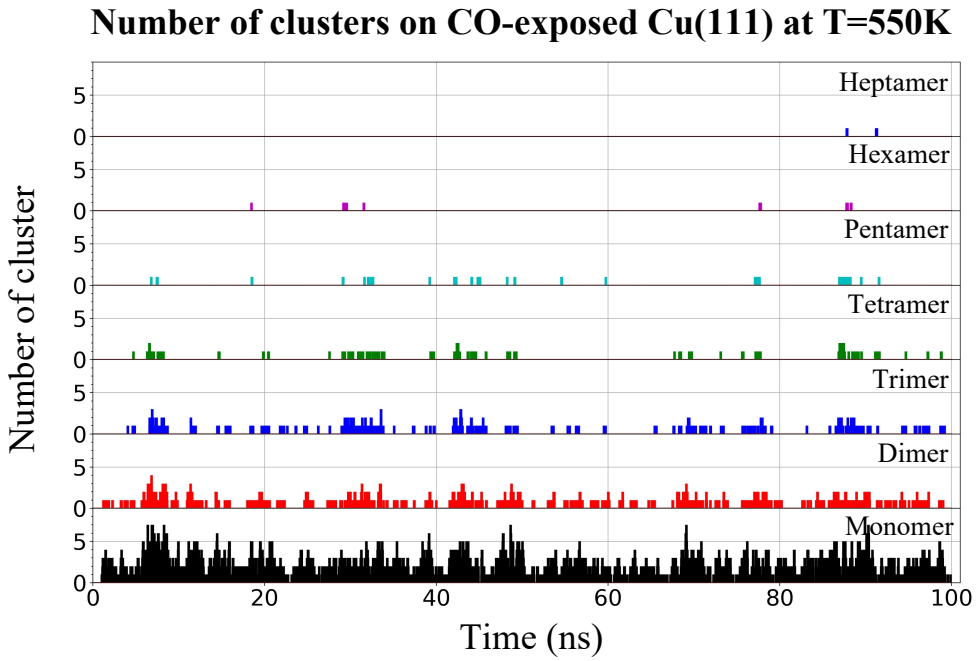
Cu + CO (450 K)



Cu + CO (550 K)

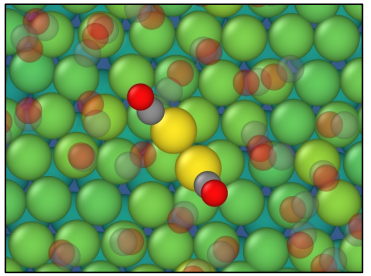




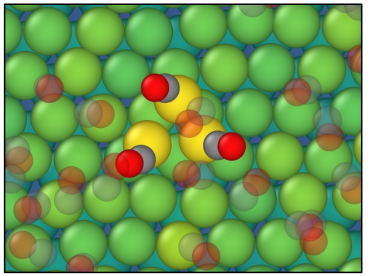


Clusters varying from **dimer** to **heptamer** are observed.

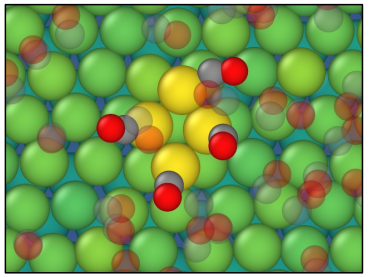
The shapes of Cu-CO clusters



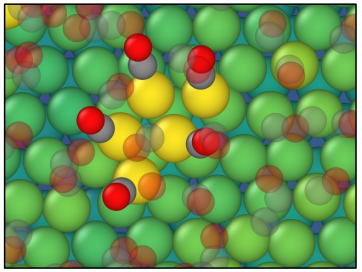
Dimer



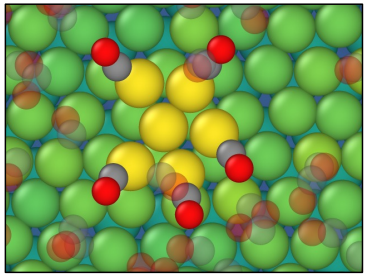
Trimer



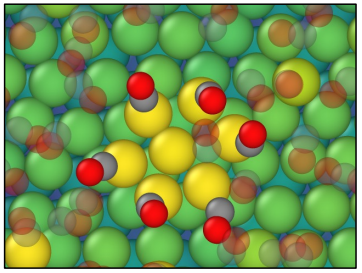
Tetramer



Pentamer



Hexamer

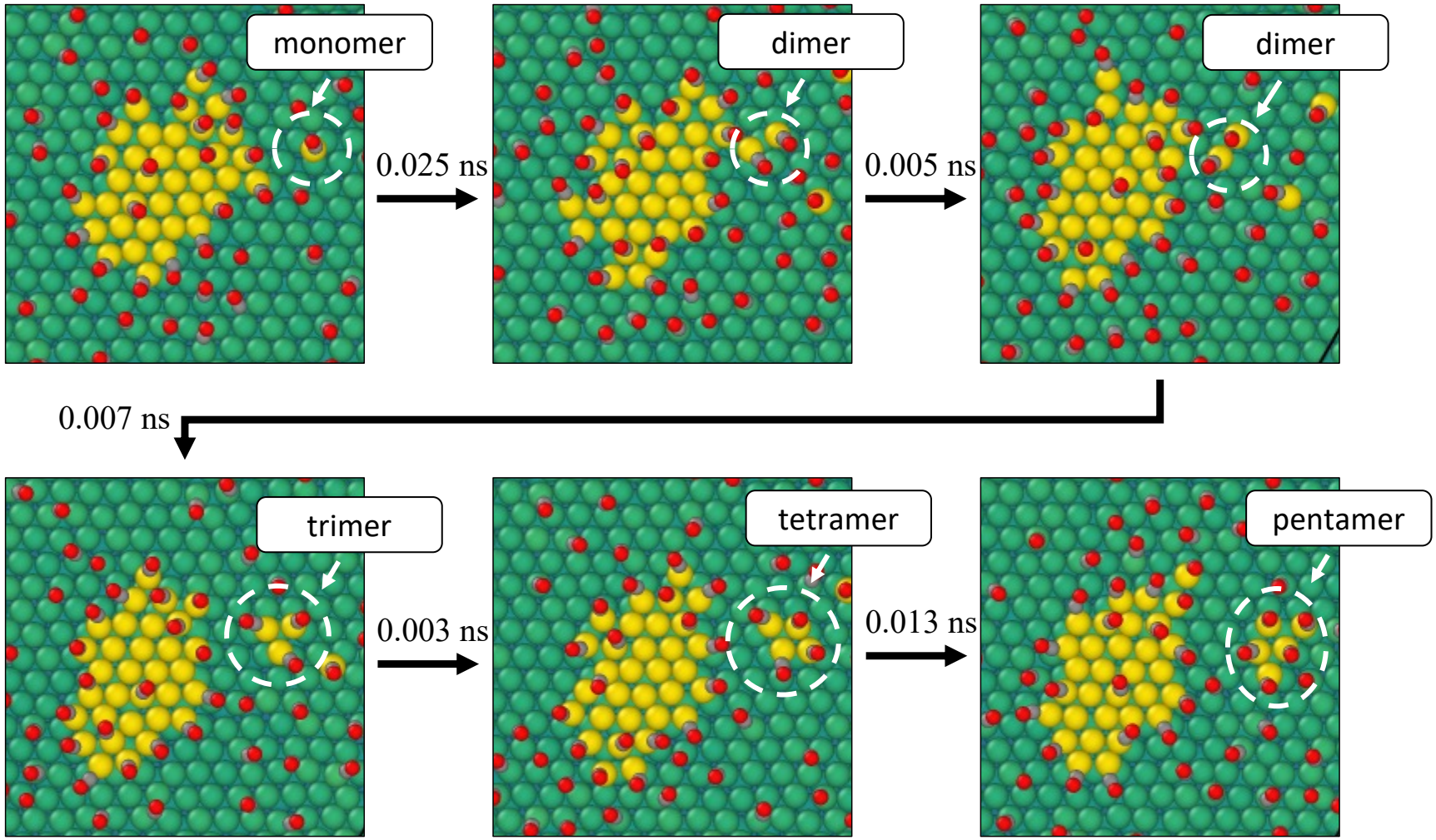


Heptamer

- Cu-CO monomers dominate the surface.
- Number of clusters reduces with the size.

Results and discussion
How are the clusters formed ?

A. Indirect formation of cluster



Clusters are formed by coalescence of smaller clusters, initiated by monomer.

Summary

- **Bridging theory and experiment is the essence of good materials science**. However, consistency is difficult because theory simplifies reality, and experiments are messy.
- **Multi-scale simulations** aided with **machine learning force-fields** can cover both limitations of theory and experiment, **thus acting as a bridge.**
- We have applied the multi-scale simulations for the following case.
  - ✓ Cu-Zn surface alloying on the step edge.
  - ✓ CO-induced cluster formation on Cu(111) surface.
  - ✓ Acceleration of WGS reaction through formation of Cu clusters.
  - ✓ H-induced reconstruction on Cu(100) surface.
  - ✓ Formate-induced step-edge fluctuation on Cu(111)-based surface.
  - ✓ Elucidation of effective normal mode during CO_2 hydrogenation.