Interaction of carbon monoxide with Cu nanoclusters grown on alumina surface

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Outline

- Motivations and state-of-the-art
- Self-seeded nucleation of Cu nanoclusters on $Al_2O_3/Ni_3Al(111)$
- CO chemistry on supported Cu nanoclusters
- Conclusions

Why CO? Why supported nanoclusters?

- **Carbon monoxide:** important reactant in many industrial catalytic processes. Dissociation is a fundamental step (e.g. in Boudouard reaction: $2CO \rightarrow CO_2+C$).

  => basis research on CO adsorption and dissociation on different catalysts using surface science techniques + quantum-mechanical calculations

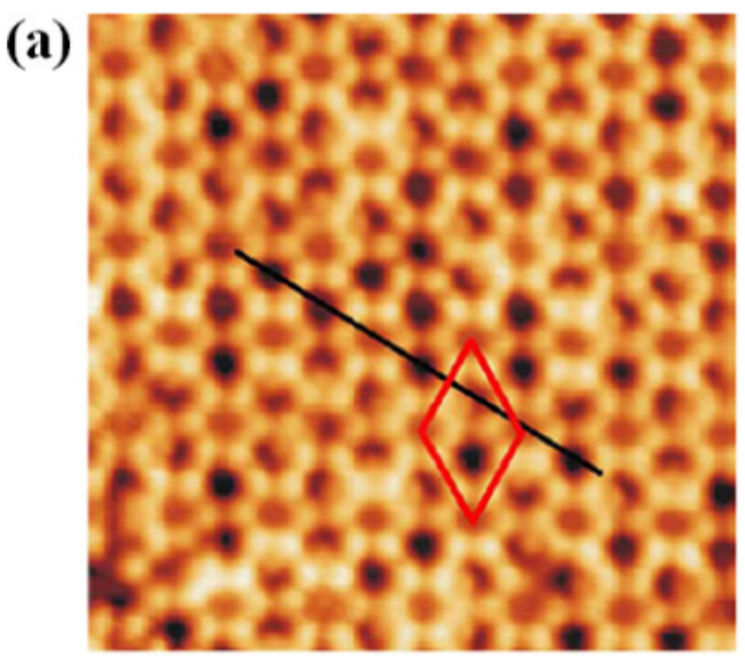
- **Metal nanoclusters or nanoparticles (NPs):** important in heterogeneous catalysis; for applicative purposes, grown on a support (useful in controlling NPs size, preventing sintering at high T, selectivity, ...)

  => the synthesis of ordered arrays of well-defined equally sized NPs is the goal of many efforts

A good template: Ultrathin films of alumina onto $Ni_3Al(111)$ substrate

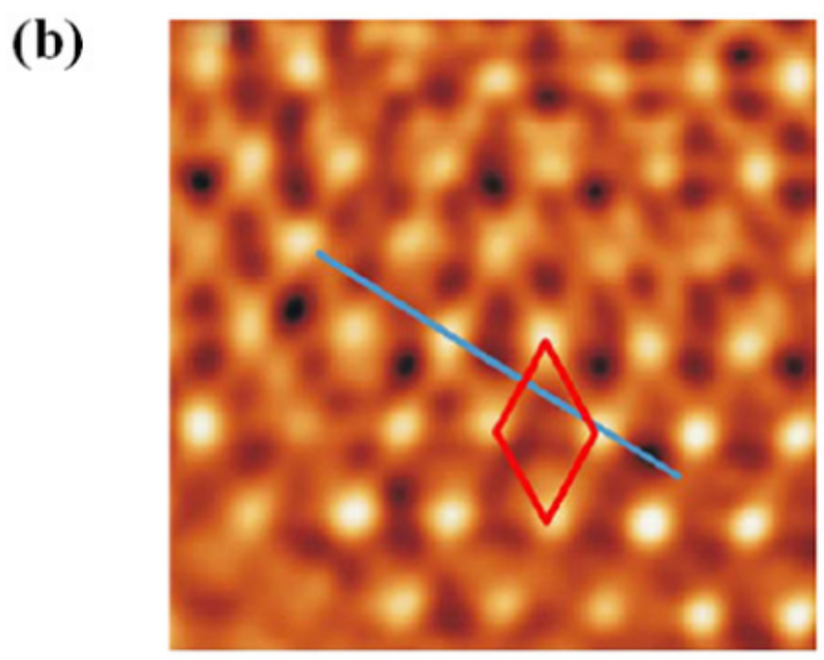
Oxide ultrathin films: recently proposed as promising substrates for growing highly ordered nanostructure arrays through self-organization of adatoms.

Alumina (Al_2O_3) on $Ni_3Al(111)$ shows a **superstructure** with two different appearances according to the voltage bias:



'network structure'

U_{bias} = 3.2 V



'dot structure'

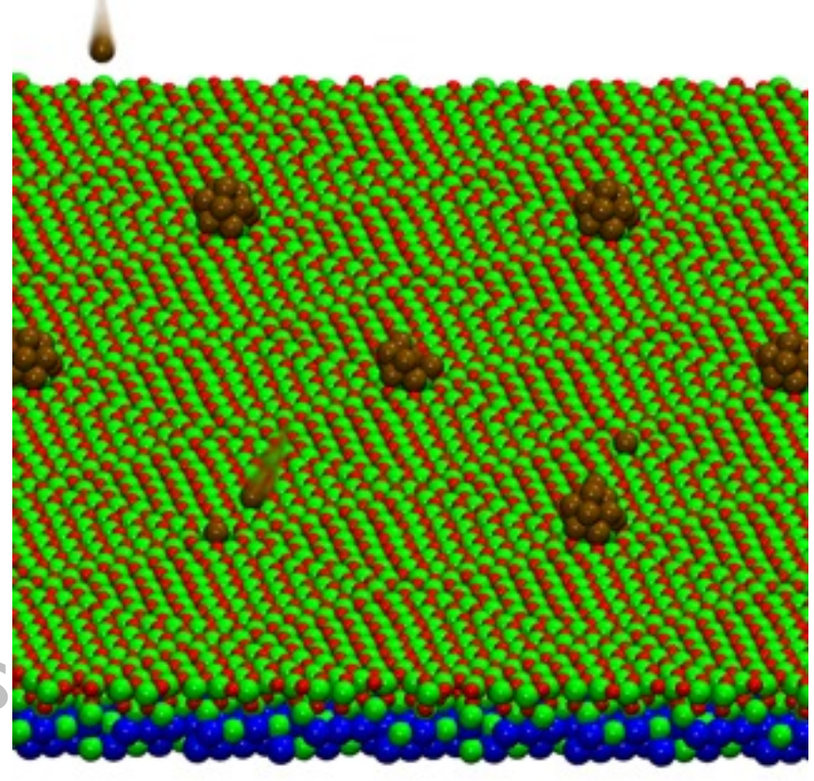
U_{bias} = 2.0 V

LT (T=23 K) - STM images

unit cell of the alumina superstructure

278 Å × 278 Å

Degen et al., *Surf. Sci.* 2005;
Moors et al., *Appl. Surf. Sci.* 2008



- Motivations and s

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A good template: Ultrathin films of alumina onto $Ni_3Al(111)$ substrate

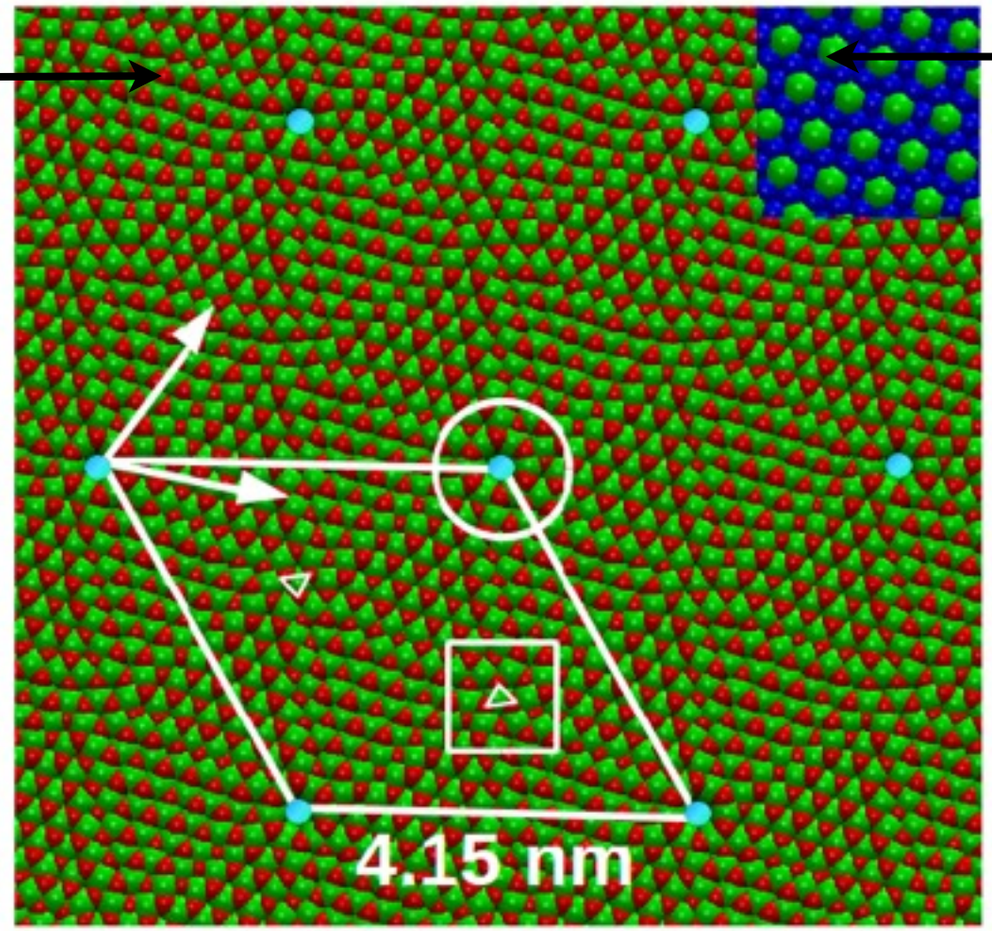
non stoichiometric Al_2O_3 →

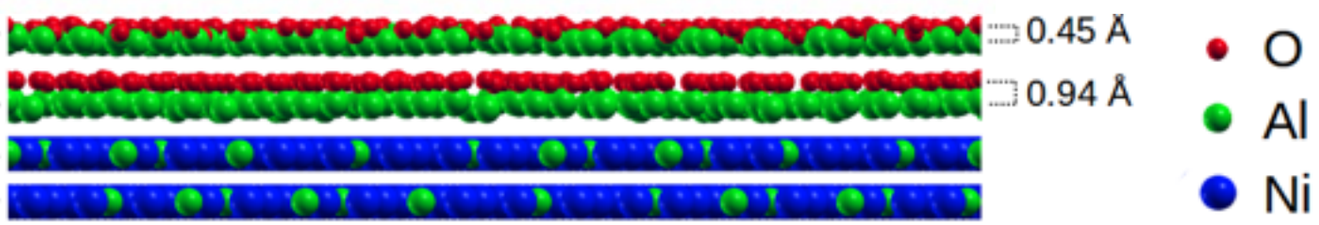
superstructure with unit cell

$(\sqrt{67} \times \sqrt{67})R12°$

with respect to the substrate

3-fold and 6-fold symmetry sites





Schmid et al., *PRL 2007;* Vesselli et al., *PRL 2010*

Technical details

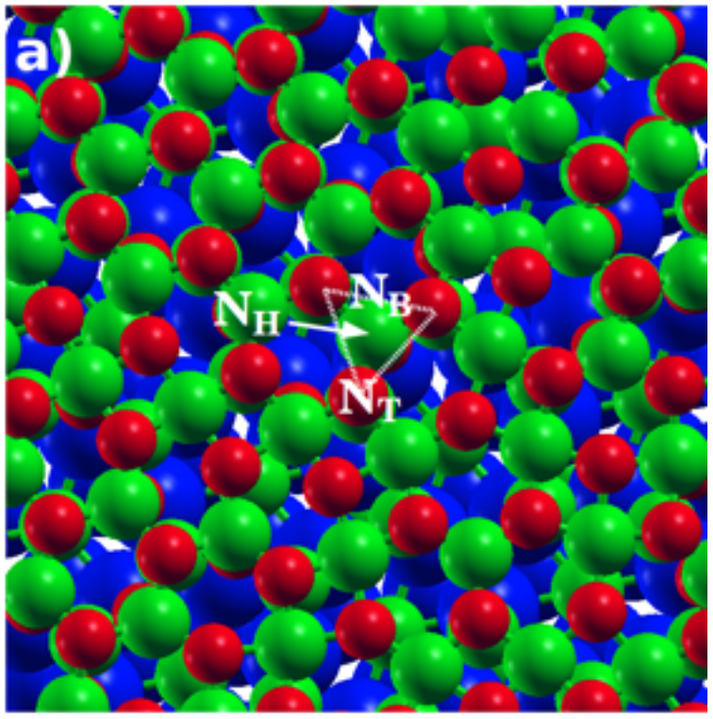
DFT calculations:

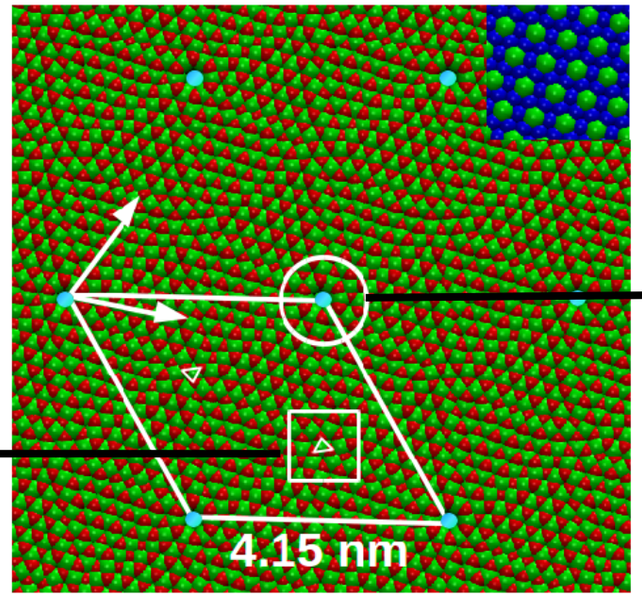
- GGA-PBE
- pseudopotentials
- reduced models (~150 atoms + vacuum in all three spatial directions)

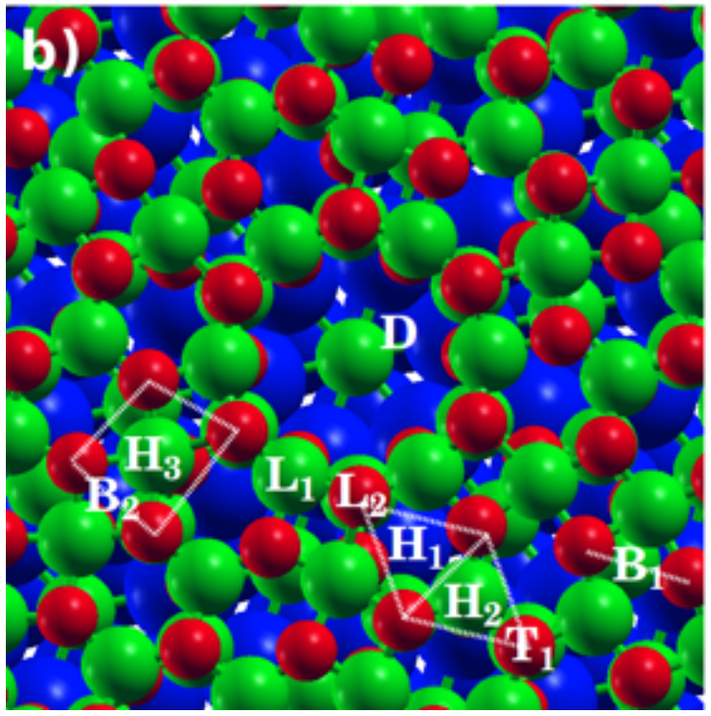
Experiments:

- $Ni_3Al(111)$ treated under UHV by sputtering & annealing recipes
- alumina obtained by thermal oxidation at 1000 K in 10^{-7} mbar O_2
- Cu deposition by CVD
- XPS spectra acquired @ SuperESCA beamline of ELETTRA Synchrotron

Single Cu atom adsorption & diffusion







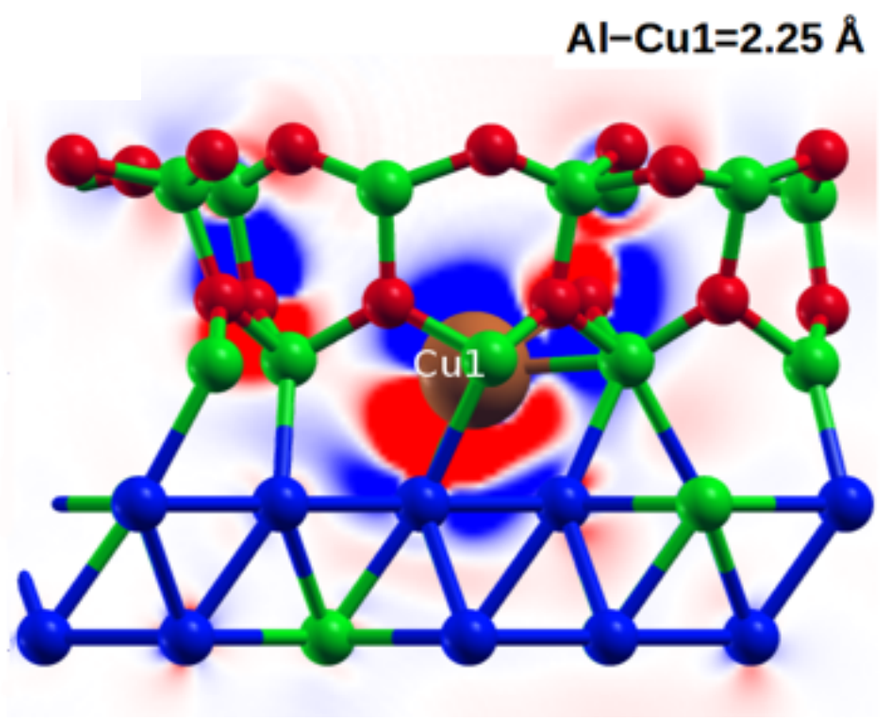
Single atom energies in the → most favored adsorption sites. In other sites, $|E^{ads}| < 1$ eV.

Site	E^{ads} (eV)
D	−2.12
N_T	−1.12
N_B	−1.33

Concerning energetics, the "dot" (D, or "hole") sites are clearly the most favored. Kinetics is not opposing to the nucleation process of Cu clusters at the holes (energy barriers for diffusion are < 0.5 eV, small enough to be easily overcome at CVD conditions)

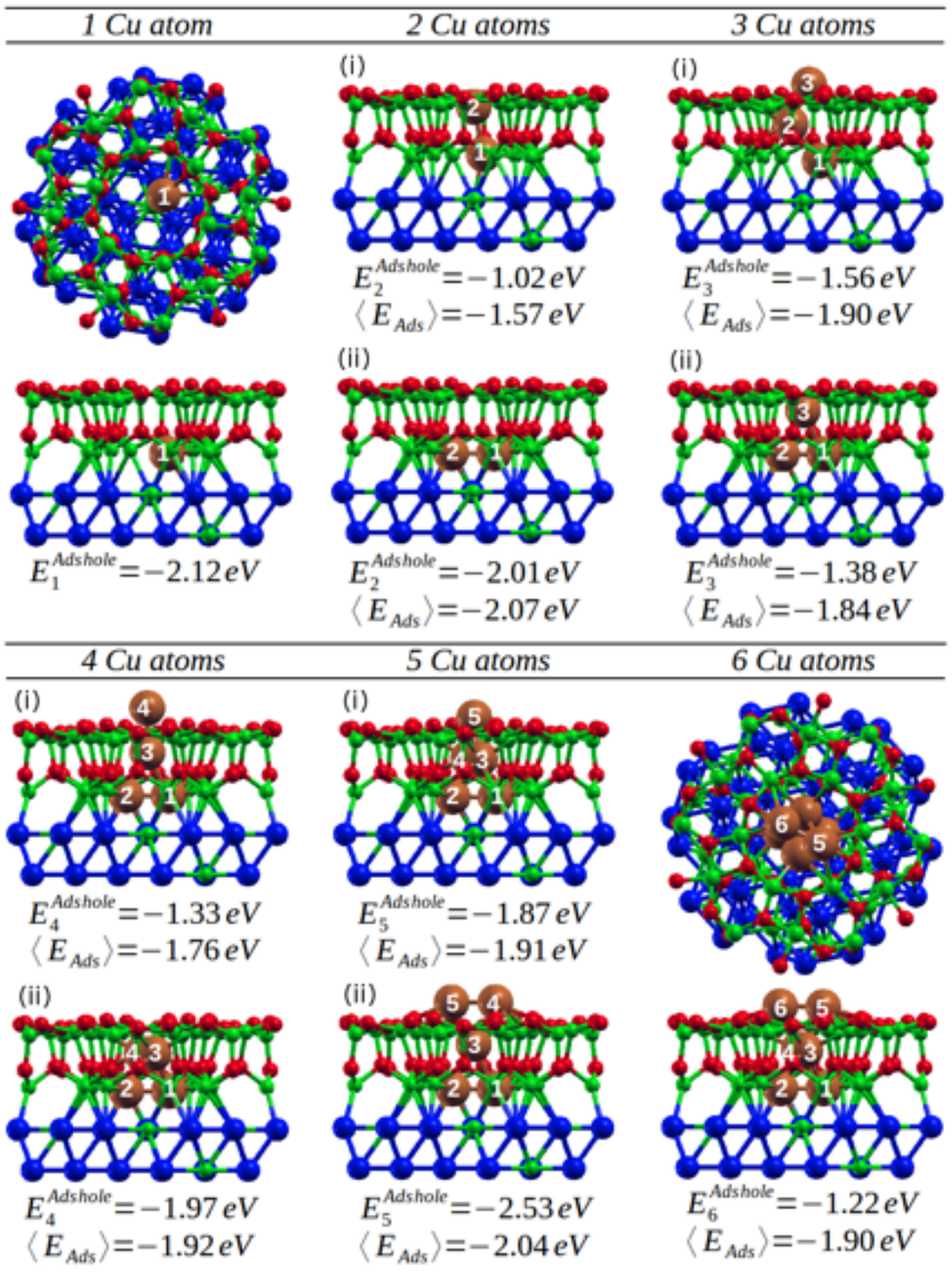
Most of the Cu atoms can eventually reach the "dot" sites and nucleate there, even taking into account their low concentration

Cu self-seeding in the hole



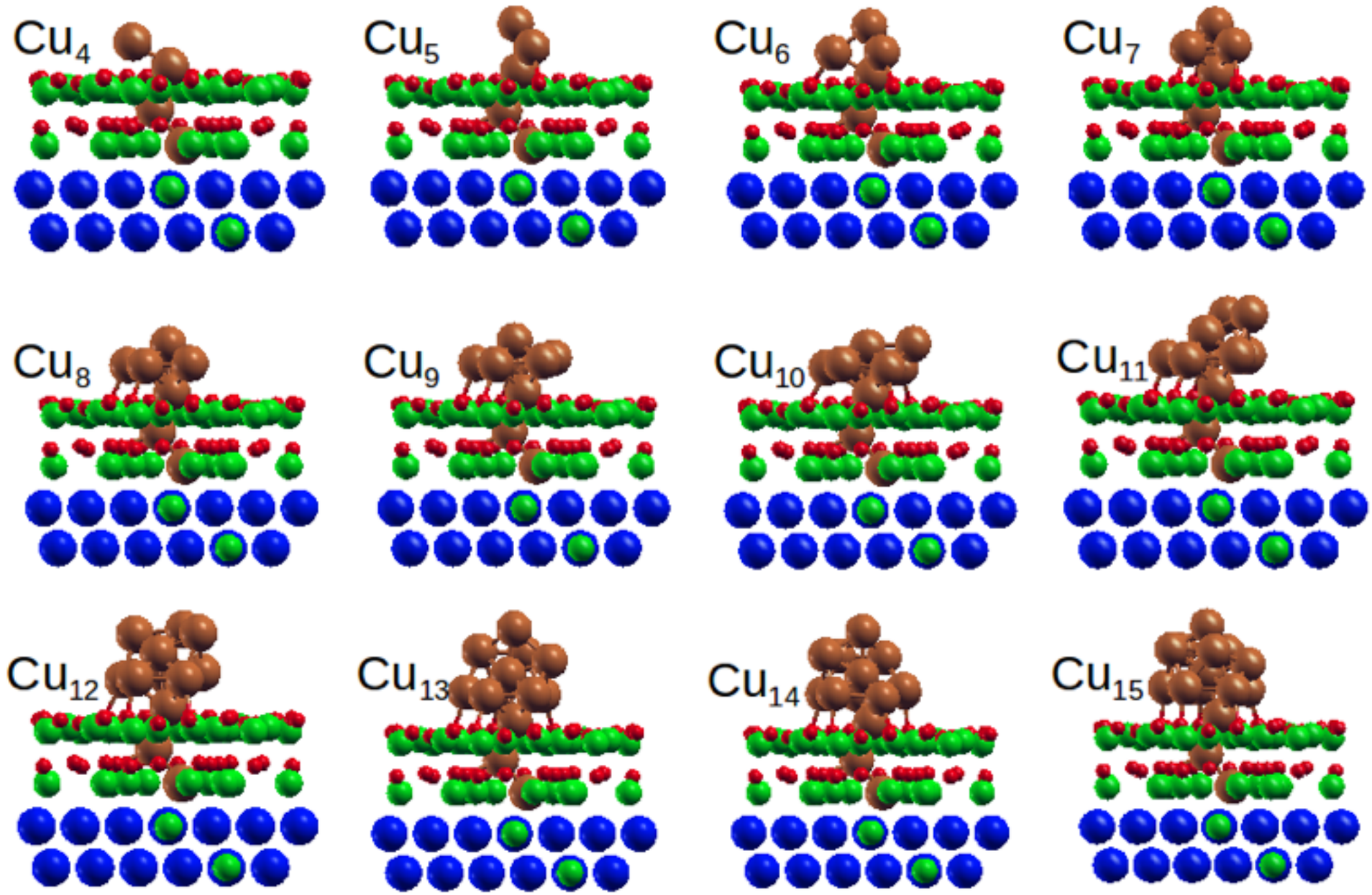
Strong adhesion of Cu to supporting metallic alloy

=> guarantees the stability of the nucleation centers, offering stiff anchoring also for multi-atomic seeds and further growth of 3D Cu NPs.



multi-atomic seeds

Seed-anchored NPs growth



Self-seeded nucleation of ordered patterns of Cu NPs proceed...

Calculations here up to Cu_{15}; exp. from CVD: minimum estimated size: Cu_{30}

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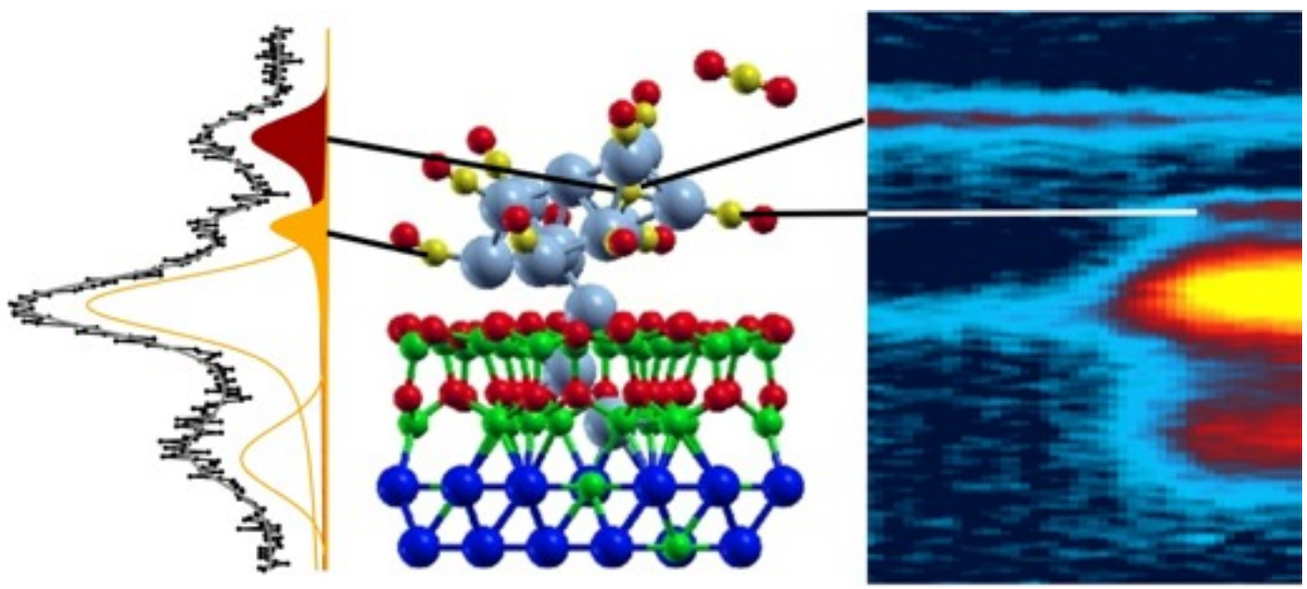


XPS on CO@Cu clusters

C 1s core level spectra measured in situ :
(i) upon exposure to CO at LN_2 , (ii) at saturation, (iii) upon heating

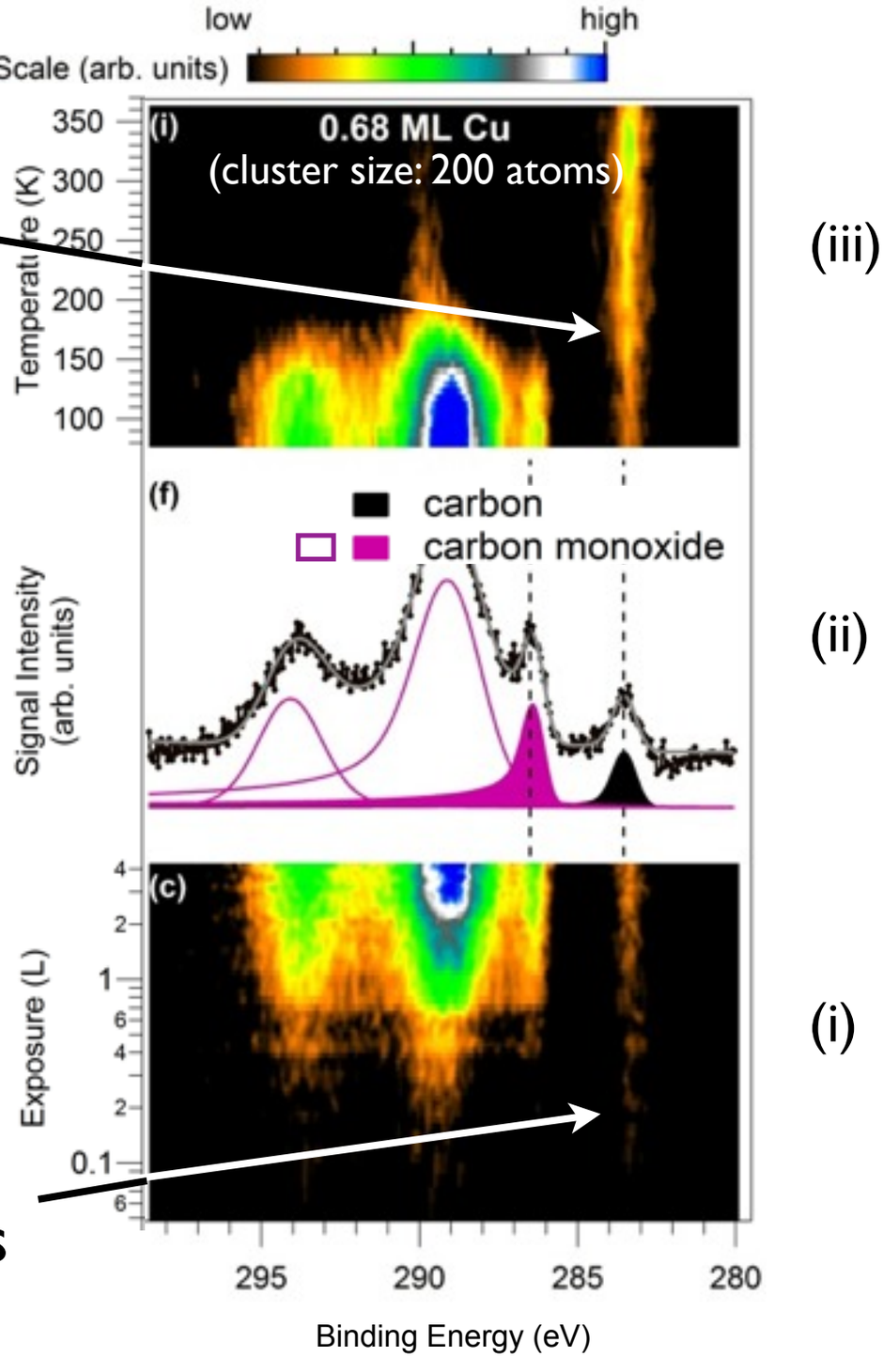
upon heating, CO desorbs, and the intensity related to the **atomic C species** increases up to a plateau, which is reached when the CO coverage drops

CO adsorption & dissociation

are influenced by

CO gas pressure (i) and
temperature (iii)

during uptake,
CO dissociates and C adsorbs on clusters



(iii)

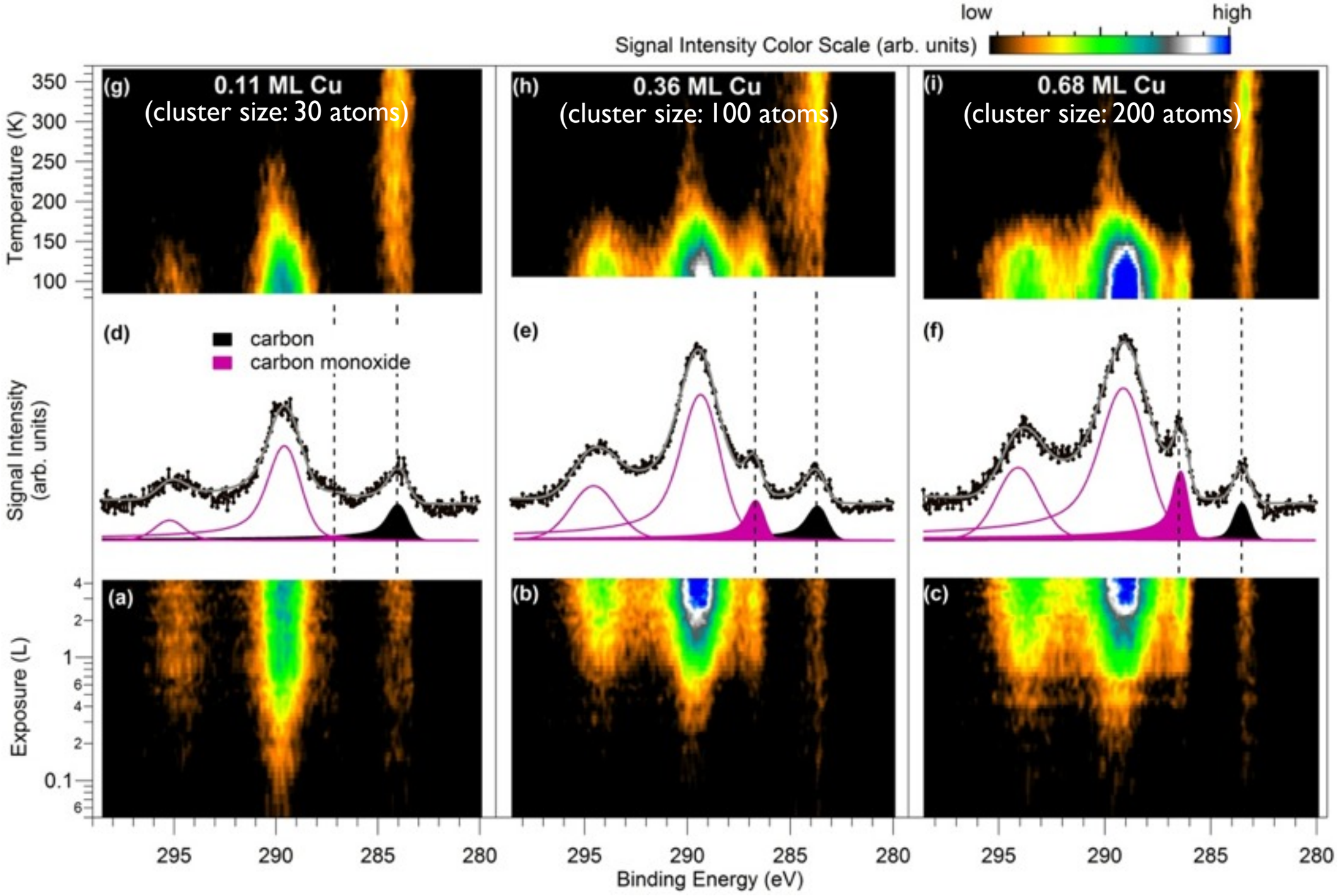
(ii)

(i)

XPS on CO@Cu clusters: cluster size

C 1s core level spectra measured in situ :

(i) upon exposure to CO at LN_2 , (ii) at saturation, (iii) upon heating, for different cluster sizes



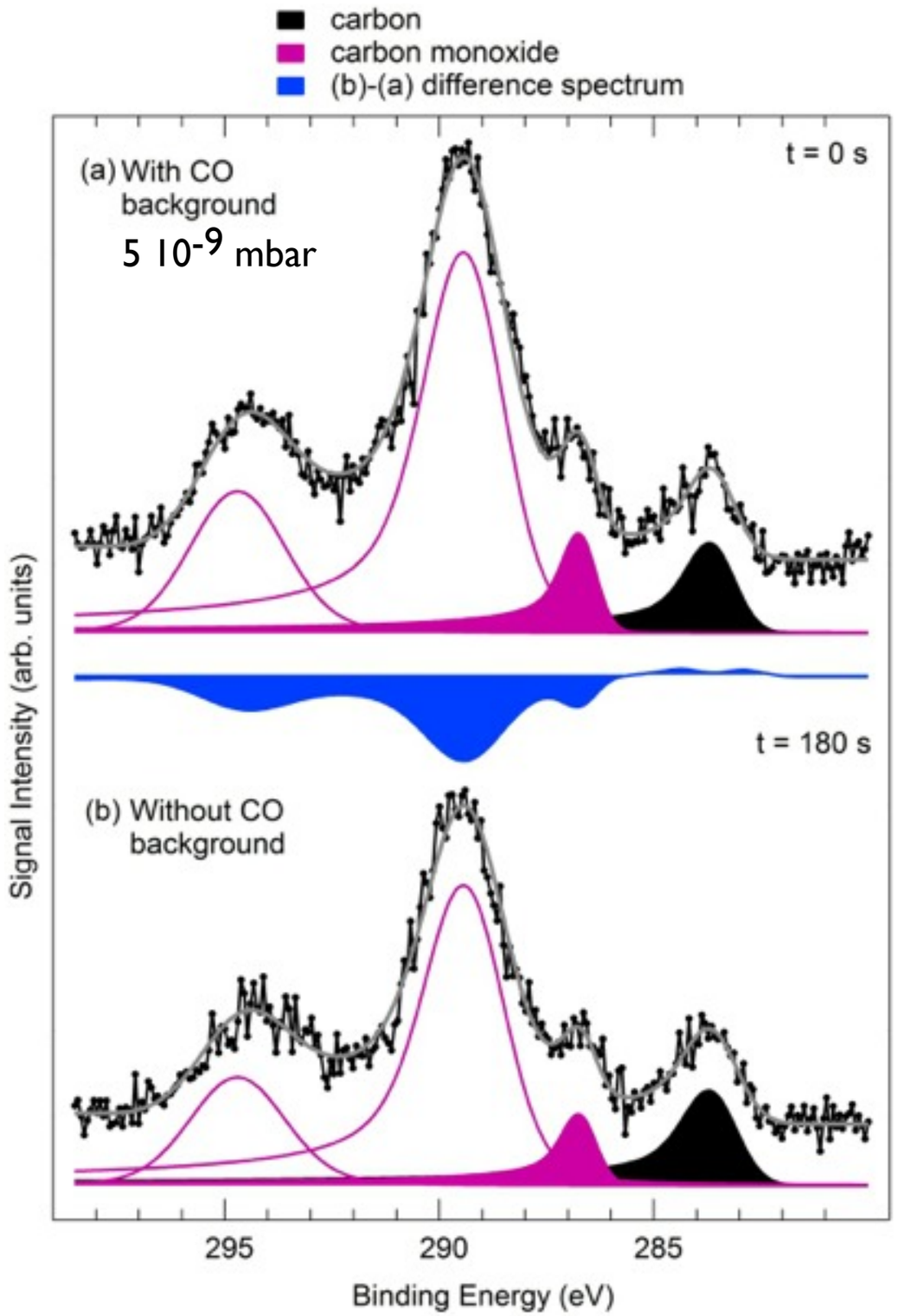
(iii)

(ii)

(i)

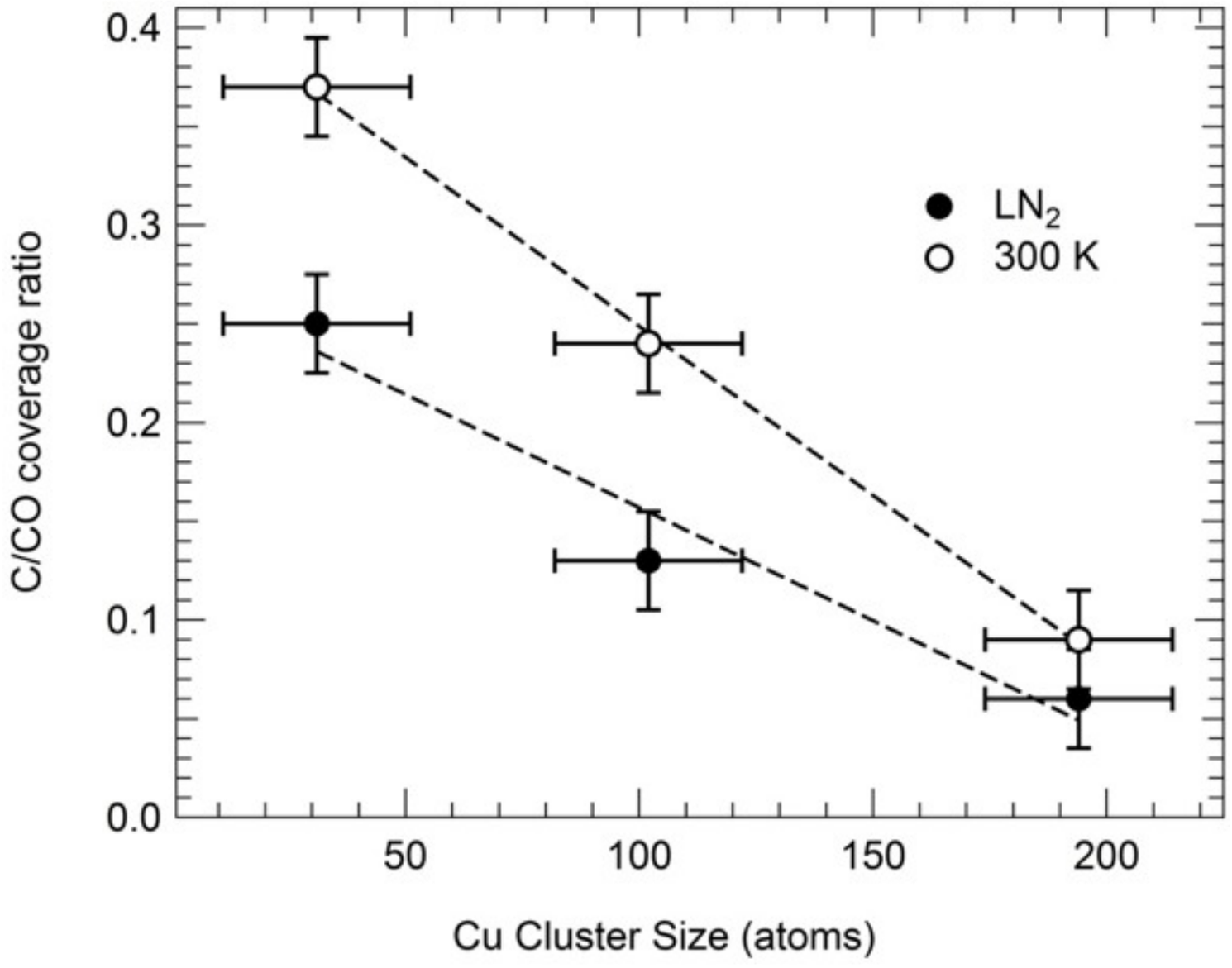
Look at C/CO and ■/□ CO: cluster size does matter!

XPS on CO@Cu clusters: CO background



Look at C/CO ratio: CO background does matter!

XPS on CO@Cu clusters: cluster size and T



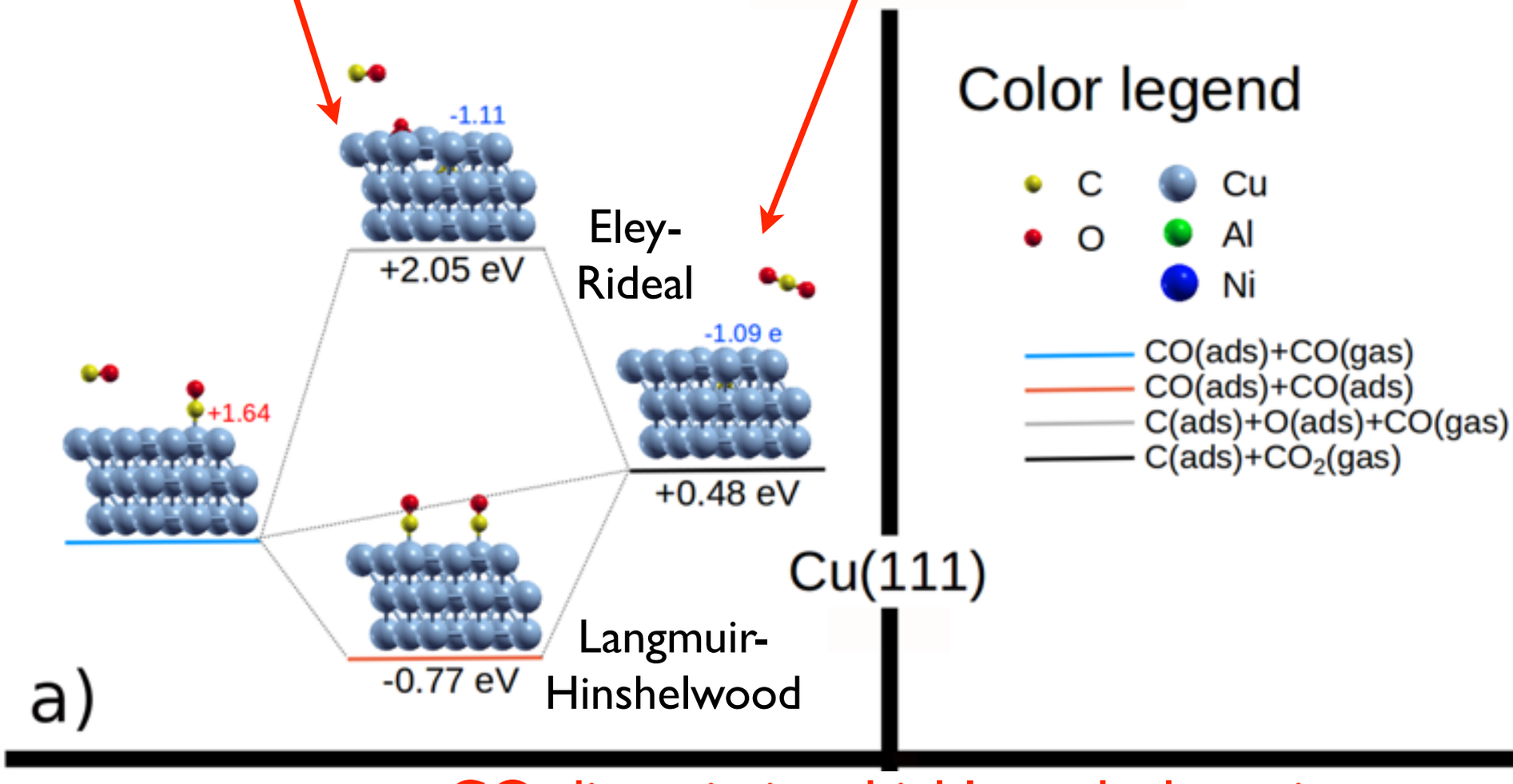
C/CO signal after exposure of the Cu clusters to CO at LN_2 temperature (filled markers) and at RT upon annealing (empty circles) in CO background:

temperature & cluster size & CO background do matter in CO dissociation

Hints from atomistic simulations:

CO dissociation & Boudouard reaction

(2CO → CO_2+C)

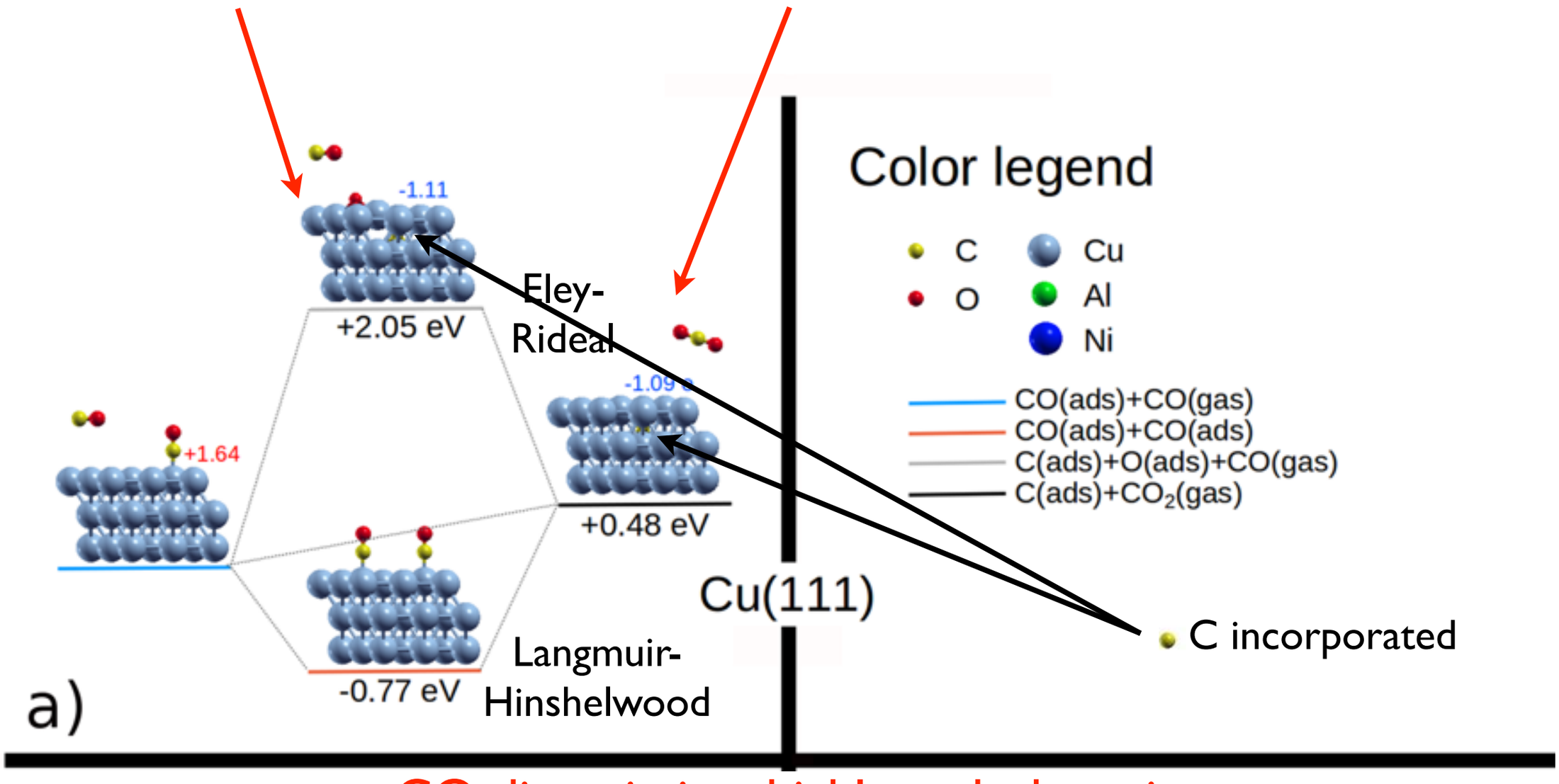


CO dissociation: highly endothermic

Boudouard reaction: also endothermic

Hints from atomistic simulations:

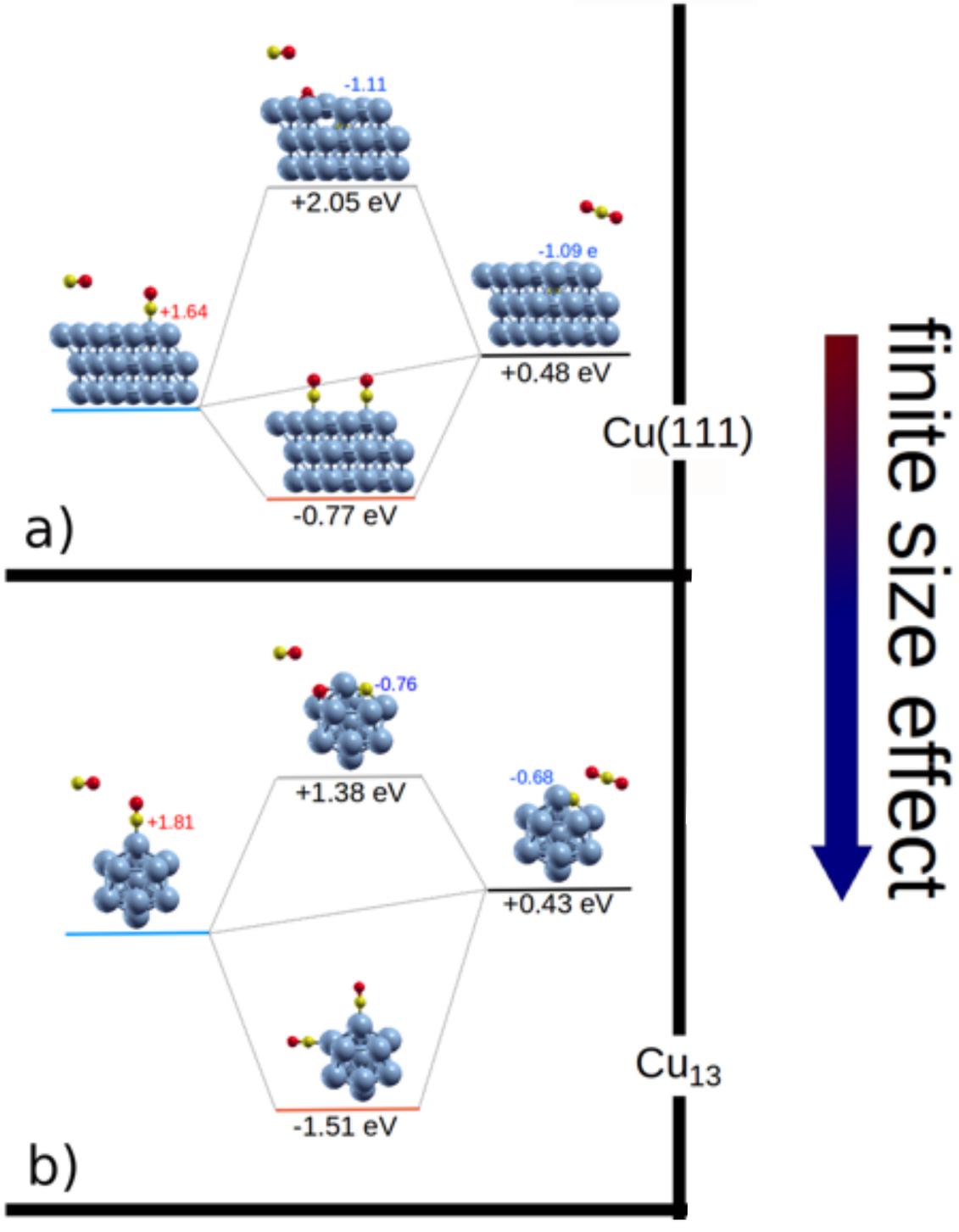
CO dissociation & Boudouard reaction



CO dissociation: highly endothermic

Boudouard reaction: also endothermic

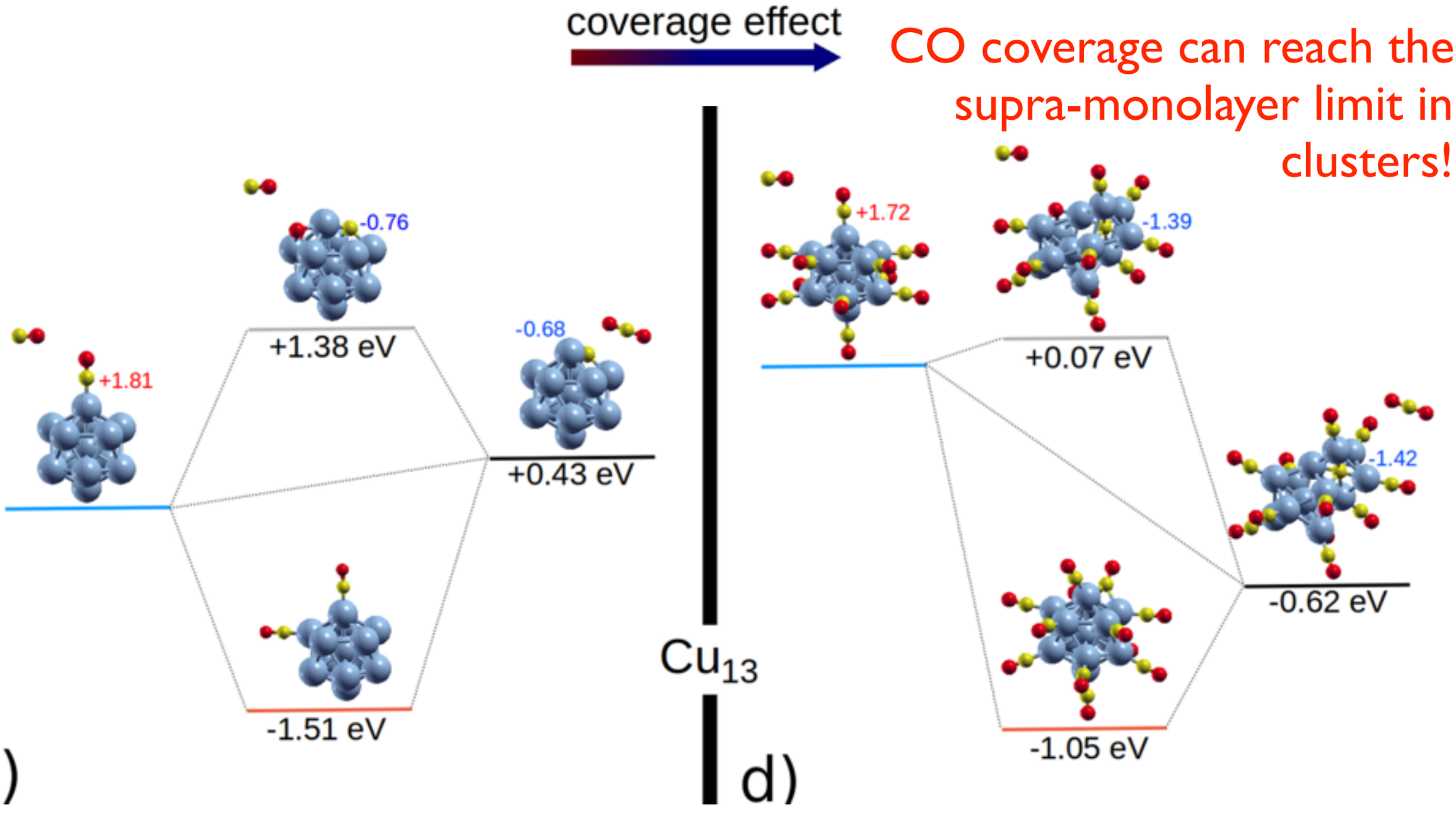
Effect of the catalyst finite size



Finite size (clusters instead of single crystal surfaces)

helps CO dissociation and coadsorption

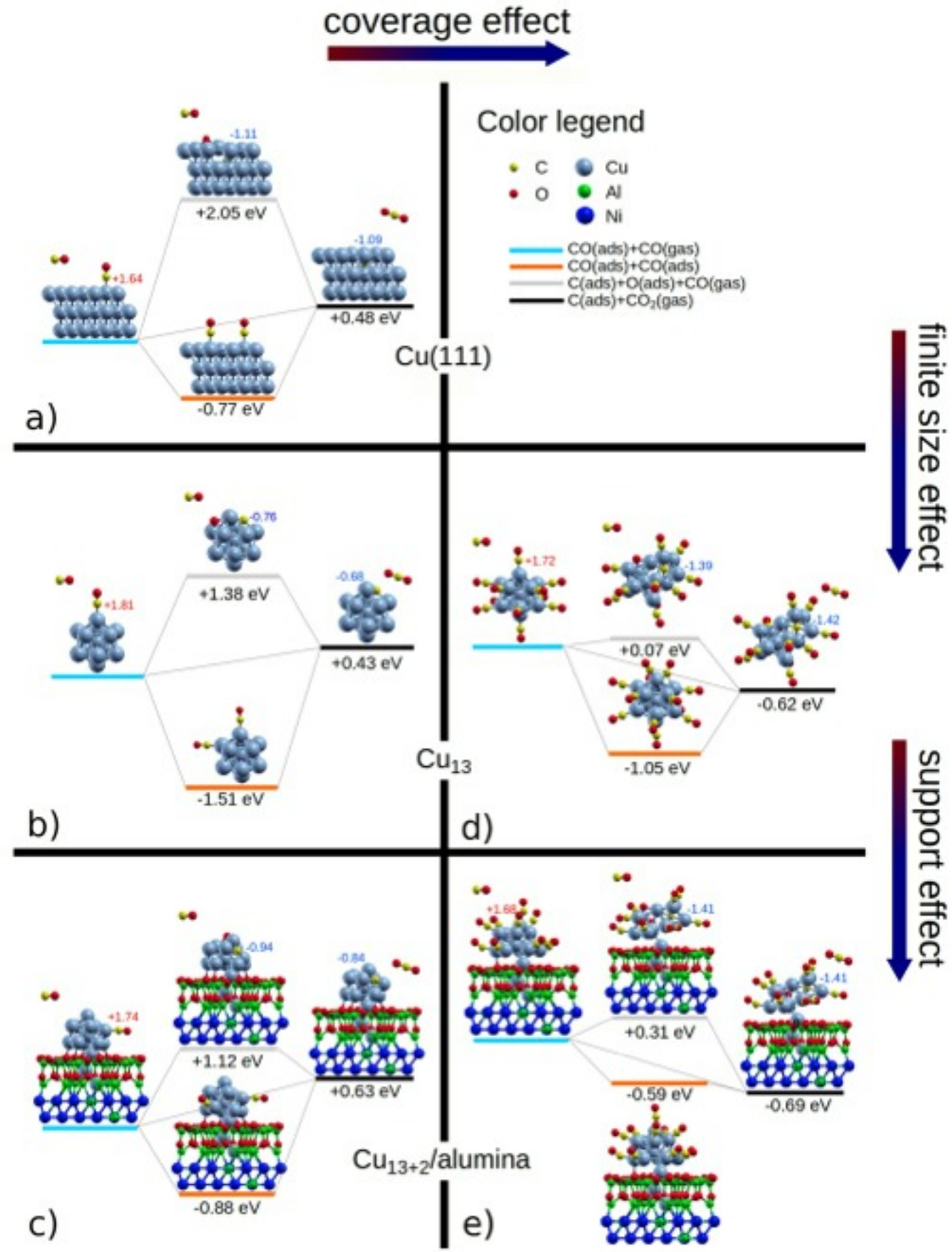
Effect of the reactant coverage



CO coverage can reach the supra-monolayer limit in clusters!

High reactant coverage improves dramatically CO dissociation and makes Boudouard reaction exothermic!

... and everything together



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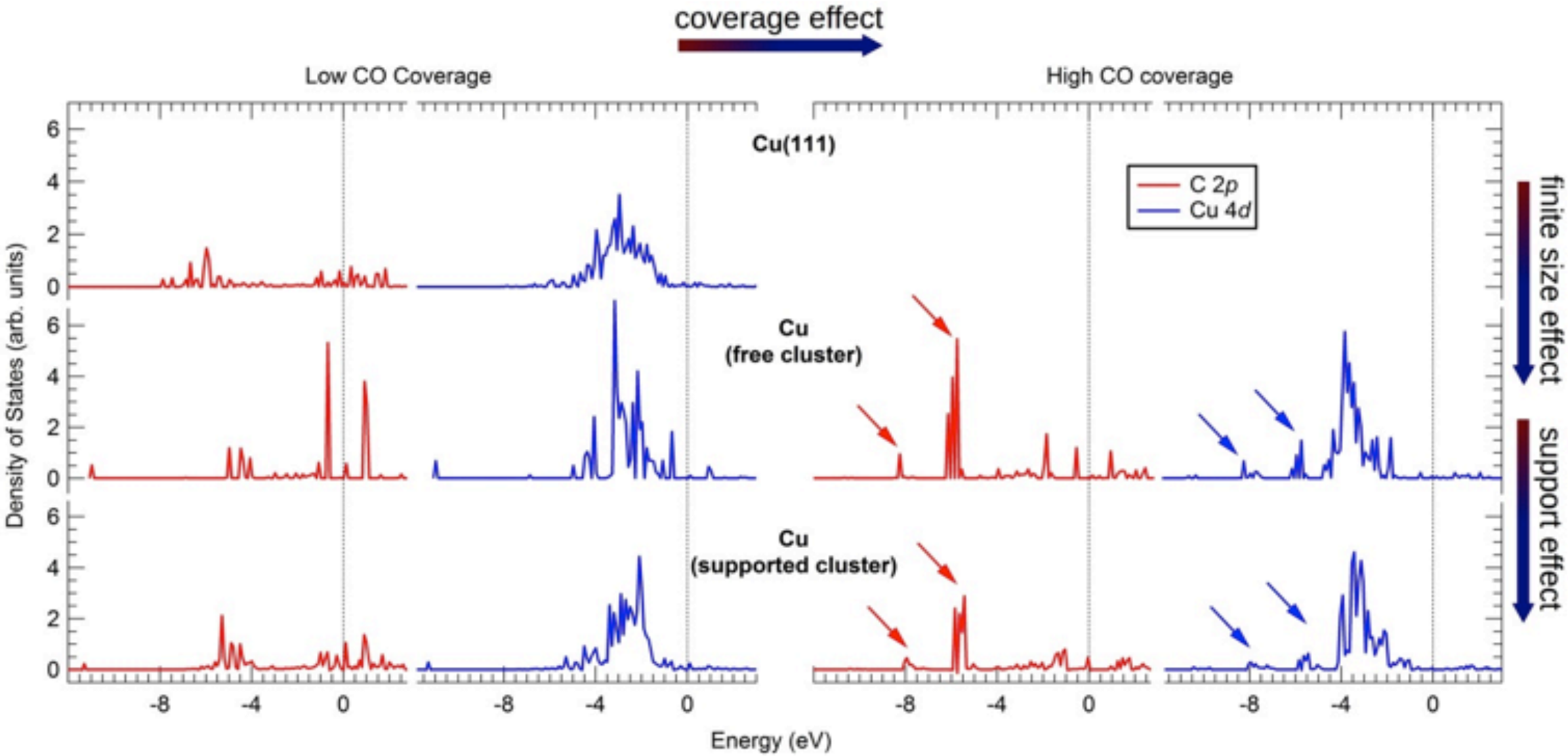


DFT projected density of states on the C atom and surrounding Cu atoms (average) after CO dissociation

Conclusions

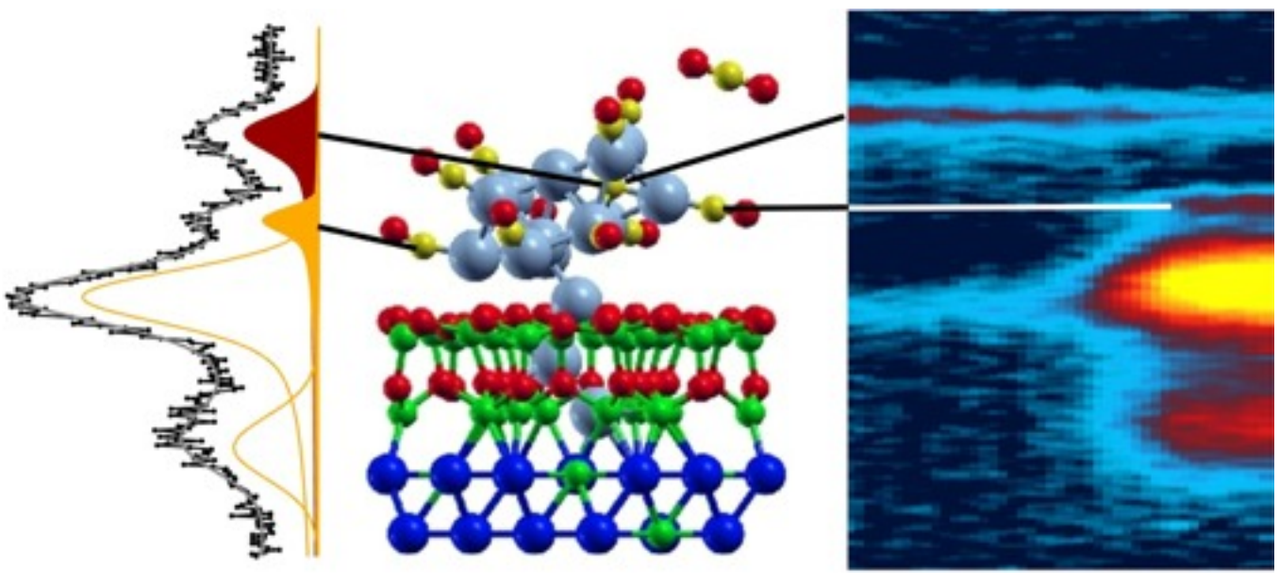
- holes of the *"dot"* structure of ultra-thin Al_2O_3 films on $Ni_3Al(111)$: preferential seeding sites for Cu, offering strong adhesion to the metal and stiff anchoring for further growth of 3D Cu clusters

- thermodynamics & kinetics contribute to make thin alumina films@Ni3Al(111) a good template for the growth of highly ordered Cu nanoclusters arrays

- finite size of Cu nanoclusters AND high reactant coverage favour the CO dissociation

- on Cu nanoclusters, supramonolayer reactant coverage can be reached!

- support makes nanoclusters more malleable



- J.A. Olmos-Asar, MP et al., in press on PCCP (2014)

- J.A. Olmos-Asar, MP et al., submitted

Thanks to: Jimena A. Olmos-Asar, Enrico Monachino, Carlo Dri, Angelo Peronio, Cristina Africh, Paolo Lacovig, Giovanni Comelli, Alfonso Baldereschi, and Erik Vesselli

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