



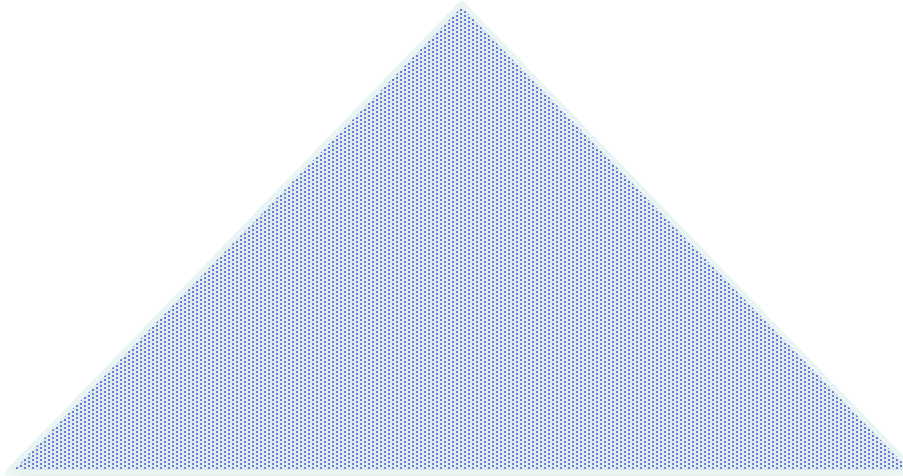
Microkinetic Modeling

Karsten Reuter

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Technische Universität München**

Catalysis Research Triangle

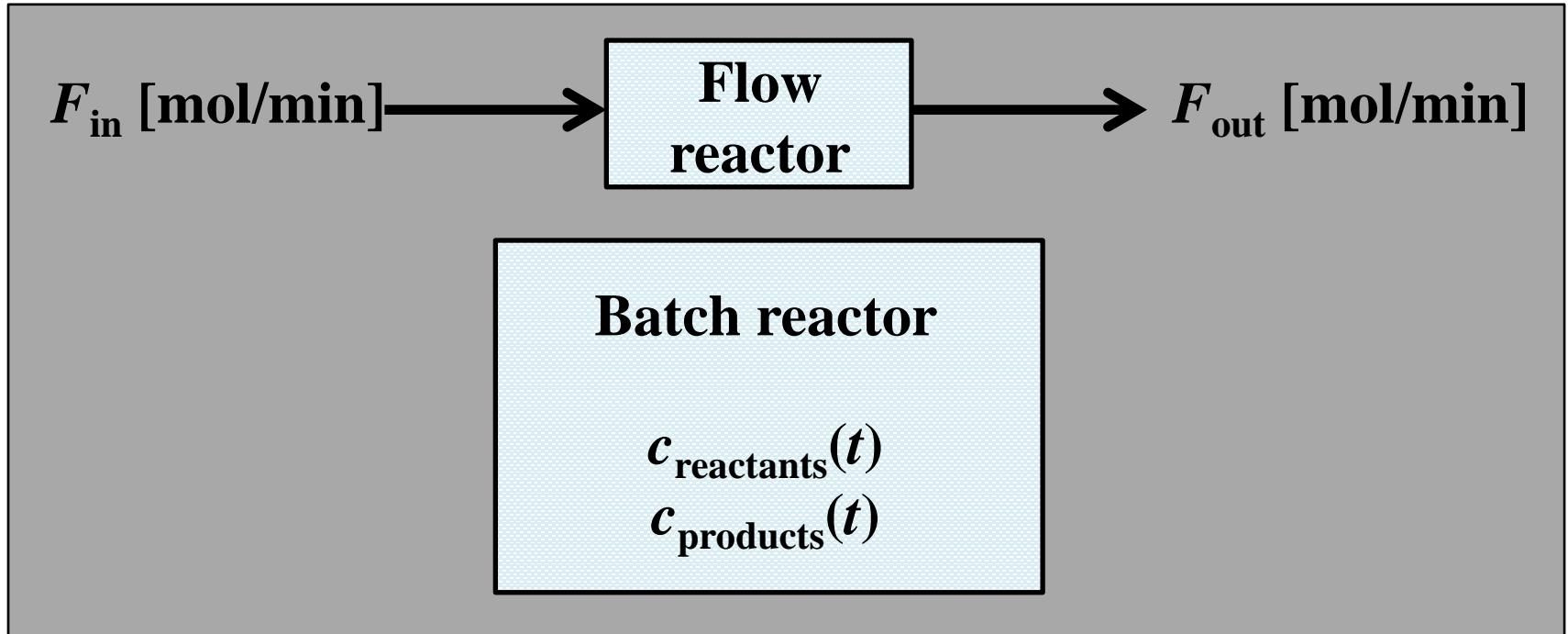
**Testing
(Kinetics)**



Preparation

Characterization

Macrokinetic studies



$r = \text{rate of reaction} = f(\text{initial gas composition, } T, p_i)$
 $f(\text{catalyst, active sites})$
 $f(\text{catalyst meso/macro structure})$
 $f(\text{reactor, flow (contact time), heat, dilution,...})$

Power law kinetics:

$$r = k \prod_i p_i^{\alpha_i}$$

From macro- to microkinetics

Reaction engineering: „Remove“ all reactor/catalyst macrostructure effects to get intrinsic rate

Normalize to rate per active site = turnover frequency

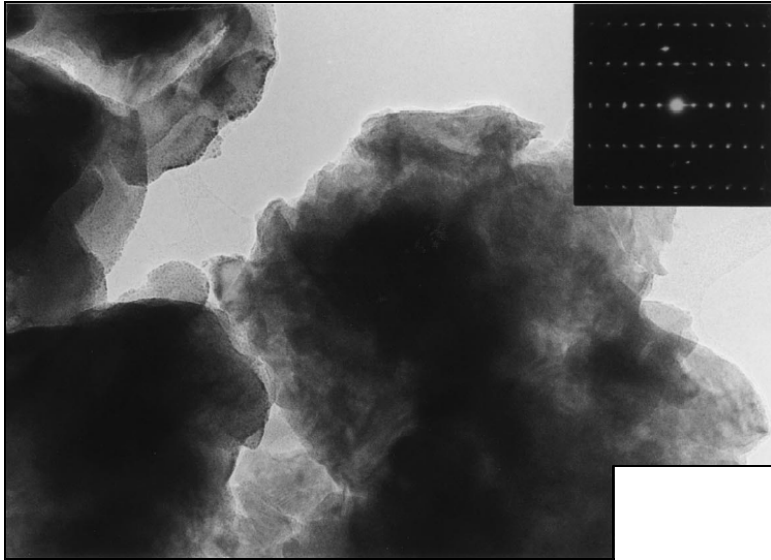
TOF = r/N [molecules site⁻¹ s⁻¹]

→ **intrinsic steady-state TOF = $\text{TOF}(T, p_i)$**

Microkinetic modeling aims to relate this to detailed mechanistic understanding:

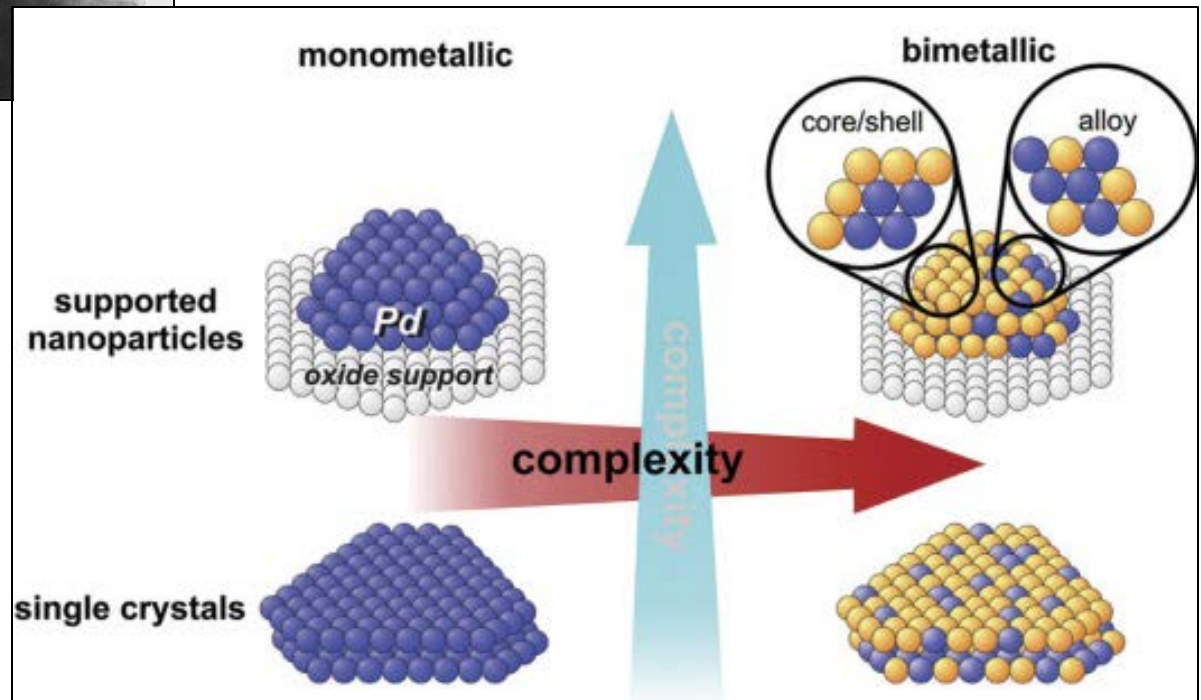
Top-down: deduce reaction mechanism from measured TOF data
Bottom-up: generate TOF data starting from first-principles calculations

Disclaimer: Mind the gap!



Supported „real“ catalyst

Model catalysts



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

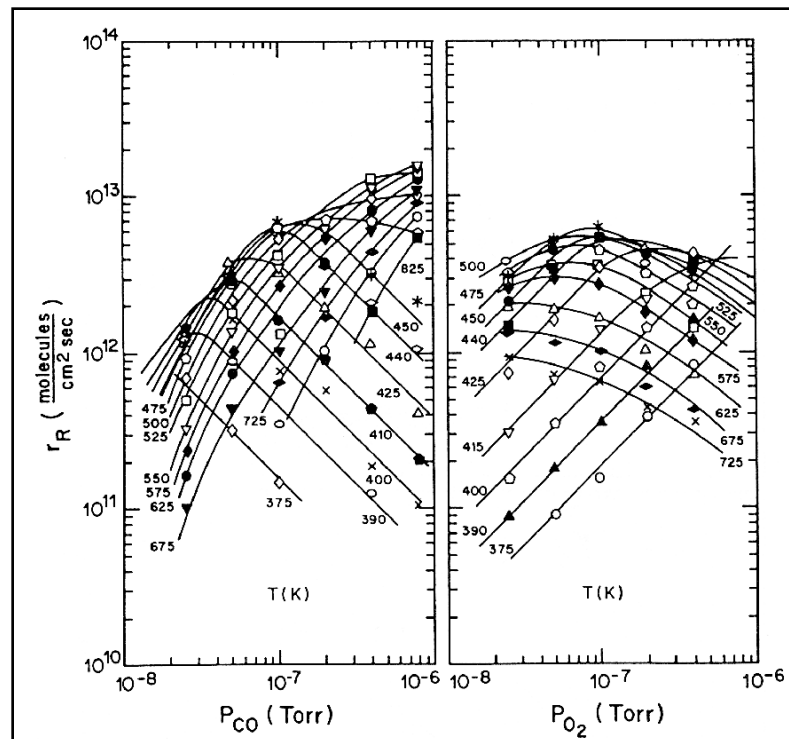
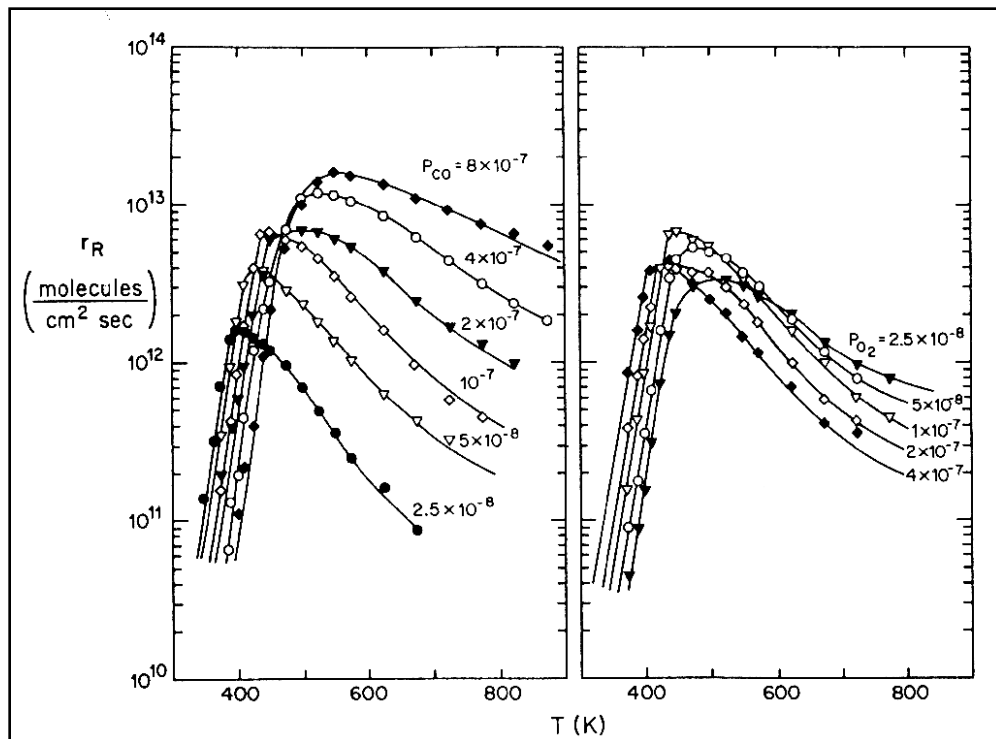
**I. The top-down approach:
Langmuir-Hinshelwood-Hougen-Watson
(LHHW) kinetics**

Chemical kinetics and catalysis,
R.A. van Santen and J.W. Niemantsverdriet,
Plenum Press (New York, 1995)

Microkinetic simulation of catalytic reactions,
P. Stoltze, Prog. Surf. Sci. 65, 65 (2000)

Step 1: Measured steady-state TOF data

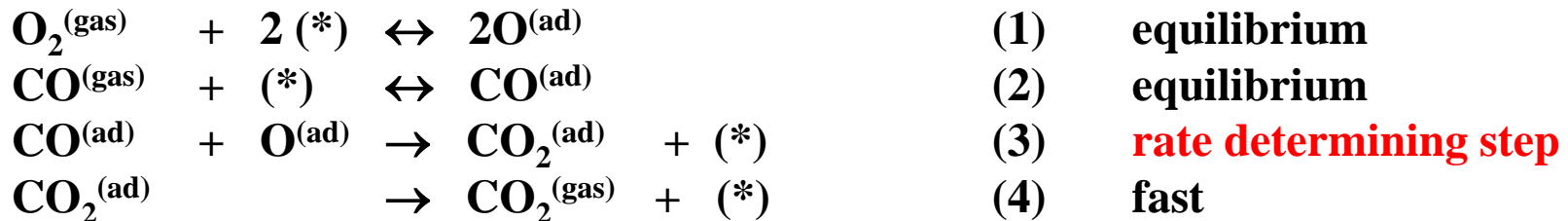
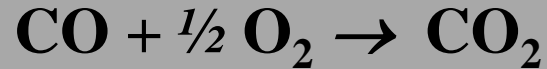
$$\text{TOF} = r/N = f(p_i, T)$$



CO oxidation over Rh(111)

TOF ~
 $10^{-2} - 10^2$ molecules site⁻¹ s⁻¹

Step 2: Formulate a reaction mechanism and rate equation



$$r(\text{CO}_2) \sim d/dt [\text{CO}_2(\text{gas})] = k_4 \theta_{\text{CO}_2(\text{ad})} \quad \text{first-order dependence (4)}$$

$$d/dt \theta_{\text{CO}_2(\text{ad})} = k_3 \theta_{\text{O}(\text{ad})} \theta_{\text{CO}(\text{ad})} - k_4 \theta_{\text{CO}_2(\text{ad})} \equiv 0 \quad \text{steady-state approximation}$$

$$r(\text{CO}_2) \sim k_3 \theta_{\text{O}(\text{ad})} \theta_{\text{CO}(\text{ad})}$$

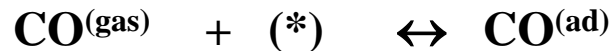
\Rightarrow determine adsorbate concentrations at the surface
in equilibrium with the gas phase

Step 3: Derive adsorption isotherms

$$\theta_{\text{eq}} = \theta_{\text{eq}}(p_i, T)$$

e.g. Langmuir:

- i) finite number of equivalent sites to hold reactants
- ii) each site can hold at most one adsorbate
- iii) no interaction between adsorbed particles



$$r_{\text{adsorption}} = k_{\text{ads}} p_{\text{CO}^{(\text{gas})}} \theta_{(*)}$$

$$r_{\text{desorption}} = k_{\text{des}} \theta_{\text{CO}^{(\text{ad})}}$$

$$r_{\text{adsorption}} = r_{\text{desorption}} \quad (\text{equilibrium})$$

$$\Rightarrow K_{\text{eq}}^{\text{CO}} = k_{\text{ads}} / k_{\text{des}} = \frac{\theta_{\text{CO}^{(\text{ad})}}}{p_{\text{CO}^{(\text{gas})}} \theta_{(*)}} = \frac{\theta_{\text{CO}^{(\text{ad})}}}{p_{\text{CO}^{(\text{gas})}} (1 - \theta_{\text{CO}^{(\text{ad})}})}$$

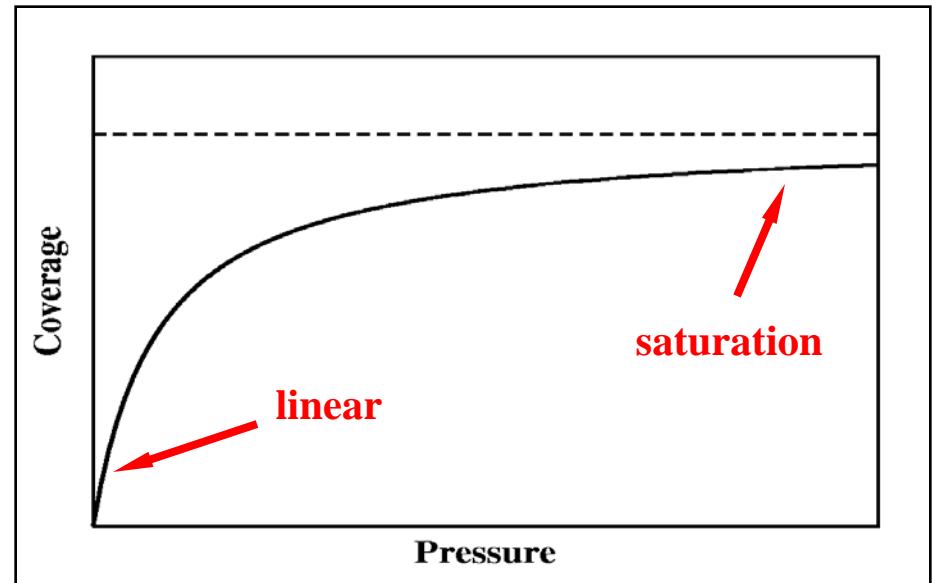
$$\theta_{\text{CO}^{(\text{ad})}} = \frac{K_{\text{eq}}^{\text{CO}} p_{\text{CO}^{(\text{gas})}}}{1 + K_{\text{eq}}^{\text{CO}} p_{\text{CO}^{(\text{gas})}}}$$

**Langmuir isotherm for
non-dissociative,
non-competitive adsorption**

Step 3: Adsorption isotherms cont'd

$$\theta_{\text{CO(ad)}} = \frac{K_{\text{eq}}^{\text{CO}} p_{\text{CO(gas)}}}{1 + K_{\text{eq}}^{\text{CO}} p_{\text{CO(gas)}}$$

- i) saturation due to finite number of sites
- ii) $K_{\text{eq}}^{\text{CO}}$ is an equilibrium property
→ thermodynamics



Similarly: molecular adsorption on several sites
 dissociative adsorption (e.g. 2 sites)
 competitive adsorption

Refinement: multiple sites
 adsorbate interactions

- Freundlich/Toth isotherms
- Tempkin/Fowler isotherms
(only averaged interactions, still analytical)
- Lattice gas Hamiltonians
(explicit interactions, no longer analytical)

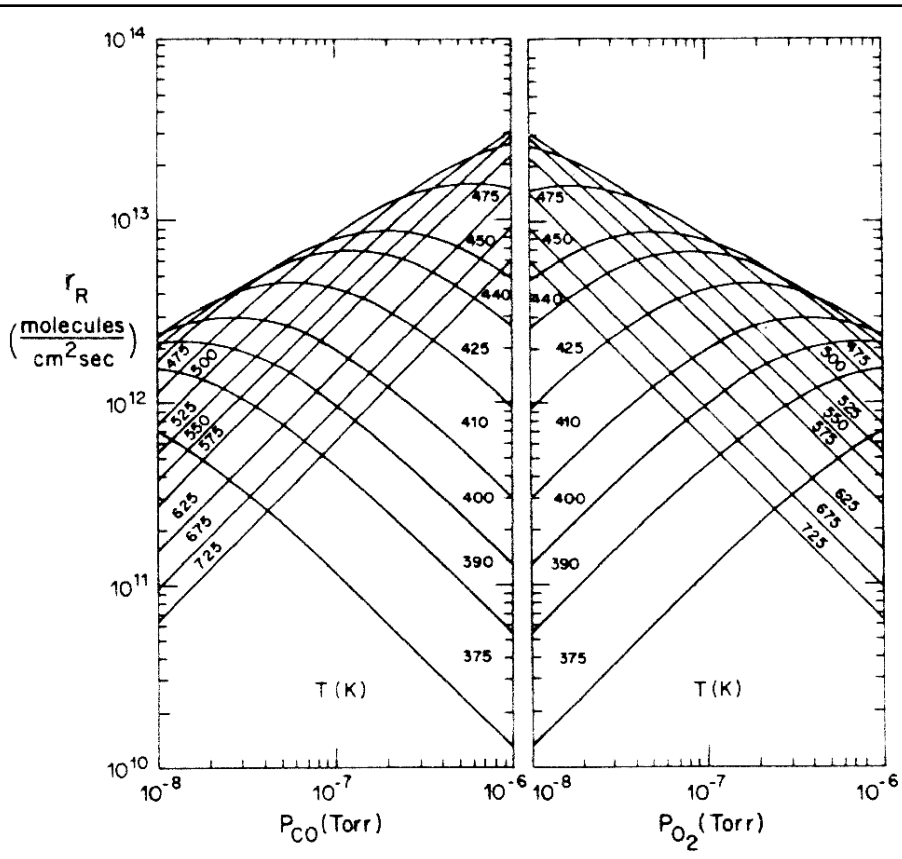
Step 4: Plug isotherms into rate equation

CO oxidation over Rh(111)

$$r(\text{CO}_2) \sim k_3 \theta_{\text{O(ad)}} \theta_{\text{CO(ad)}}$$

$$\theta_{\text{CO(ad)}} = \frac{K_{\text{eq}}^{\text{CO}} p_{\text{CO(gas)}}}{1 + K_{\text{eq}}^{\text{CO}} p_{\text{CO(gas)}} + K_{\text{eq}}^{\text{O}_2} p_{\text{O}_2(\text{gas})}}$$

$$\theta_{\text{O(ad)}} = \frac{K_{\text{eq}}^{\text{O}_2} p_{\text{O}_2(\text{gas})}}{1 + K_{\text{eq}}^{\text{CO}} p_{\text{CO(gas)}} + K_{\text{eq}}^{\text{O}_2} p_{\text{O}_2(\text{gas})}}$$



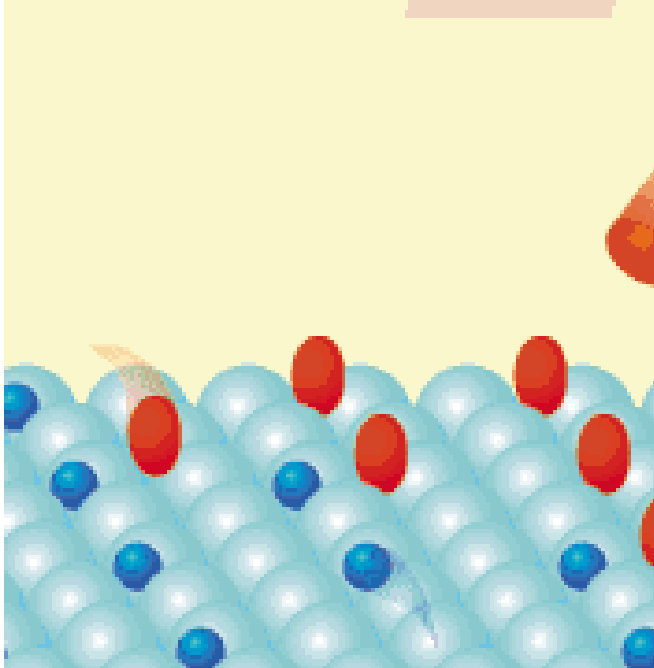
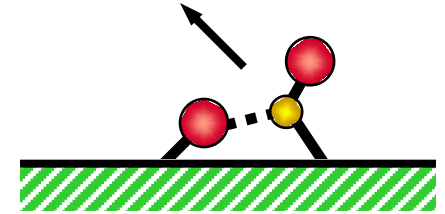
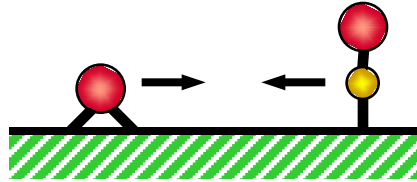
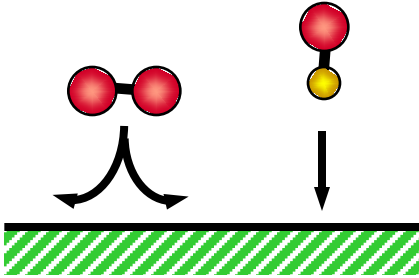
Langmuir isotherms
 competitive adsorption of O and CO
 rapid O_2 dissociation (first order in $\theta_{\text{O(ad)}}$)

Fits perfectly...

II: The bottom-up approach: First-principles kinetic Monte Carlo simulations

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 (2009). <http://www.fhi-berlin.mpg.de/th/paper.html>

Elementary processes and catalytic function



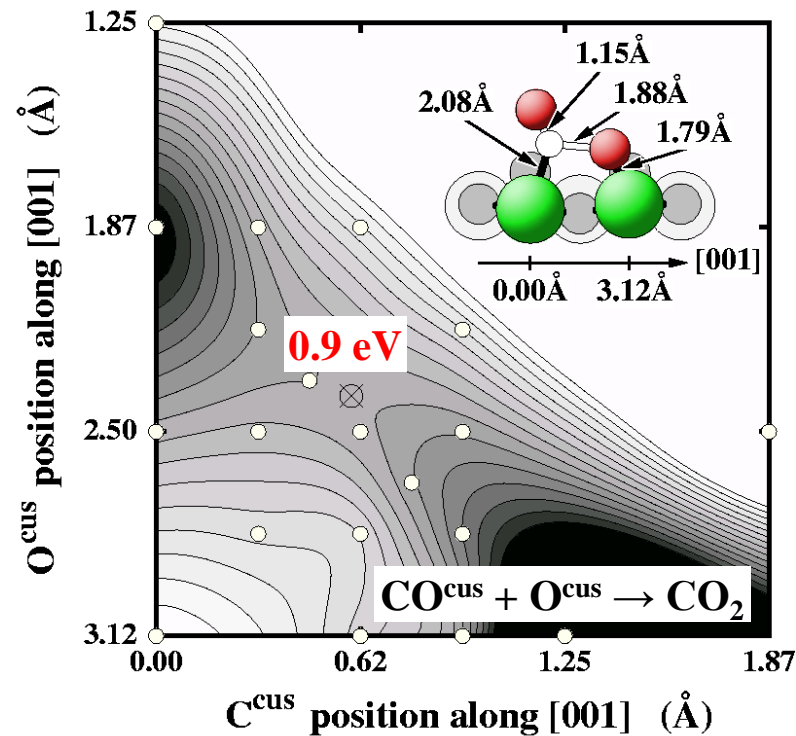
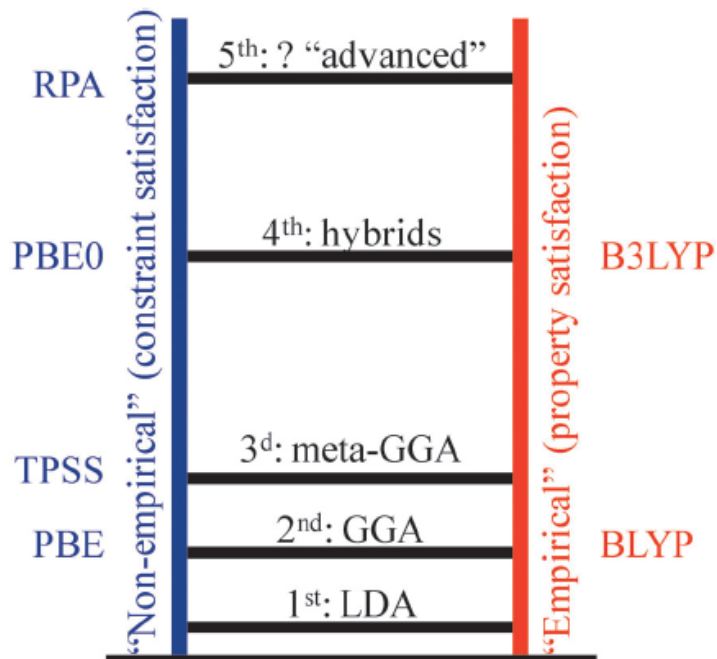
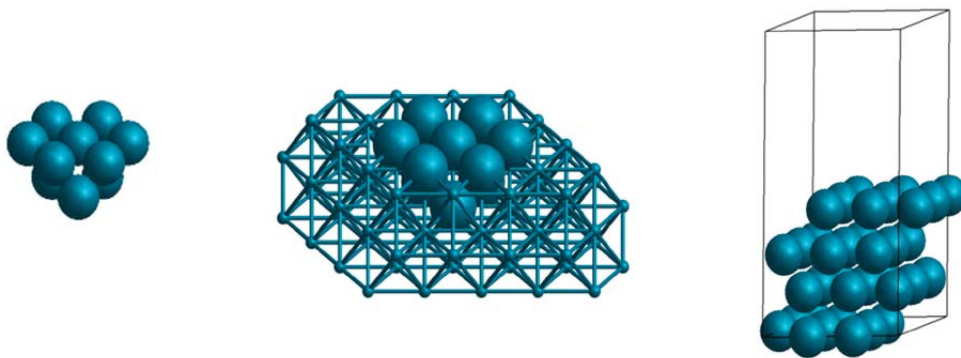
- Continuous bond making and breaking

Challenge I: predictive-quality QM energetics

- Rare event time scale: $> \sim \text{msec}$

Challenge II: long time-scale simulations

First-principles modeling of surface reactions



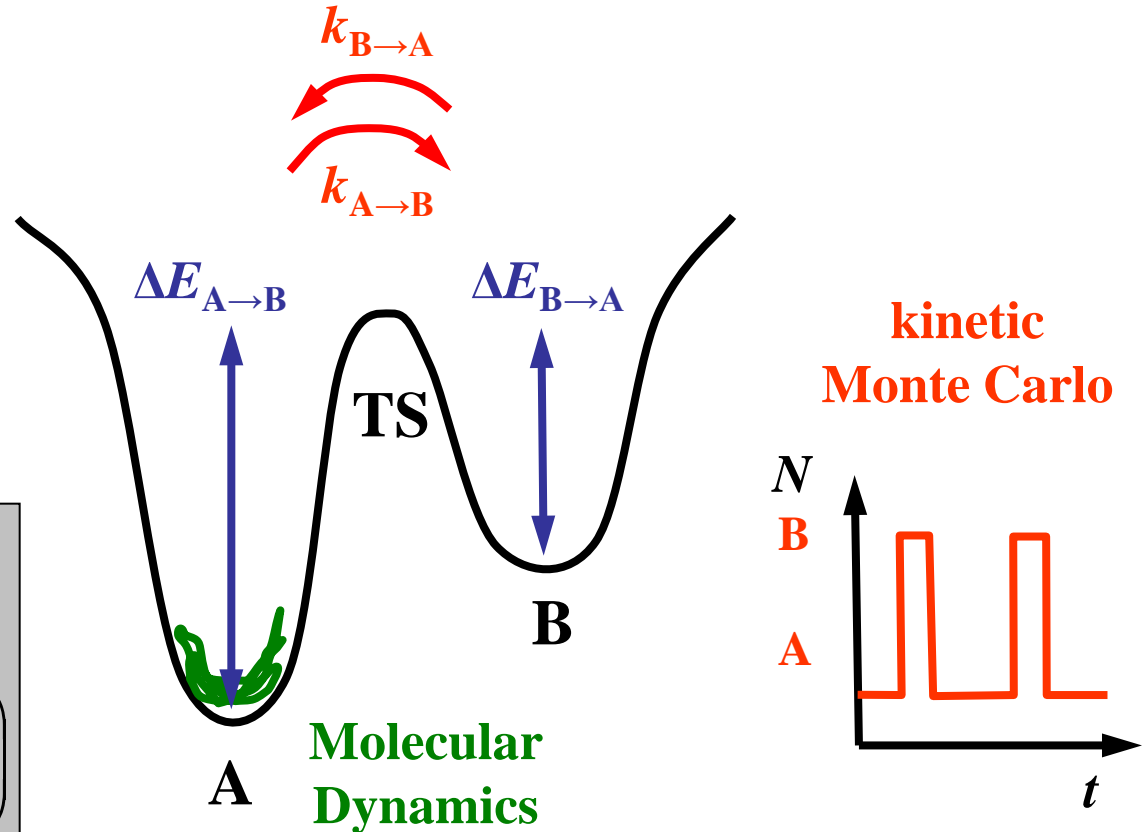
- Active site model

- „Level of theory“

Markovian state dynamics: Kinetic Monte Carlo simulations

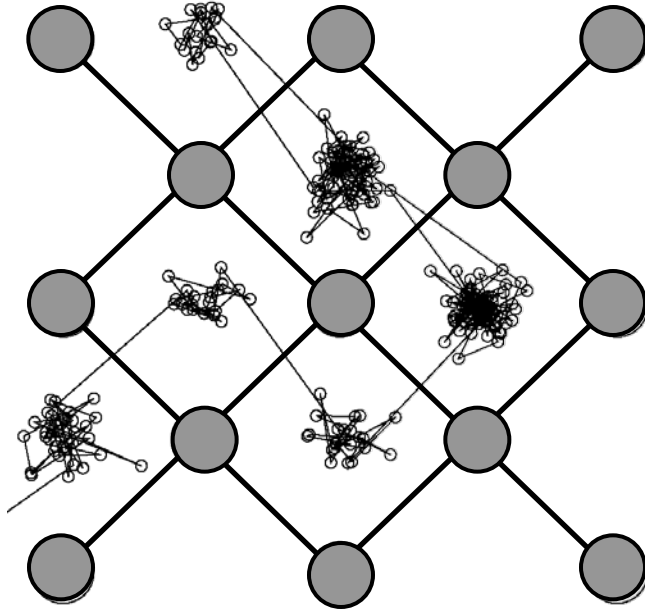
Transition State Theory

$$k_{i \rightarrow j} = \left(\frac{k_B T}{h} \right) \frac{Z_{\text{TS}(i \rightarrow j)}}{Z_i}$$
$$= \Gamma_0 \exp\left(\frac{-\Delta E_{i \rightarrow j}}{k_B T} \right)$$



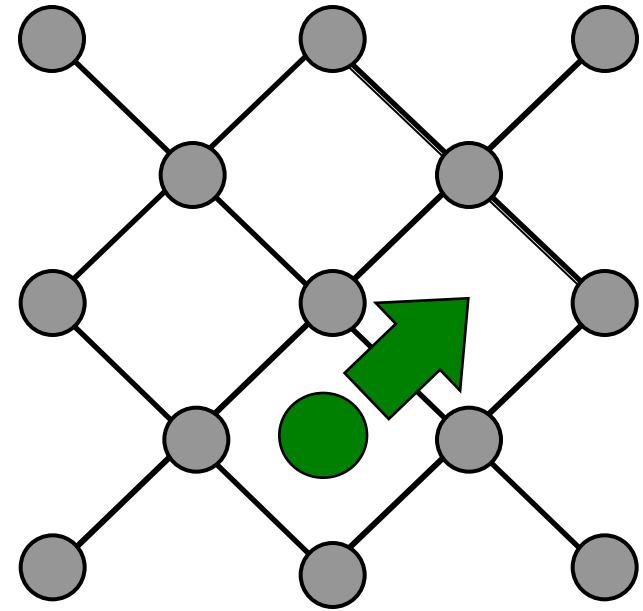
$$\frac{dP_i(t)}{dt} = -\sum_j k_{i \rightarrow j} P_i(t) + \sum_j k_{j \rightarrow i} P_j(t)$$

Kinetic Monte Carlo: essentially „coarse-grained MD“



**Molecular Dynamics:
the whole trajectory**

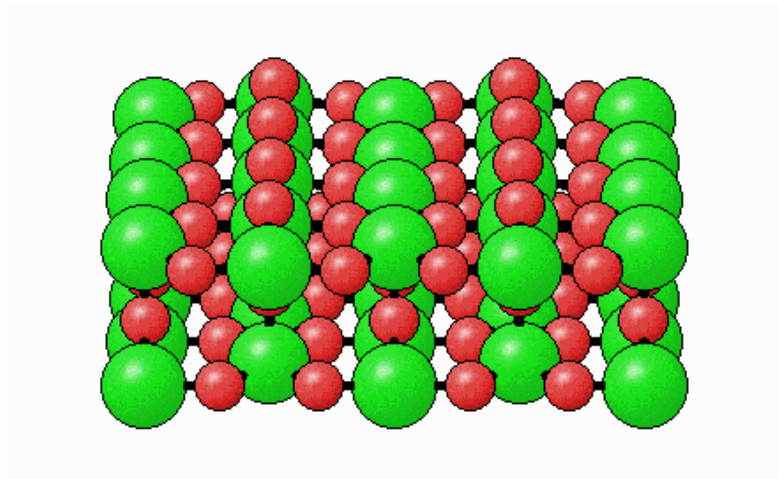
***ab initio* MD:
up to 50 ps**



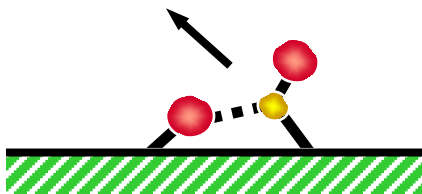
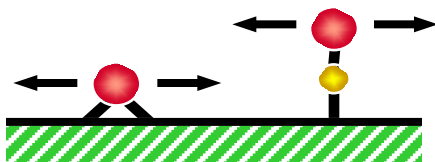
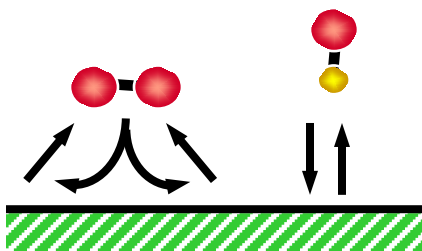
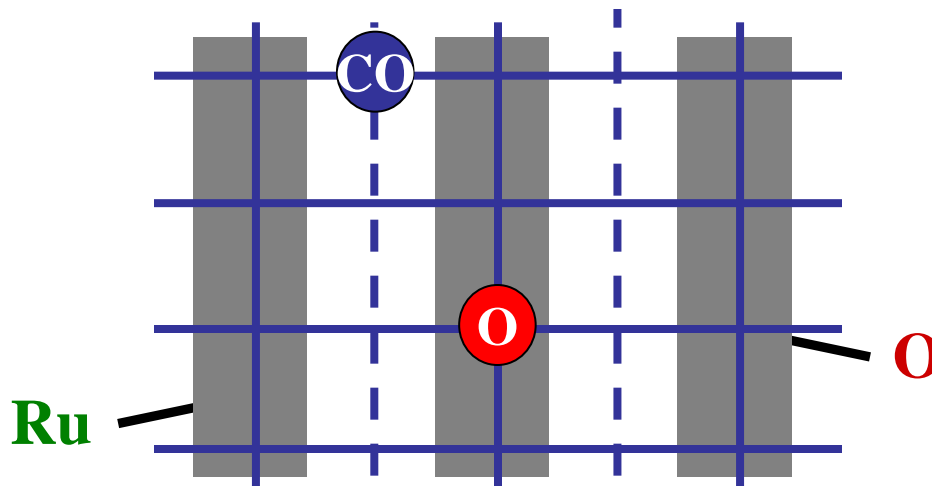
**Kinetic Monte Carlo:
coarse-grained hops**

***ab initio* kMC:
up to minutes**

Building a first-principles kinetic Monte Carlo model



CO oxidation @ RuO₂(110)



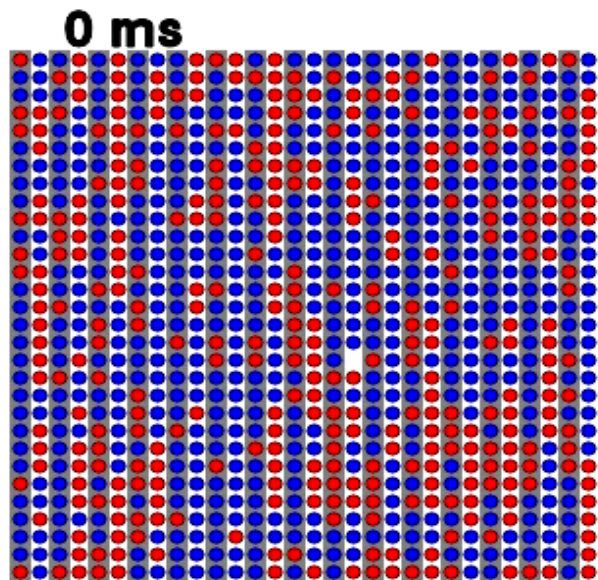
26 elementary processes (site-specific):

- O₂ adsorption/desorption (dissociative/associative)
- CO adsorption/desorption (unimolecular)
- O and CO diffusion
- CO + O reaction

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

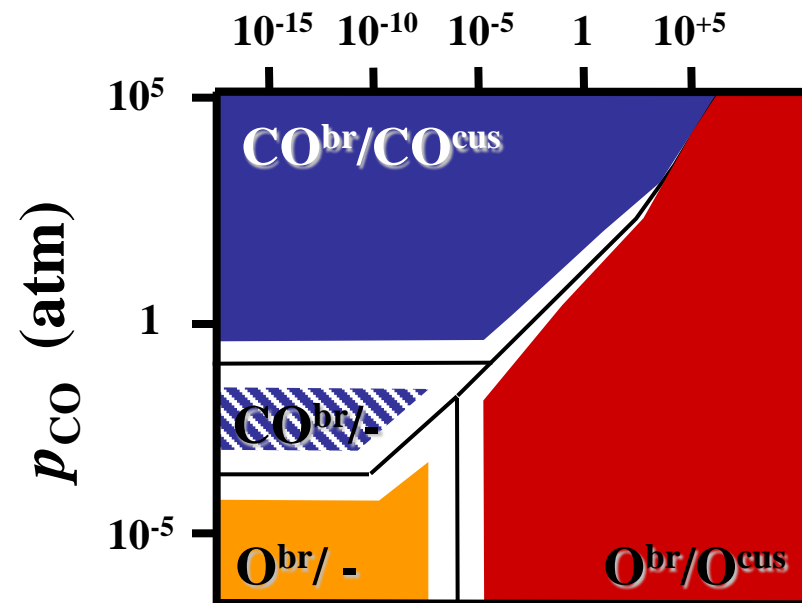
K. Reuter and M. Scheffler, Phys. Rev. B 73, 045433 (2006)

Surface structure and composition in the reactive environment

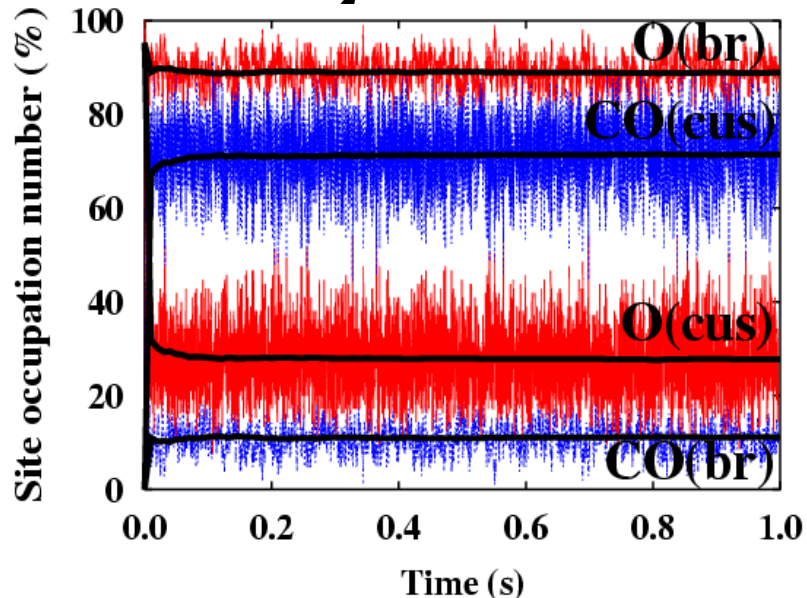


CO oxidation at RuO₂(110)

600 K p_{O_2} (atm)



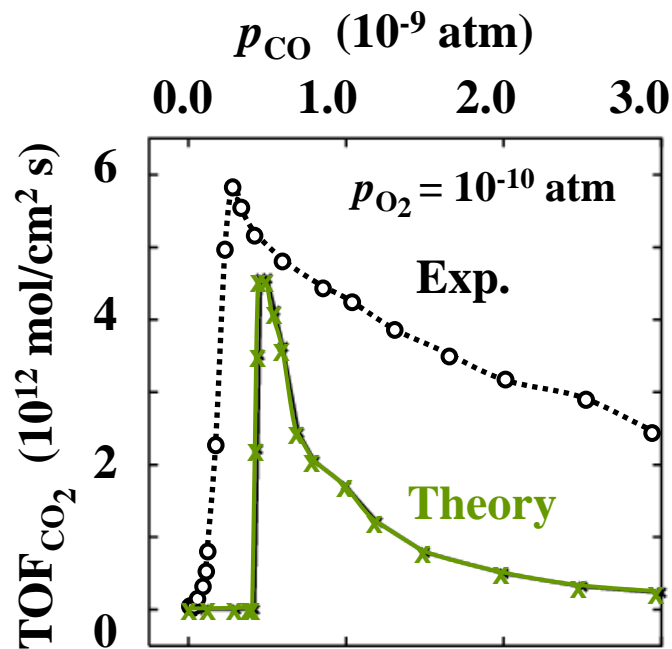
$T = 600$ K, $p_{O_2} = 1$ atm, $p_{CO} = 7$ atm



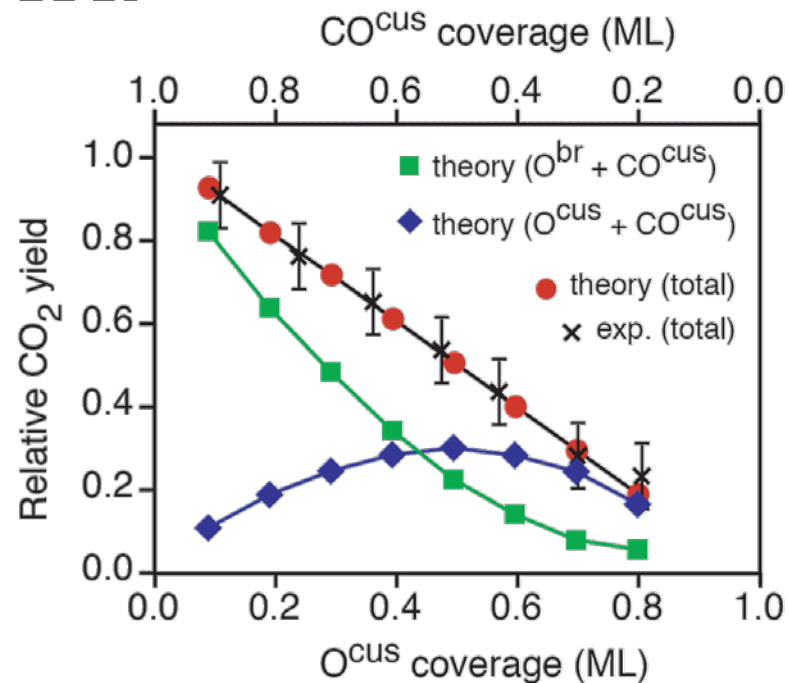
K. Reuter, D. Frenkel and M. Scheffler,
Phys. Rev. Lett. 93, 116105 (2004)

Steady-state and transient parameter-free turnover frequencies

350 K



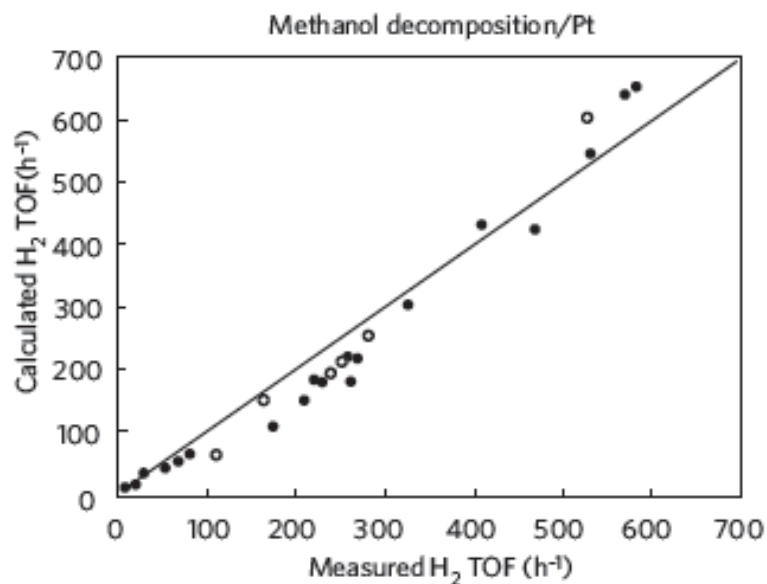
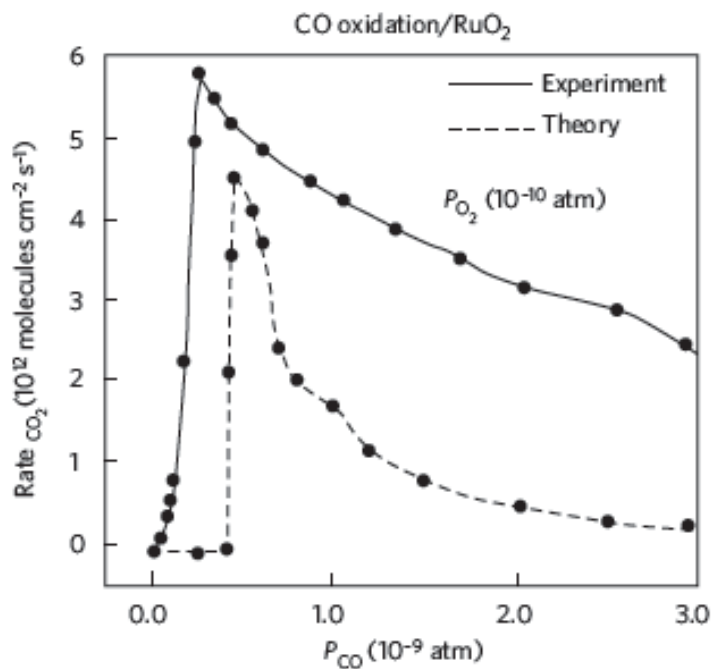
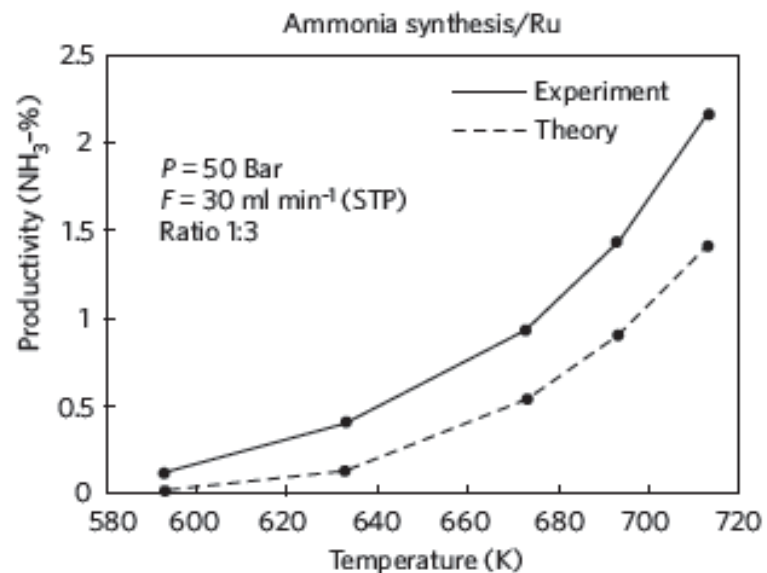
TPR



The dawn of a new era



J.K. Nørskov *et al.*,
Nature Chem. 1, 37 (2009)



III. Towards error-controlled first-principles microkinetic models

Key ingredients to „predictive-quality“ microkinetic modeling

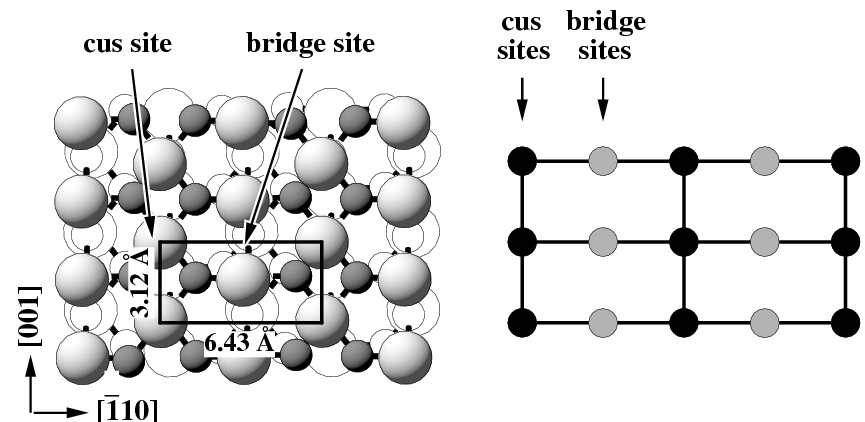
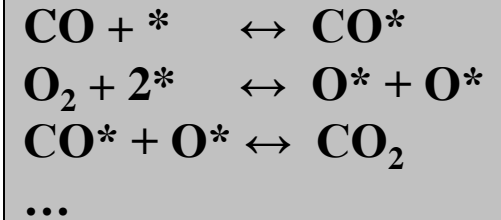
Accurate rate constants:

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

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

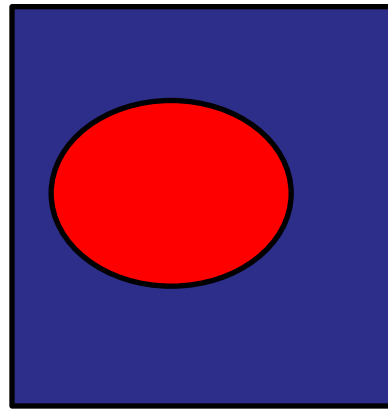
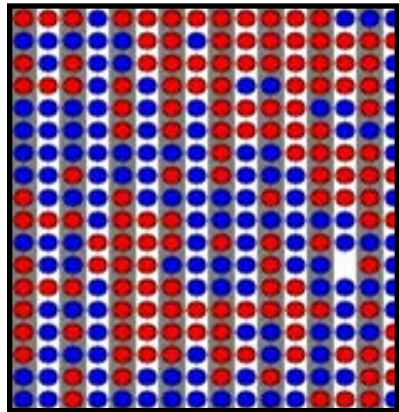
Reaction mechanism:

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



Mean-field approximation: Phenomenological rate equations

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



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

$P(\text{O}^{\text{br}}, \text{CO}^{\text{cus}}, t)$



$\theta(\text{O}^{\text{br}}, t) \cdot \theta(\text{CO}^{\text{cus}}, t)$

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

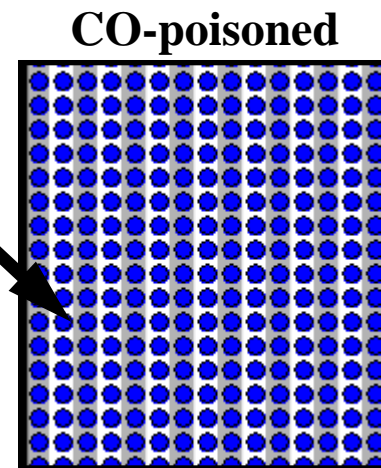
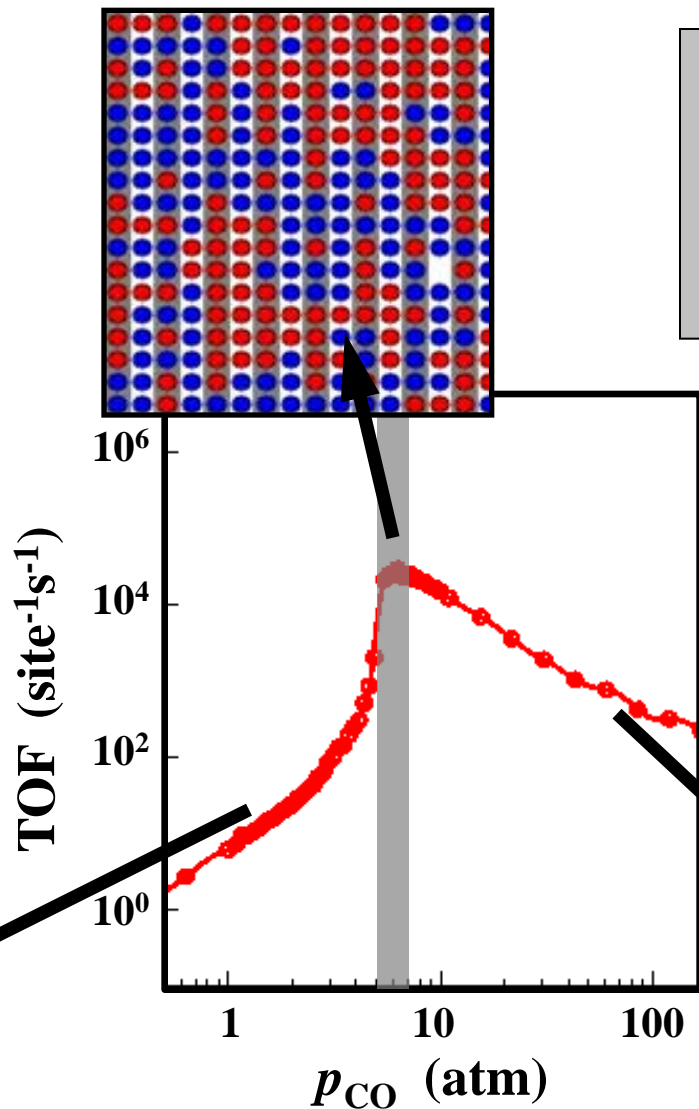
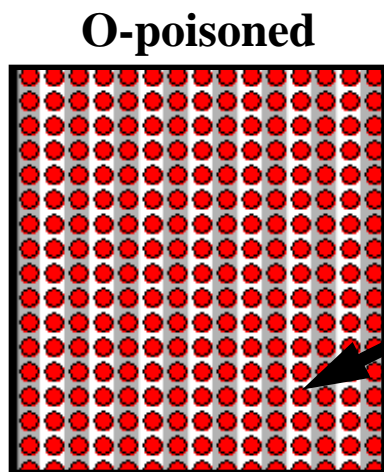
$$\frac{d\theta(\text{O}^{\text{br}}, t)}{dt} = f_2 \left\{ k_{i \rightarrow j}, \theta(\text{O}^{\text{cus}}, t), \theta(\text{O}^{\text{br}}, t), \theta(\text{CO}^{\text{cus}}, t), \theta(\text{CO}^{\text{br}}, t) \right\}$$

...

Spatial arrangement and catalytic activity

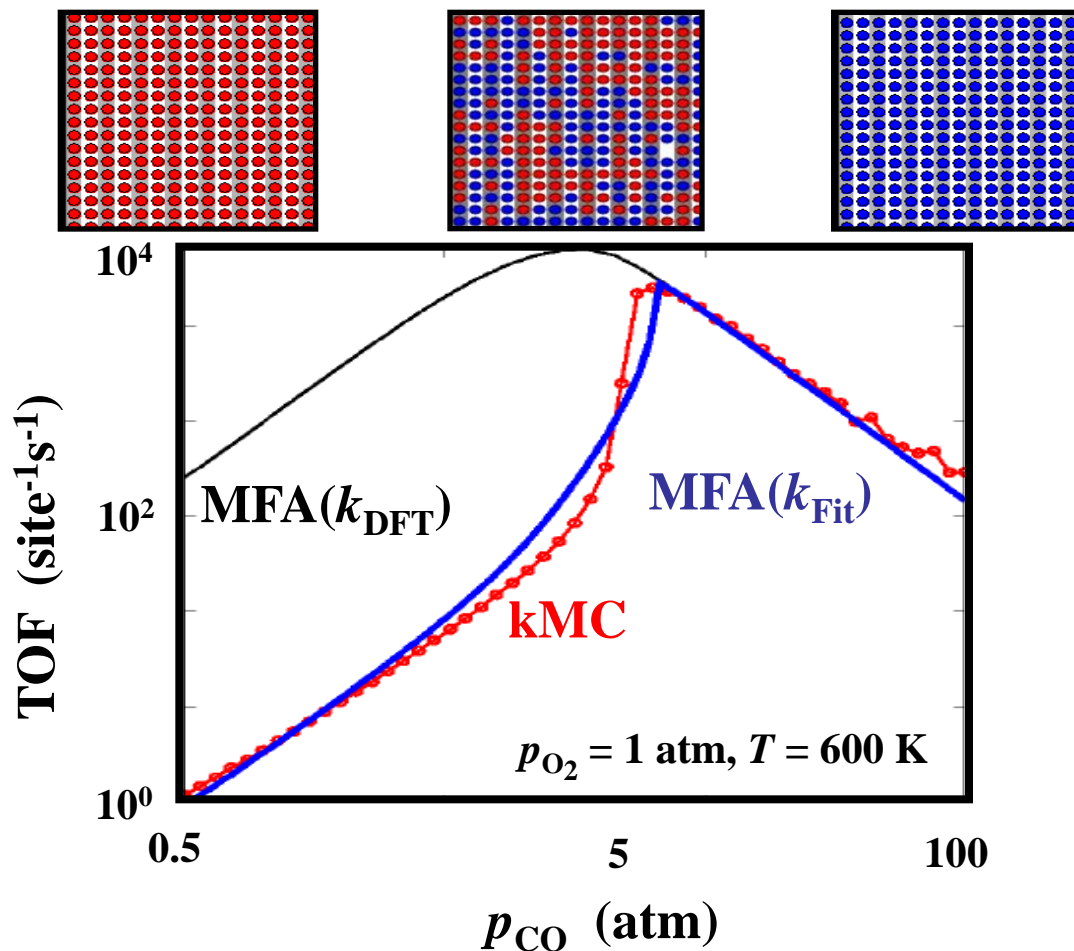
$T = 600 \text{ K}$
 $p_{\text{O}_2} = 1 \text{ atm}$

→ Inhomogeneous spatial distribution even in absence of lateral interactions in kMC model



The „power“ of fitting

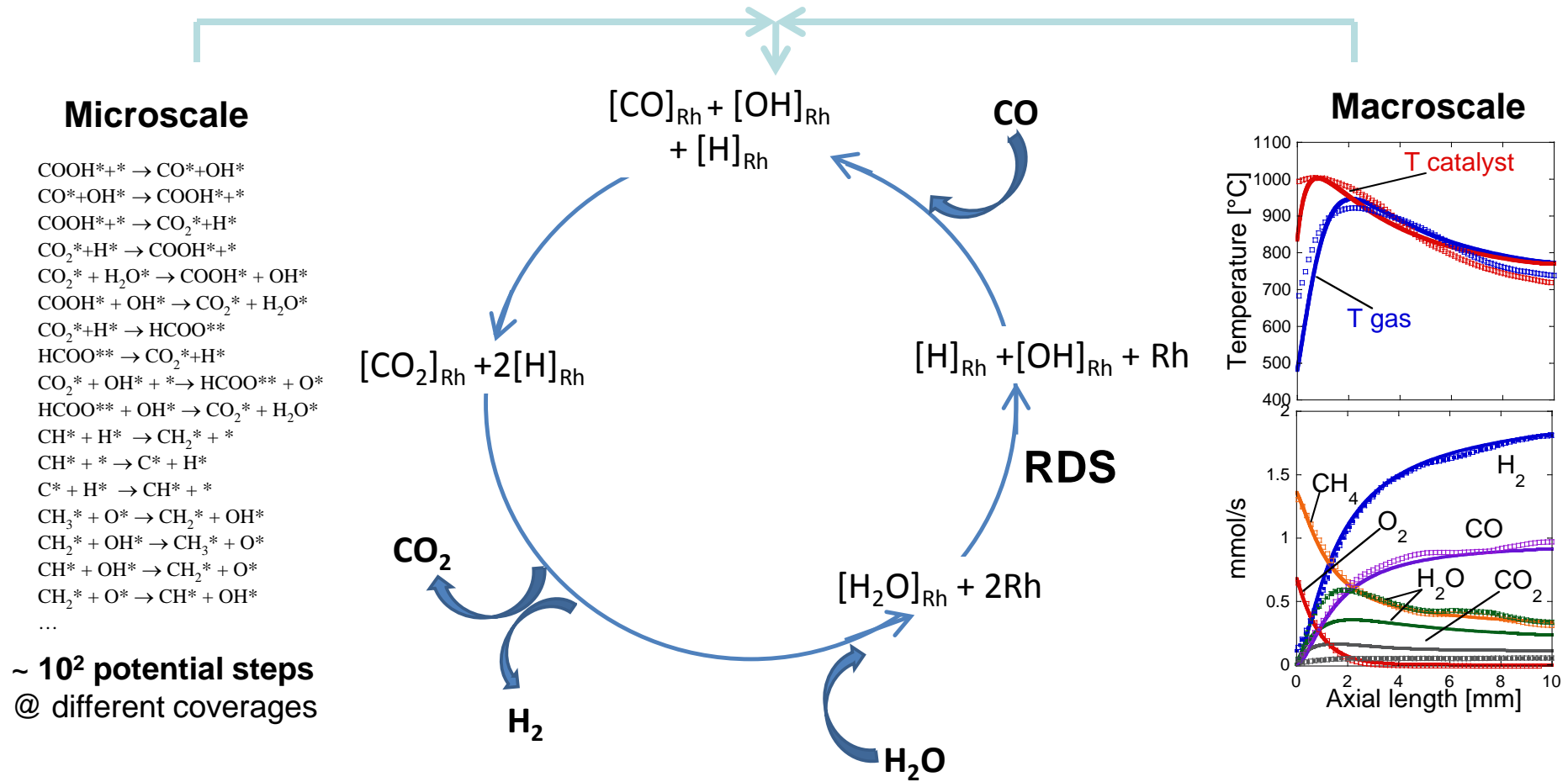
CO oxidation
at RuO₂(110)



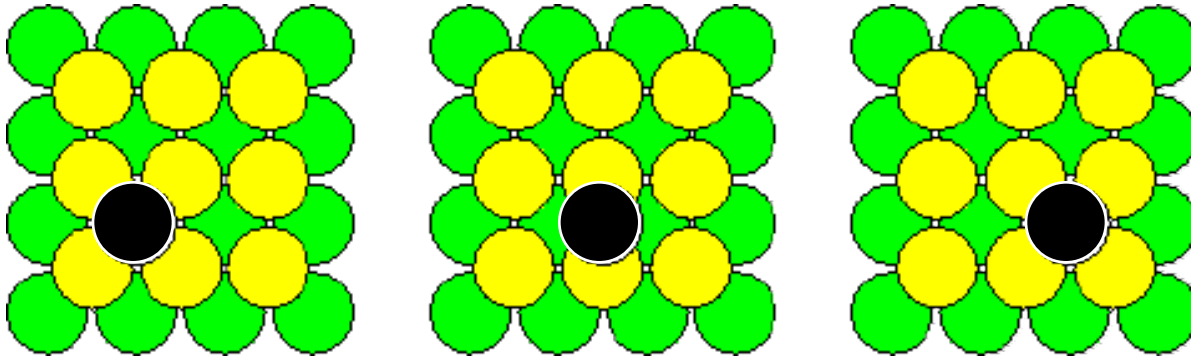
Fitted rate constants deviate from “real” rate constants
by up to two orders in magnitude for dominant processes

Effective parameters without microscopic meaning

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



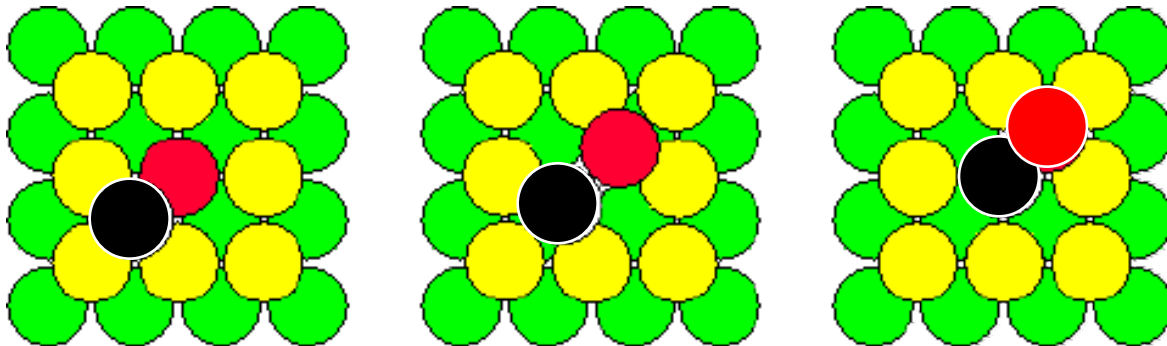
Diffusion at metal surfaces: surprises...



Hopping mechanism

Ag(100) $\Delta E = 0.45$ eV

Au(100) $\Delta E = 0.83$ eV



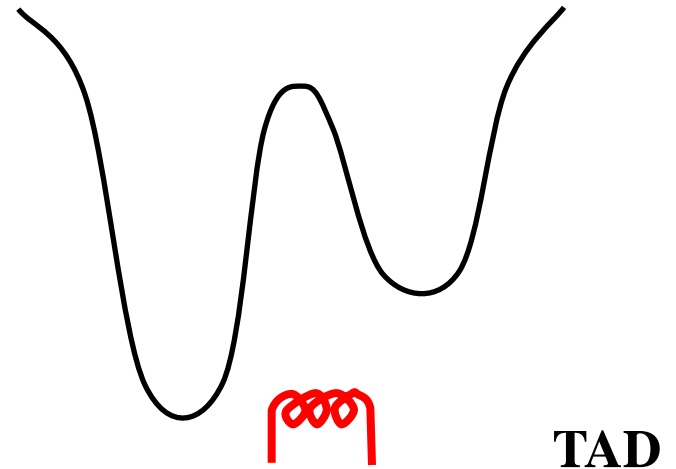
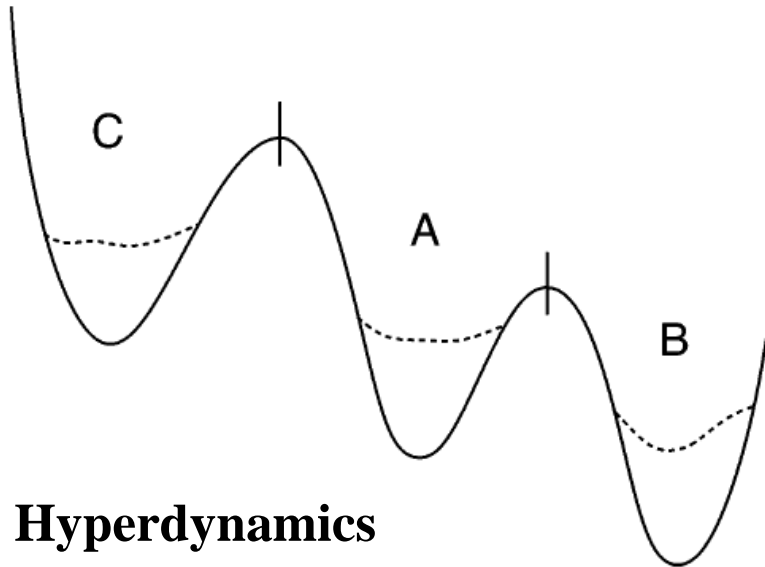
Exchange mechanism

Ag(100) $\Delta E = 0.73$ eV

Au(100) $\Delta E = 0.65$ eV

Automatized process identification

Accelerated molecular dynamics:



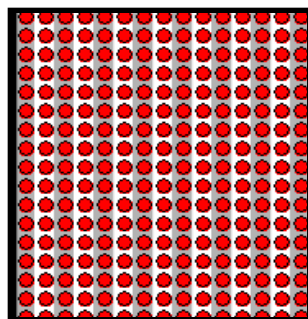
Other approaches:

- metadynamics
- dimer method
- ...

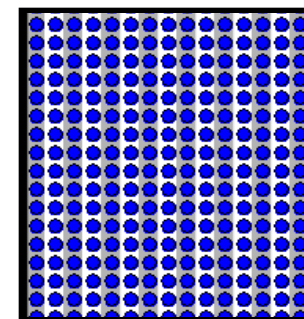
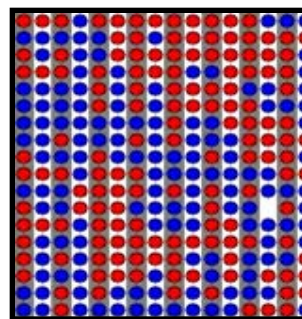
Extending the Time Scale in Atomistic Simulation of Materials,
A.F. Voter, F. Montalenti and T.C. Germann,
Annu. Rev. Mater. Res. 32, 321 (2002)

Error propagation through rate-determining steps

CO oxidation at RuO₂(110)



O-poisoned

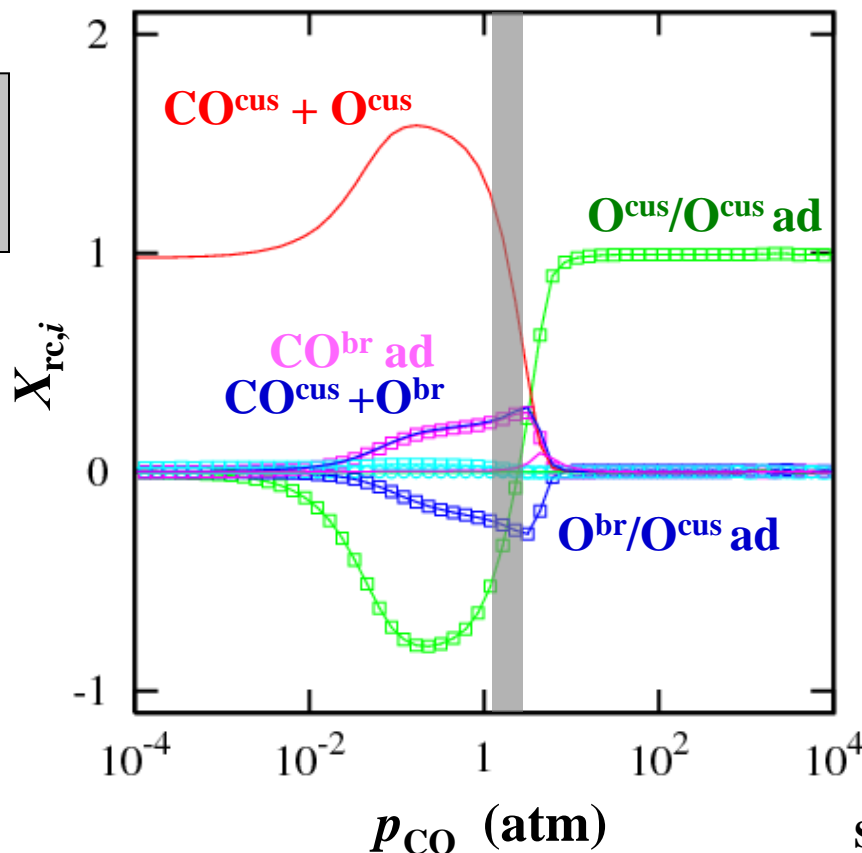


CO-poisoned

Sensitivity analysis:

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

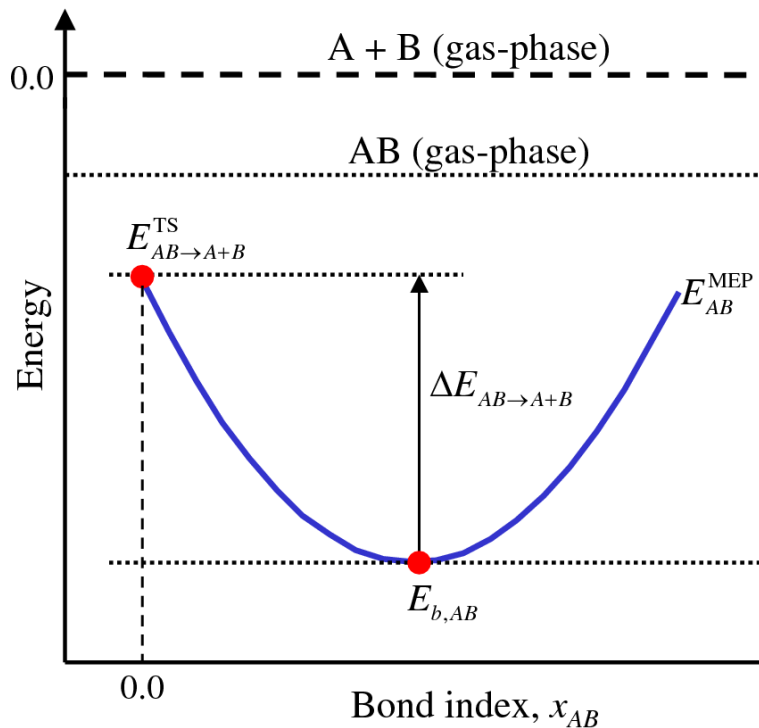
C.T. Campbell,
J. Catal. 204, 520 (2001);
Nature 432, 282 (2004)



$p_{\text{O}_2} = 1$ atm
 $T = 600$ K

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

Source for „rough“ rate constants: Hybrid UBI-QEP ?!

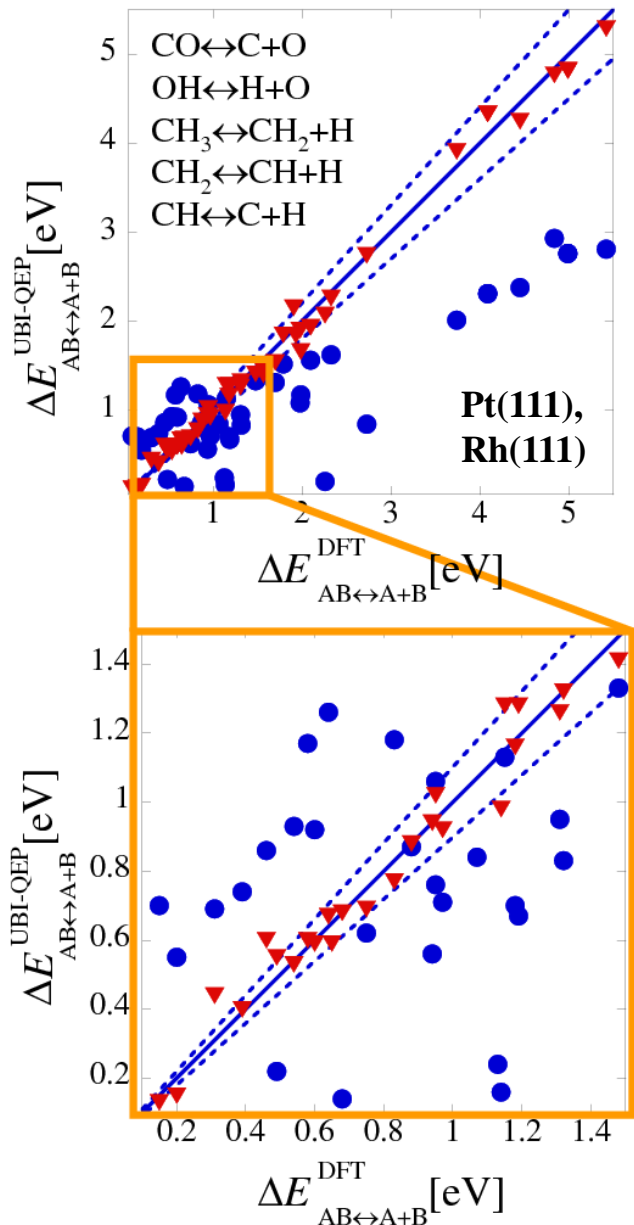


Unity Bond-Index Quadratic Exponential Potential

$$\Delta E_{AB \rightarrow A+B}^{UBI-QEP} = \phi \left[E_{AB \rightarrow A+B}^{TS} - \min_{x_{AB}} (E_{AB}^{MEP}) \right] = \phi \left[\frac{(P - D_{AB})^2}{(P + D_{AB})} \right]$$

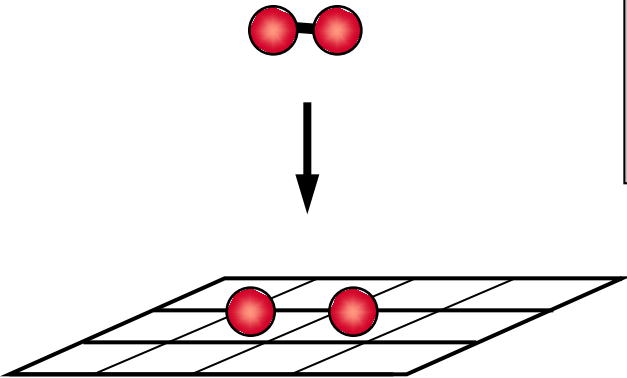
E. Shustorovich and H. Sellers, Surf. Sci. Rep. 31, 5 (1998)

M. Maestri and K. Reuter, Angew. Chemie Int. Ed. 123, 1226 (2011)

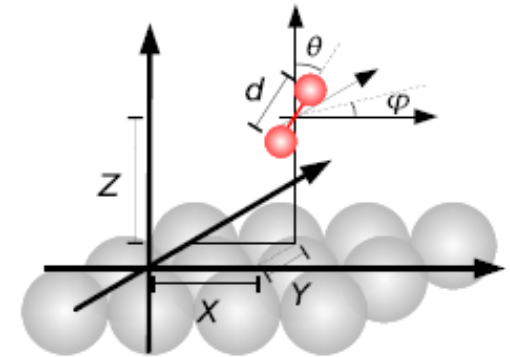


More than Markov?

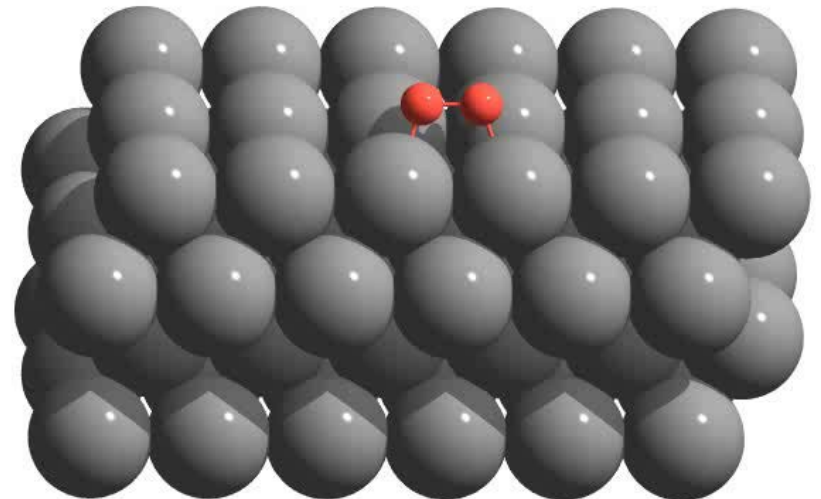
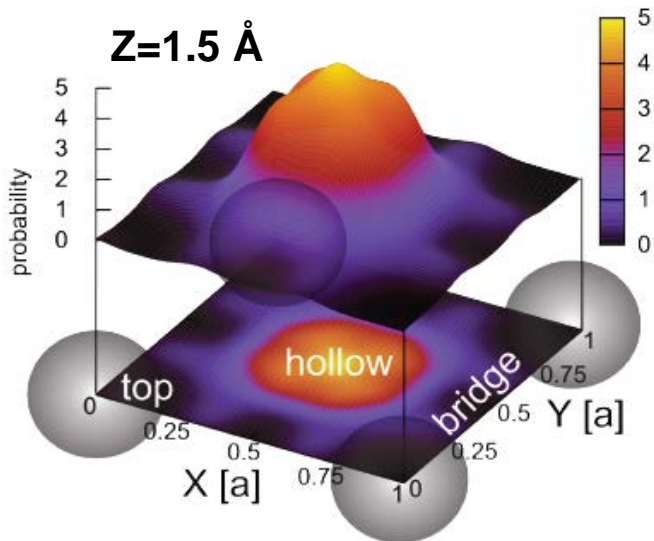
Heat dissipation during dissociative adsorption: O₂/Pd(100)



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



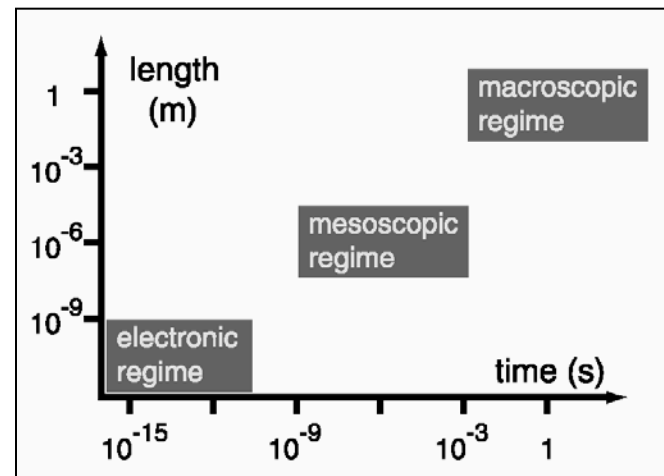
$$V_{\text{fsa}} = (X, Y, Z, d, \theta, \varphi)$$



First-Principles Microkinetic Modeling: Where do we stand?

State-of-the-art in catalysis modeling:

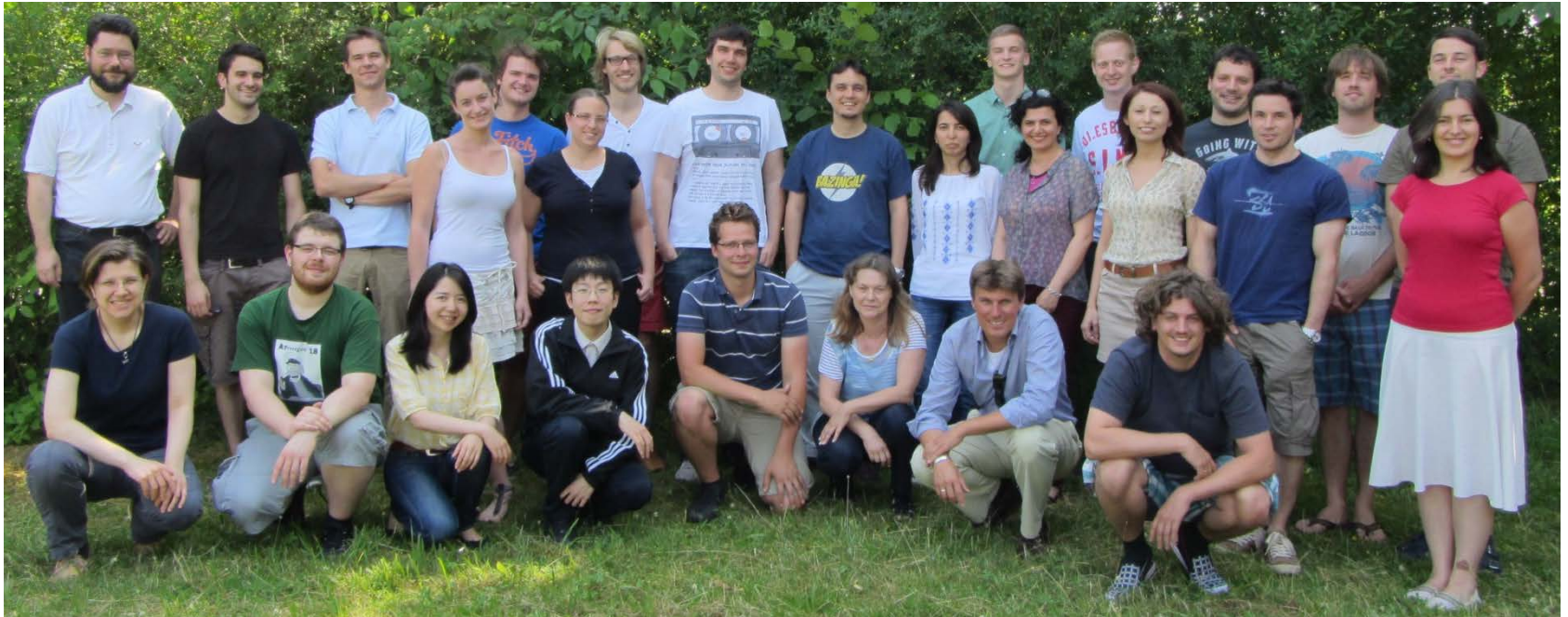
- **Prevalence of highly coarse-grained models based on effective parameters without true microscopic meaning**
 - rate equation theory*
 - based on empirical rate constants*
- **Emergence of *ad-hoc* 1p-microkinetic models**
 - kMC and mean-field*
 - model catalysts, show case reactions*



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 reactor models*
- **Robust links between theories that enable reverse-mapping**
 - sensitivity analysis to control flow of error across scales*

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