Bistability during CO oxidation at Pd(100): Atomistic origin from first-principles kinetic Monte Carlo simulations

Max J. Hoffmann[1], Matthias Scheffler[2], Karsten Reuter[1]

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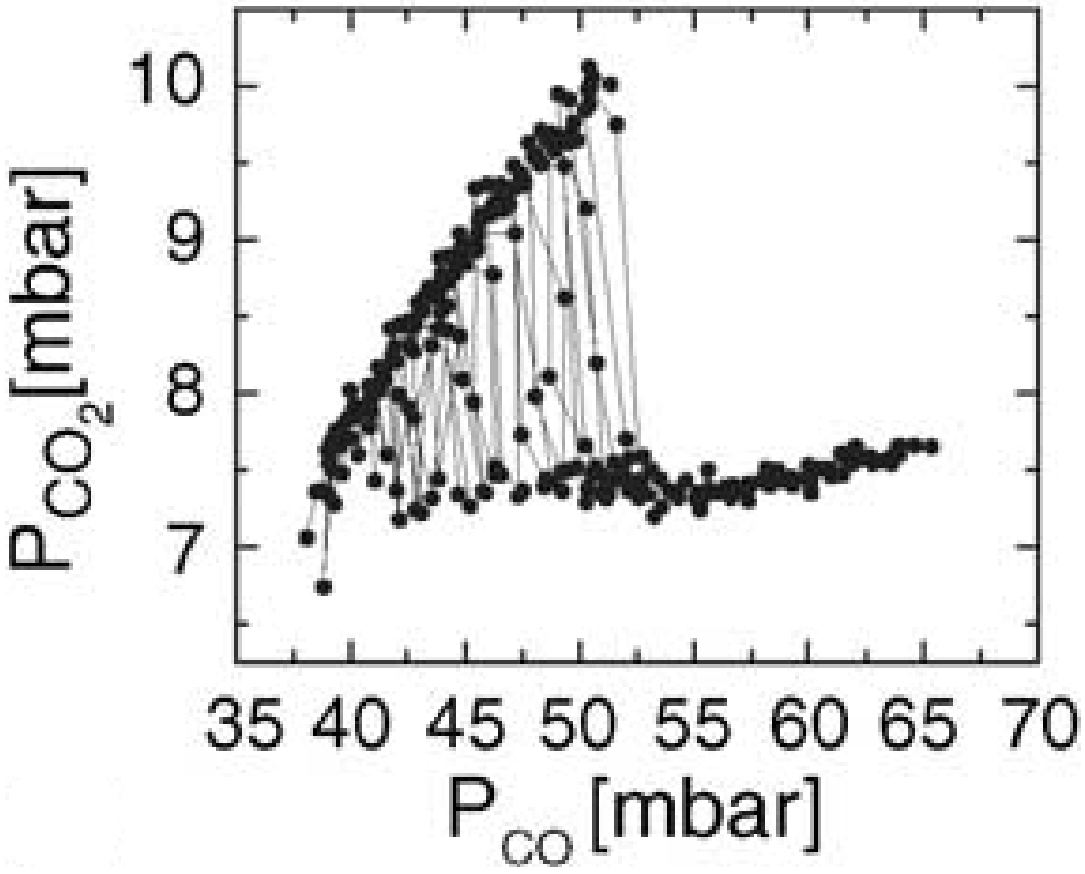
March 11, 2013

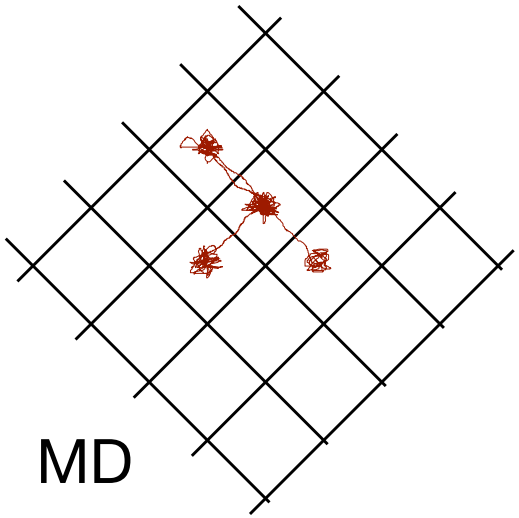
One surface-two reactivities

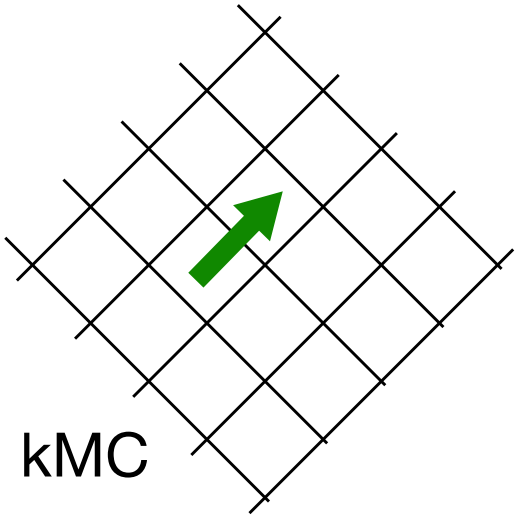


CO_2 production over Pd(100) at ambient pressure $T = 408\,\mathrm{K}$

Hendriksen *et al.*, Catal. Today 105 2, 234 (2005)

Method: First-principles Kinetic Monte Carlo





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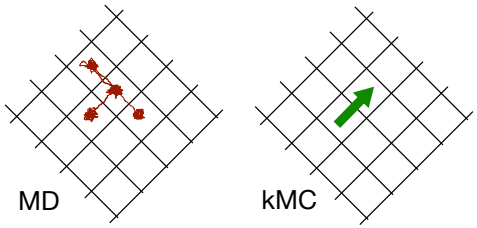

Follow rare-event time evolution by numerically solving
Markovian master equation:

$$\dot{\rho}_i = \sum_j (-k_{ji}\rho_i + k_{ij}\rho_j)$$

Using harmonic transition state theory

$$k_{ij} = f^{\mathrm{TST}} \frac{k_\mathrm{B}T}{h} \exp\left(\frac{-\Delta E_{ij}}{k_\mathrm{B}T}\right)$$

Reuter and Scheffler, PRB **73, 4**, (2006), 045433.

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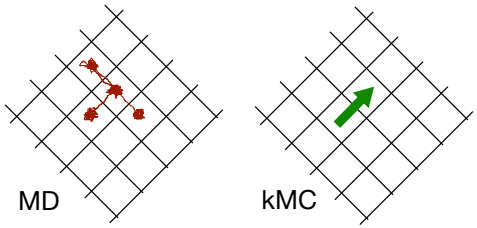

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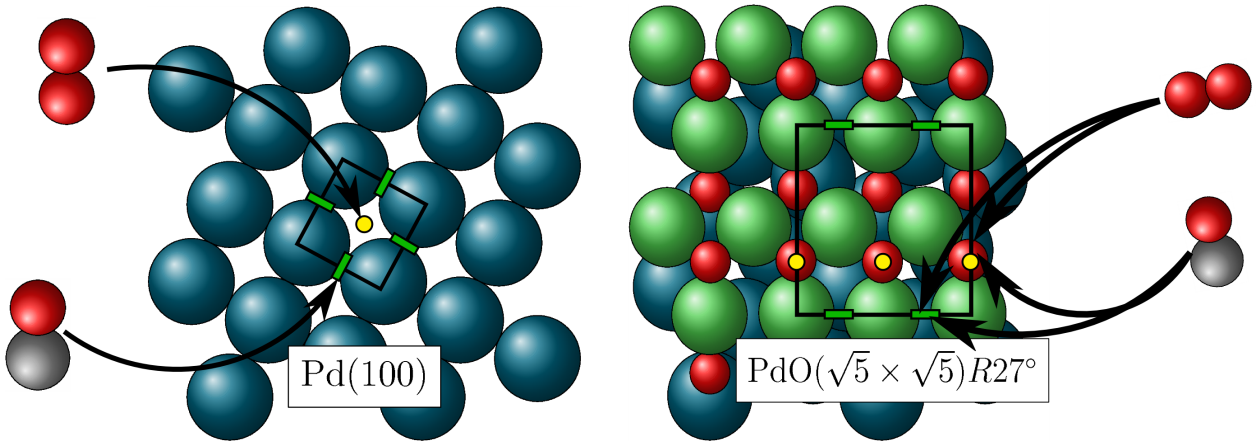
DFT(vibrations, barriers)
CASTEP GGA-PBE
$E_{\mathrm{cut}} = 400$ eV, U.S.-PP,
4-layer slabs

Reuter and Scheffler, PRB **73, 4**, (2006), 045433.

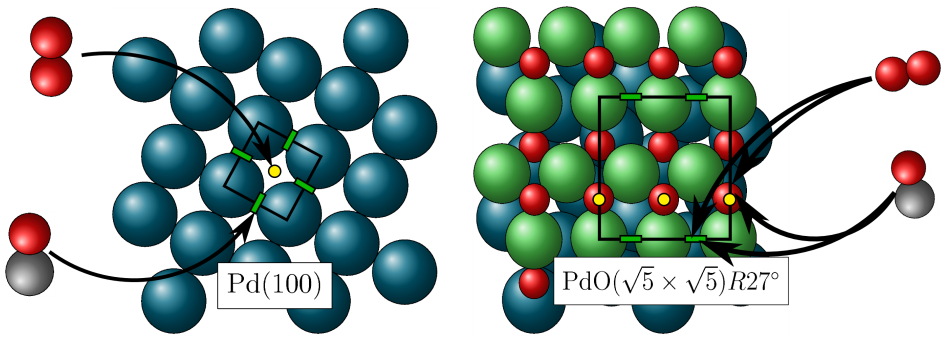
Lattice Model & Elementary Processes



metal vs. oxide

Lattice Model & Elementary Processes

- CO: molecular adsorption, desorption, diffusion
- O_2: dissocative adsorption, desorption, diffusion
- $CO + \frac{1}{2}O_2 \rightarrow CO_2$ reaction



Pd(100)

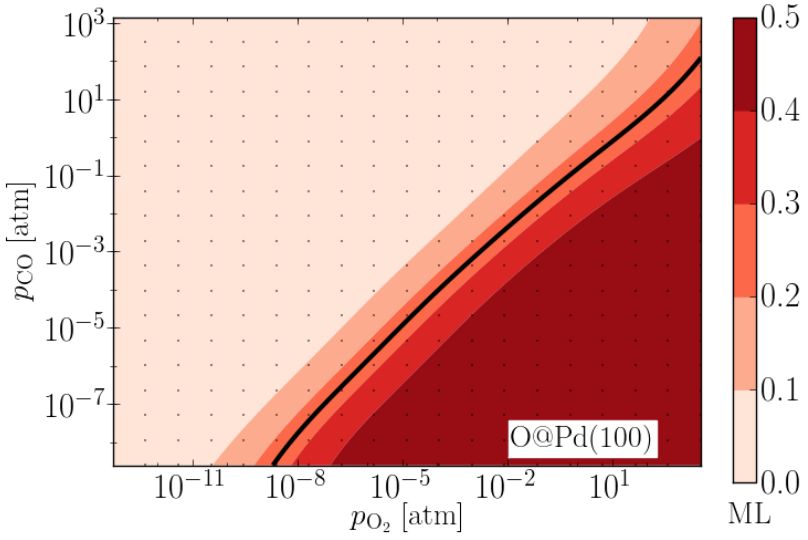
- lateral interactions through n.n. site blocking

PdO$\left(\sqrt{5} \times \sqrt{5}\right)$ R27°

- no lateral interactions, DFT binding energies for intact surface oxide
- Eley-Rideal reaction

Kinetic phases overlap

$T = 600\,\mathrm{K}$



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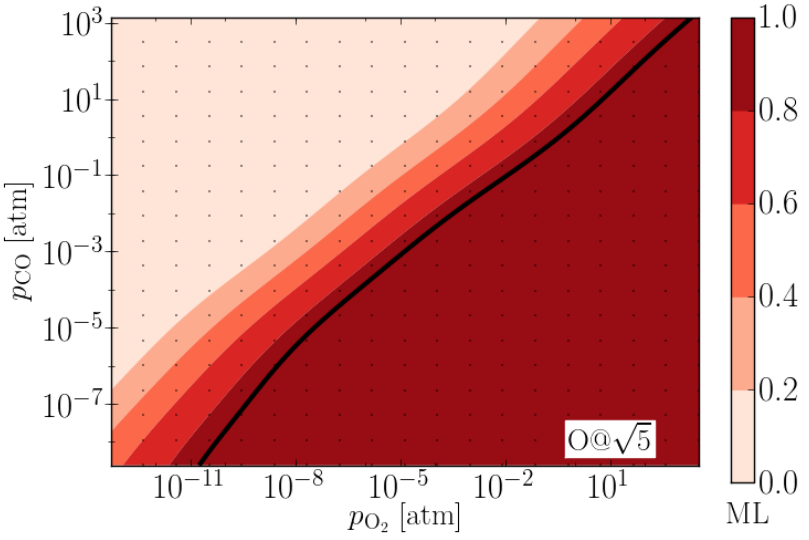

PdO($\sqrt{5} \times \sqrt{5}$)$R27°$

MJH, K. Reuter, Topics Catal. (submitted), arXiv:1301.3285

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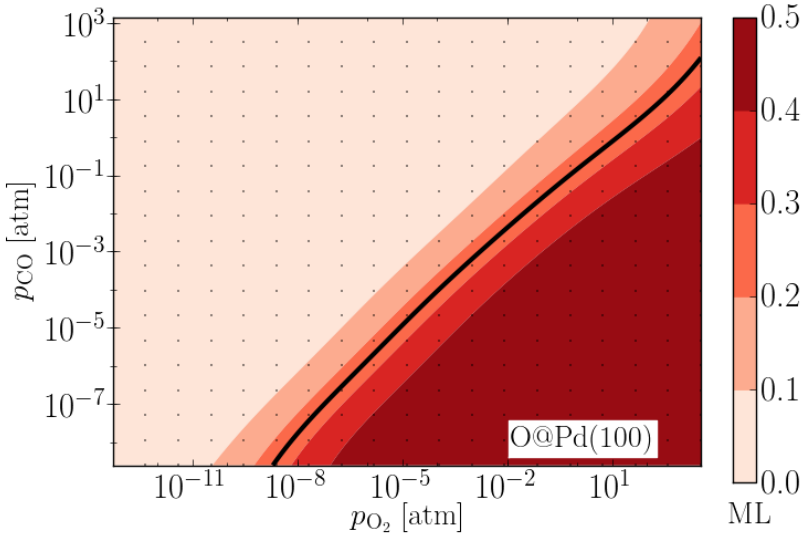

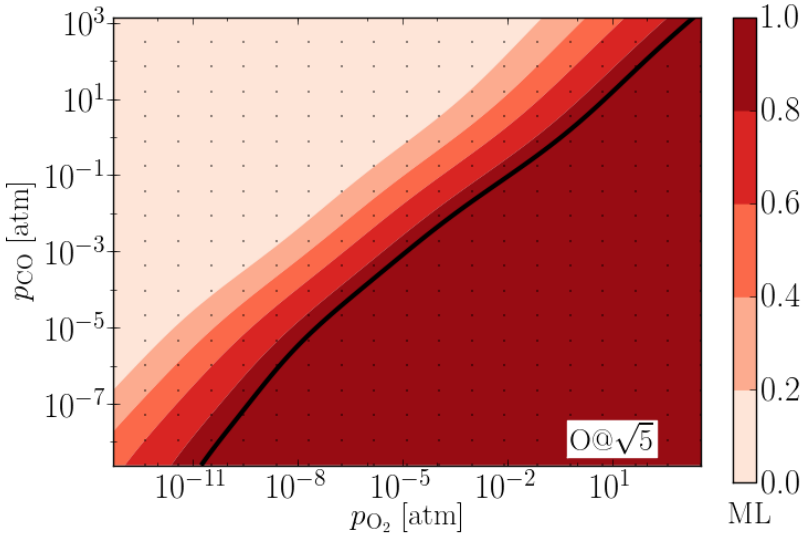

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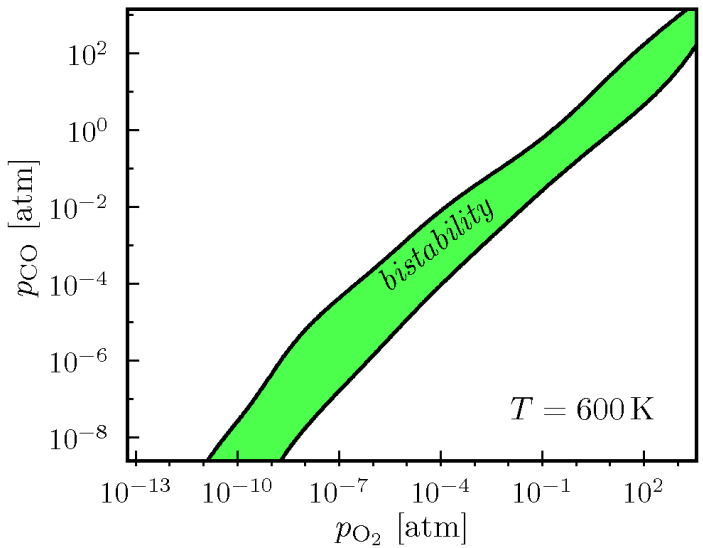

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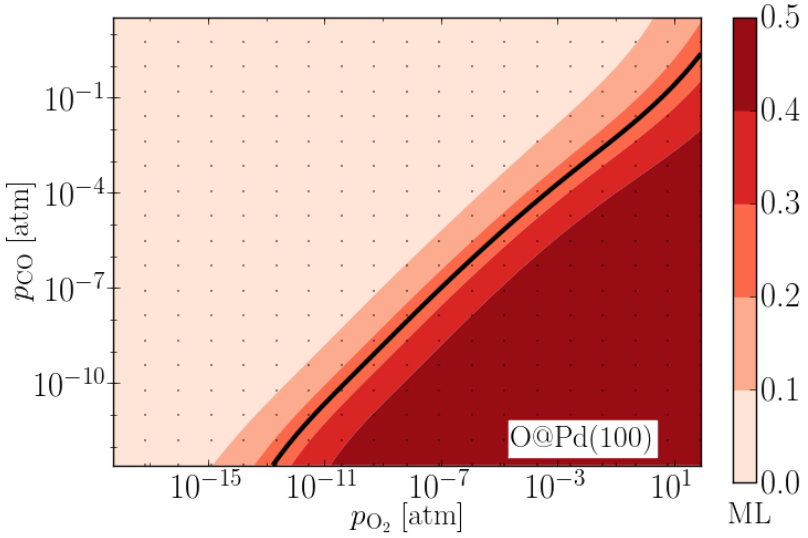
Kinetic phases overlap

$T = 500\,\mathrm{K}$



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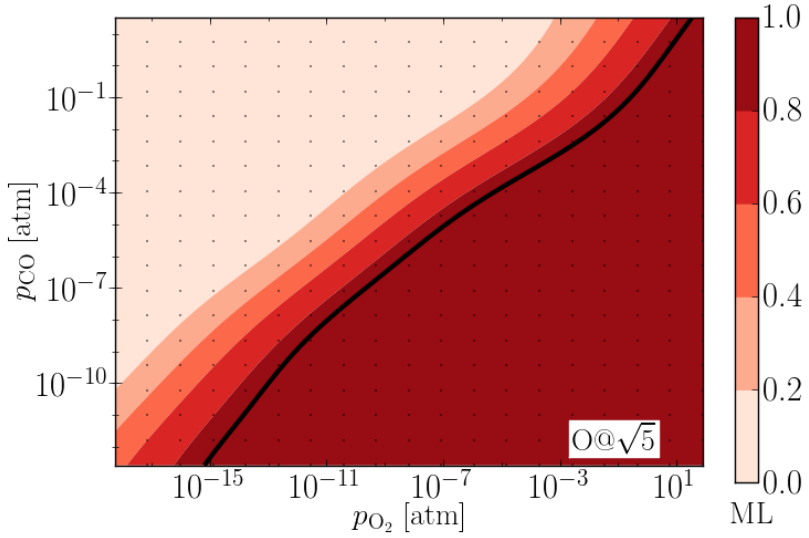

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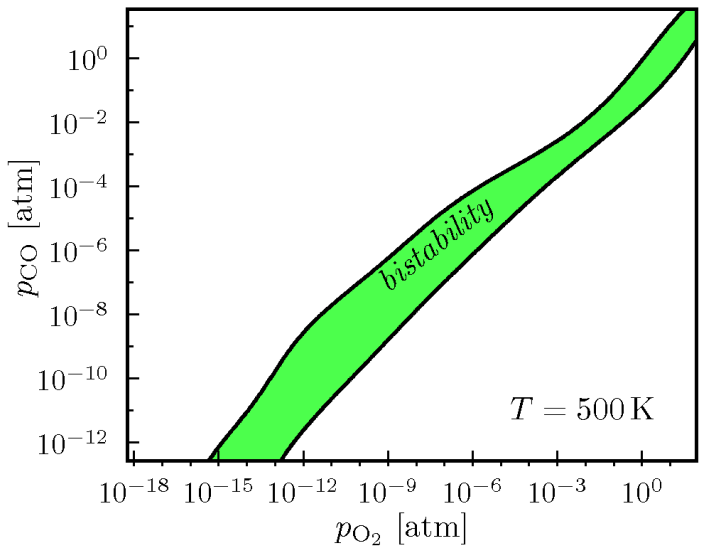

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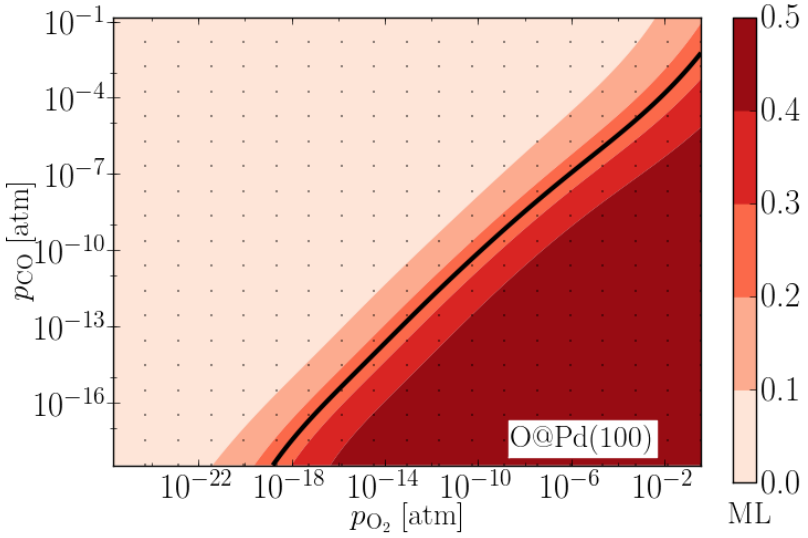
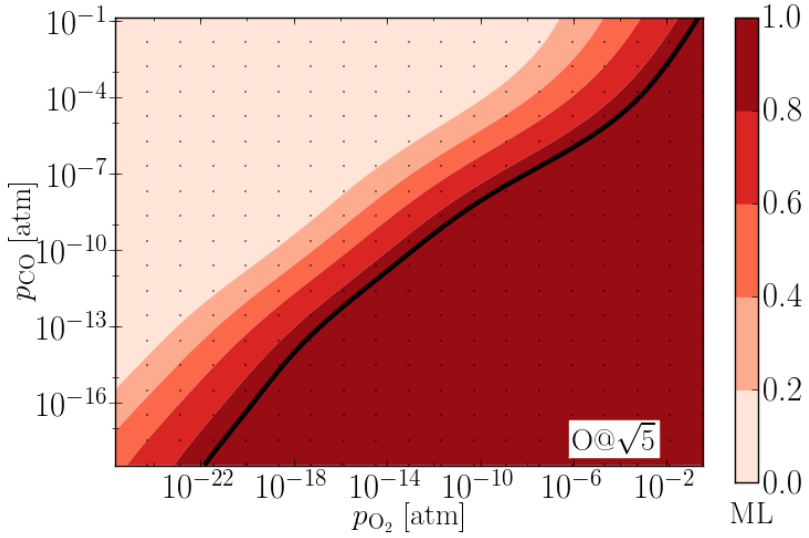
Kinetic phases overlap

$T = 400\,\mathrm{K}$





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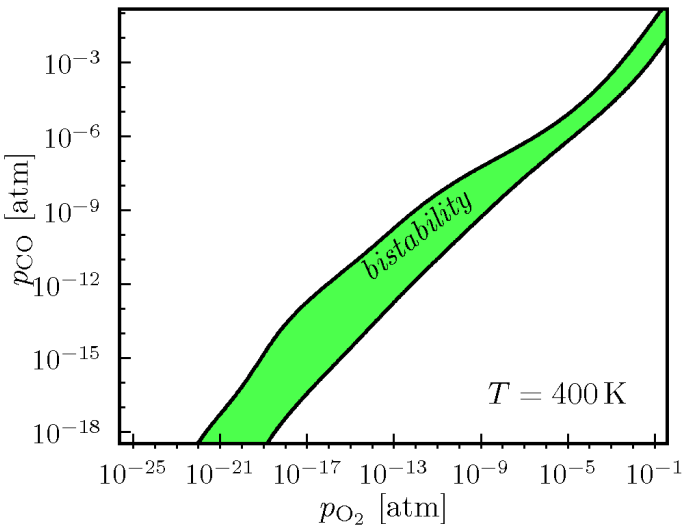

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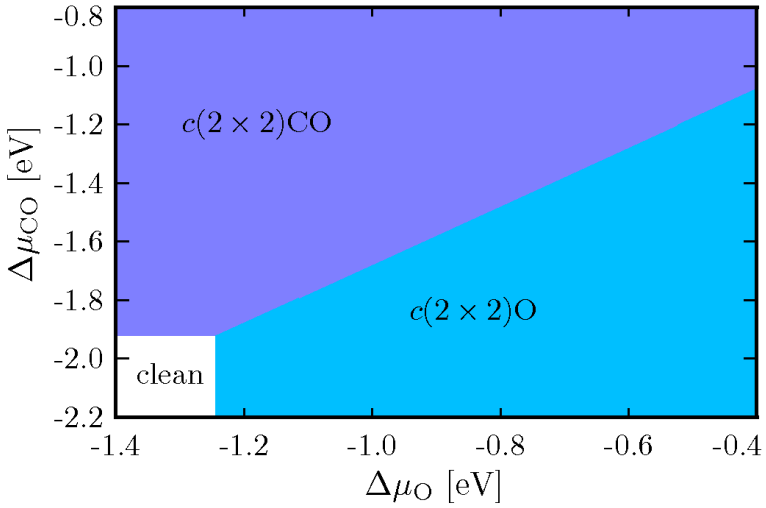
Thermodynamic phases overlap, too!



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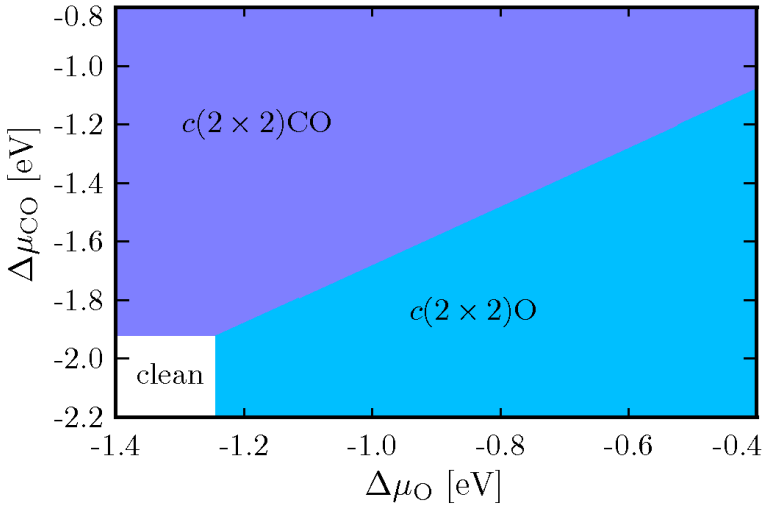

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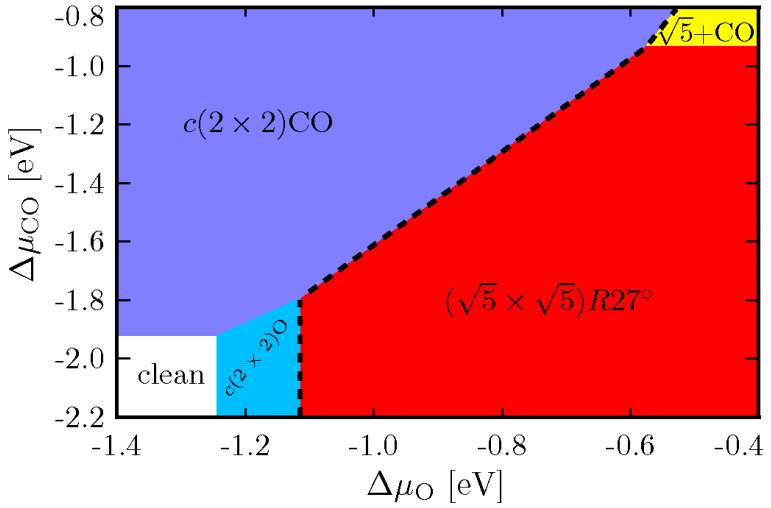

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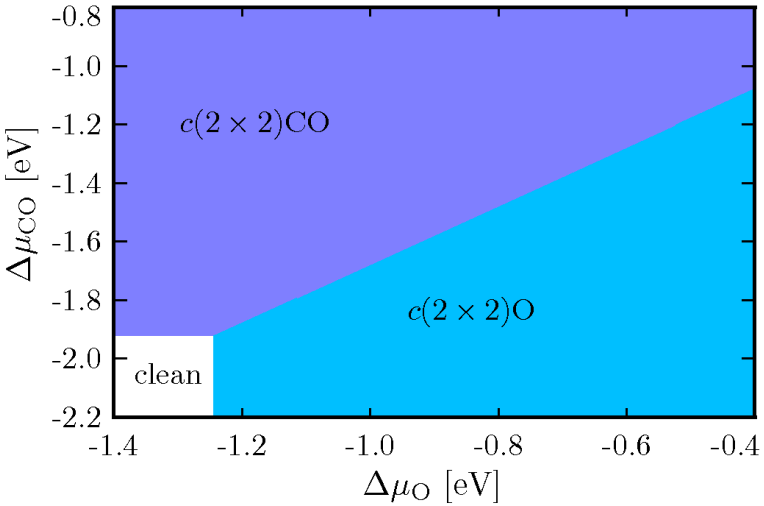

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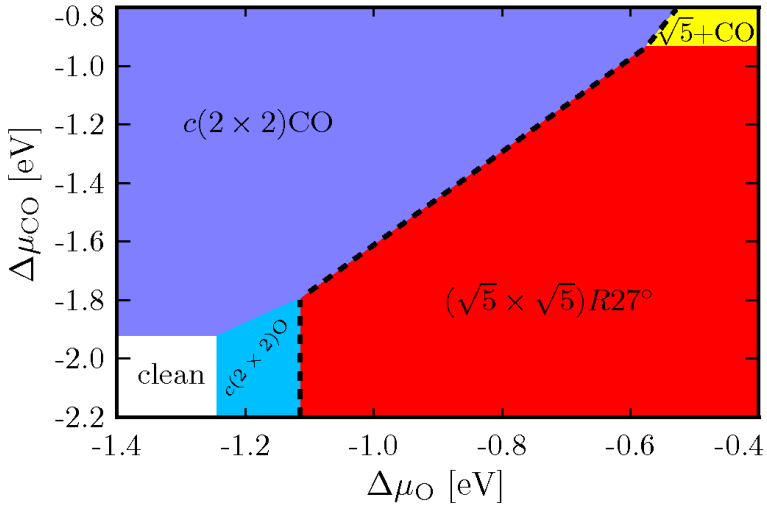

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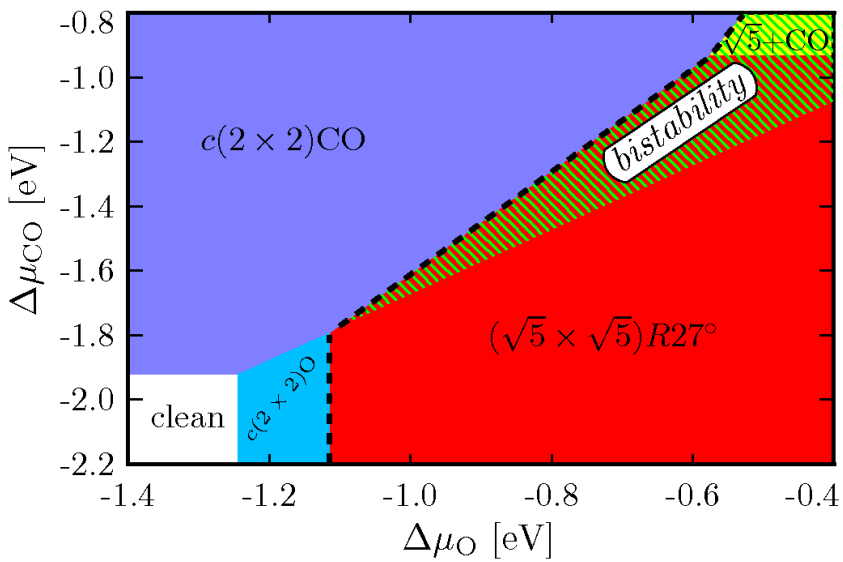
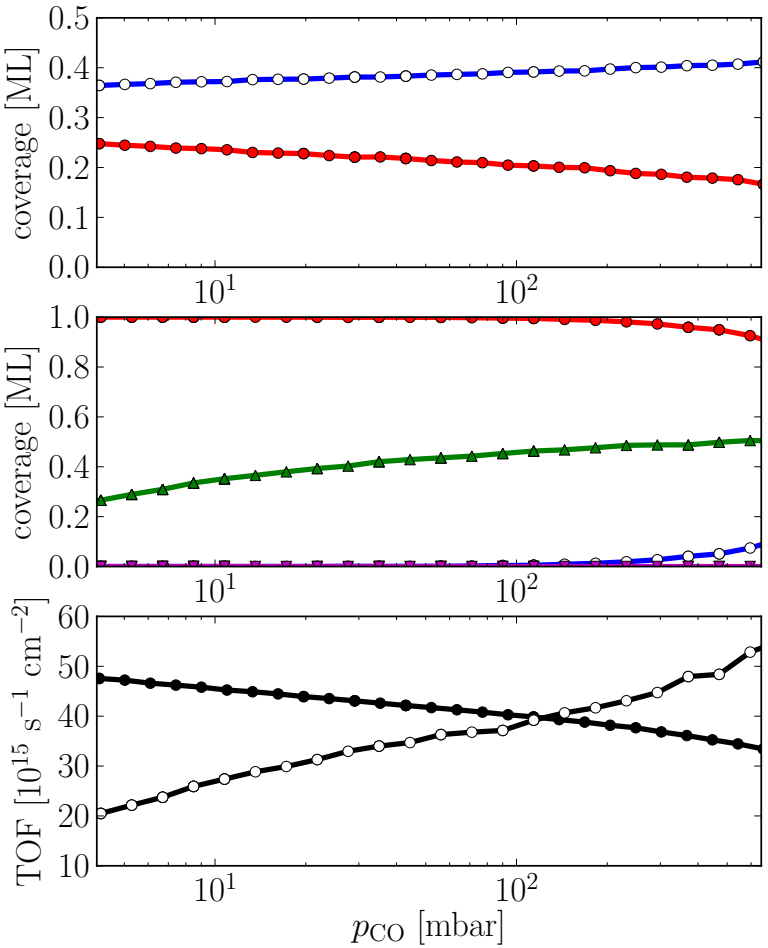


Reaction kinetics revisited

$T = 408\,\mathrm{K}$



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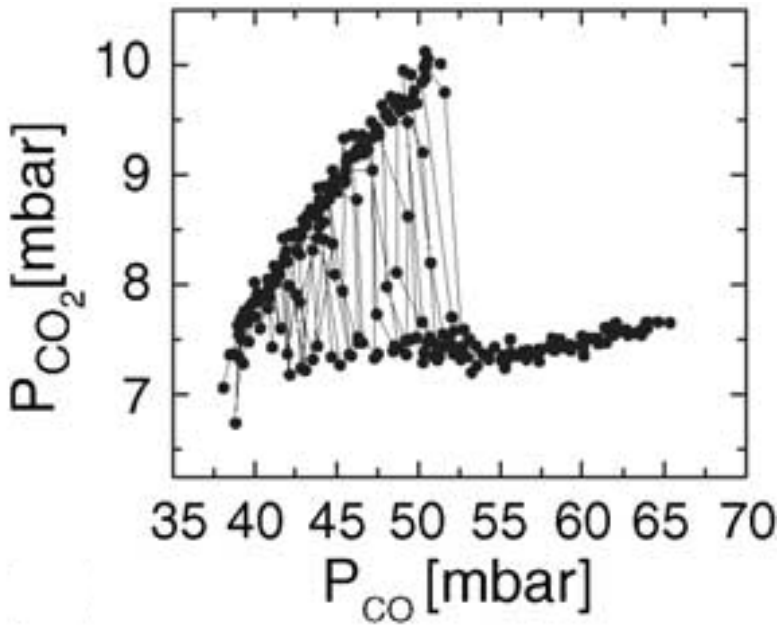

Hendriksen *et al.*, Catal. Today 105 2, 234 (2005)

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- bistability can be rationalized from thermodynamics
- kinetics show that CO coverage and lateral interaction hinder surface oxide formation
- reactivity of both surfaces may be very similar

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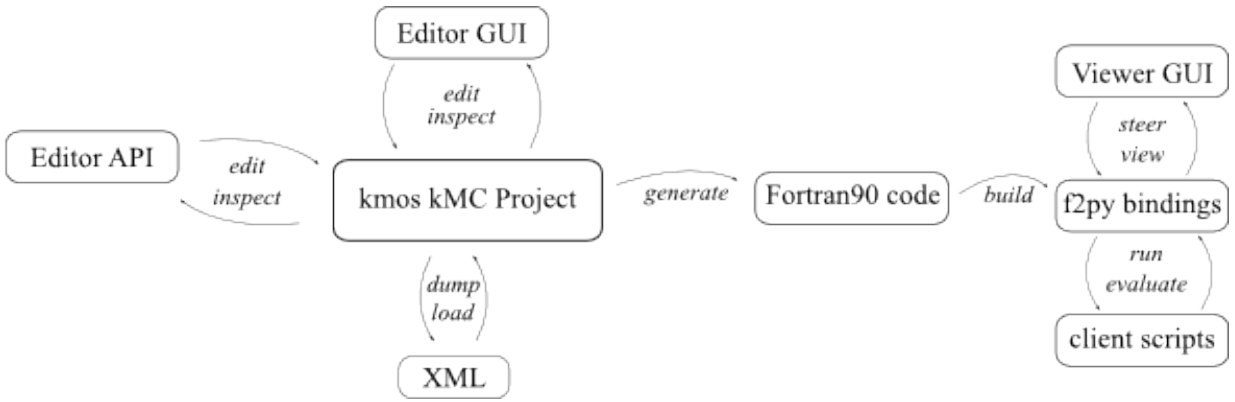
Thank you for your attention (please stay tuned for **O 20.6**).

kmos: kMC Framework

- implement kMC models at the speed of thought
- exchange format for models
- GUI Editor and Viewer

github.com/mhoffman/kmos



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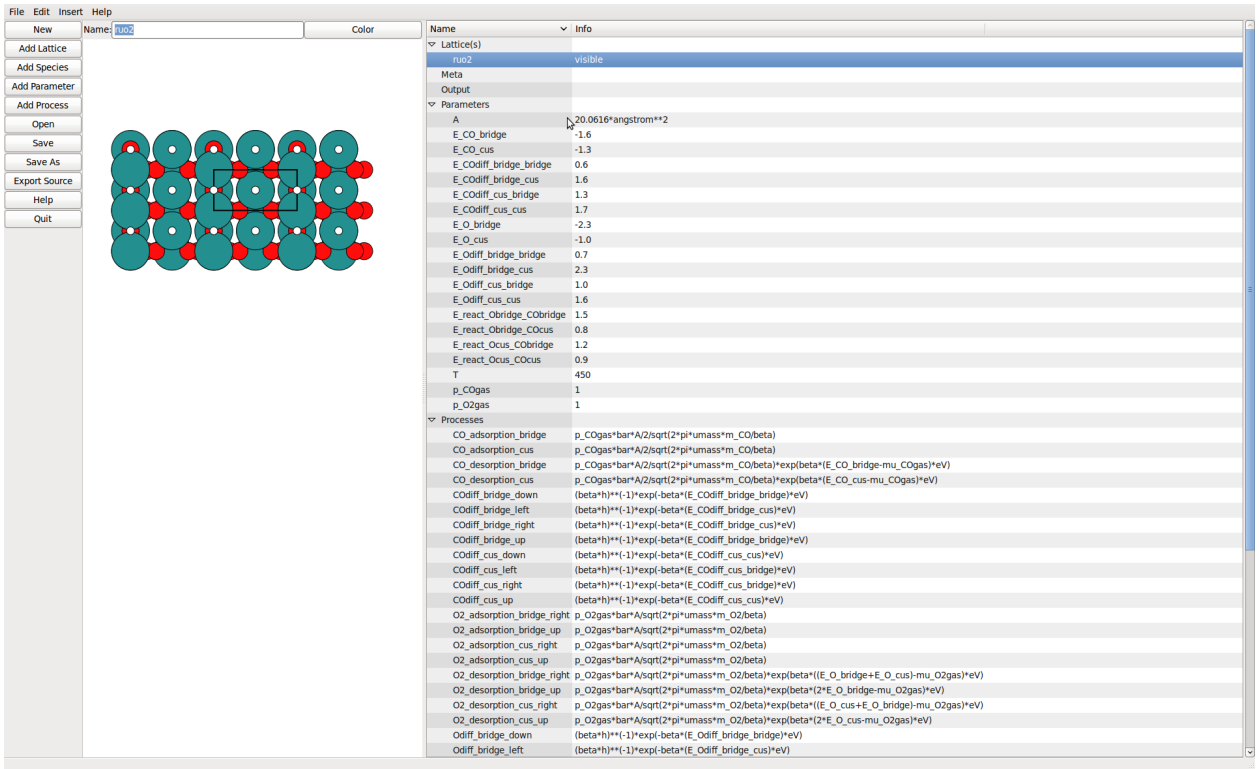

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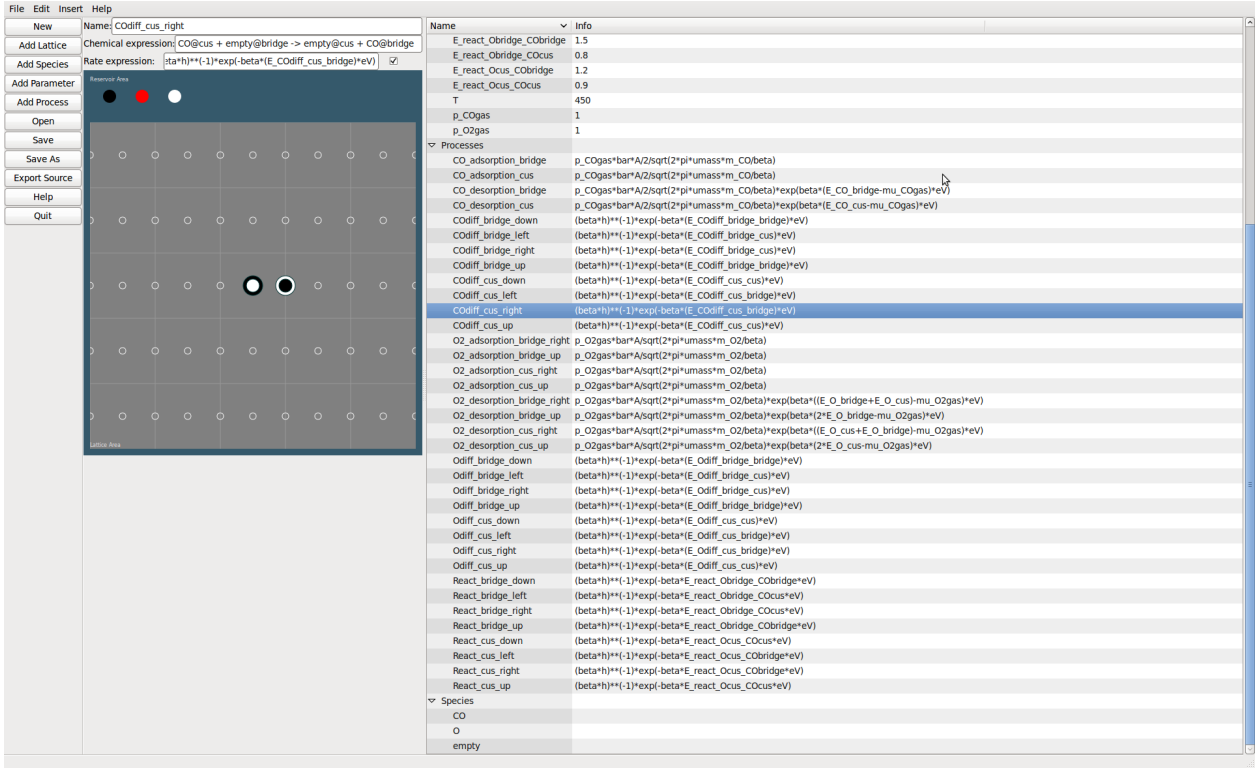

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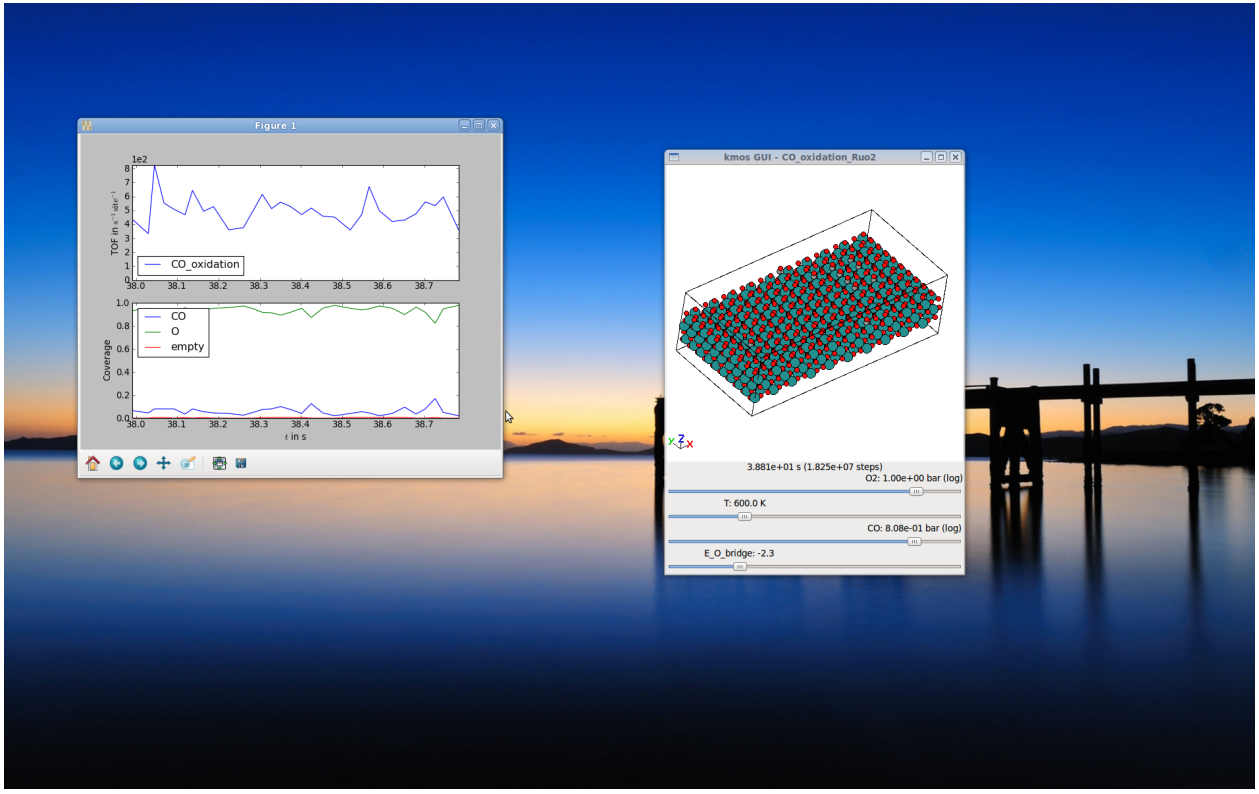

kmos: kMC Framework

- "Kinetic Monte Carlo modeling of the catalytic hydrogenation of benzene on Pt(111)" Maxime Van den Bossche, Master Thesis, 2012, Universiteit Gent
- "First-principles Modelling of Diffusion and Entropy in Battery Materials", Dipl-Chem. Steffen Hartung, TUM Create Singapore
- "First-principles kinetic Monte Carlo based reactor modeling", Dr. Sebastian Matera, TUM
- "Configurational Entropy Contributions in Adsorbate Spatial Distributions", Dr. Aditya (Ashi) Savara, Northwestern Univsersity
- "Multi-lattice kinetic Monte Carlo for CO Oxidation on Pd(100)/PdO(101)$\sqrt{5}$", MJH

Treatment of Lateral Interaction

Nearest-neighbor cluster expansion on $(\sqrt{5}\times\sqrt{5})$R27°

- "CO Oxidation on Pd(100) at Technologically Relevant Pressure Conditions: A First-Principles Kinetic Monte Carlo Study"
  J. Rogal, K. Reuter, and M. Scheffler, Phys. Rev. B 77, 155410 (2008).

Oxygen-oxygen interaction on Pd(100)

- "First-Principles Statistical Mechanics Approach to Step Decoration at Surfaces"
  Y. Zhang and K. Reuter, Chem. Phys. Lett 465, 303 (2008).