When atomic-scale resolution is not enough:

Heat and mass transfer effects in *in-situ* model catalyst studies

Karsten Reuter

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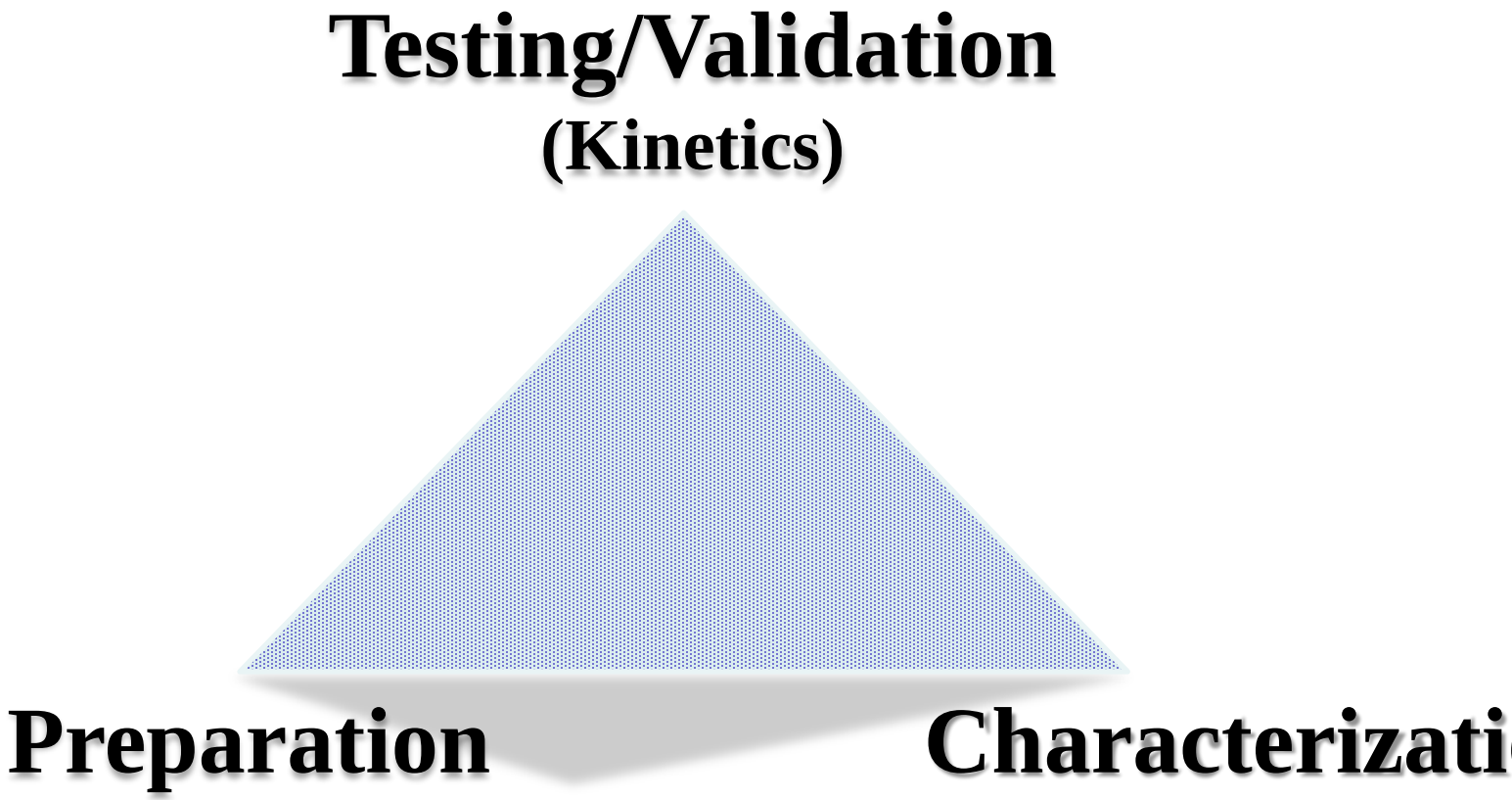
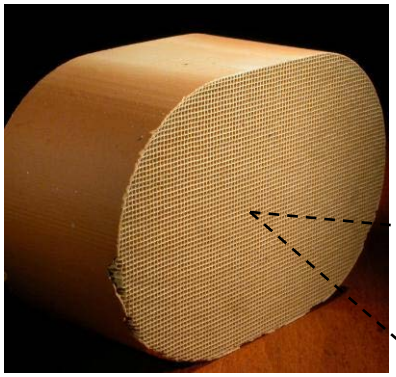
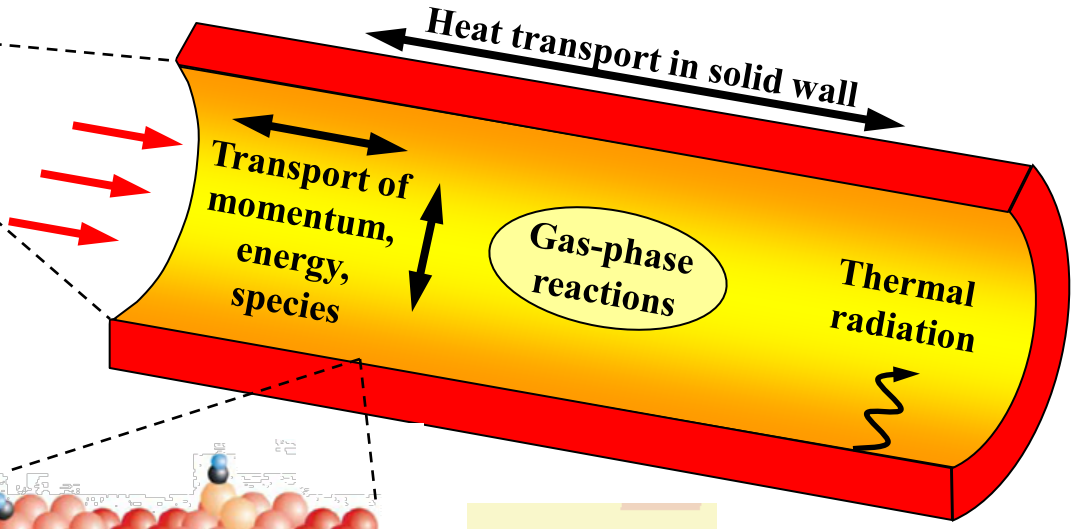
Catalysis research triangle



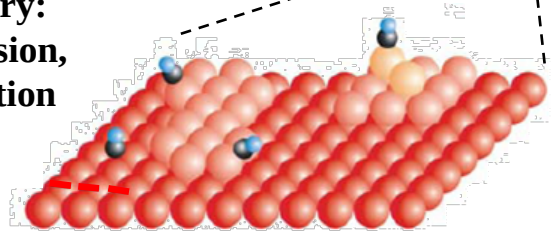
Challenges across the scales

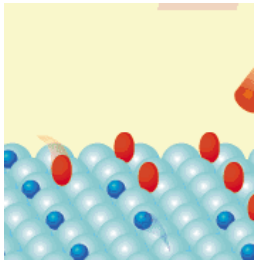


Self-consistent coupling to reactive flow field and appropriate heat balance



Surface chemistry: adsorption, diffusion, reaction, desorption

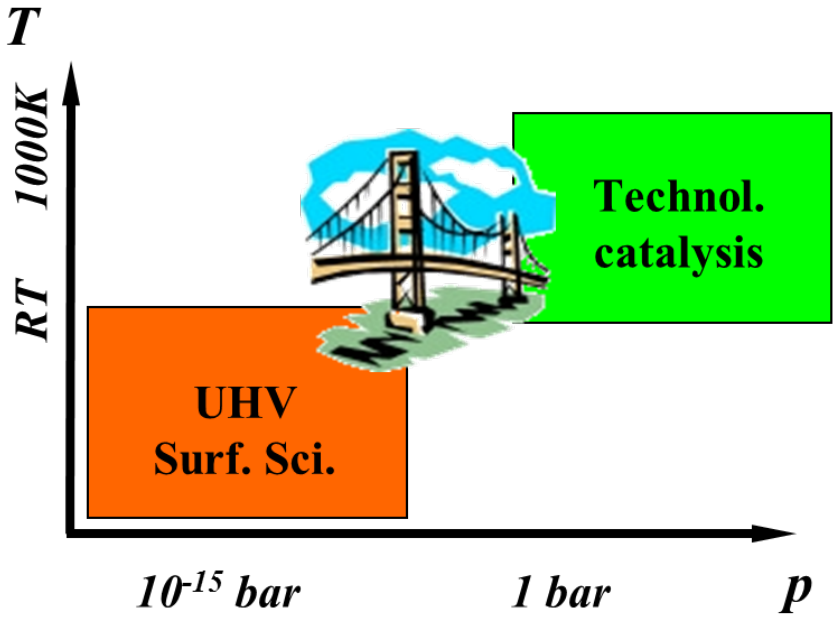


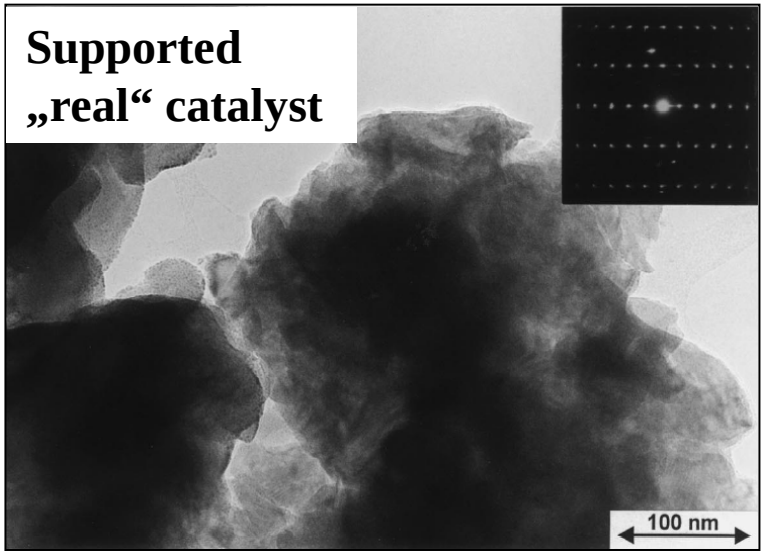


Accurate (first-principles) energetics of individual elementary processes

Quantitative transient and steady-state surface kinetics

The Surface Science disclaimer: Mind the gap(s)!

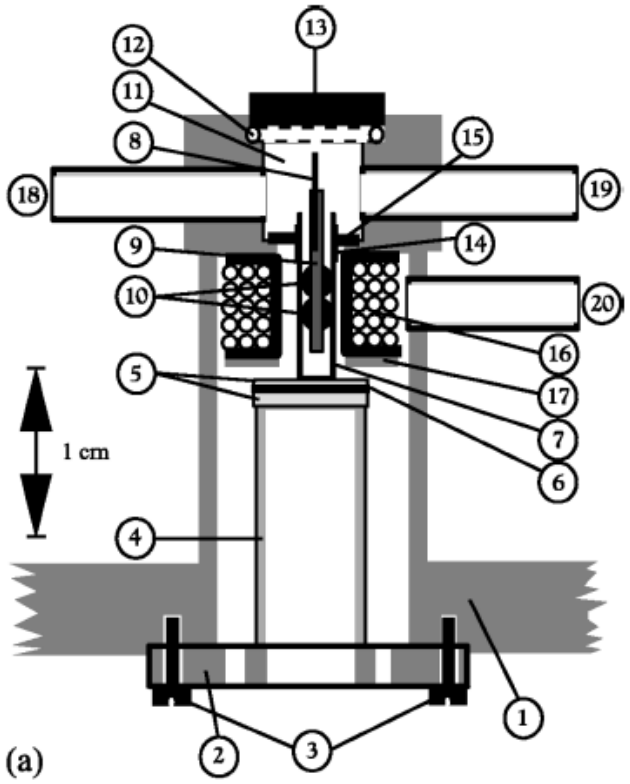




Courtesy: G. Rupprechter and Ch. Weiland, NanoToday 2, 20 (2007)

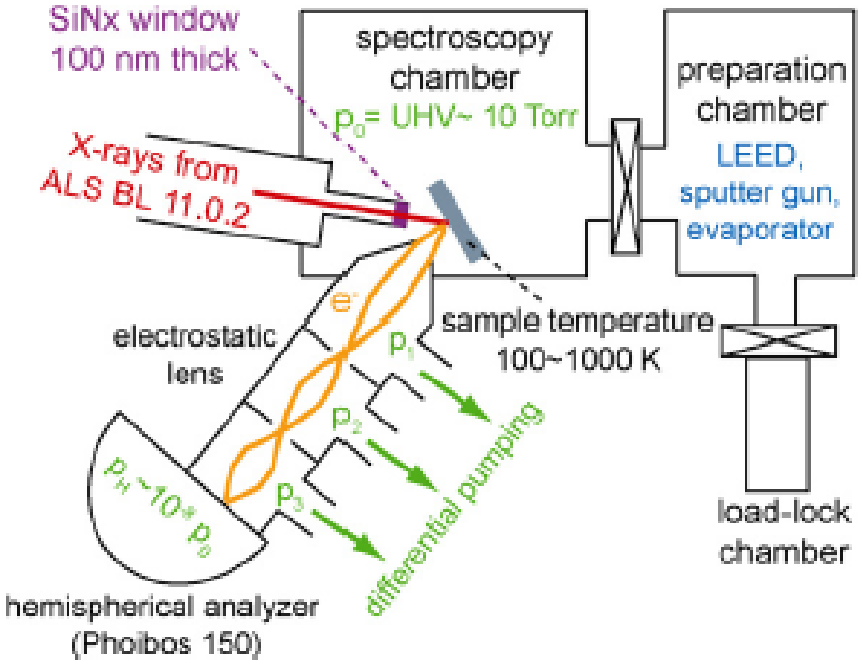
Going *in situ*: It's not just like opening a valve…

Reactor STM



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

in situ XPS



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

A. Stierle and A.M. Molenbroek (Eds.), MRS Bull. 32 (2007)

A tour from electrons to the reactor

Part I First-principles microkinetics

Part II Integrating 1p-kMC into CFD

The “Quantum Engines”: Electronic structure methods

Potential energy for fixed nuclear positions $\{\mathbf{R}_I\}$:

$$E_0(\{\mathbf{R}_I\}) = \mathrm{Min}_\Psi \langle\Psi| H^e\{\mathbf{R}_I\} |\Psi\rangle$$

1. Wavefunction based methods („Quantum Chemistry“)

Ansatz for Ψ: Hartree-Fock, post-HF (MP2, CI, CC,…)

2. Density-functional theory $\Psi = \Psi[n(\mathbf{r})]$ (Hohenberg-Kohn, 1964)

$$\Rightarrow E_0(\{\mathbf{R}_I\}) = \mathrm{Min}_{n(\mathbf{r})} E_{\{\mathbf{R}_I\}}[n]$$

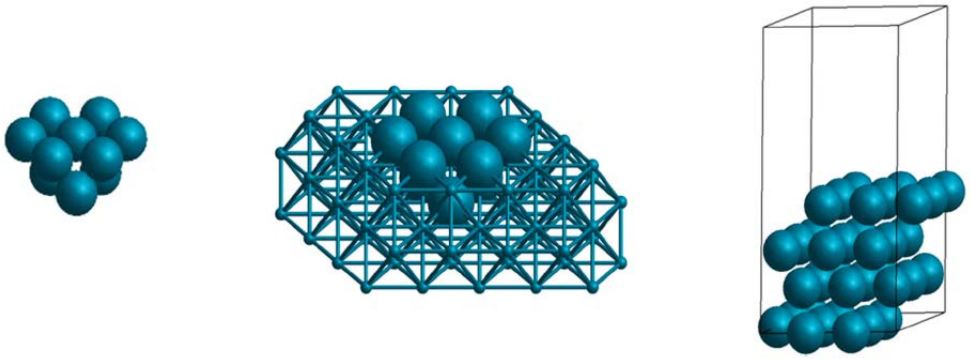
$$E_{\{\mathbf{R}_I\}}[n] = T_s[n] + \int d^3r\, v^{\mathrm{nuc}}_{\{\mathbf{R}_I\}}(\mathbf{r}) n(\mathbf{r}) + \frac{1}{2}\int\int d^3r d^3r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + E^{\mathrm{xc}}[n]$$

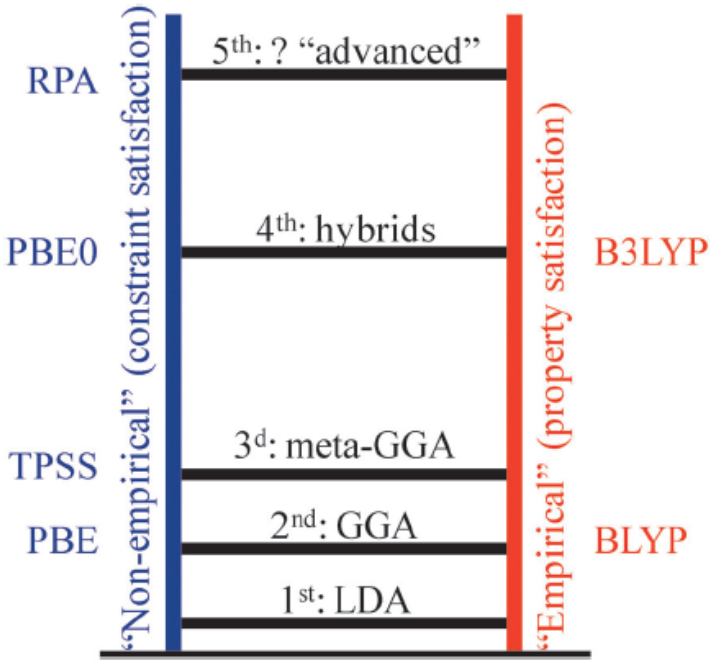
(Kohn-Sham, 1965)

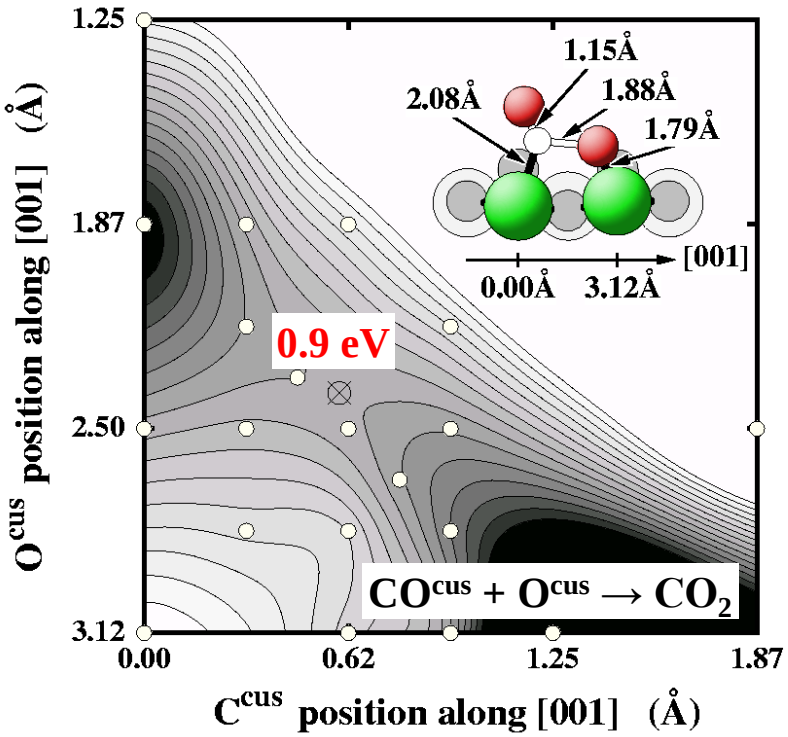
$$E^{XC}_{LDA}[n] = \int d^3r\, n(r)\, \varepsilon^{XC}(n_o)\Big|_{n_o=n(r)}$$

$$E^{XC}_{GGA}[n] = \int d^3r\, n(r) \varepsilon^{XC}(n_o, \nabla n_o)\Big|_{n_o=n(r)}$$

Electronic regime: Energetics of elementary processes







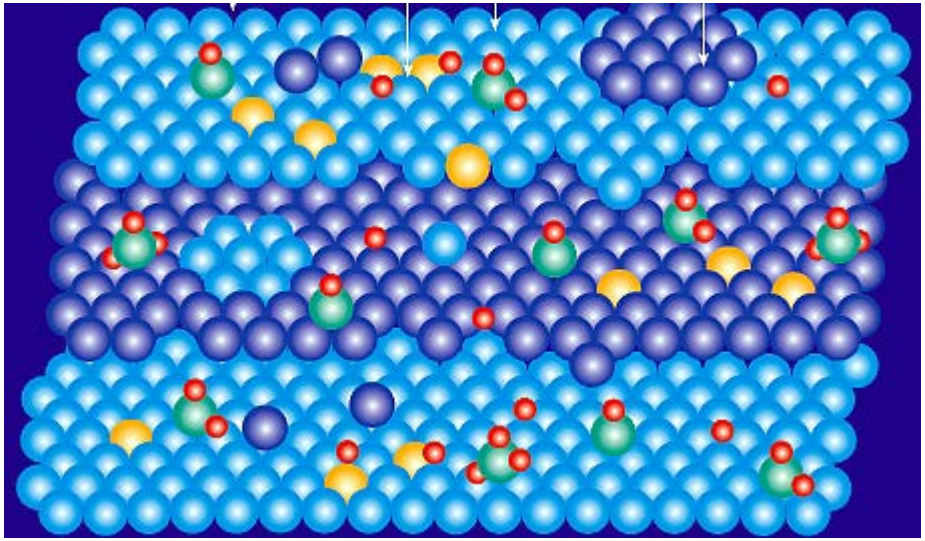
- **Active site model**
- **„Level of theory“**

M. Sabbe, M.F. Reyniers, and K. Reuter, Catal. Sci. Technol. 2, 2010 (2012)

„The“ active site: The effective to atomistic gap

*

vs.



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

- **Lately: move towards „multi-site“ models (multi = 2,…)**

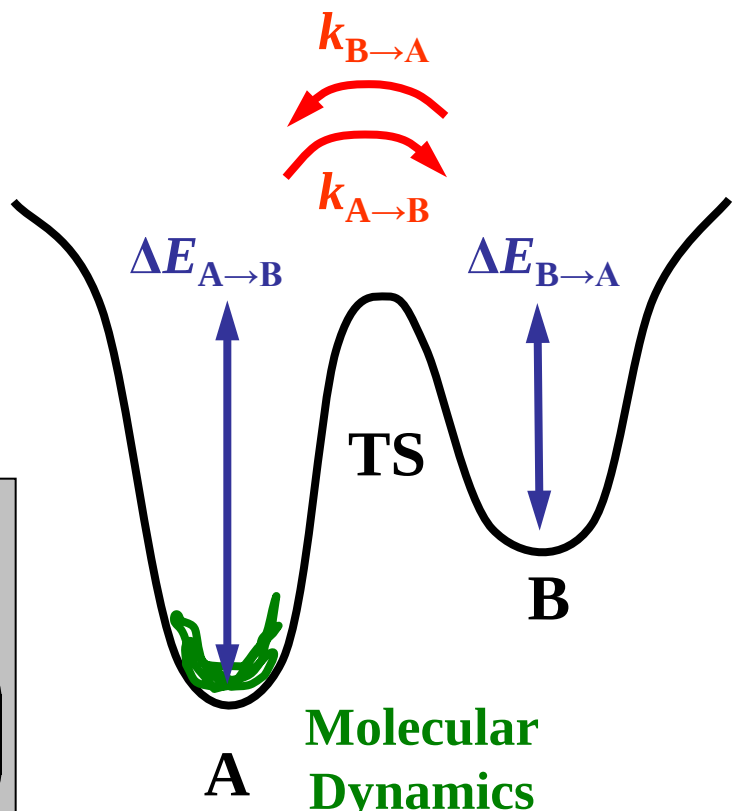
- **Atomistic active site model**
  every atom counts
  generally insufficient experimental characterization

- **Manifold of possibly active site types**
  on which one to focus?
  consider how many?

Mesoscopic regime: Tackling rare-event time scales

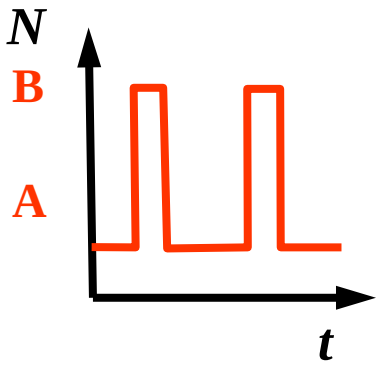
Transition State Theory

$$k_{i\to j} = \left(\frac{k_B T}{h}\right)\frac{Z_{TS(i\to j)}}{Z_i} = \Gamma_\circ \exp\left(\frac{-\Delta E_{i\to j}}{k_B T}\right)$$



Molecular Dynamics

kinetic Monte Carlo

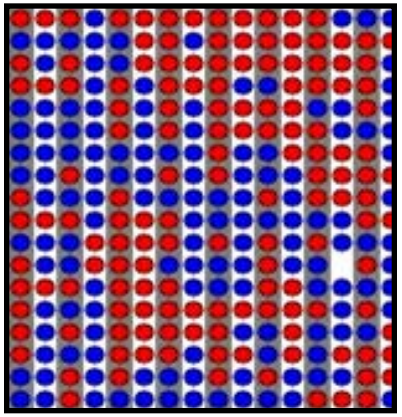


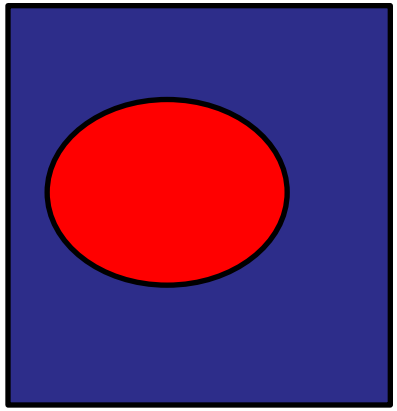
$$\frac{dP_i(t)}{dt} = -\sum_j k_{i\to j} P_i(t) + \sum_j k_{j\to i} P_j(t)$$

First-principles kinetic Monte Carlo simulations for heterogeneous catalysis: Concepts, status and frontiers
K. Reuter, in "Modeling Heterogeneous Catalytic Reactions: From the Molecular Process to the Technical System", (Ed.) O. Deutschmann, Wiley-VCH, Weinheim (2011). http://www.fhi-berlin.mpg.de/th/paper.html

Mean-field approximation: Rate equations

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



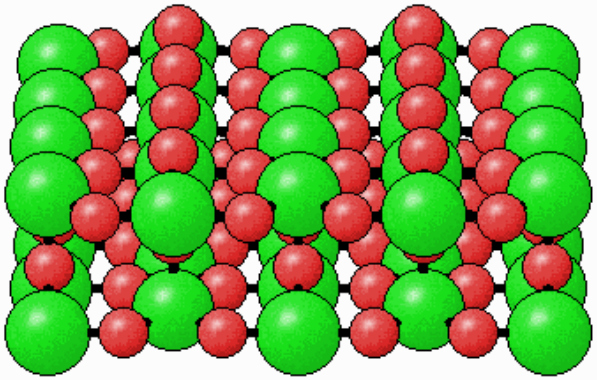


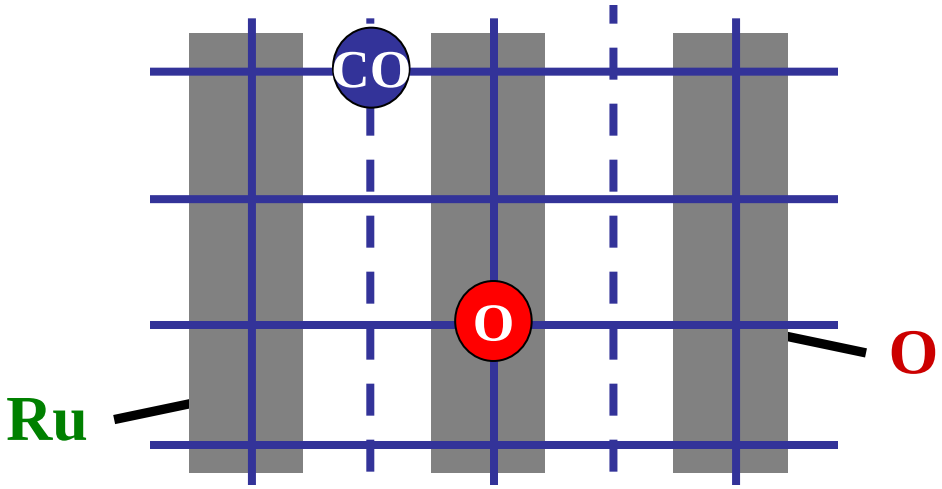
$\theta(\mathrm{O}^{\mathrm{cus}})$
$\theta(\mathrm{O}^{\mathrm{br}})$
$\theta(\mathrm{CO}^{\mathrm{cus}})$
$\theta(\mathrm{CO}^{\mathrm{br}})$

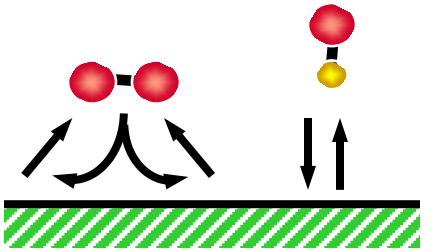
$$P(\mathrm{O}^{\mathrm{br}}, \mathrm{CO}^{\mathrm{cus}}, t)$$
$$\downarrow$$
$$\theta(\mathrm{O}^{\mathrm{br}}, t) \cdot \theta(\mathrm{CO}^{\mathrm{cus}}, t)$$

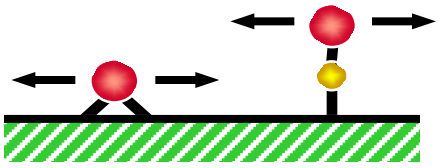
$$\frac{d\theta(\mathrm{O}^{\mathrm{cus}}, t)}{dt} = f_1\left\{k_{i\to j}, \theta(\mathrm{O}^{\mathrm{cus}}, t), \theta(\mathrm{O}^{\mathrm{br}}, t), \theta(\mathrm{CO}^{\mathrm{cus}}, t), \theta(\mathrm{CO}^{\mathrm{br}}, t)\right\}$$
$$\frac{d\theta(\mathrm{O}^{\mathrm{br}}, t)}{dt} = f_2\left\{k_{i\to j}, \theta(\mathrm{O}^{\mathrm{cus}}, t), \theta(\mathrm{O}^{\mathrm{br}}, t), \theta(\mathrm{CO}^{\mathrm{cus}}, t), \theta(\mathrm{CO}^{\mathrm{br}}, t)\right\}$$
$$\ldots$$

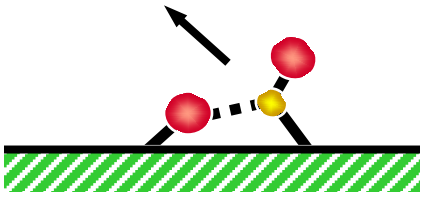
CO oxidation at $RuO_2(110)$: 1p-kMC model











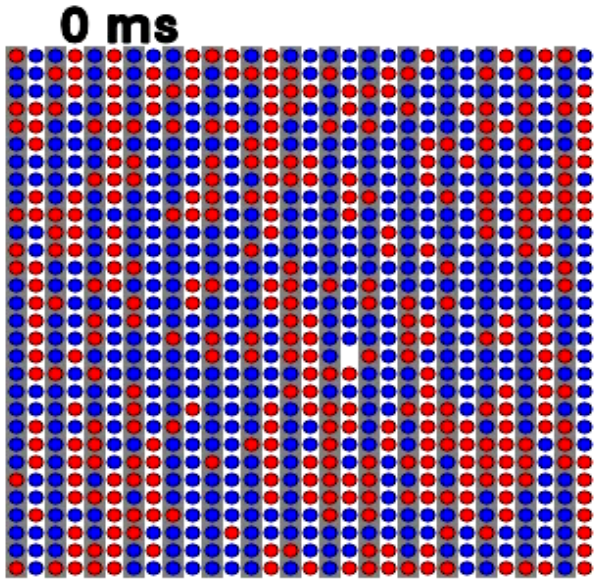
26 elementary processes (site-specific):

- O_2 adsorption/desorption (dissociative/associative)
- CO adsorption/desorption (unimolecular)
- O and CO diffusion
- CO + O reaction

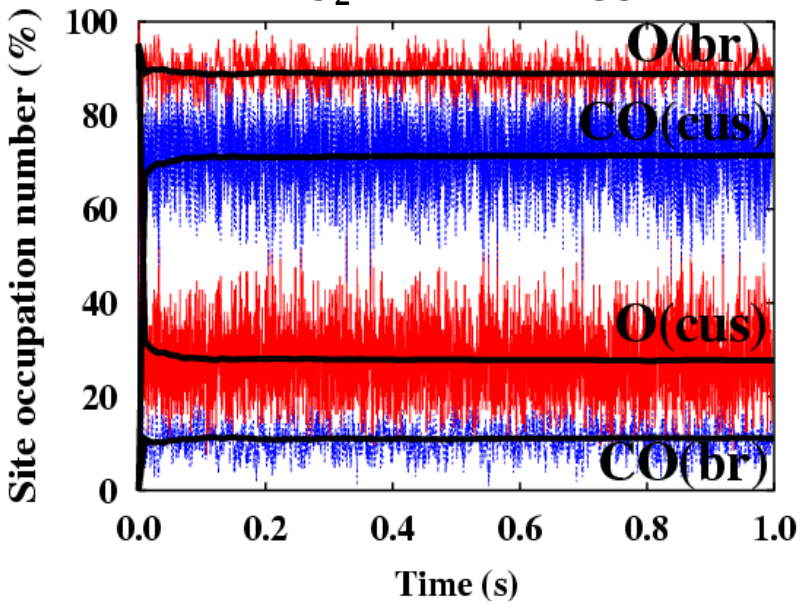
K. Reuter, Oil&Gas Sci. Technol. 61, 471 (2006)

K. Reuter and M. Scheffler, Phys. Rev. B 73, 045433 (2006)

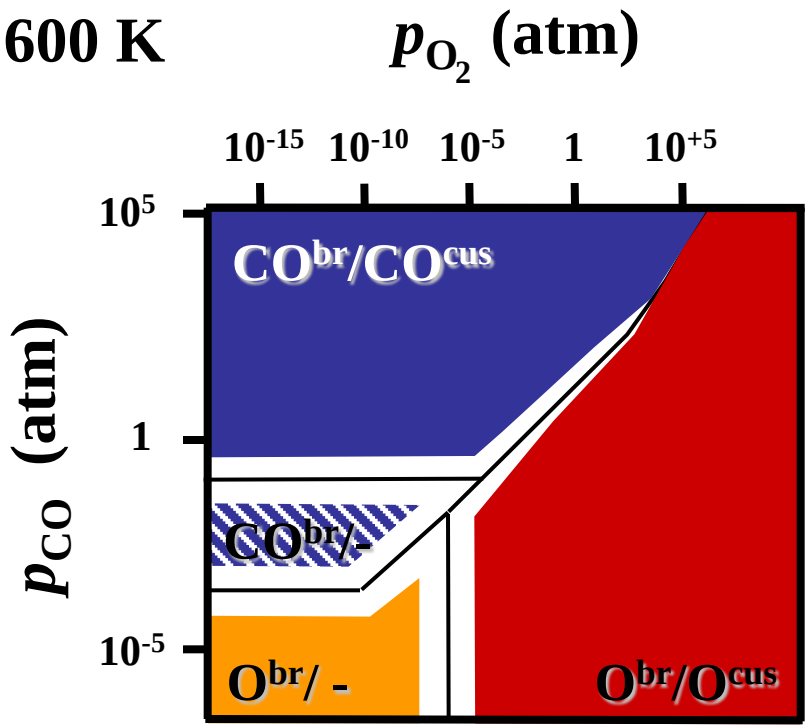
Surface structure and composition in the reactive environment



T = 600 K, p_{O_2} = 1 atm, p_{CO} = 7 atm



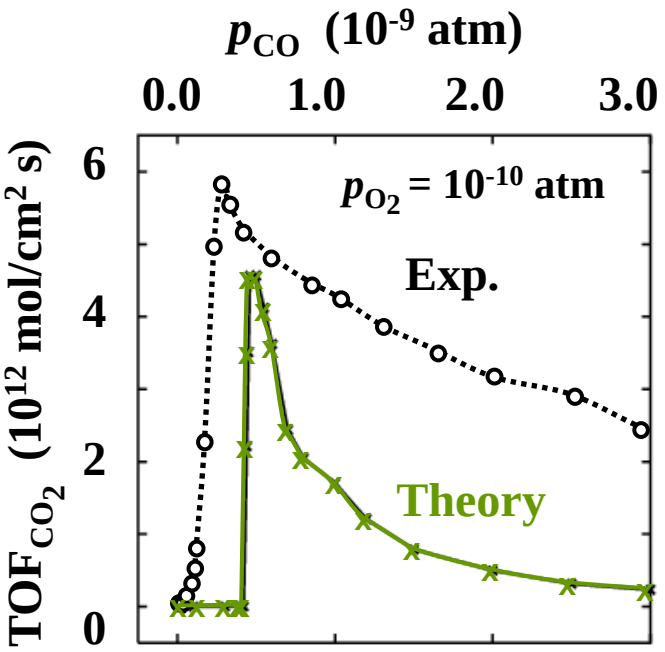
CO oxidation at RuO_2(110)



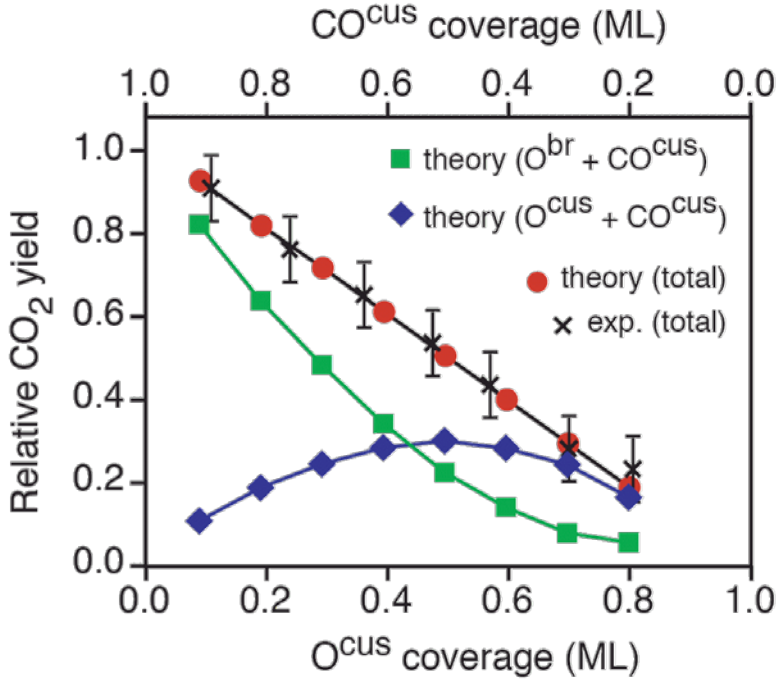
K. Reuter, D. Frenkel and M. Scheffler, Phys. Rev. Lett. 93, 116105 (2004)

Steady-state and transient parameter-free turnover frequencies

350 K



TPR



K. Reuter and M. Scheffler,
Phys. Rev. B 73, 045433 (2006)

M. Rieger, J. Rogal, and K. Reuter,
Phys. Rev. Lett. 100, 016105 (2008)

Key ingredients to „predictive-quality“ microkinetic modeling

Accurate rate constants:

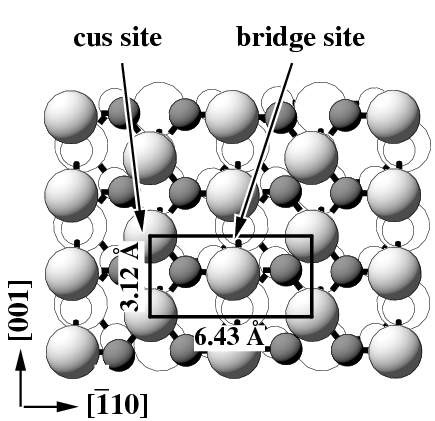
$$k_{i\to j} = \Gamma_{\circ} \exp\left(\frac{-\Delta E_{i\to j}}{k_{\mathrm{B}} T}\right)$$

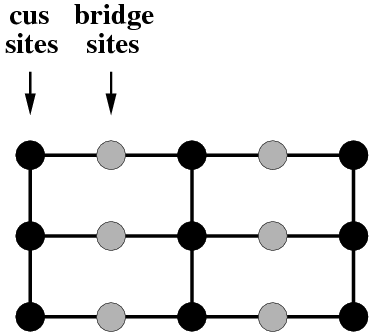
Transition state theory and beyond
DFT functionals: „self-interaction“
van der Waals interactions

Reaction mechanism:

Process identification
Lattice mapping / spatial distributions
„Hot chemistry“ beyond Markov

$$\mathrm{CO} + * \leftrightarrow \mathrm{CO}*$$
$$\mathrm{O_2} + 2* \leftrightarrow \mathrm{O}* + \mathrm{O}*$$
$$\mathrm{CO}* + \mathrm{O}* \leftrightarrow \mathrm{CO_2}$$
$$\ldots$$



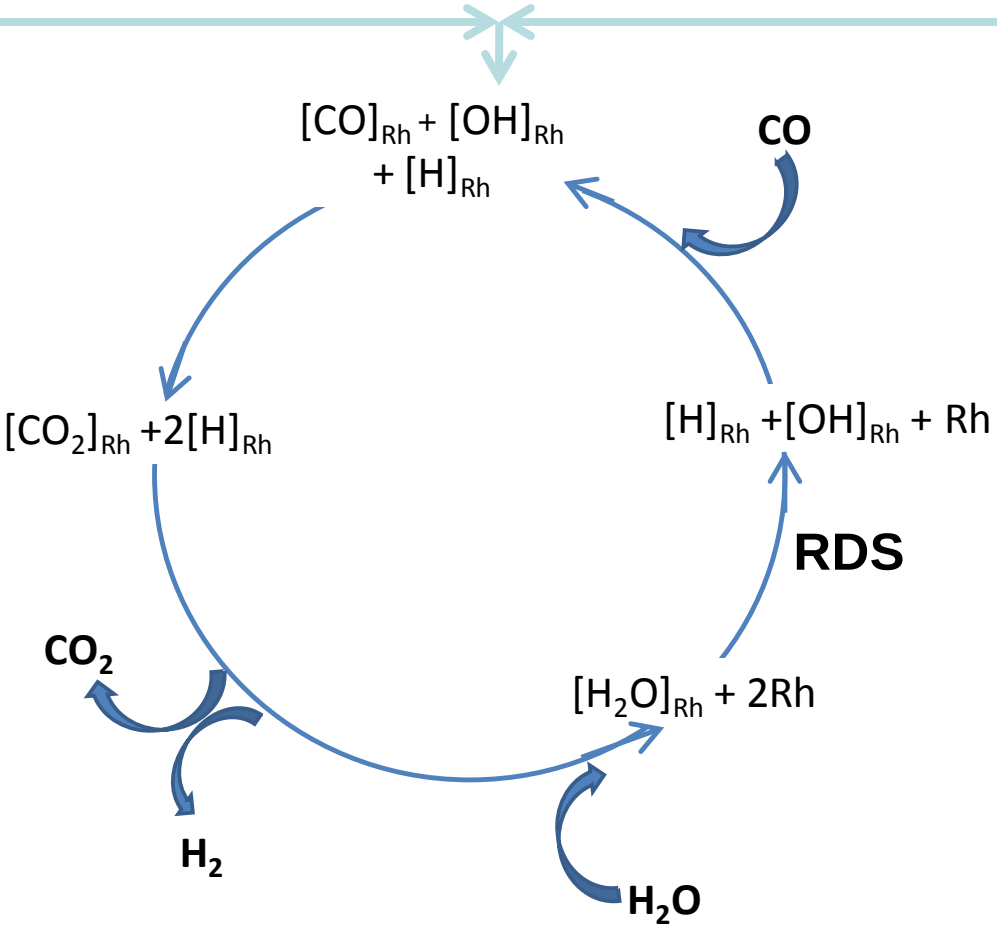


„E pluribus unum“: Water-gas-shift at Rh(111)

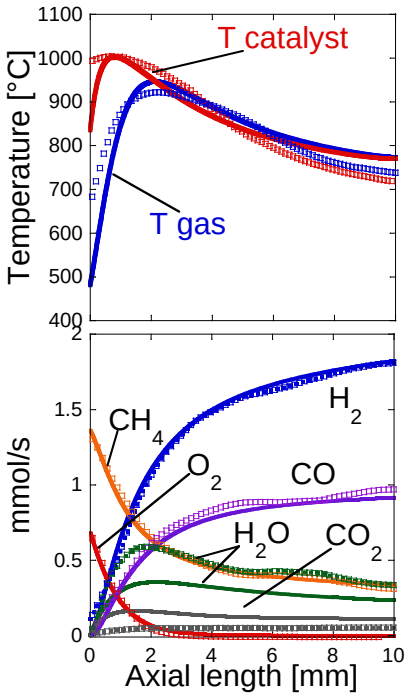
Microscale

$COOH^*+^* \rightarrow CO^*+OH^*$
$CO^*+OH^* \rightarrow COOH^*+^*$
$COOH^*+^* \rightarrow CO_2^*+H^*$
$CO_2^*+H^* \rightarrow COOH^*+^*$
$CO_2^* + H_2O^* \rightarrow COOH^* + OH^*$
$COOH^* + OH^* \rightarrow CO_2^* + H_2O^*$
$CO_2^*+H^* \rightarrow HCOO^{**}$
$HCOO^{**} \rightarrow CO_2^*+H^*$
$CO_2^* + OH^* + ^* \rightarrow HCOO^{**} + O^*$
$HCOO^{**} + OH^* \rightarrow CO_2^* + H_2O^*$
$CH^* + H^* \rightarrow CH_2^* + ^*$
$CH^* + ^* \rightarrow C^* + H^*$
$C^* + H^* \rightarrow CH^* + ^*$
$CH_3^* + O^* \rightarrow CH_2^* + OH^*$
$CH_2^* + OH^* \rightarrow CH_3^* + O^*$
$CH^* + OH^* \rightarrow CH_2^* + O^*$
$CH_2^* + O^* \rightarrow CH^* + OH^*$
…

~ 10^2 potential steps
@ different coverages



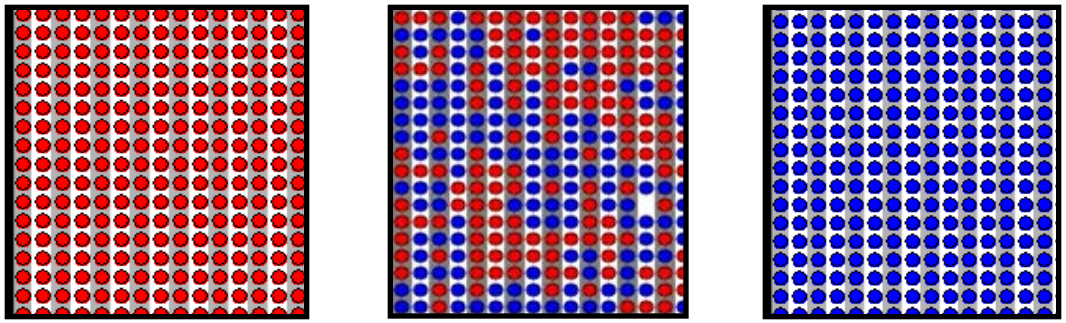
Macroscale



M. Maestri and K. Reuter, Chem. Eng. Sci. 74, 296 (2012)

Error propagation through rate-determining steps

CO oxidation at $RuO_2(110)$

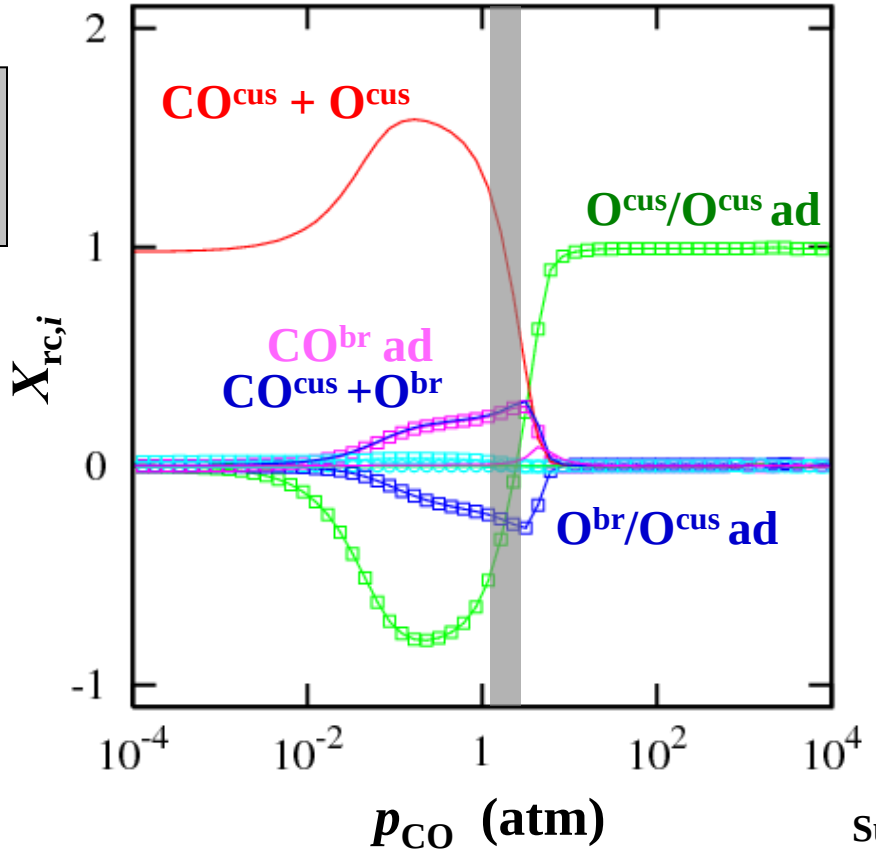


O-poisoned CO-poisoned

Sensitivity analysis:

$$X_{\mathrm{rc},i} = \left(\frac{k_i}{\mathrm{TOF}}\right)\left(\frac{\partial \mathrm{TOF}}{\partial k_i}\right)_{k_j, K_i}$$

C.T. Campbell, J. Catal. 204, 520 (2001); Nature 432, 282 (2004)

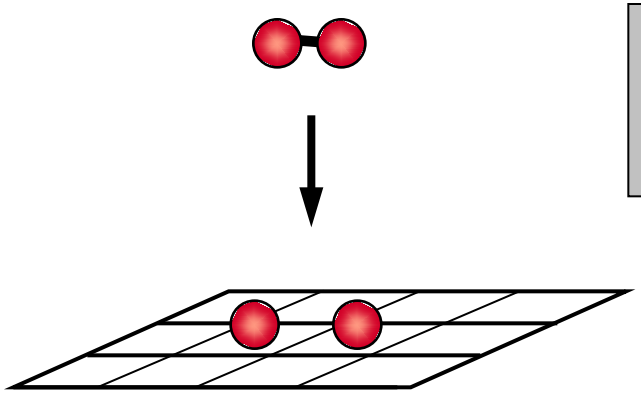


p_{O_2} = 1 atm
T = 600 K

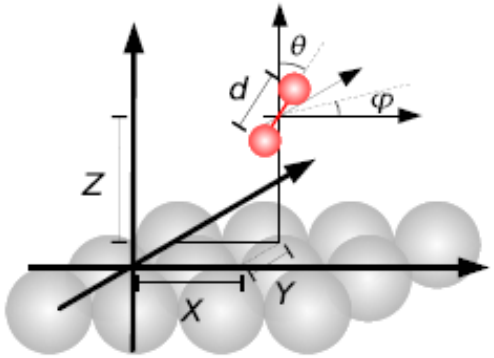
H. Meskine *et al.*, Ertl Special Issue Surf. Sci. 603, 1724 (2009)

More than Markov?

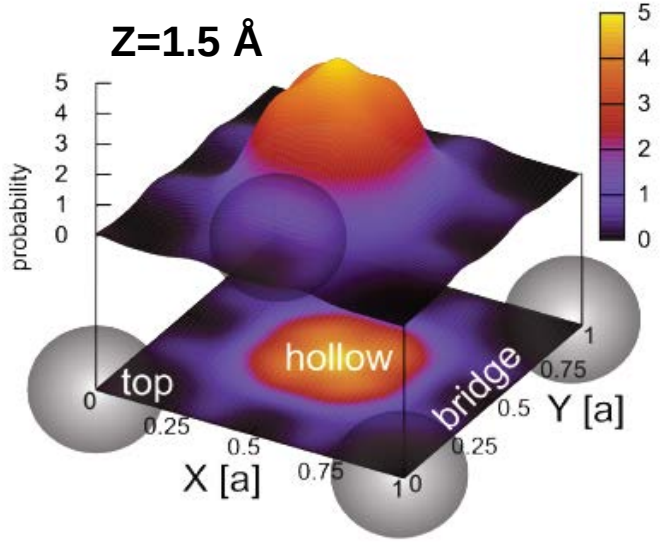
Heat dissipation during dissociative adsorption: O_2/Pd(100)

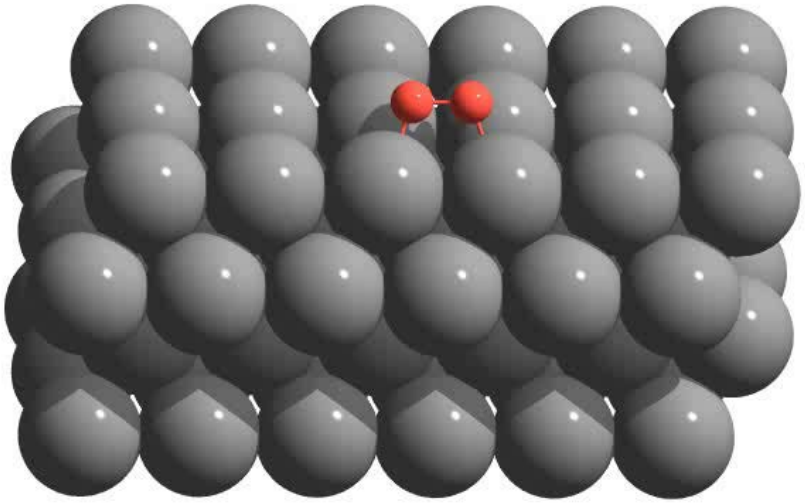


$$k = \tilde{S}_{\circ}(T)\frac{pA_{uc}}{\sqrt{2\pi m k_B T}}$$



$$V_{fsa} = (X, Y, Z, d, \theta, \varphi)$$





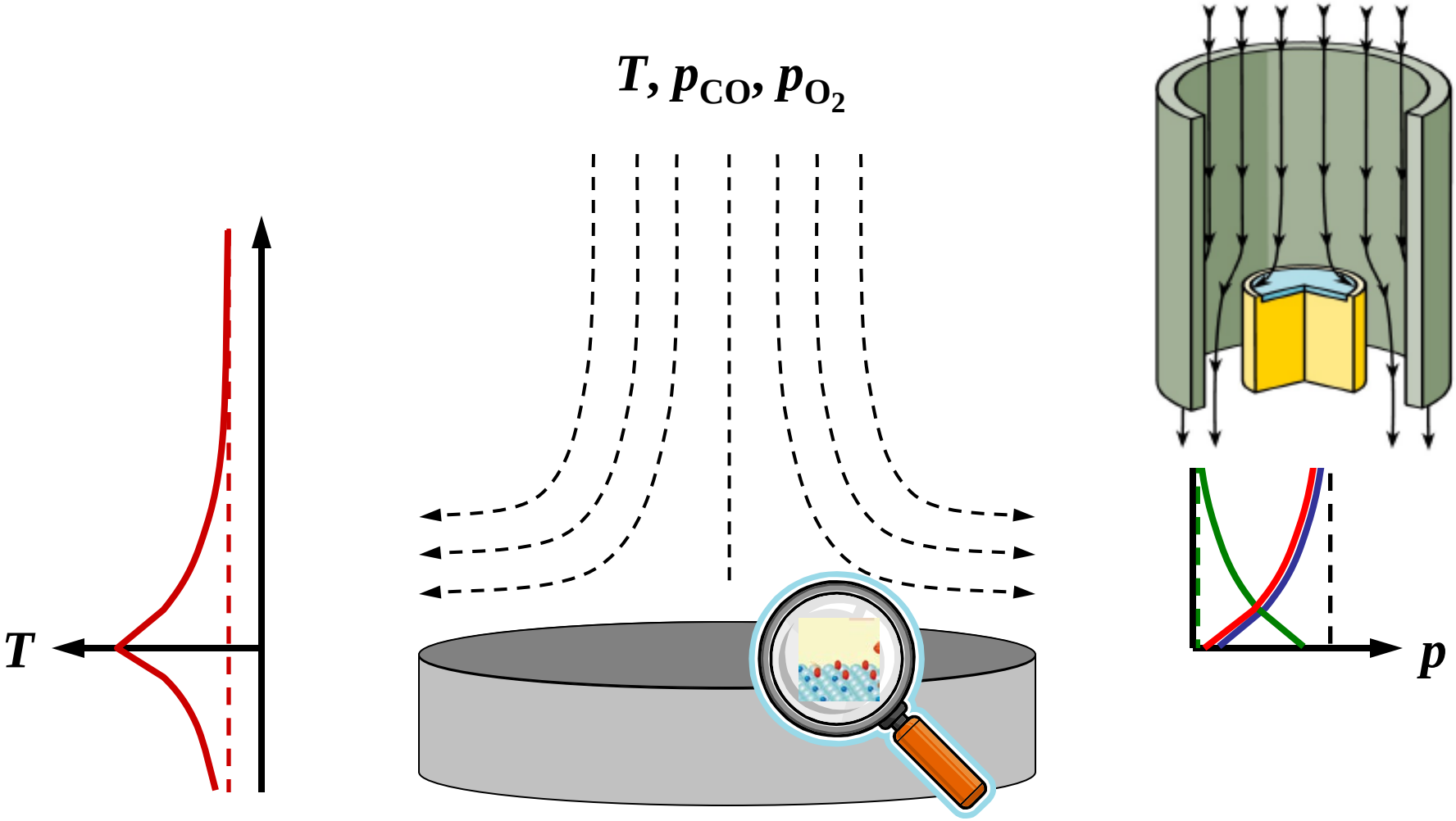
J. Meyer and K. Reuter (in preparation)

A tour from electrons to the reactor

Part I First-principles microkinetics

Part II Integrating 1p-kMC into CFD

Stagnation flow: Heat and mass transfer



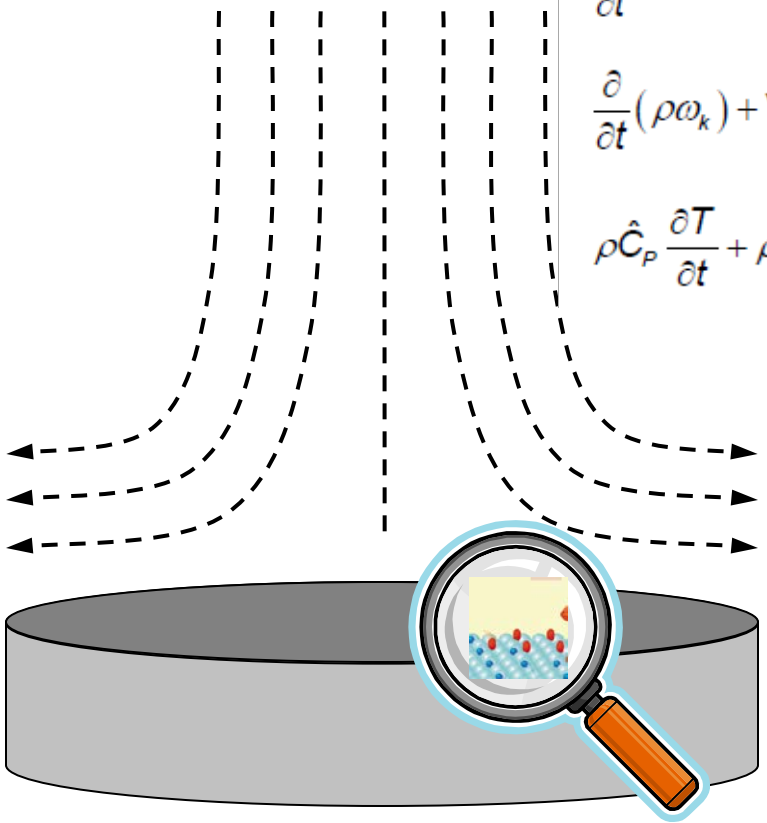
Self-consistent coupling to the flow field

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

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

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



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

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

Linking the scales: Quasi-instantaneous steady-state approximation

On time scales relevant to changes in flow profile surface chemistry adapts quasi-instantaneously to new steady-state

e.g. O. Deutschmann, "*Computational Fluid Dynamics Simulation of Catalytic Reactors*", In: Handbook of Heterogeneous Catalysis (2008)

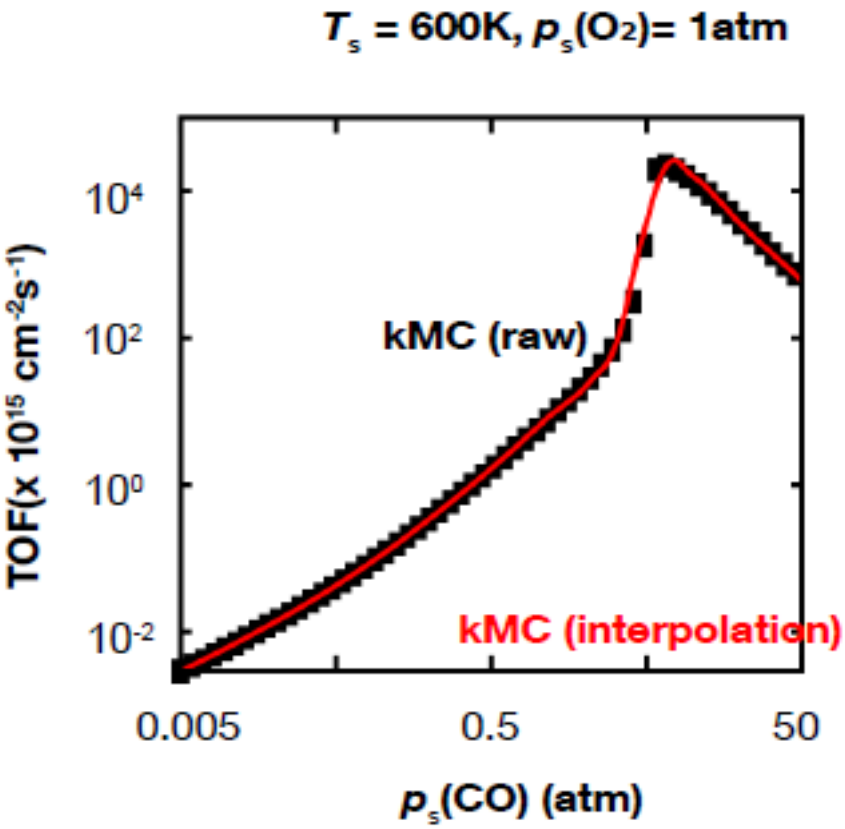
Precompute steady-state 1p-kMC TOFs on dense grid in (T, p_{O_2}, p_{CO})-space

↓

Interpolate using modified Shepard (ideal for grid-less scattered data)

↓

Run CFD using continuous representation as boundary condition



S. Matera and K. Reuter, Phys. Rev. B 82, 085446 (2010)

The CatalyticFOAM project

Pre-Processing

- OpenFOAM® BlockMesh
- GAMBIT, Ansys, CFX, etc.

OpenFOAM® Framework

Convection + Diffusion

- segregated approach
- discretization on unstructured meshes

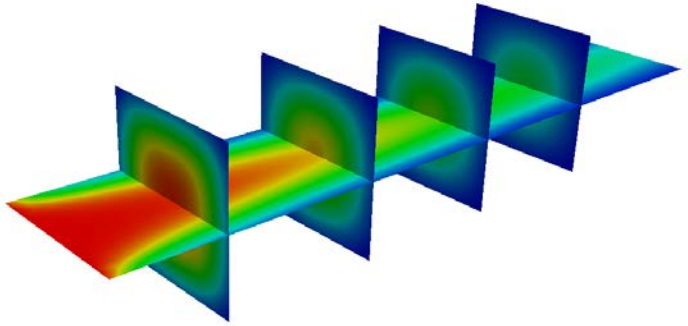
CatalyticFOAM Framework

Reactions

- coupled approach
- stiff ODE solvers

Paraview ®

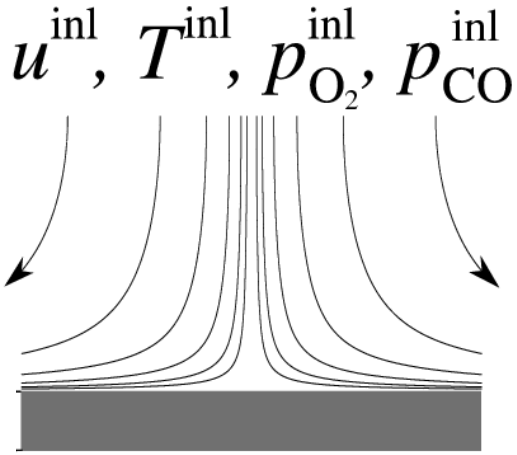
Post-processing



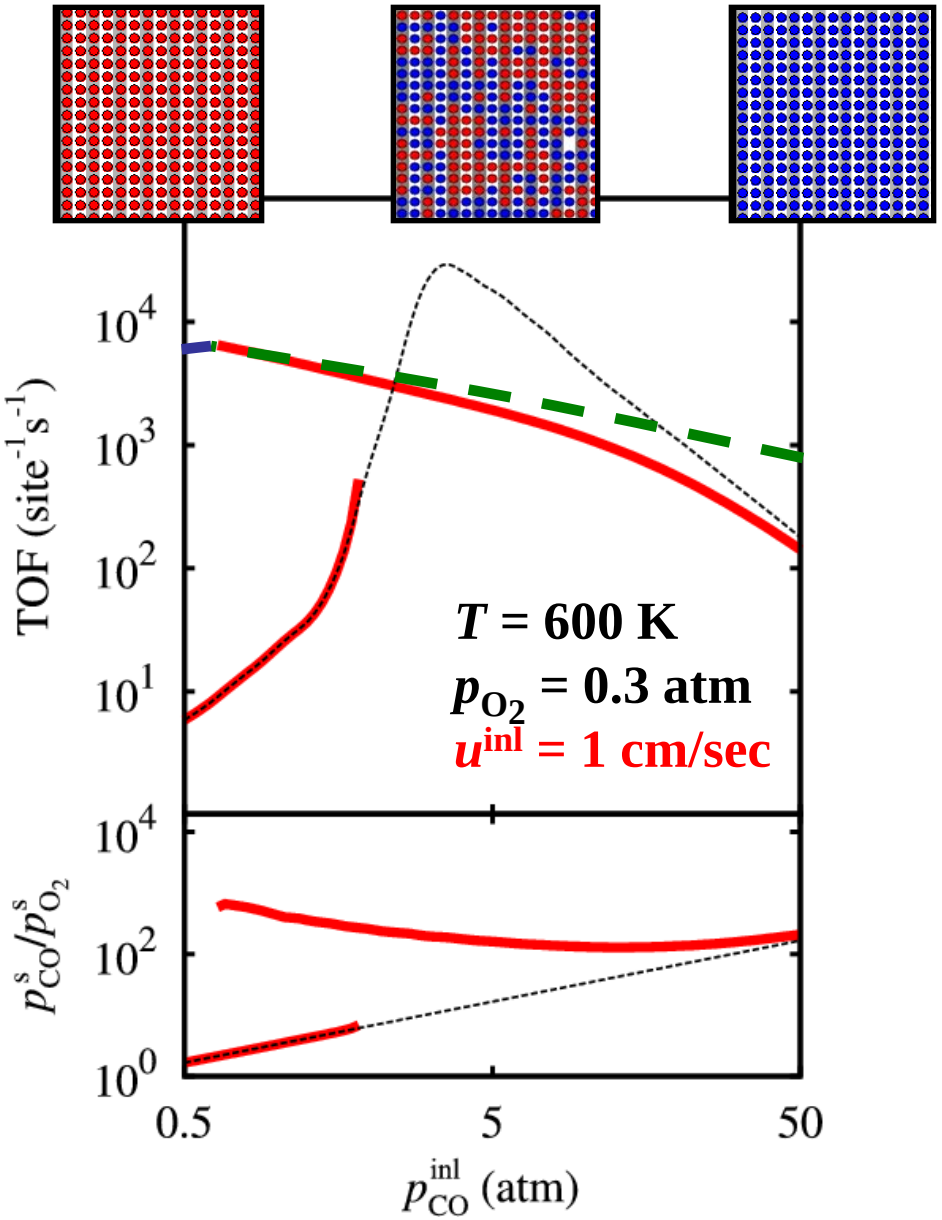
M. Maestri **A. Cuoci**

www.catalyticfoam.polimi.it

In situ TOFs in the isothermal limit: Mass transfer limitations

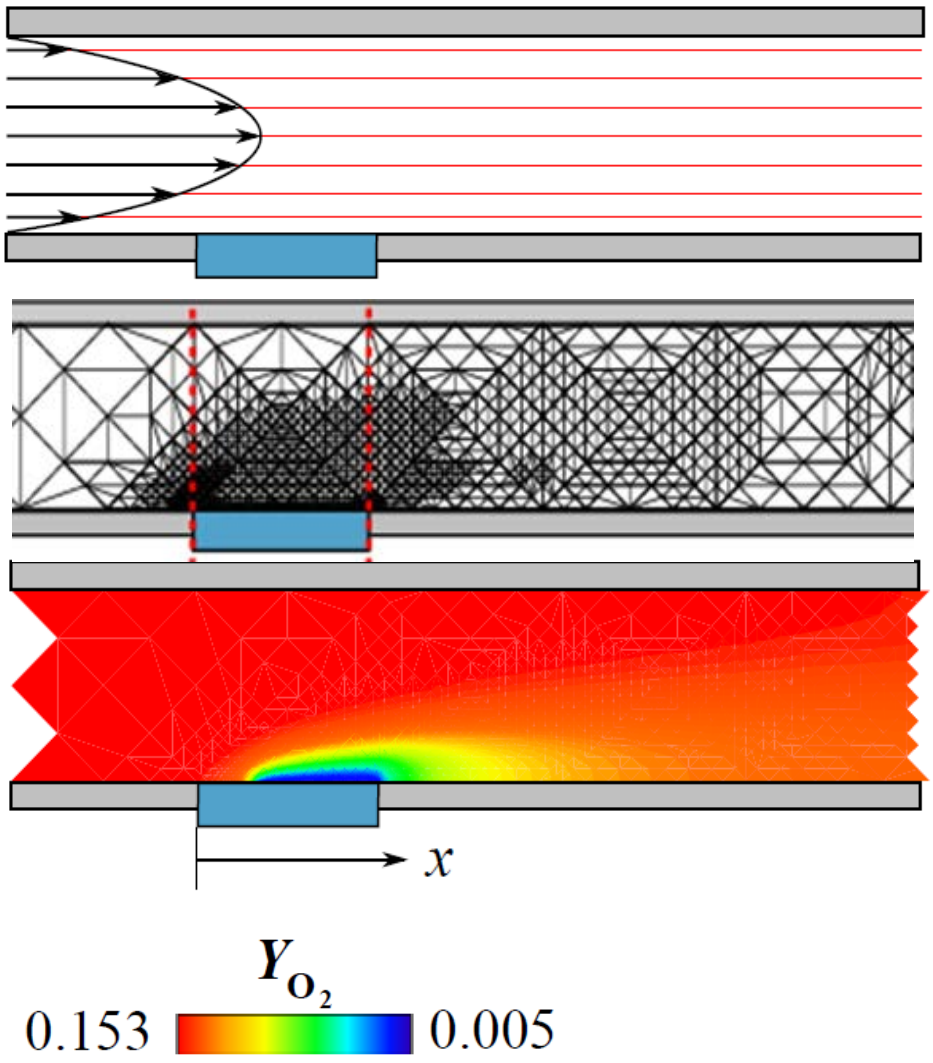


T = const

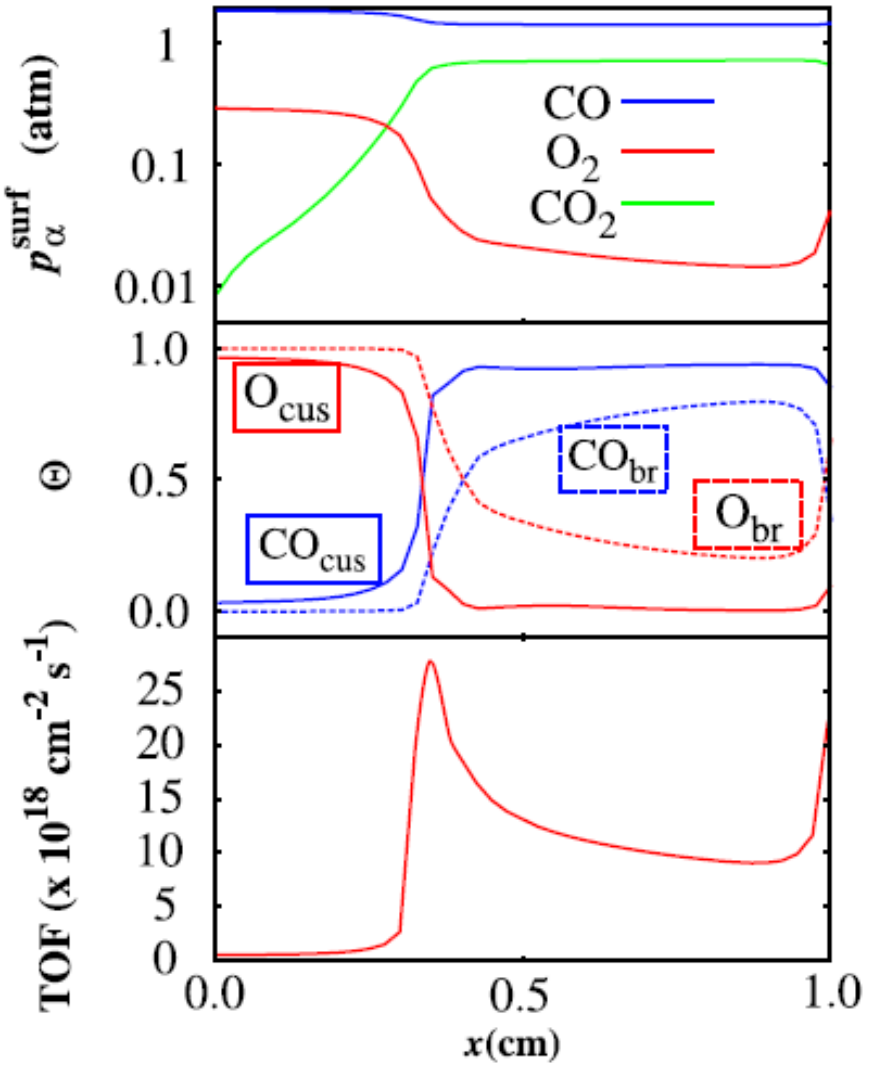


S. Matera and K. Reuter, Catal. Lett. 133, 156 (2009)

When atomic scale resolution is not enough



T = 600 K, $u_{inl(max)}$ = 20 cm/sec
p_{O_2} = 0.3 atm, p_{CO} = 1.9 atm

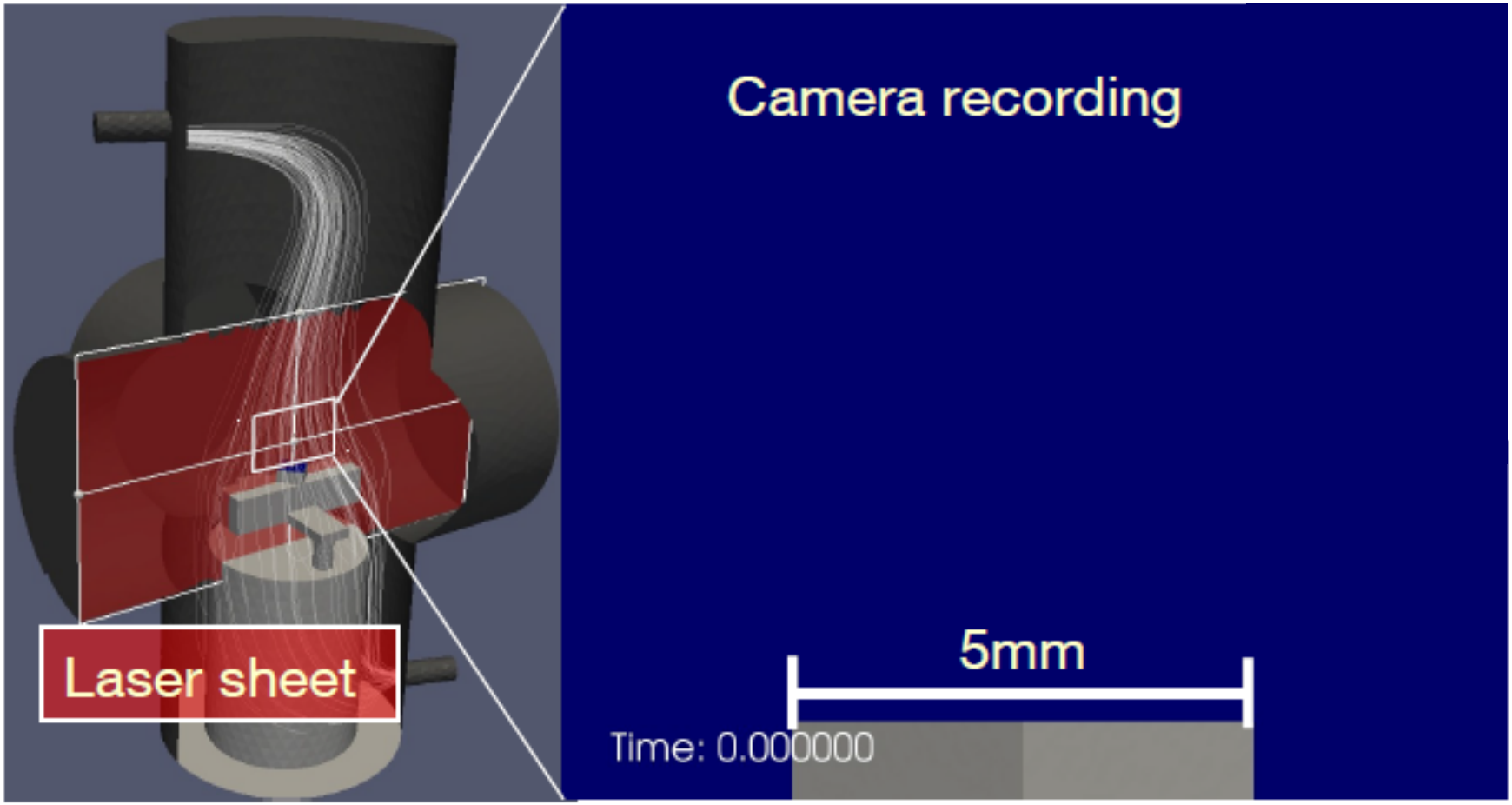


S. Matera and K. Reuter, J. Catal. 295, 261 (2012)

Planar Laser Induced Fluorescence (PLIF)

Laser-sheet stimulation of known excitation (here: CO_2 vibration)

→ 2D concentration profile above catalyst

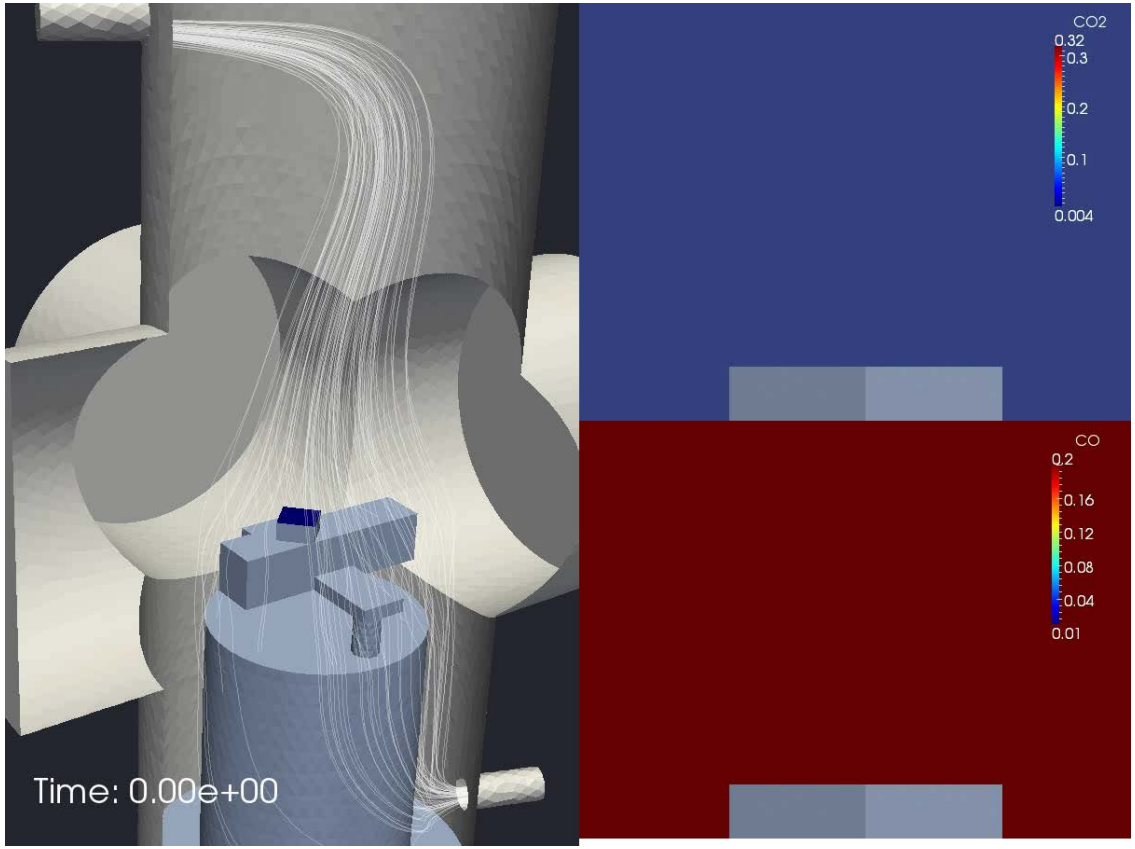


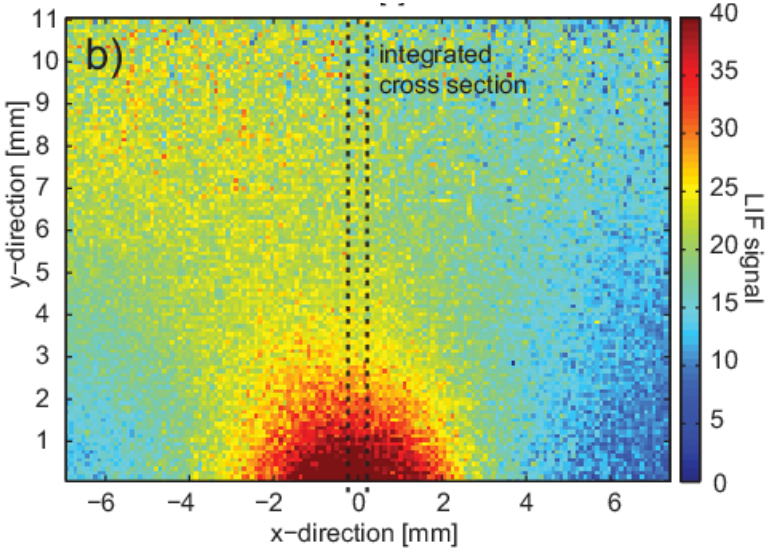
Y. Zetterberg *et al.*, Rev. Sci. Instrum. 83, 053104 (2012)

Making mass transfer limitations „visible“

***in situ* PLIF measurements of ambient CO oxidation at Pd(100)**

together with
E. Lundgren *et al*. (Lund University)





$CO:O_2$ = 1:1, p_{tot} = 1 atm

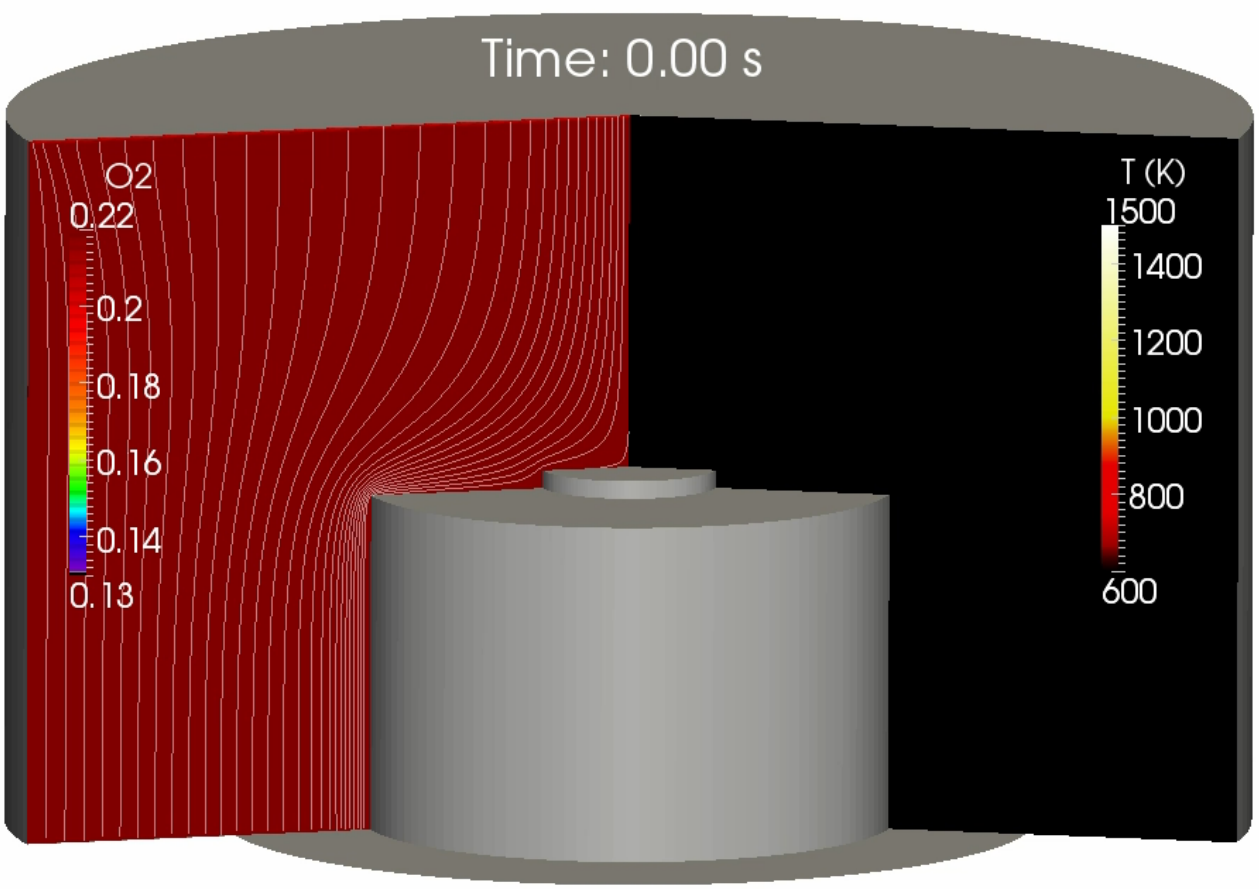
S. Blomberg, M.J. Hoffmann *et al*.,
Phys. Rev. Lett. 110, 117601 (2013)

S. Matera *et al*., in preparation

Incomplete heat dissipation in a real stagflow reactor: Rayleigh-Bénard convection

CO oxidation at $RuO_2(110)$

$CO:O_2$ = 4:1, p_{tot} = 1 atm
T_{inlet} = 500K, adiabatic limit

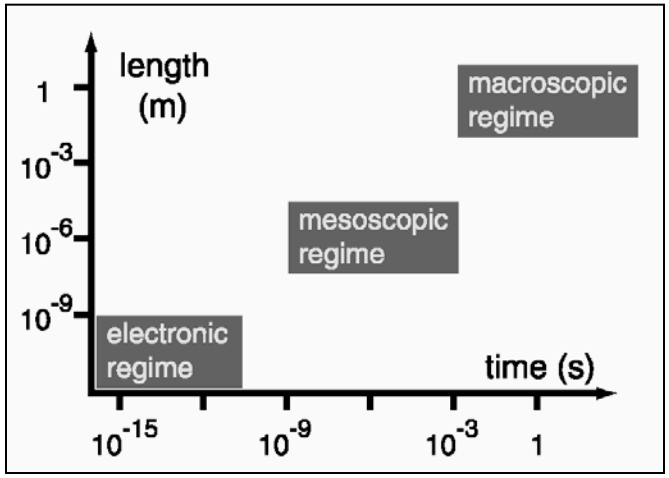


S. Döpking, S. Matera

First-Principles Multiscale Modeling: Where do we stand?

State-of-the-art in catalysis modeling:

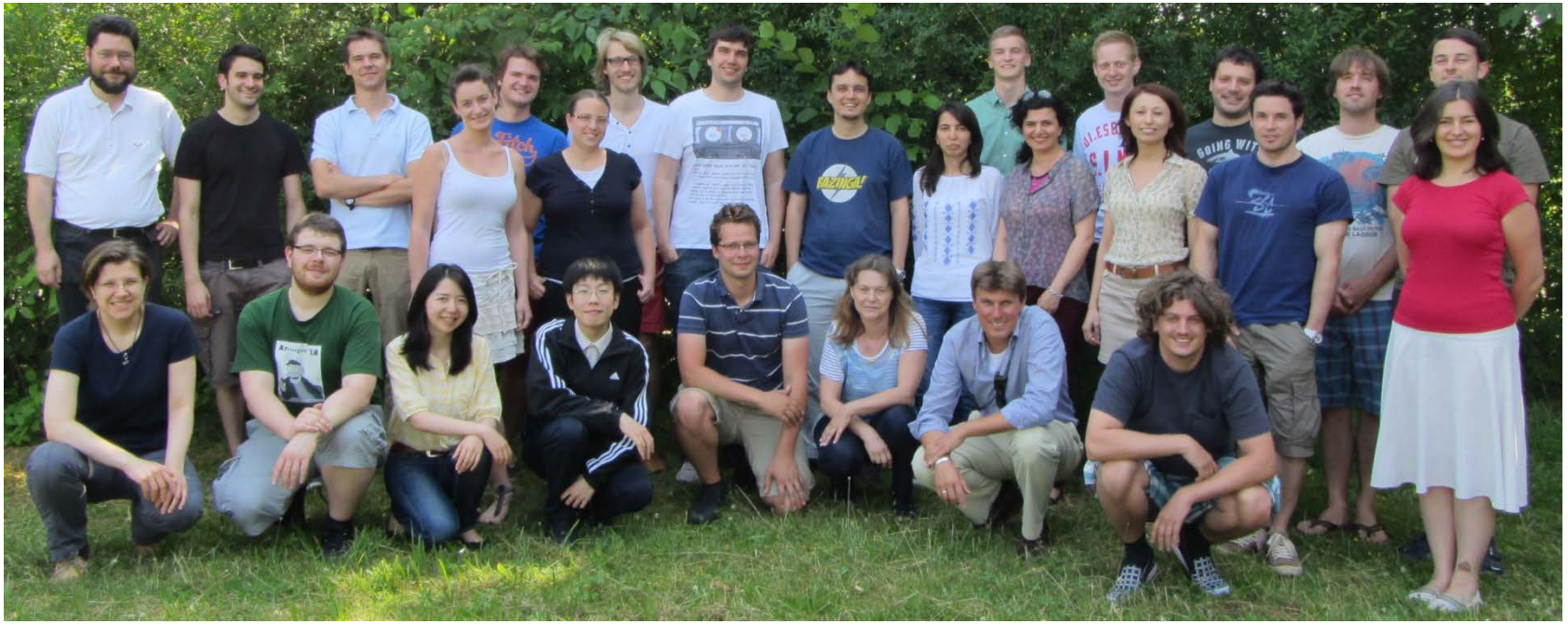
- **Prevalence of highly coarse-grained models based on effective parameters without true microscopic meaning**
  - *rate equation theory*
  - *based on empirical rate constants*
  - *1D flow models*
- **Emergence of *ad-hoc* 1p-microkinetic models**
  - *kMC and mean-field for*
  - *model catalysts & show case reactions*



Steps towards a predictive character multiscale catalysis modeling:

- **Replace effective parameters by clean first-principles data**
  - *fitted vs. DFT-based rate constants*
  - *battle the curse of complexity (off-lattice, complex networks)*
  - *electronic non-adiabaticity, heat dissipation*
- **Refined modeling at each individual level**
  - *reliable and efficient 1p-rate constants (where needed)*
  - *necessity to resolve spatial arrangement at surface*
  - *integrate 1p-surface chemistry into detailed reactor models*
- **Robust links between theories that enable reverse-mapping**
  - *sensitivity analysis to control flow of error across scales*

Thanks so much!!!



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