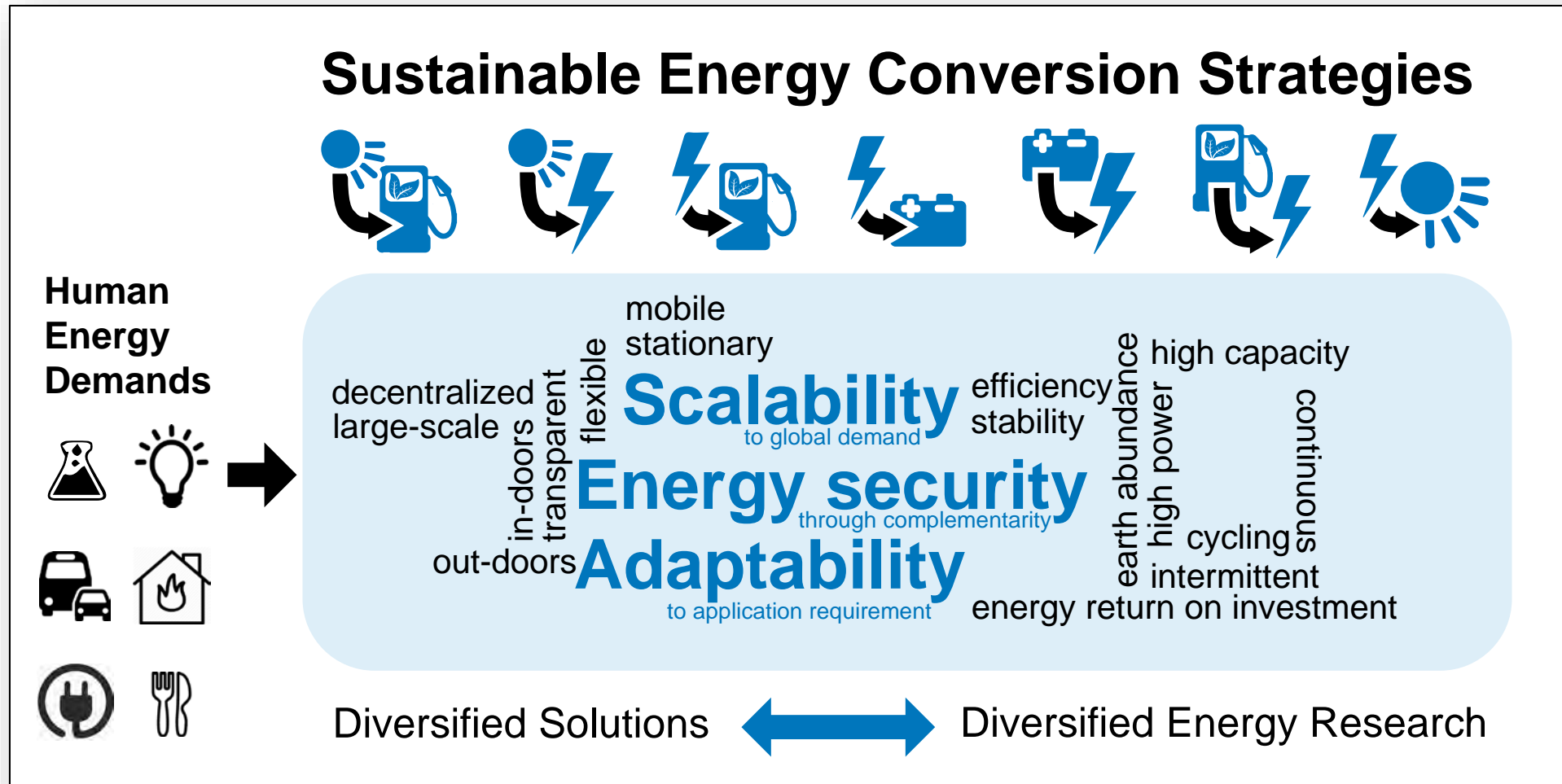


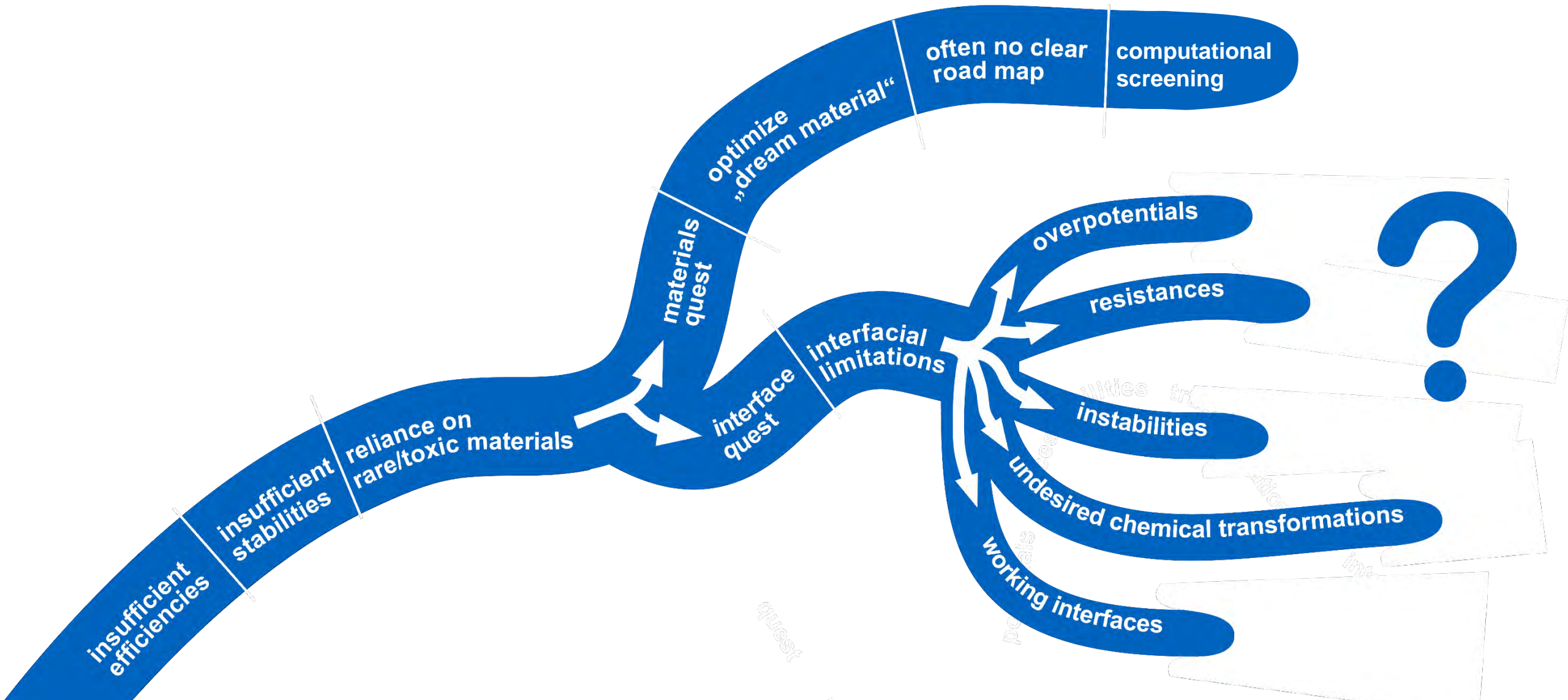


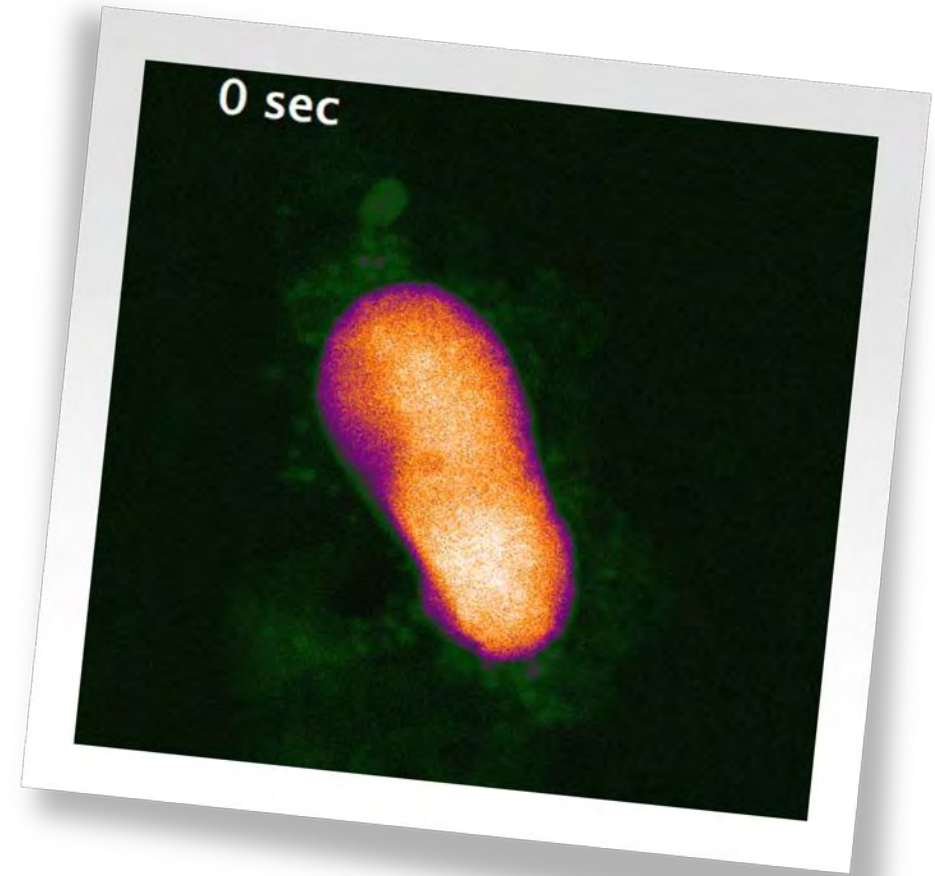
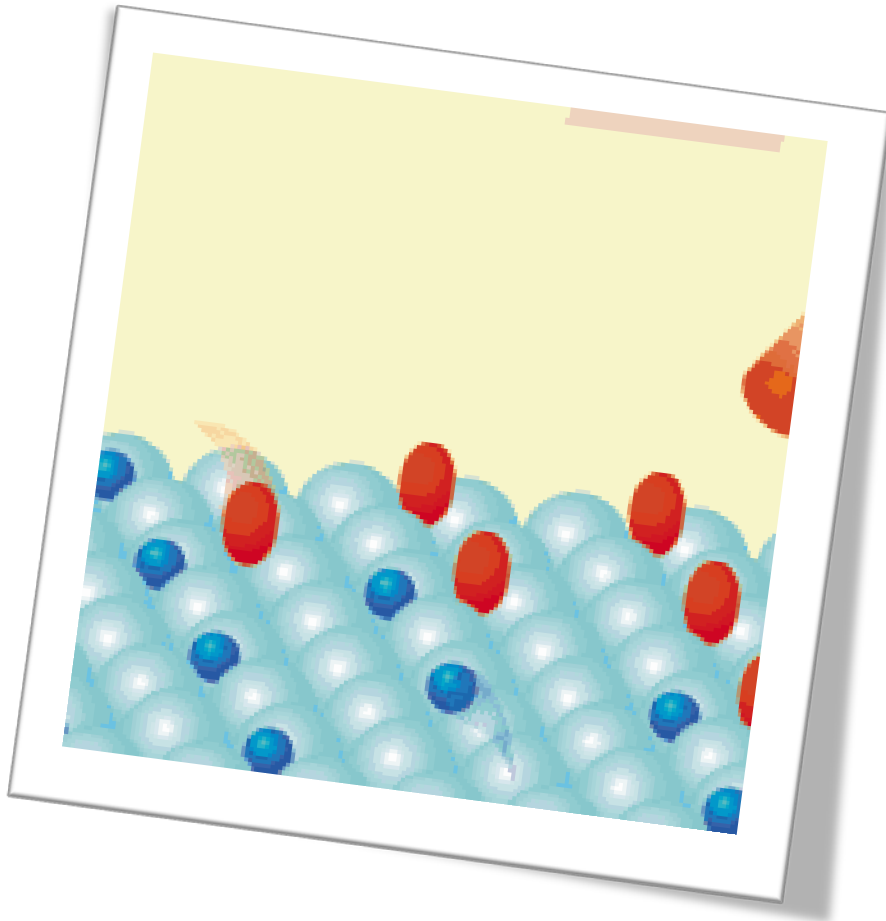
Multiscale Theory of *Operando* Energy Conversion Systems

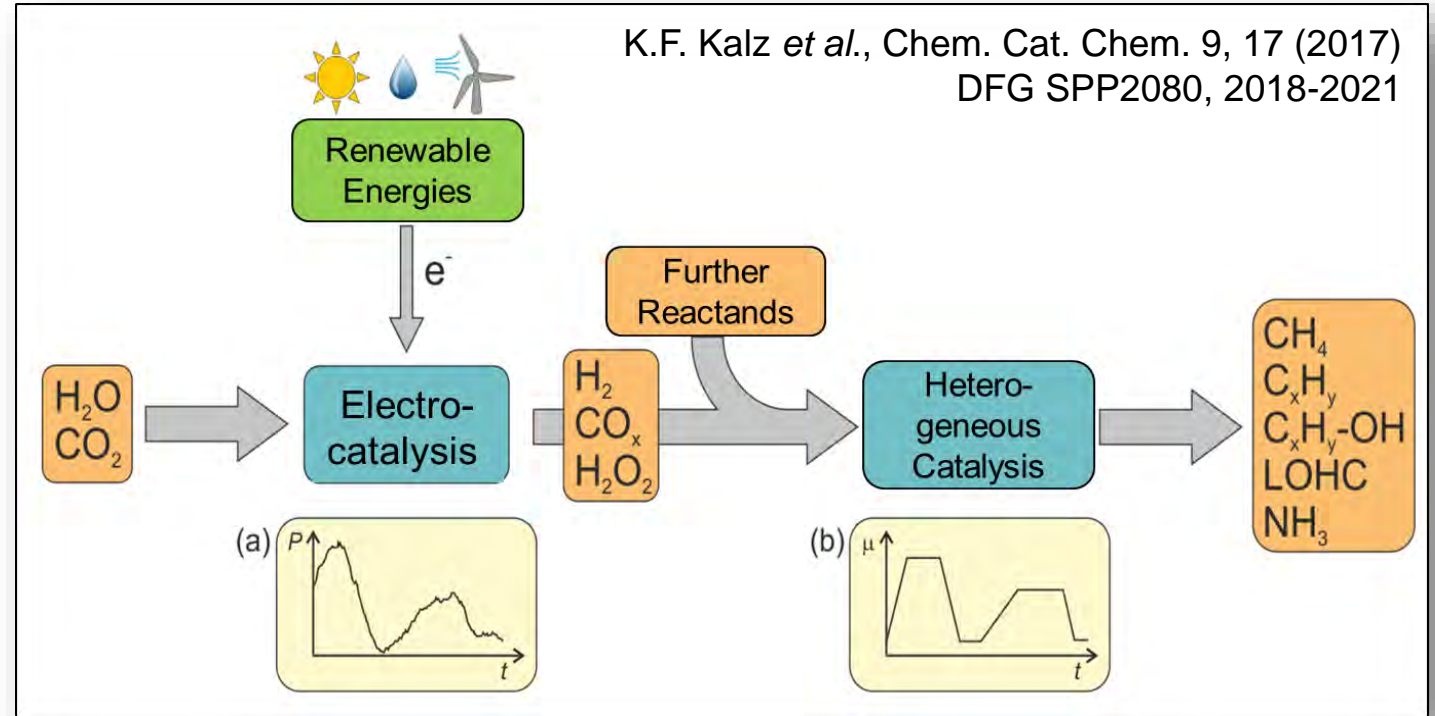
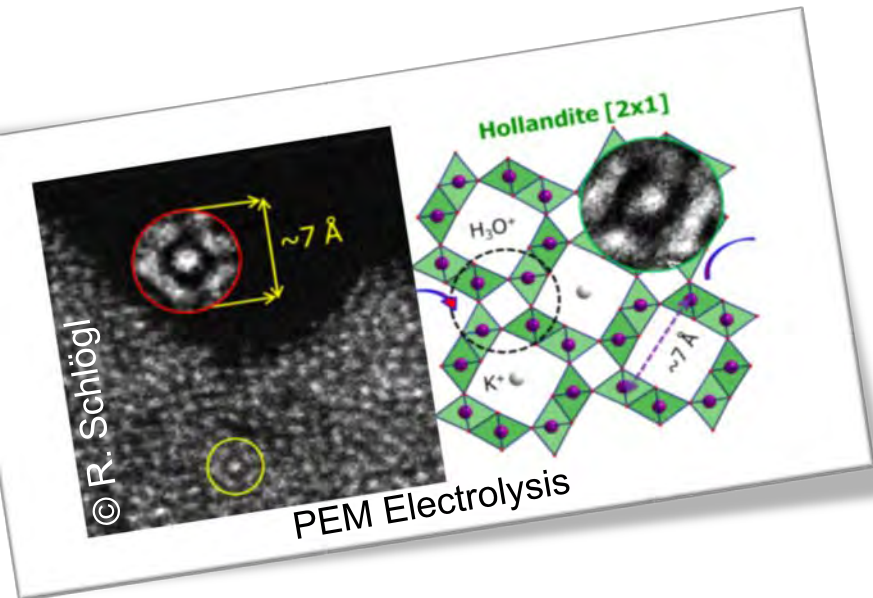
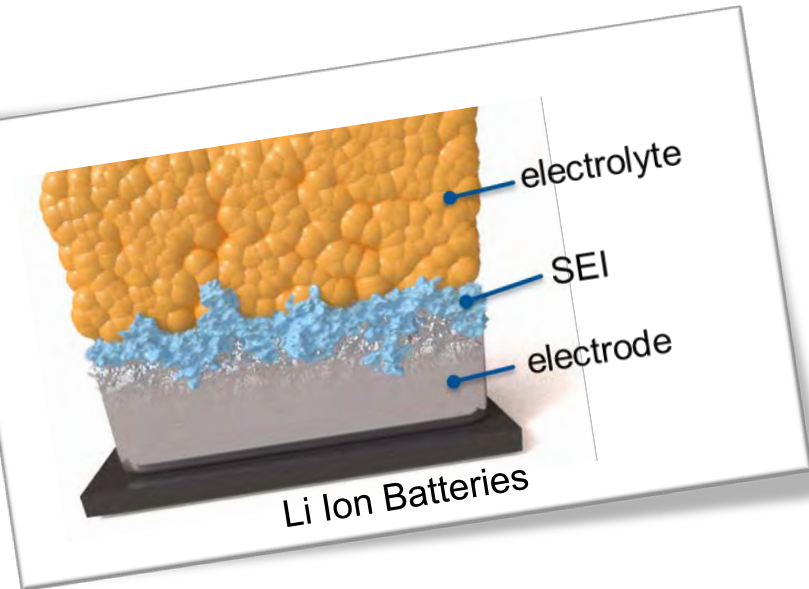
Karsten Reuter

**Chemistry Department and Catalysis Research Center
Technische Universität München**

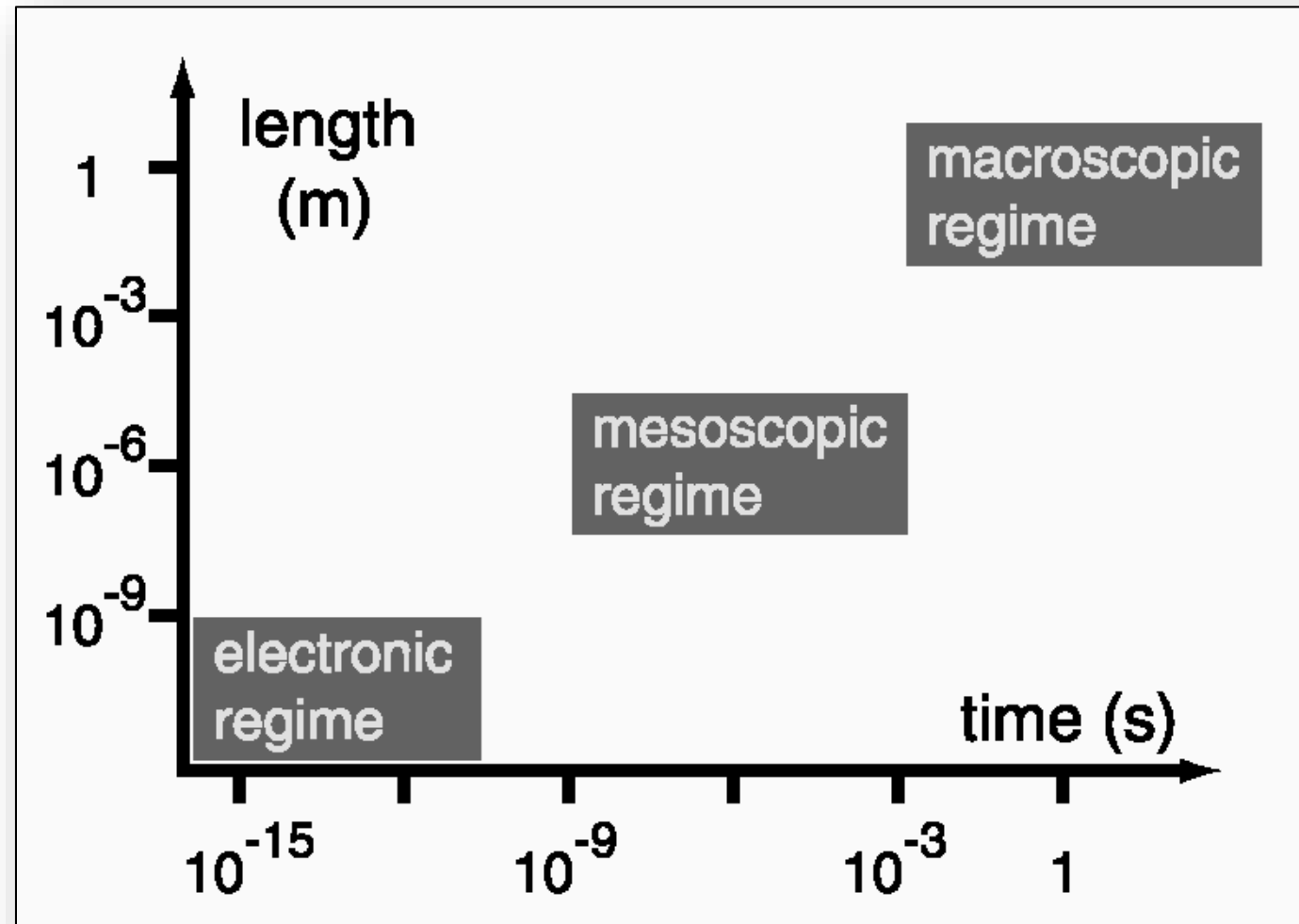






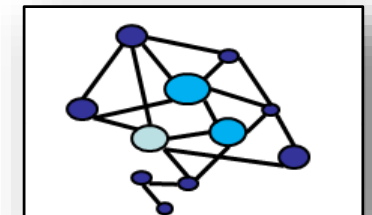
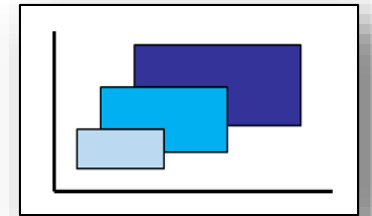


- *Operando* studies
- Microscopic processes and macroscopic environment

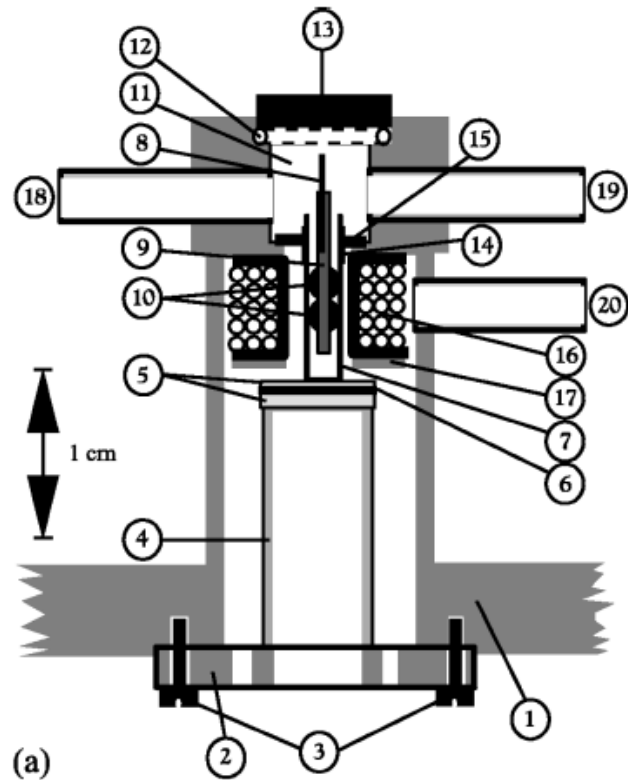


- i) Oxide Formation in Oxidation Catalysis:
Hierarchical multiscale modeling from electrons to the reactor

- ii) On the Way to Adaptive Multiscale Modeling:
Machine learning as gateway to structural complexity

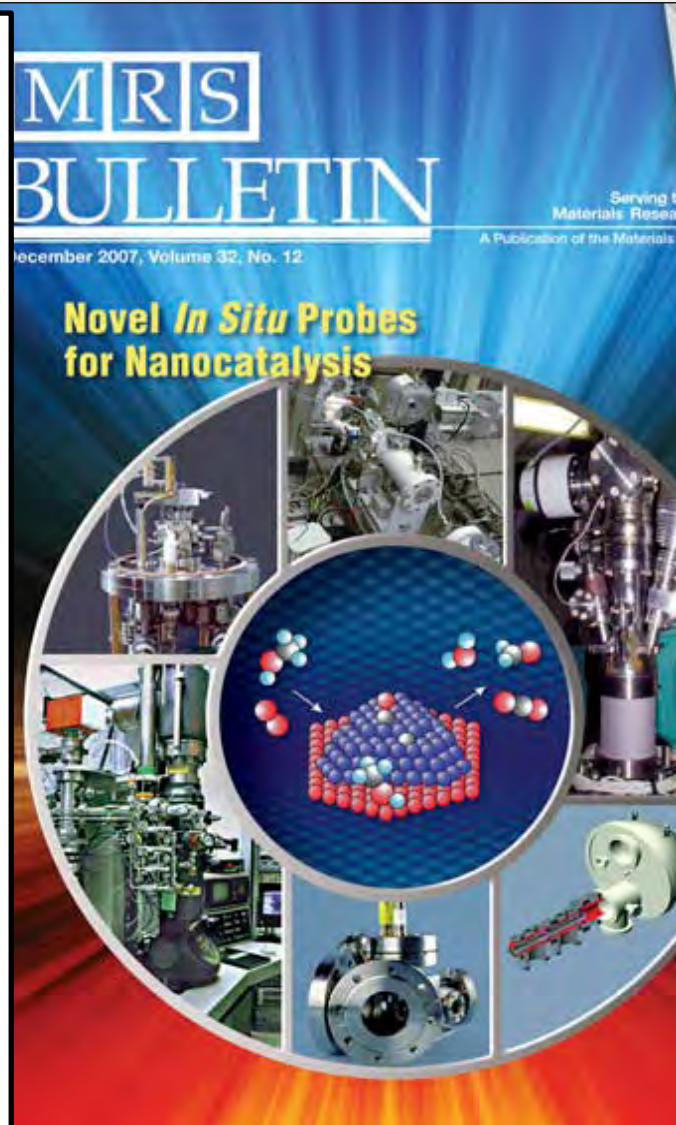


Reactor STM

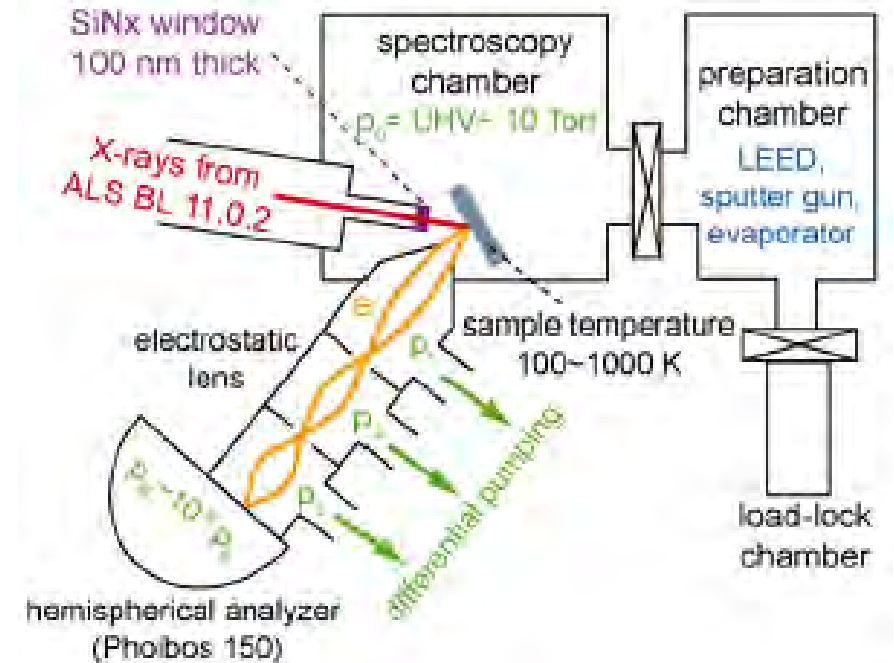


(a)

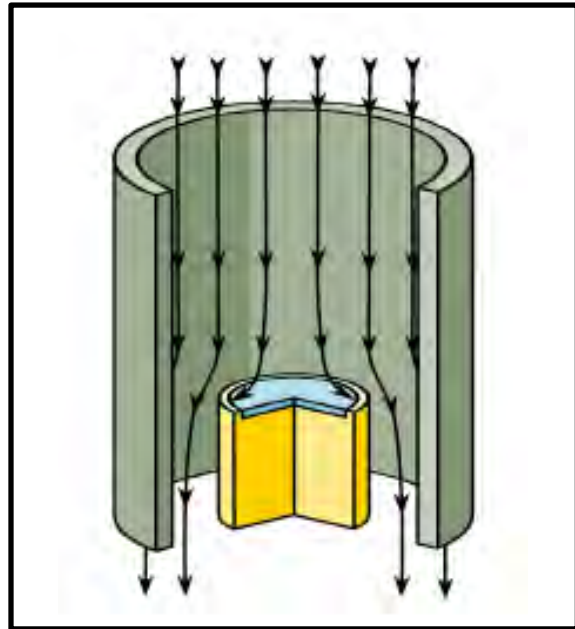
P.B. Rasmussen *et al.*,
Rev. Sci. Instrum. 69, 3879 (1998)



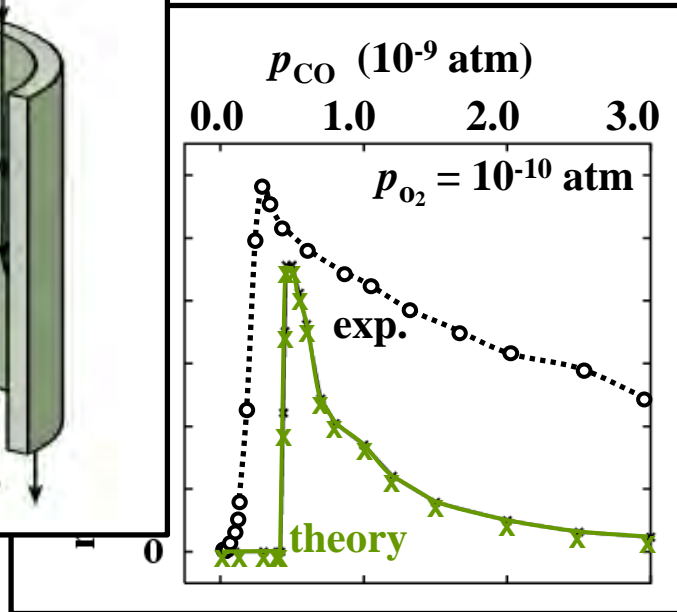
in situ XPS



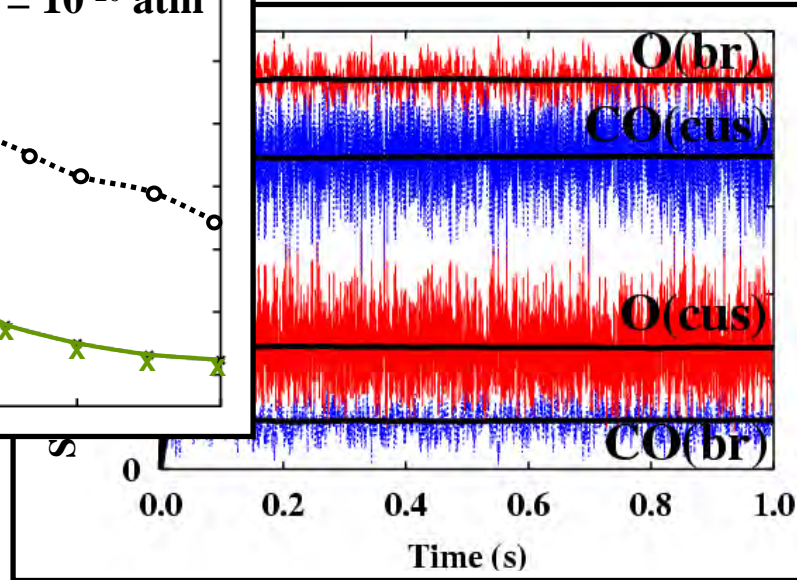
S. Yamamoto *et al.*,
J. Phys. CM 20, 184025 (2008)



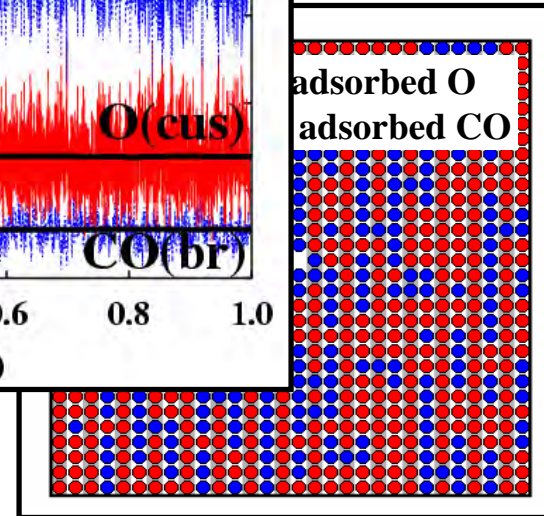
Heat and mass transport



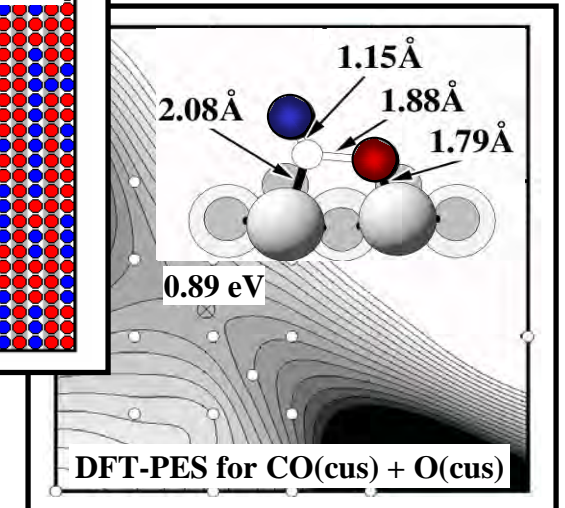
Intrinsic catalytic activity

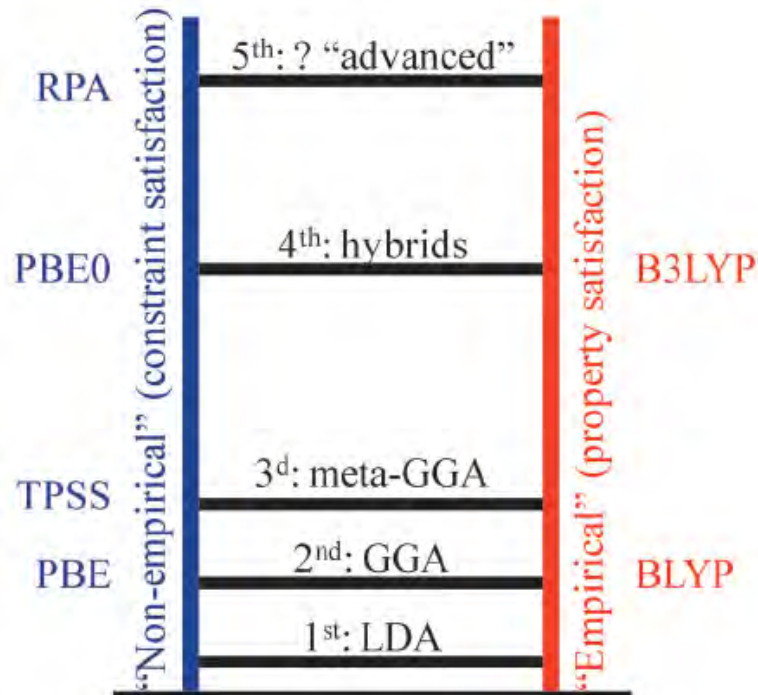
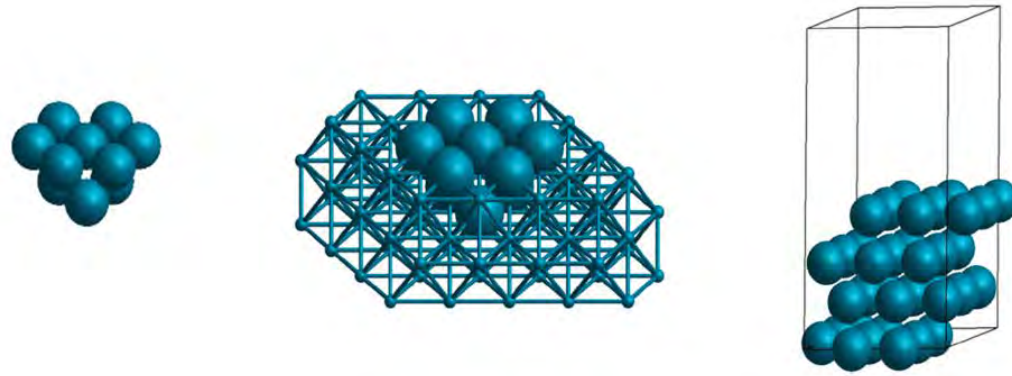


Microkinetic model

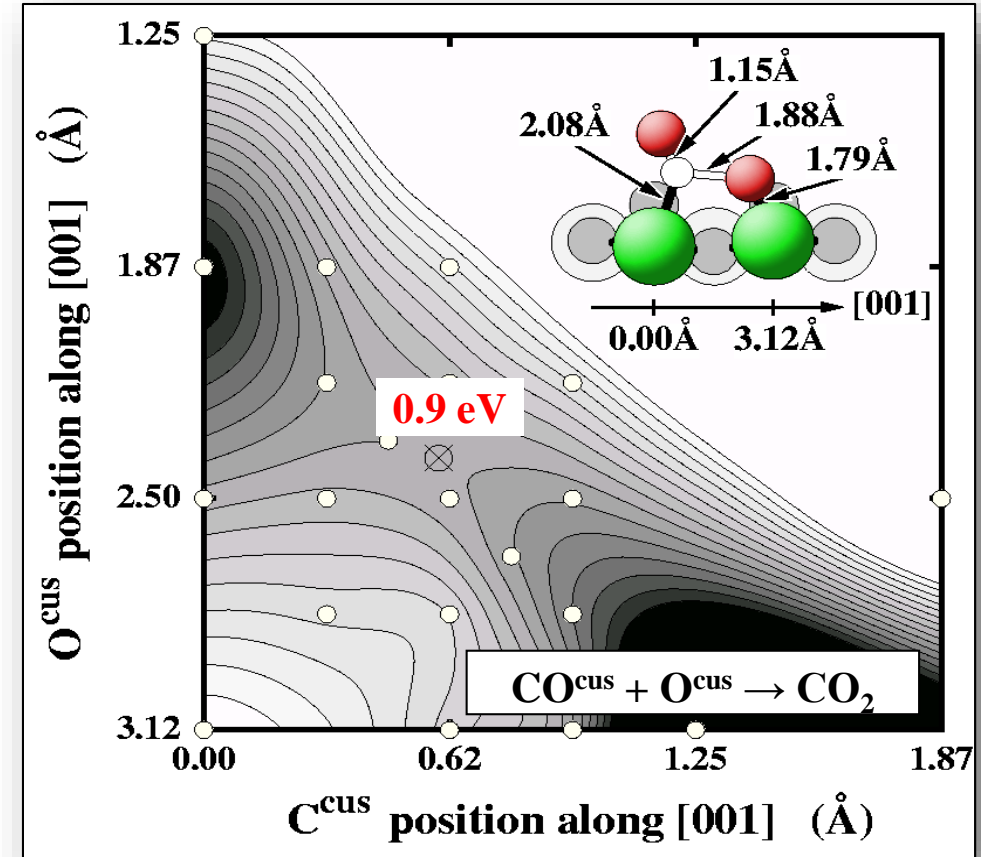


Elementary processes





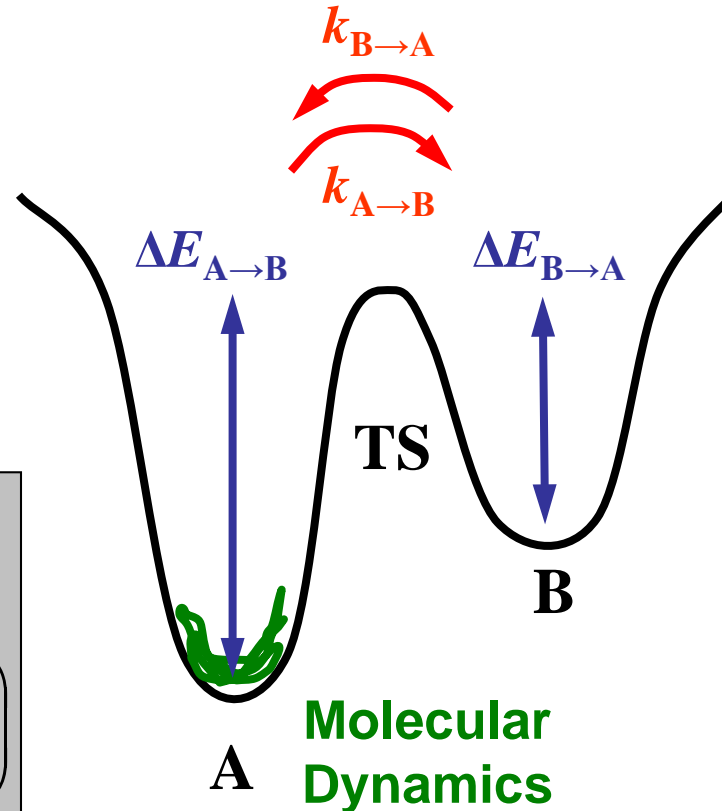
Active site model
„Level of theory“



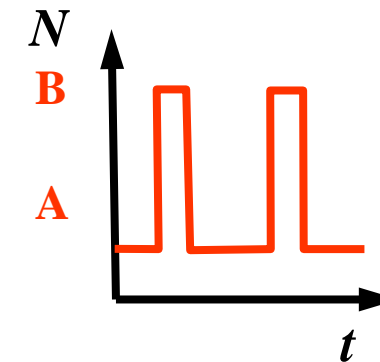
Transition State Theory

$$k_{i \rightarrow j} = \left(\frac{k_B T}{h} \right) \frac{Z_{\text{TS}(i \rightarrow j)}}{Z_i}$$

$$= \Gamma_0 \exp\left(\frac{-\Delta E_{i \rightarrow j}}{k_B T} \right)$$



kinetic Monte Carlo



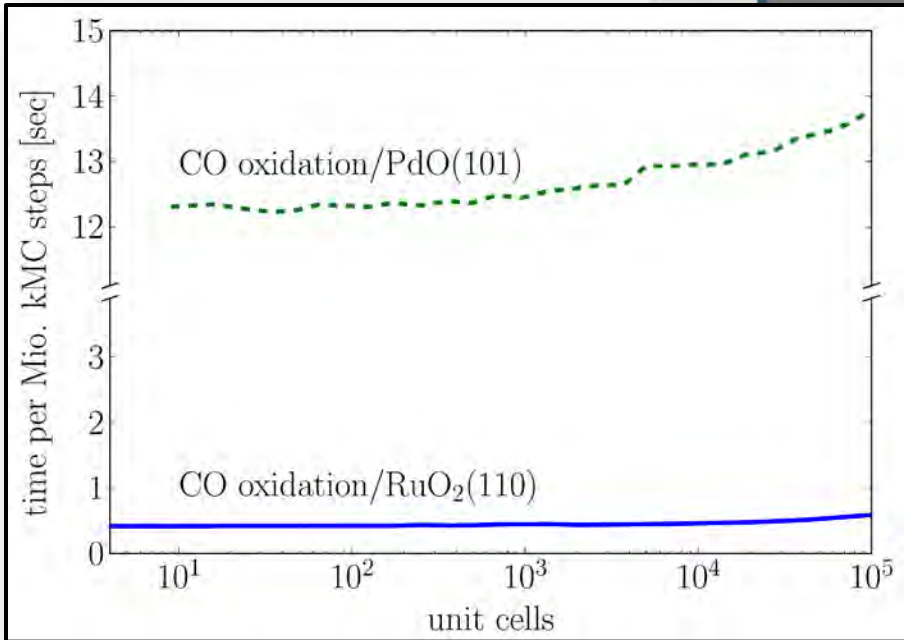
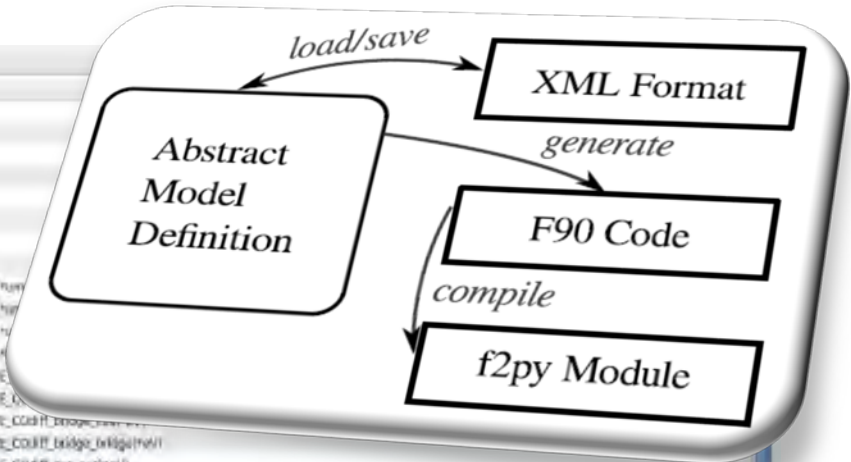
$$\frac{dP_i(t)}{dt} = -\sum_j k_{i \rightarrow j} P_i(t) + \sum_j k_{j \rightarrow i} P_j(t)$$

kmos: A Lattice kMC Framework

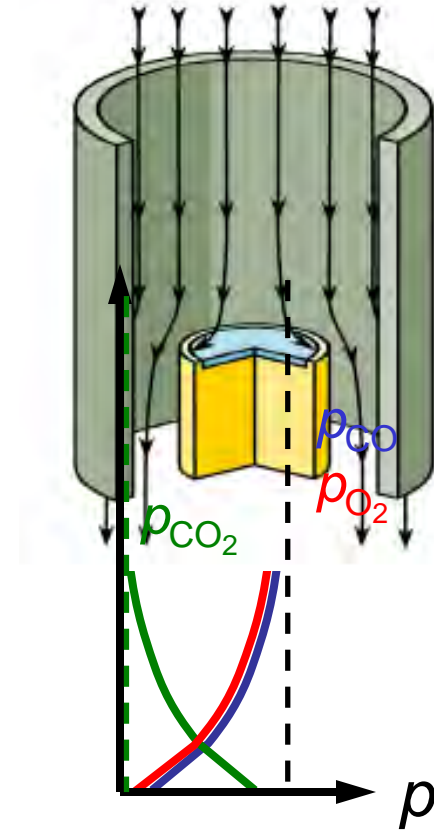
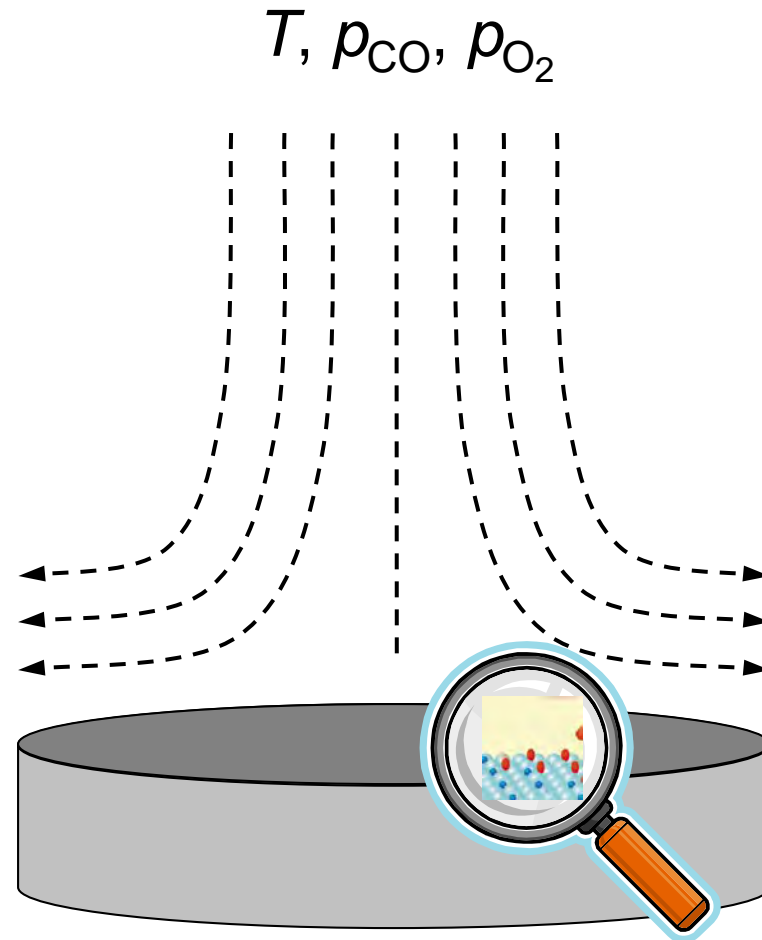
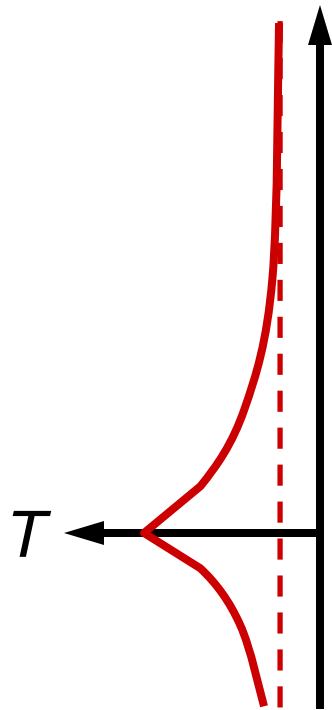
github.com/mhoffman/kmos
kmos

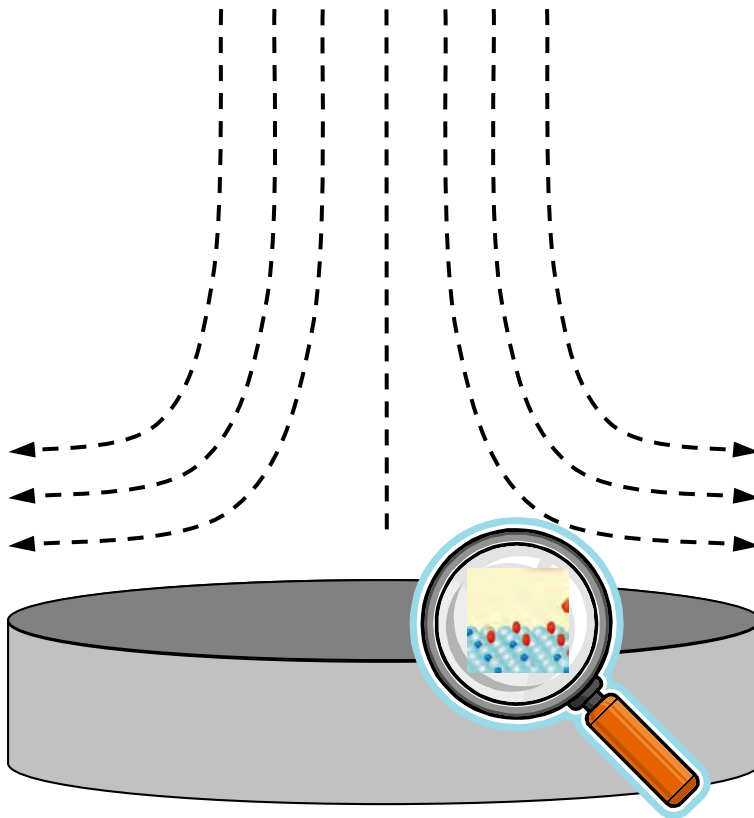
The screenshot shows the kmos software interface. On the left, there are tabs for 'Name', 'Lattice', 'Species', 'Parameters', 'Process', 'Jobs', 'View', 'New As', 'Export Source', 'Help', and 'Quit'. The main window displays a chemical reaction network with various species and reactions. On the right, there is a list of species and reactions with their respective rates and information.

Name	Info
E_react_bridge_CObridge	1.5
E_react_bridge_COdown	0.8
E_react_bridge_CObridge	1.2
E_react_bridge_COdown	0.9
g_COgas	1
p_COgas	1
CO_adsorption_bridge_right	$\mu_{COgas} + \beta \mu_{bridge} - 2 \mu_{CObridge}$
CO_adsorption_bridge_down	$\mu_{COgas} + \beta \mu_{bridge} - \mu_{CObridge} - \mu_{COdown}$
CO_adsorption_bridge_left	$\mu_{COgas} + \beta \mu_{bridge} - \mu_{CObridge} - \mu_{COleft}$
CO_adsorption_CO_up	$\mu_{COgas} + \beta \mu_{COup} - \mu_{CObridge}$
CO_desorption_bridge_right	$\mu_{CObridge} - \mu_{COgas} - \beta \mu_{bridge}$
CO_desorption_bridge_down	$\mu_{CObridge} - \mu_{COgas} - \beta \mu_{bridge} - \mu_{COdown}$
CO_desorption_bridge_left	$\mu_{CObridge} - \mu_{COgas} - \beta \mu_{bridge} - \mu_{COleft}$
CO_desorption_CO_down	$\mu_{CObridge} - \mu_{COup} - \beta \mu_{COdown}$
CO_desorption_CO_up	$\mu_{CObridge} - \mu_{COup} - \beta \mu_{COdown}$
CO_diff_bridge_down	$\beta \mu_{bridge} - \beta \mu_{bridge} - \mu_{COdiff_bridge_down}$
CO_diff_bridge_left	$\beta \mu_{bridge} - \beta \mu_{bridge} - \mu_{COdiff_bridge_left}$
CO_diff_bridge_right	$\beta \mu_{bridge} - \beta \mu_{bridge} - \mu_{COdiff_bridge_right}$
CO_diff_CO_down	$\beta \mu_{bridge} - \beta \mu_{bridge} - \mu_{COdiff_CO_down}$
CO_diff_CO_left	$\beta \mu_{bridge} - \beta \mu_{bridge} - \mu_{COdiff_CO_left}$
CO_diff_CO_right	$\beta \mu_{bridge} - \beta \mu_{bridge} - \mu_{COdiff_CO_right}$
CO_diff_CO_up	$\beta \mu_{bridge} - \beta \mu_{bridge} - \mu_{COdiff_CO_up}$
React_bridge_down	$\beta \mu_{bridge} - \beta \mu_{bridge} - \mu_{react_bridge_down}$
React_bridge_left	$\beta \mu_{bridge} - \beta \mu_{bridge} - \mu_{react_bridge_left}$
React_bridge_right	$\beta \mu_{bridge} - \beta \mu_{bridge} - \mu_{react_bridge_right}$
React_bridge_down	$\beta \mu_{bridge} - \beta \mu_{bridge} - \mu_{react_bridge_down}$
React_CO_down	$\beta \mu_{bridge} - \beta \mu_{bridge} - \mu_{react_CO_down}$
React_CO_left	$\beta \mu_{bridge} - \beta \mu_{bridge} - \mu_{react_CO_left}$
React_CO_right	$\beta \mu_{bridge} - \beta \mu_{bridge} - \mu_{react_CO_right}$
React_CO_up	$\beta \mu_{bridge} - \beta \mu_{bridge} - \mu_{react_CO_up}$



e.g. CO oxidation





$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0$$

continuity

$$\frac{\partial}{\partial t} (\rho \mathbf{v}) + \nabla \cdot (\rho \mathbf{v} \mathbf{v}) = -\nabla p + \nabla \cdot \left[\mu (\nabla \mathbf{v} + \nabla \mathbf{v}^T) - \frac{2}{3} \mu (\nabla \mathbf{v}) \mathbf{I} \right] + \rho \mathbf{g}$$

momentum

$$\frac{\partial}{\partial t} (\rho \omega_k) + \nabla \cdot (\rho \omega_k \mathbf{v}) = -\nabla \cdot (\rho \omega_k \mathbf{V}_k) + \dot{\Omega}_k^{\text{hom}} \quad k = 1, \dots, NG$$

mass

$$\rho \hat{C}_p \frac{\partial T}{\partial t} + \rho \hat{C}_p \mathbf{v} \nabla T = \nabla \cdot (\lambda \nabla T) - \rho \sum_{k=1}^{NG} \hat{C}_{p,k} \omega_k \mathbf{V}_k - \sum_{k=1}^{NG} \hat{H}_k^{\text{hom}} \dot{\Omega}_k^{\text{hom}}$$

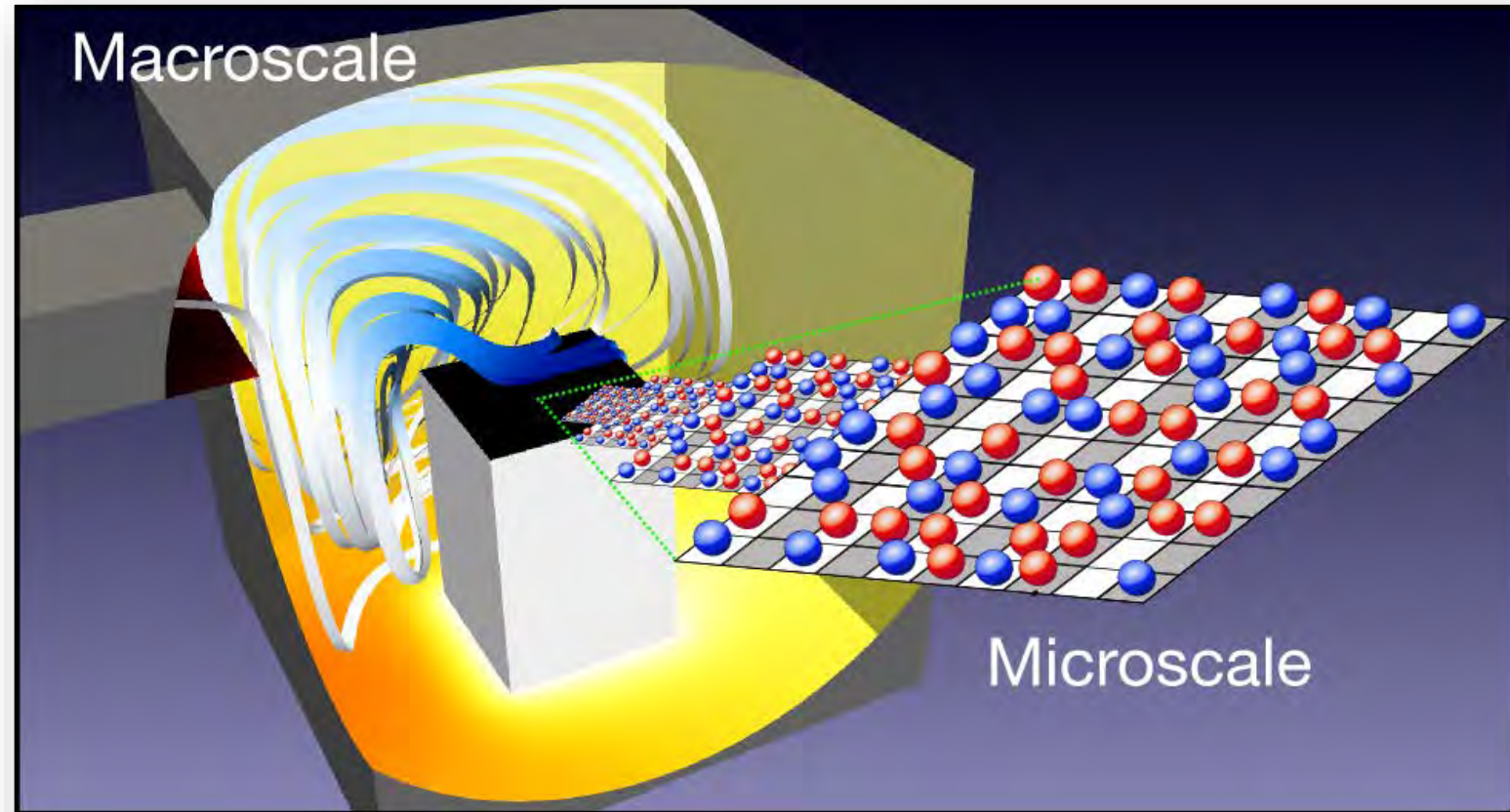
energy

Computational Fluid Dynamics
with chemical source terms
from 1p-kMC

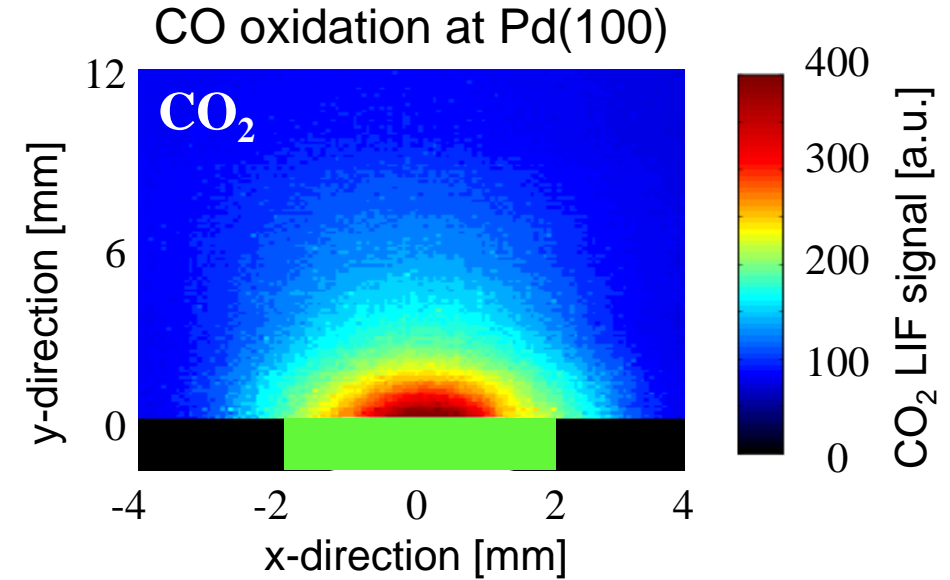
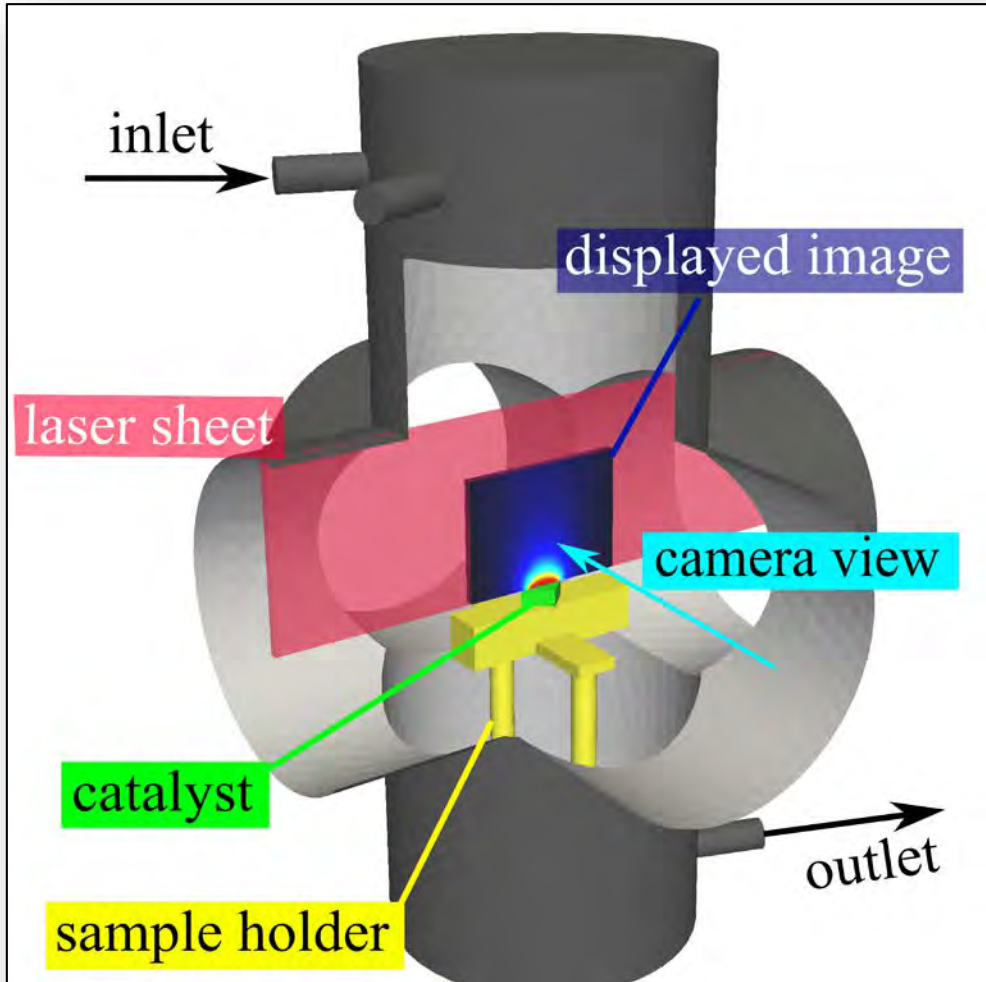
$$k_{\text{ad}} = S(T) \frac{\rho A_{\text{uc}}}{\sqrt{2\pi m k_B T}}$$



with
M. Maestri and A. Cuoci
(Politecnico Milan)



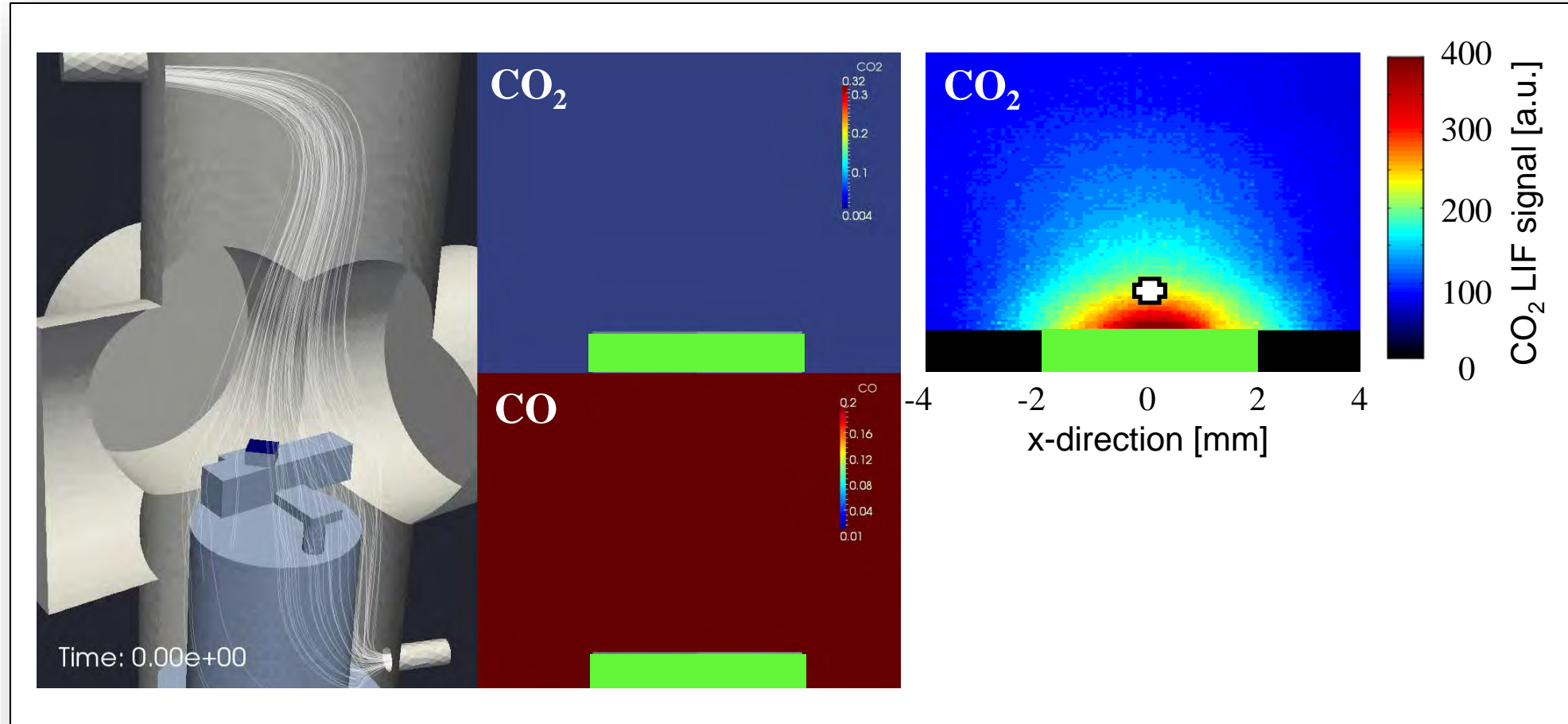
E. Lundgren, J. Gustafson *et al.*
(Lund University)



Stimulation of known excitation (here: CO₂ vibration)

→ 2D concentration profile above catalyst

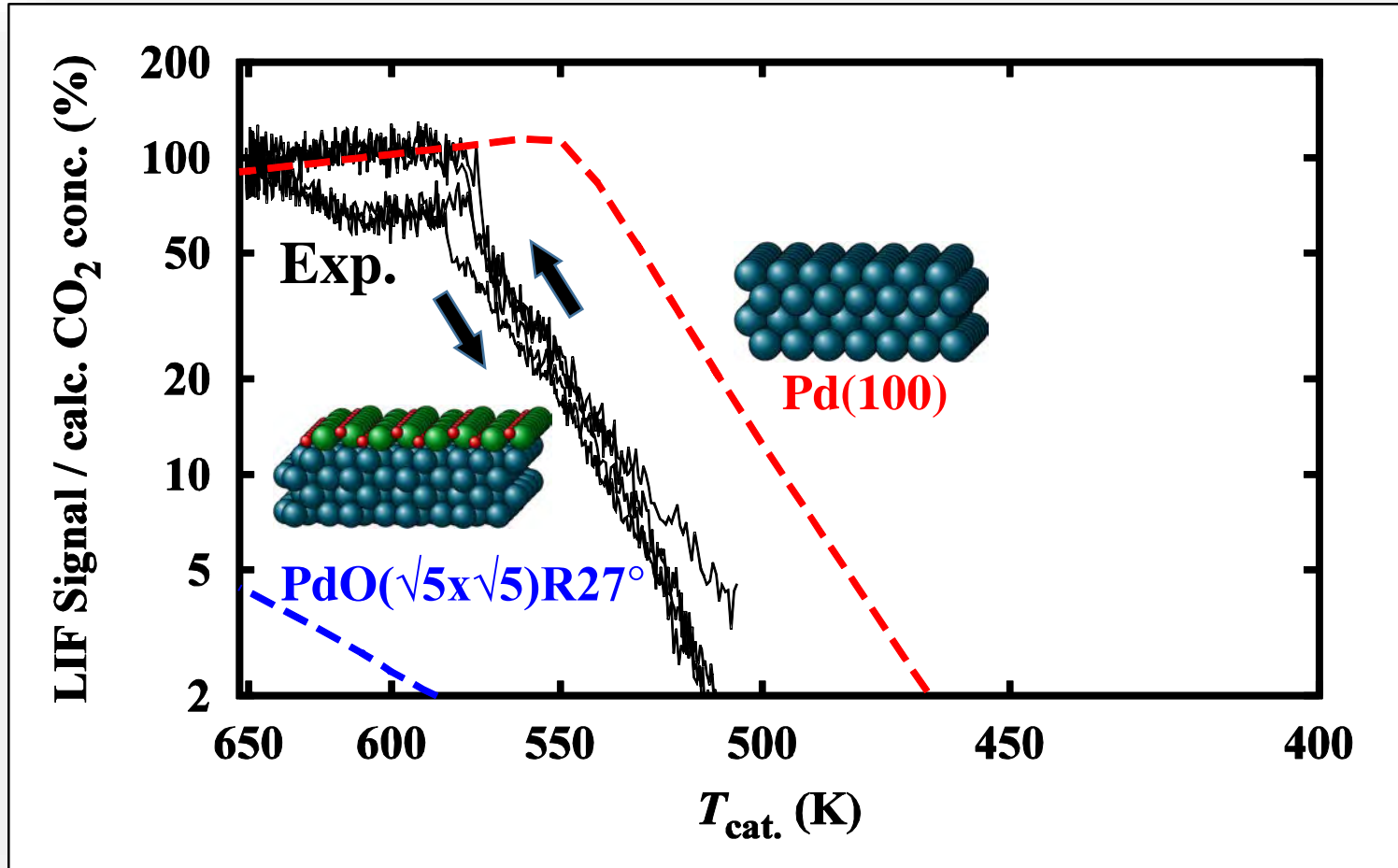
1p-kMC/CFD simulation vs. *in situ* LIF measurements
of near-ambient CO oxidation at Pd(100)



CO : O₂ = 1 : 4, $p_{\text{tot}} = 0.18$ atm, $T = 600$ K, 72 ml_n/min, 50% Ar

S. Matera, M. Maestri, A. Cuoci, and K. Reuter,
ACS Catal. 4, 4081 (2014)

with E. Lundgren, J. Gustafson *et al.*
(Lund University)

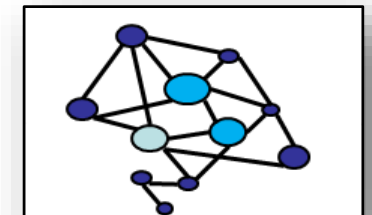
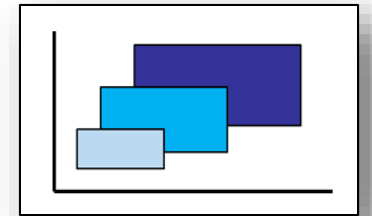


Active Pd(100)
as a minority phase
on the surface?!

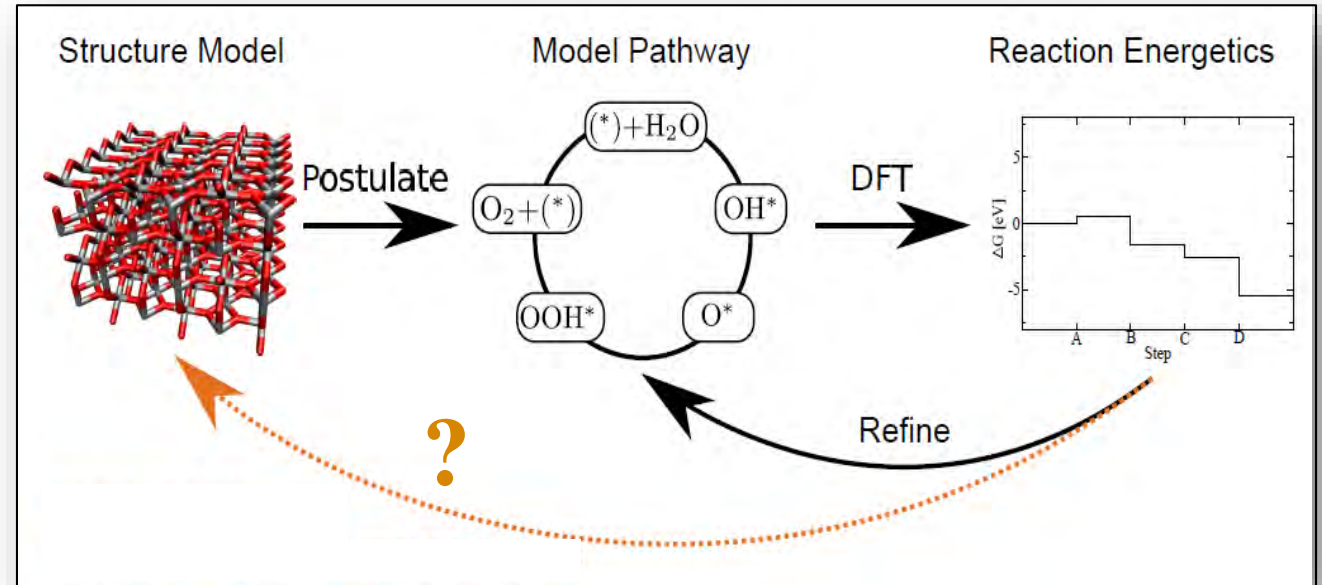
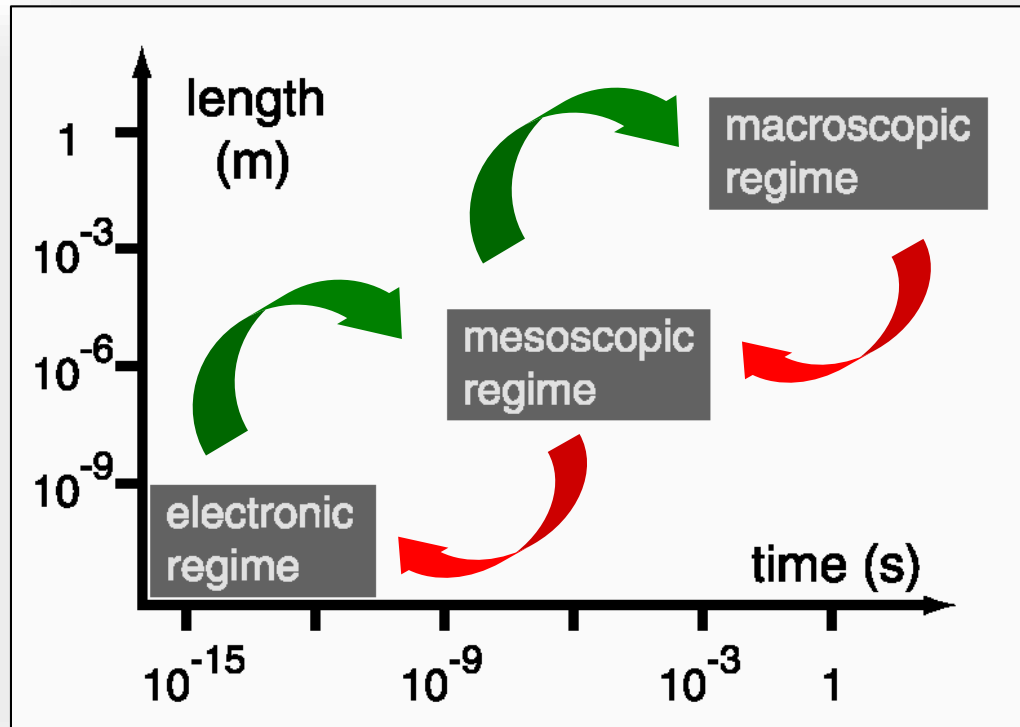
$p_{\text{tot}} = 0.18 \text{ atm}$
72 ml_n/min, 50% Ar

- i) Oxide Formation in Oxidation Catalysis:
Hierarchical multiscale modeling from electrons to the reactor

- ii) On the Way to Adaptive Multiscale Modeling:
Machine learning as gateway to structural complexity

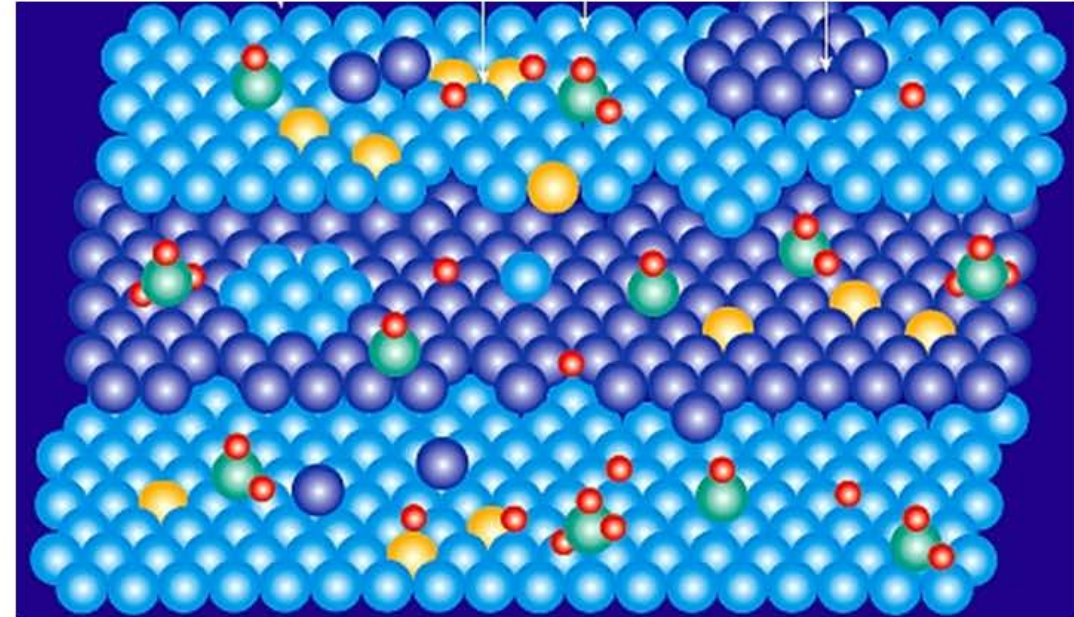


From Static to Adaptive Multiscale Modeling





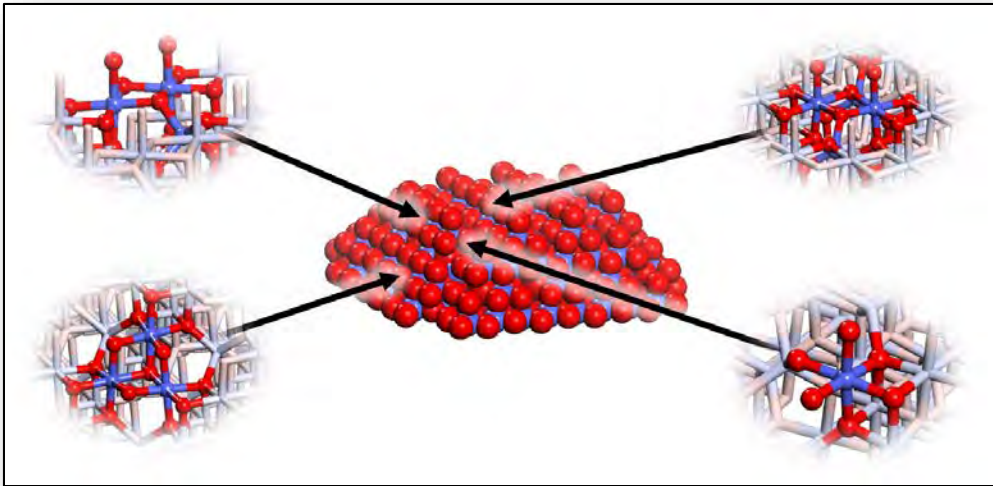
vs.



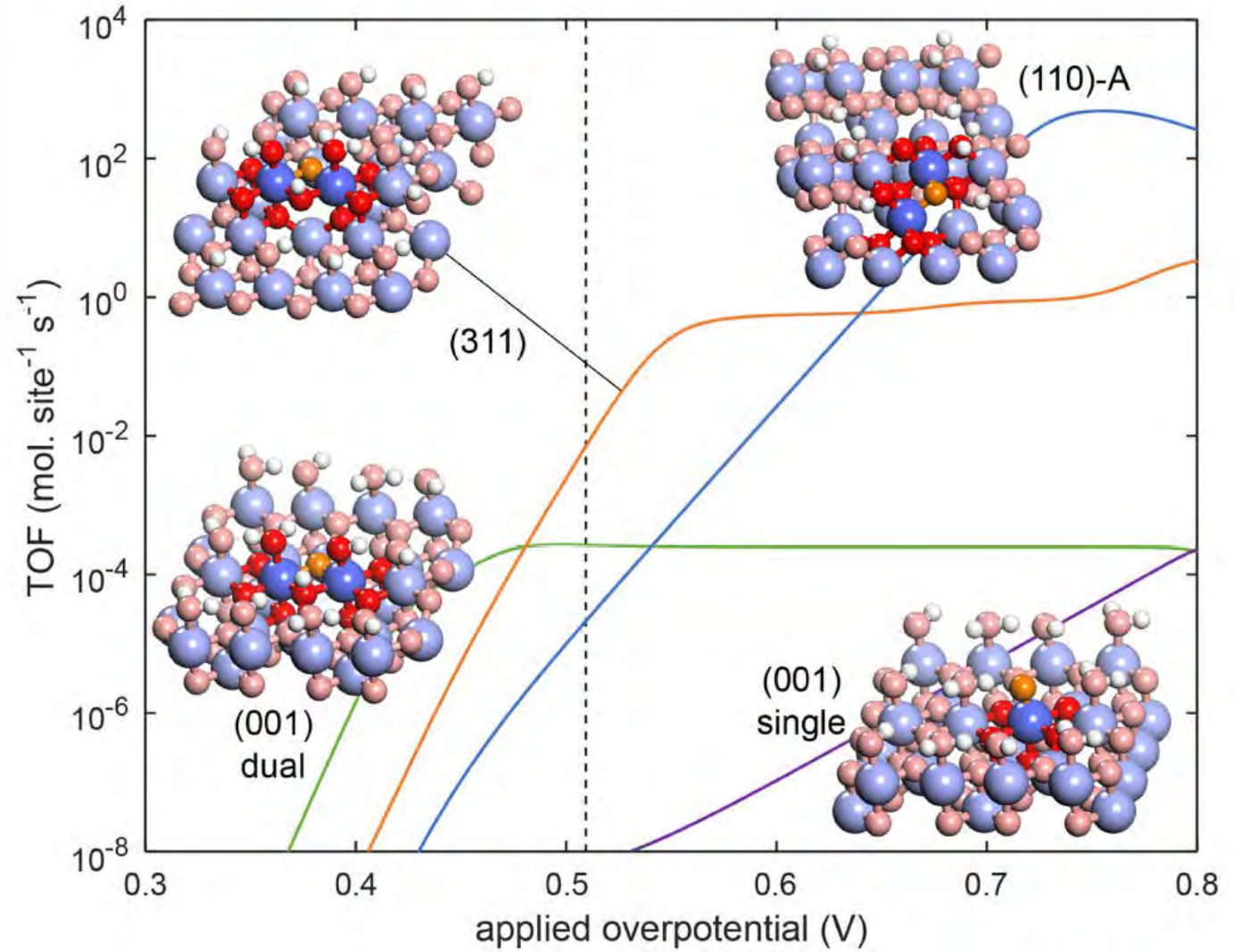
- Generic active site independent of operation conditions dominant over other sites (one site model)

- Atomistic active site model
 - every atom counts
 - generally insufficient experimental characterization
 - might change drastically *operando*

The Active Site in OER at Co_3O_4

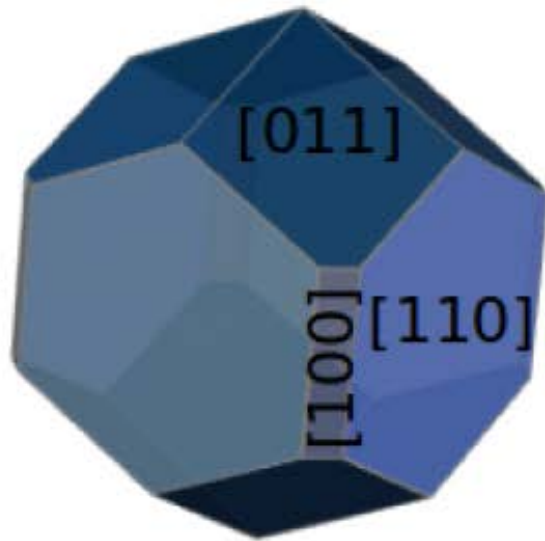


Active site changes with applied potential

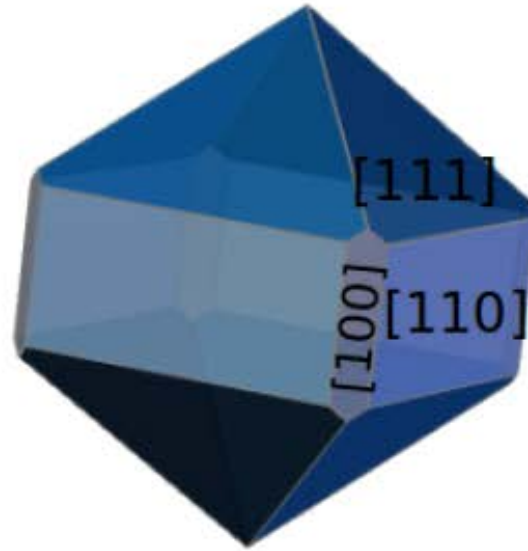


C.P. Plaisance *et al.*,
J. Am. Chem. Soc. 137, 14660 (2015);
C.P. Plaisance, K. Reuter, and R.A. van Santen,
Faraday Disc. 188, 199 (2016)

Ab initio thermodynamics



$U = 0\text{ V}$



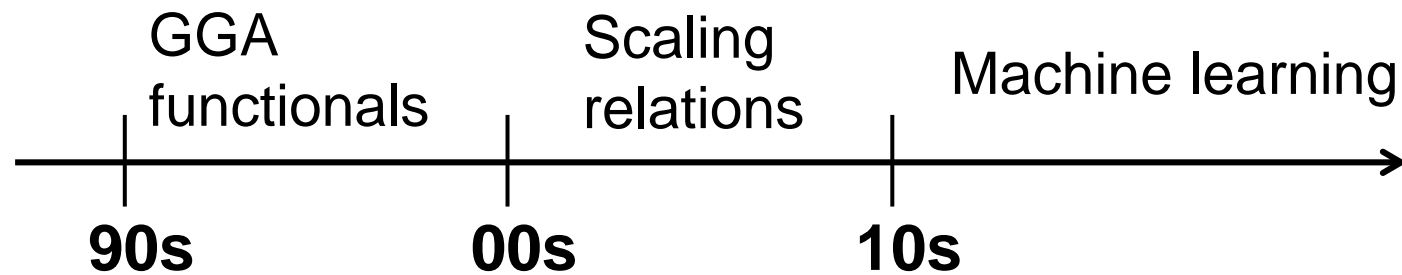
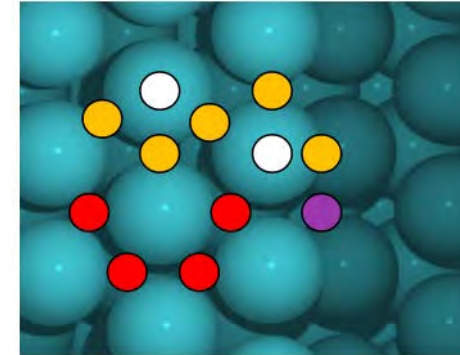
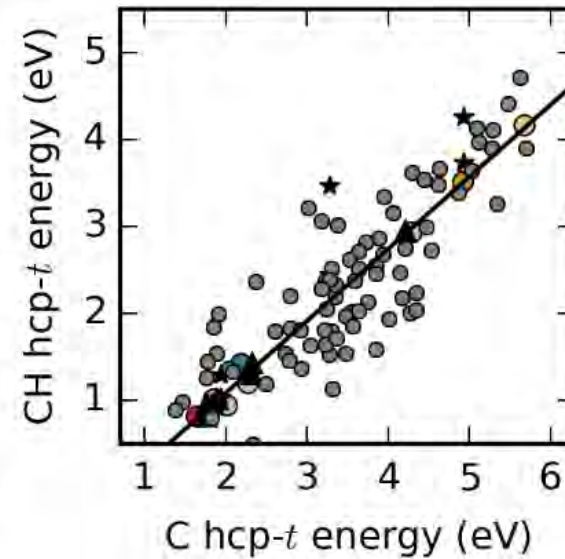
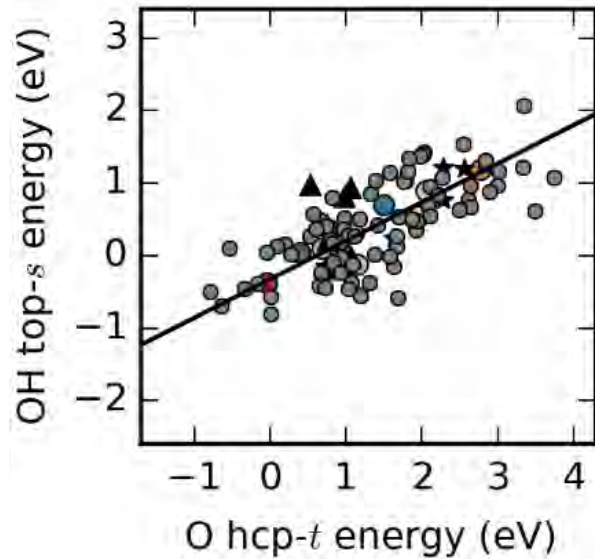
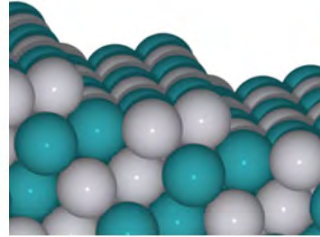
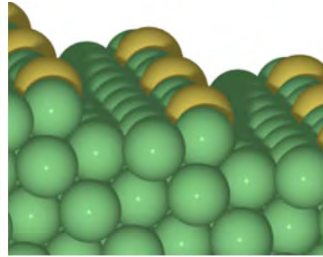
$U = 0.6\text{ V}$



$U = 1.2\text{ V}$

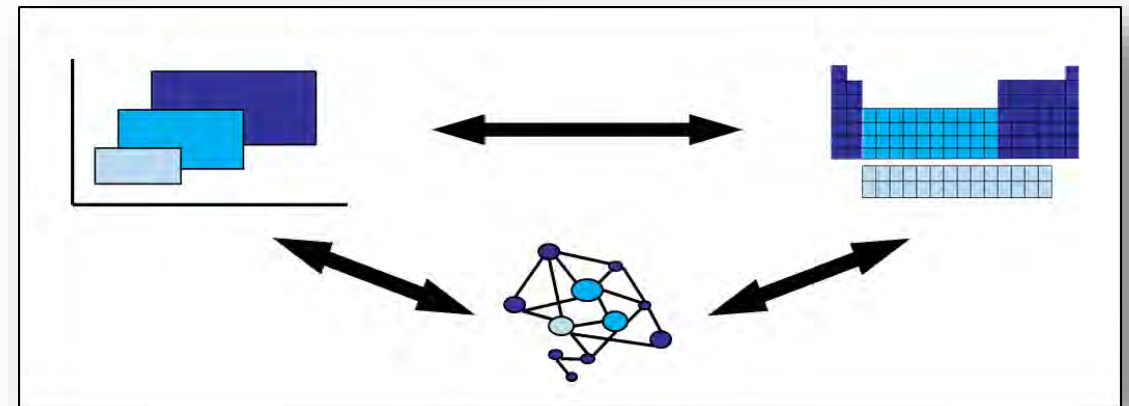
Stabilization of {111} facets at operating potentials

Computing Approaches to Adsorption Energies



We've come a long way to reach half way...

- Present set of computational tools well developed to tackle „static“ catalytic problems (→ computational screening)
- Addressing near-ambient *in situ* studies requires multiscale modeling from electrons to the reactor
- Present microkinetic approaches fall short in scrutinizing potentially crucial dynamical transformations of the active surface. A self-fulfilling prophecy?!
- Machine learning approaches likely the game changer to tackle the real complexity of working catalysts



THANK YOU!



Mie Andersen
 Albert Bruix
 Johannes Margraf
 Harald Oberhofer

Daniel Opalka
 Matteo Maestri (→Polimi)
 Sebastian Matera (→FU Berlin)
 Craig Plaisance (→LSU)

J. Gustafson, E. Lundgren (U Lund)
 A.J. Medford, J. K. Nørskov (DTU)
 S.V. Levchenko, M. Scheffler (FHI Berlin)