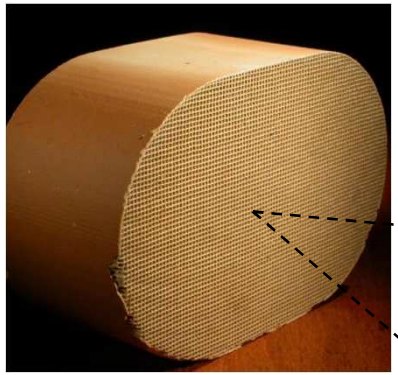
Towards a First-Principles Chemical Engineering

Karsten Reuter

Chemistry Department and Catalysis Research Center
Technische Universität München

Challenges across the scales



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

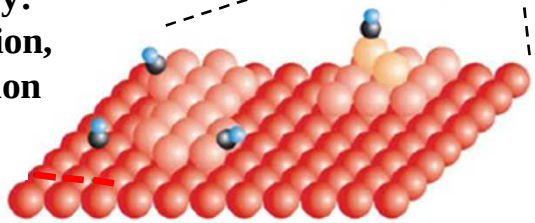
Heat transport in solid wall

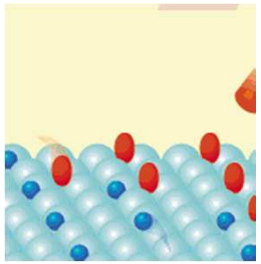
Transport of momentum, energy, species

Gas-phase reactions

Thermal radiation

Surface chemistry: adsorption, diffusion, reaction, desorption

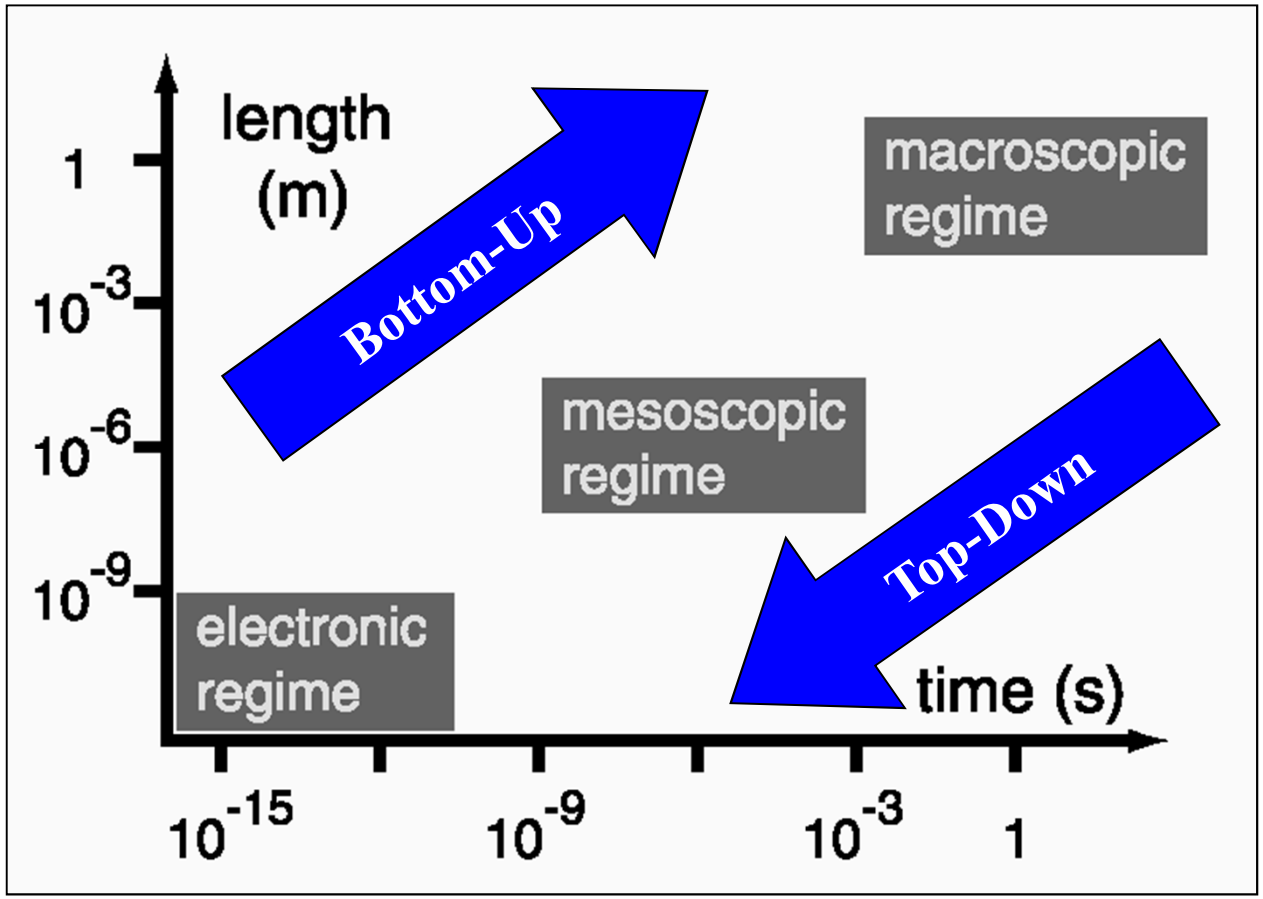




Accurate (first-principles) energetics of individual elementary processes

Quantitative transient and steady-state surface kinetics

Multiscale modeling

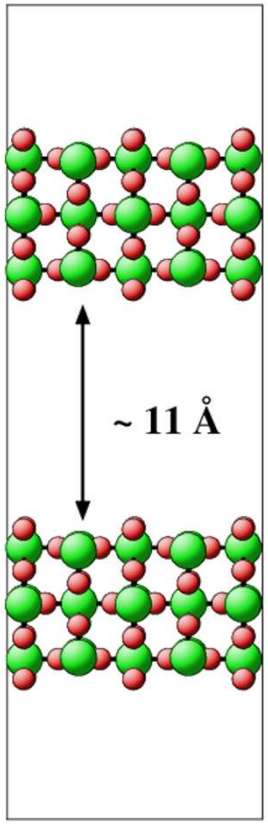


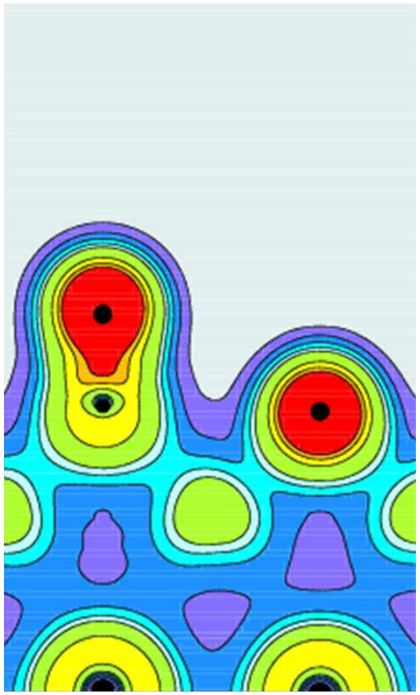
Ab initio atomistic thermodynamics and statistical mechanics of surface properties and functions
K. Reuter, C. Stampfl, and M. Scheffler, in: Handbook of Materials Modeling Vol. 1, (Ed.) S. Yip, Springer (Berlin, 2005). http://www.fhi-berlin.mpg.de/th/paper.html

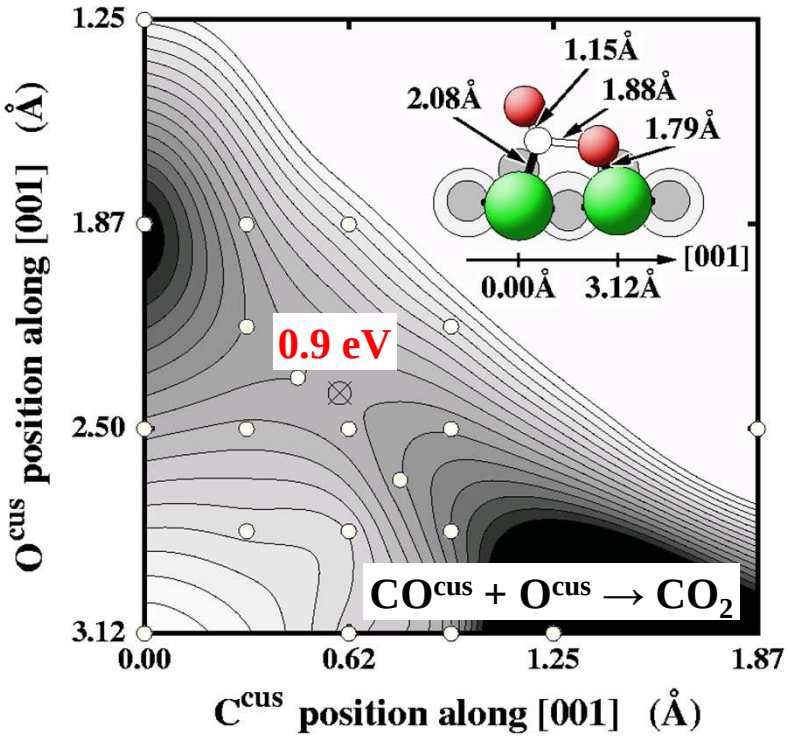
I. „Bottom up best practice“:

Multiscale modeling approach to in-situ CO oxidation at $RuO_2(110)$

Electronic regime: Energetics of elementary processes





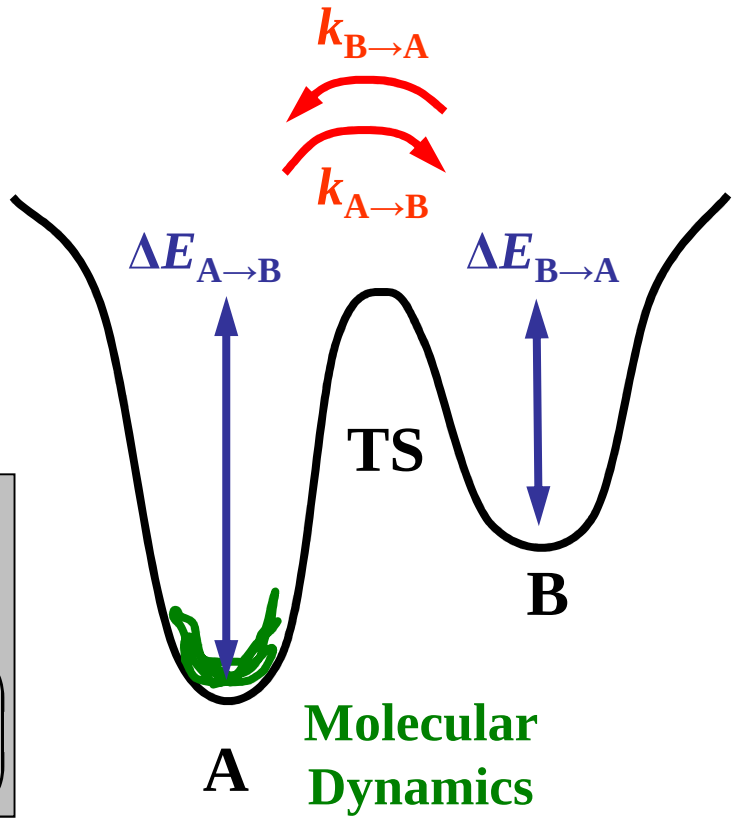


Density-Functional Theory

V_{xc} = GGA (PBE…)

K. Reuter and M. Scheffler, Phys. Rev. B 68, 045407 (2003)

Mesoscopic regime: Tackling rare-event time scales

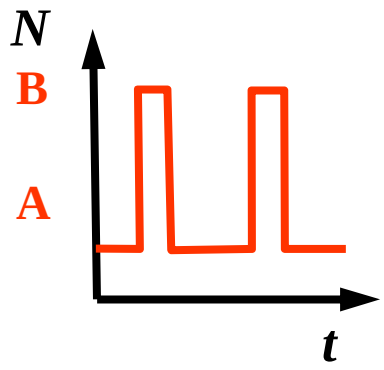


Transition State Theory

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

Molecular Dynamics

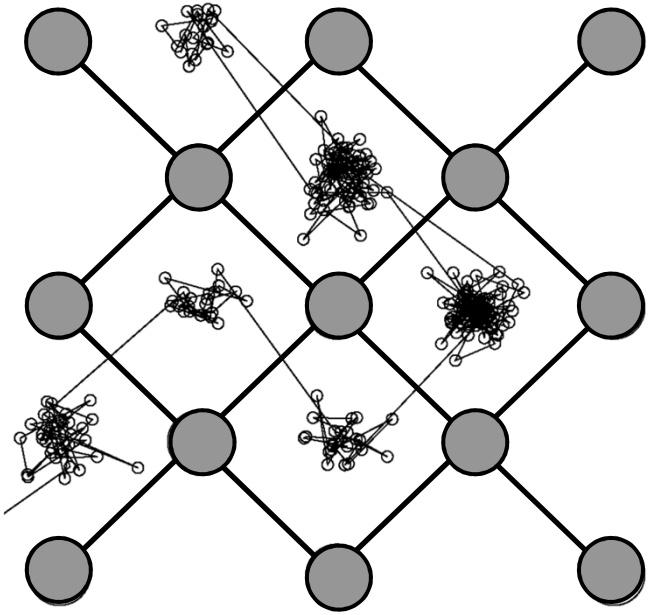
kinetic Monte Carlo



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

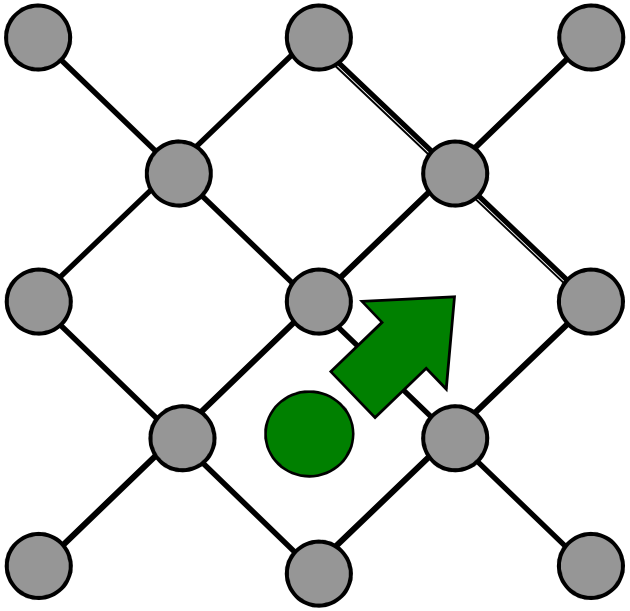
First-principles kinetic Monte Carlo simulations for heterogeneous catalysis: Concepts, status and frontiers
K. Reuter, in "Modeling Heterogeneous Catalytic Reactions: From the Molecular Process to the Technical System", (Ed.) O. Deutschmann, Wiley-VCH, Weinheim (2011). http://www.fhi-berlin.mpg.de/th/paper.html

Kinetic Monte Carlo: essentially „coarse-grained MD“



Molecular Dynamics:
the whole trajectory

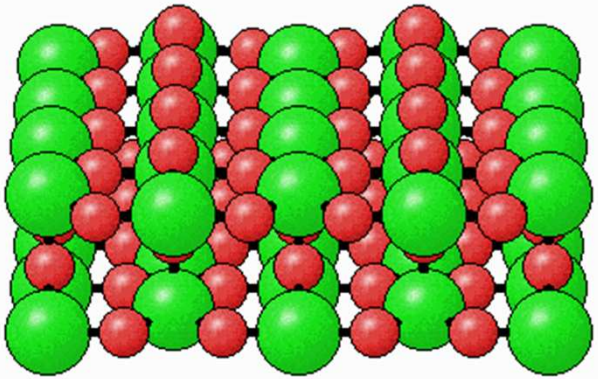
***ab initio* MD:**
up to 50 ps

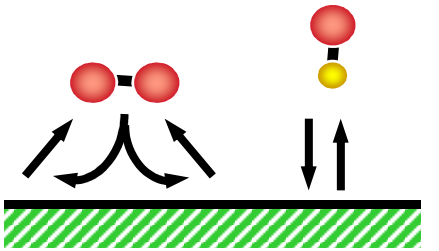


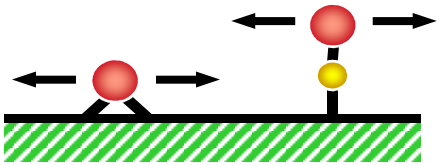
Kinetic Monte Carlo:
coarse-grained hops

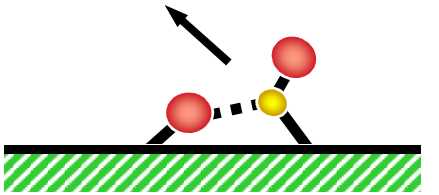
***ab initio* kMC:**
up to minutes

Building a first-principles kinetic Monte Carlo model

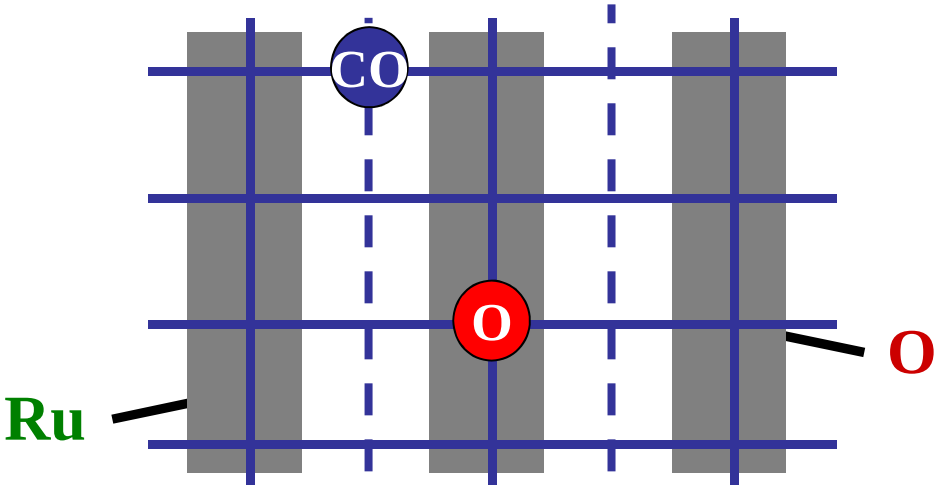








CO oxidation @ RuO_2(110)

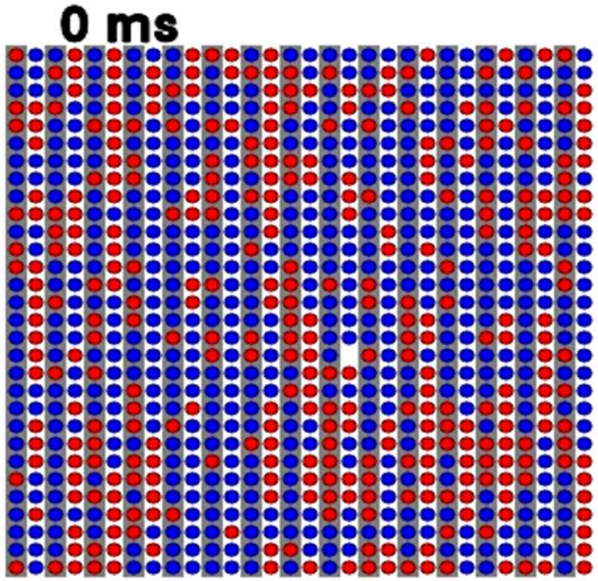


26 elementary processes (site-specific):

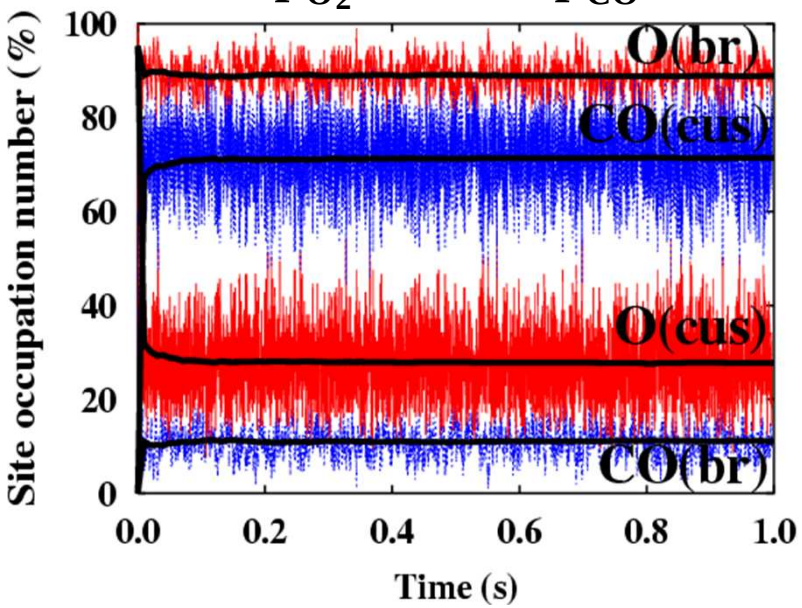
- **O_2 adsorption/desorption (dissociative/associative)**
- **CO adsorption/desorption (unimolecular)**
- **O and CO diffusion**
- **CO + O reaction**

K. Reuter, Oil&Gas Sci. Technol. 61, 471 (2006)
K. Reuter and M. Scheffler, Phys. Rev. B 73, 045433 (2006)

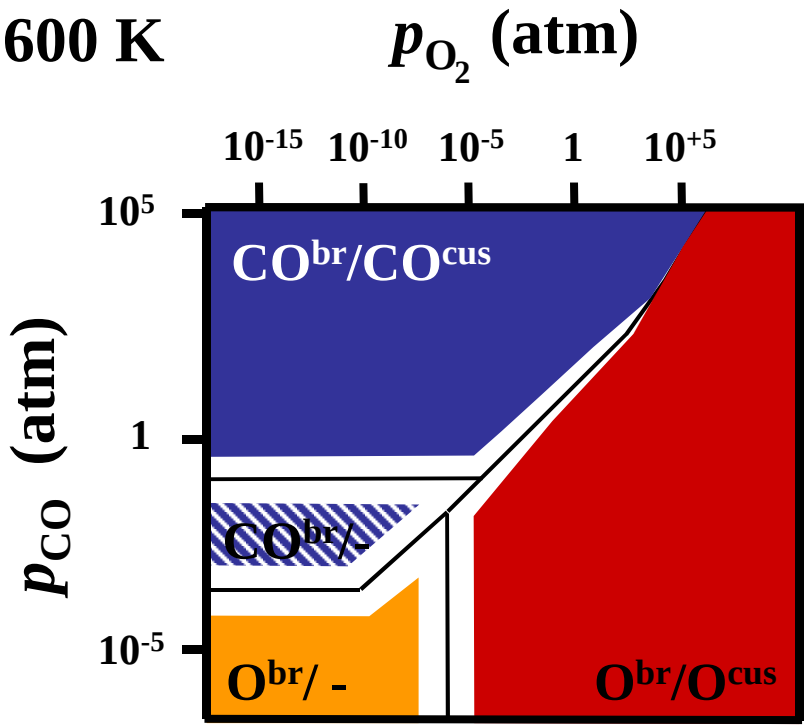
Surface structure and composition in the reactive environment



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

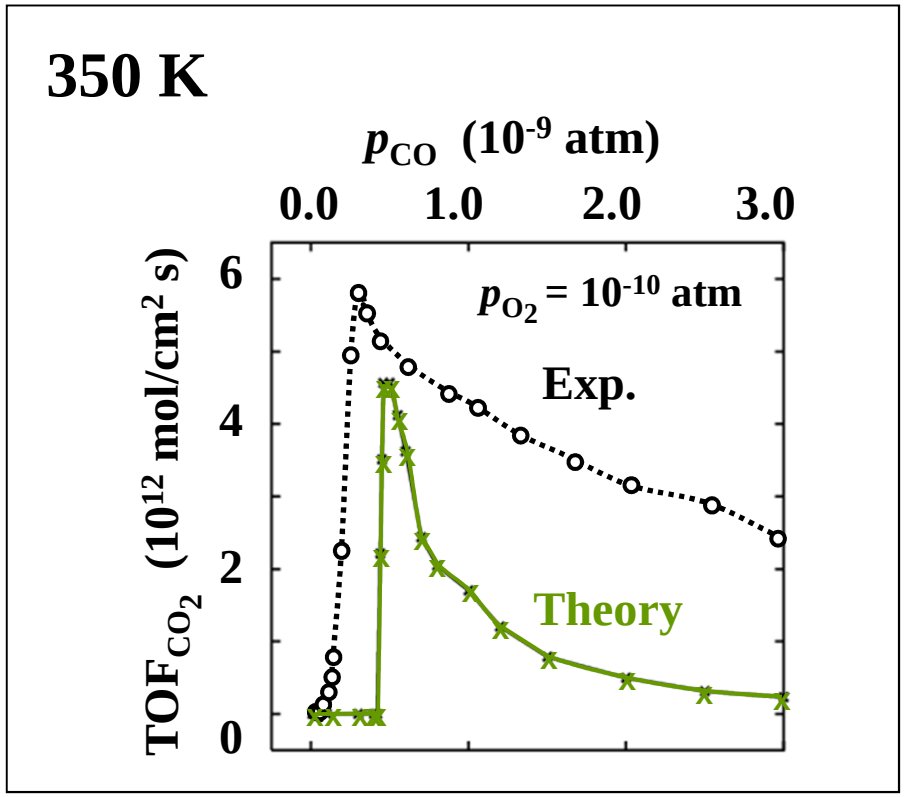


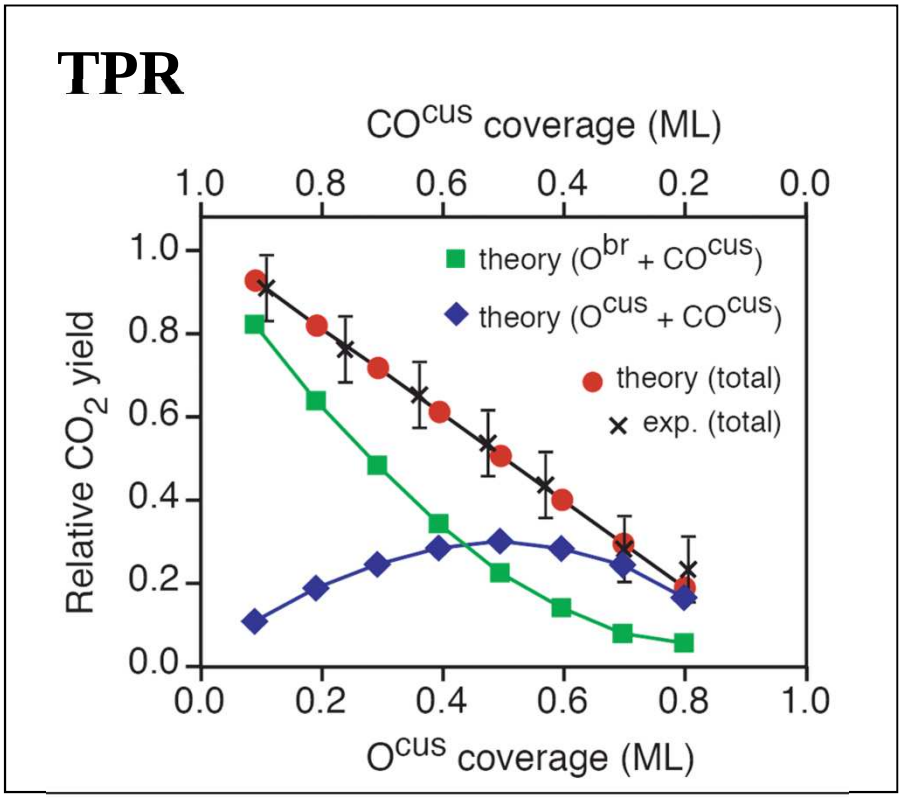
CO oxidation at RuO_2(110)



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

Steady-state and transient parameter-free turnover frequencies



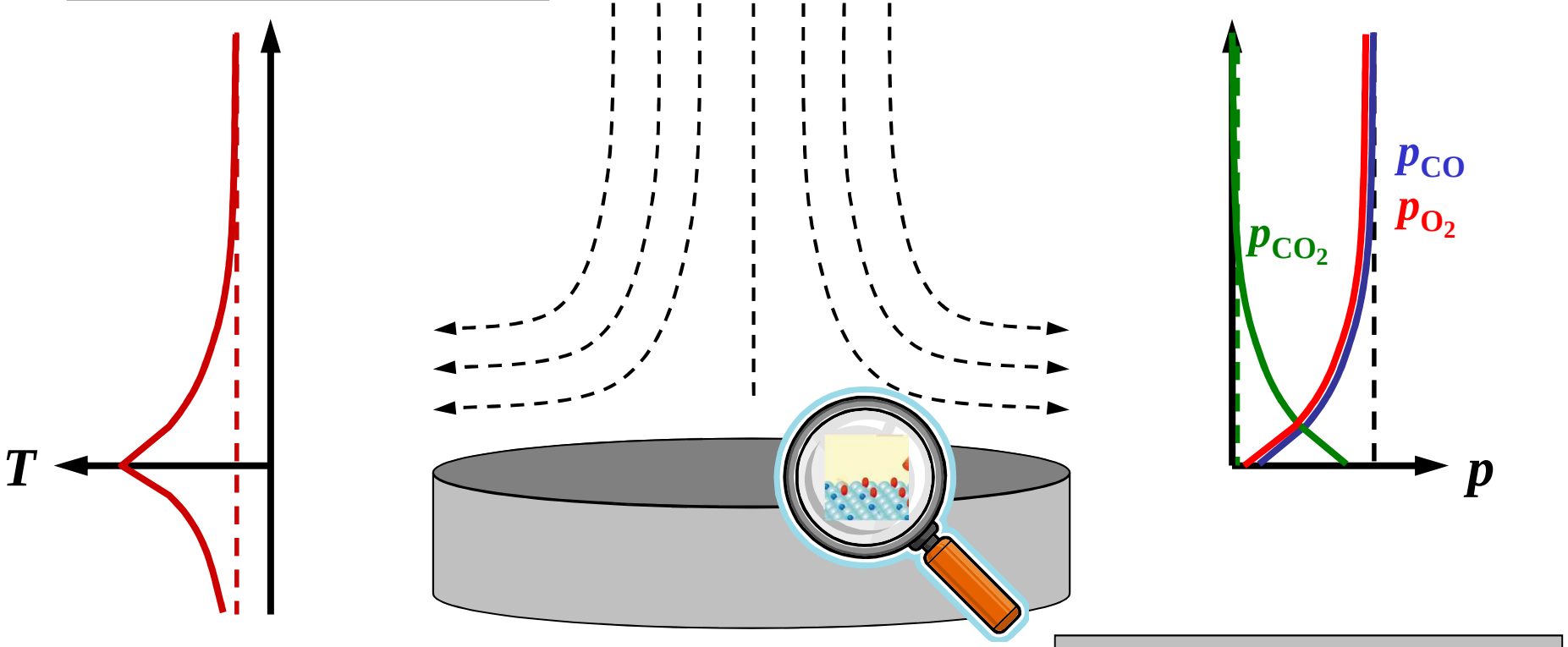


K. Reuter and M. Scheffler,
Phys. Rev. B 73, 045433 (2006)

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

Macroscopic regime: Heat and mass transfer

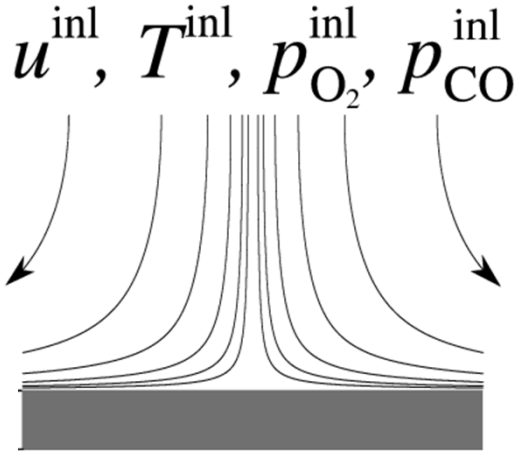
Computational Fluid Dynamics: Stationary stagnation point flow



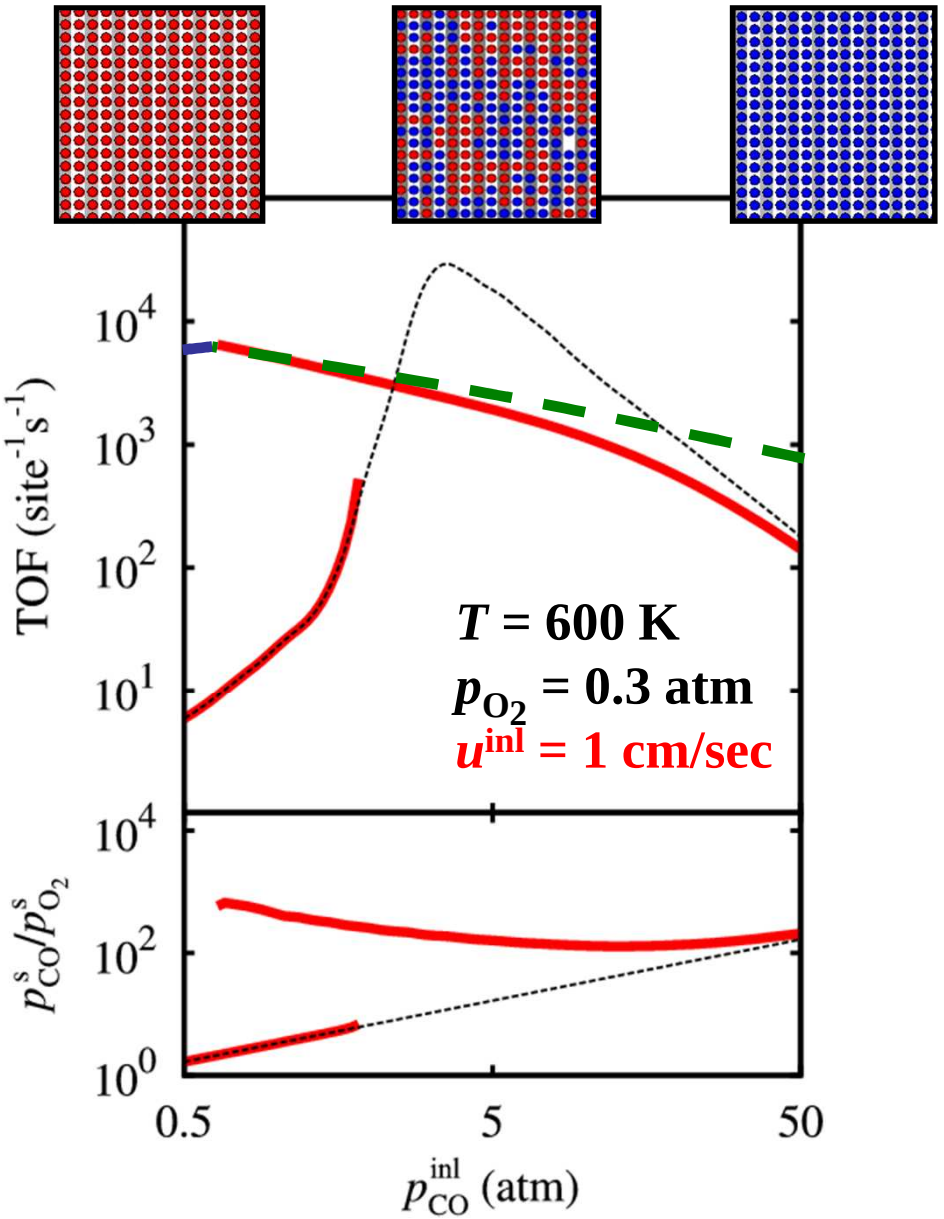
Chemical source terms from 1p-kMC

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

Isothermal limit: Mass transfer limitations



T = const



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

II. Towards error-controlled first-principles microkinetic models

Key ingredients to „predictive-quality“ microkinetic modeling

Accurate rate constants:

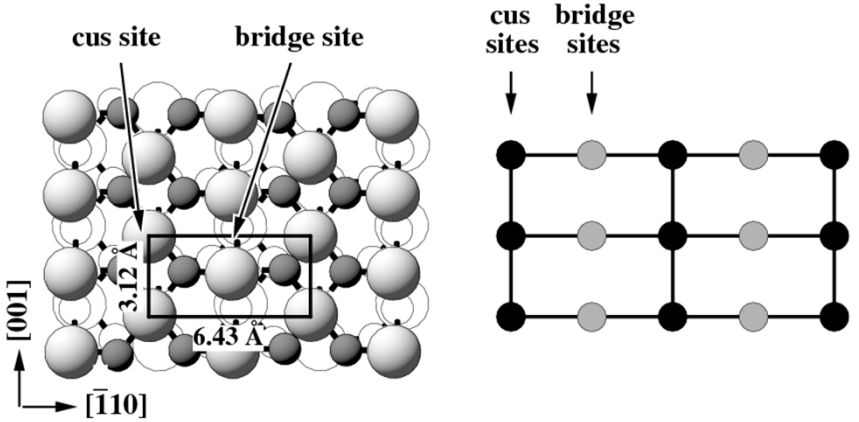
$$k_{i\to j} = \Gamma_{\circ} \exp\left(\frac{-\Delta E_{i\to j}}{k_{\mathrm{B}} T}\right)$$

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

Reaction mechanism:

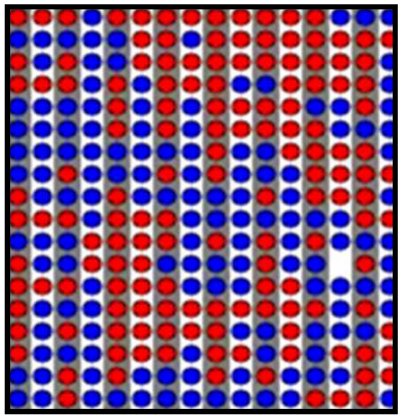
Process identification
Lattice mapping / spatial distributions
„Hot chemistry“ beyond Markov

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



Mean-field approximation: Phenomenological rate equations

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



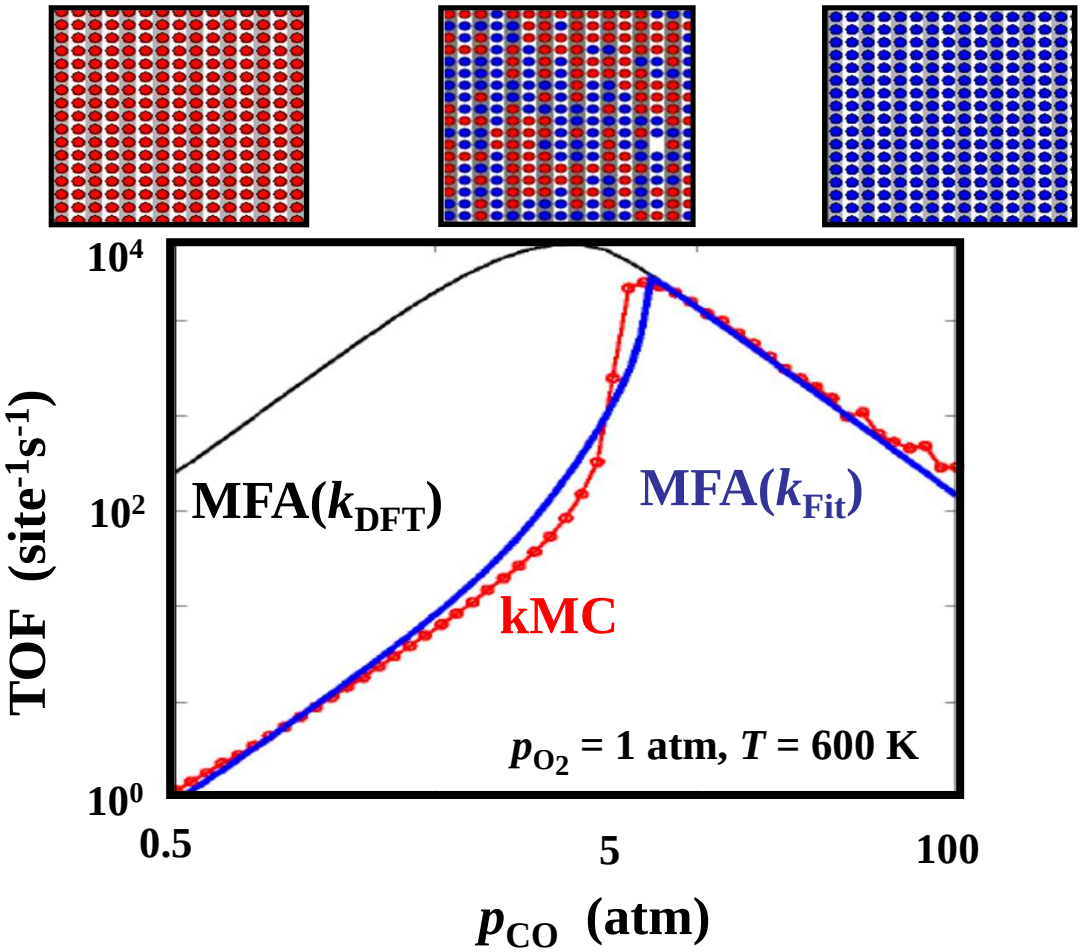
$\theta(\mathrm{O}^{\mathrm{cus}})$
$\theta(\mathrm{O}^{\mathrm{br}})$
$\theta(\mathrm{CO}^{\mathrm{cus}})$
$\theta(\mathrm{CO}^{\mathrm{br}})$

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

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

The „power“ of fitting

CO oxidation at $RuO_2(110)$

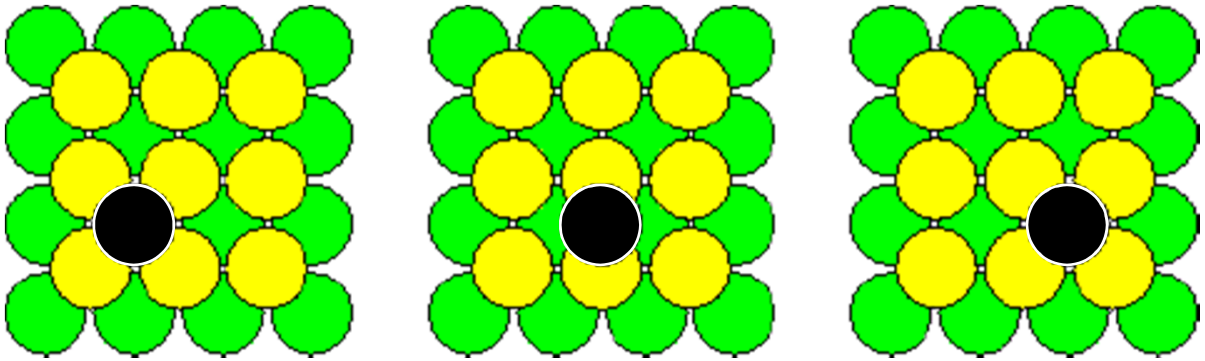


Fitted rate constants deviate from “real” rate constants by up to two orders in magnitude for dominant processes

Effective parameters without microscopic meaning

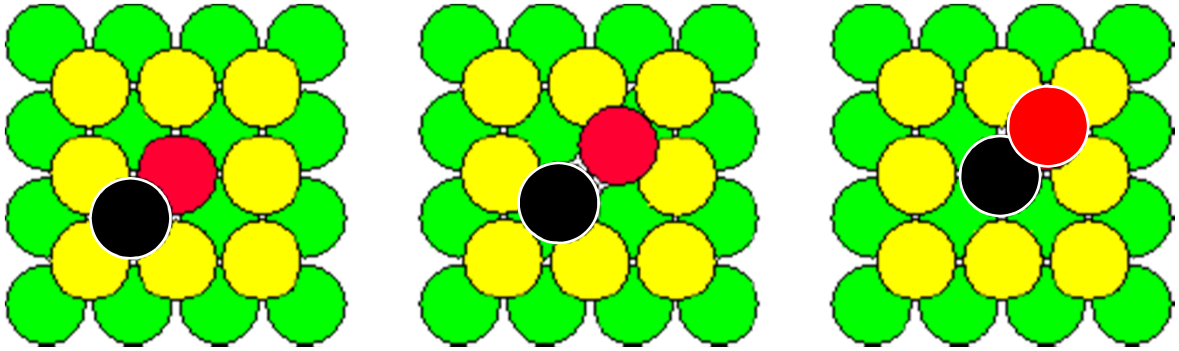
B. Temel *et al.*,
J. Chem. Phys. 126, 204711 (2007)

Diffusion at metal surfaces: surprises…



Hopping mechanism

Ag(100) ΔE **= 0.45 eV**
Au(100) ΔE **= 0.83 eV**



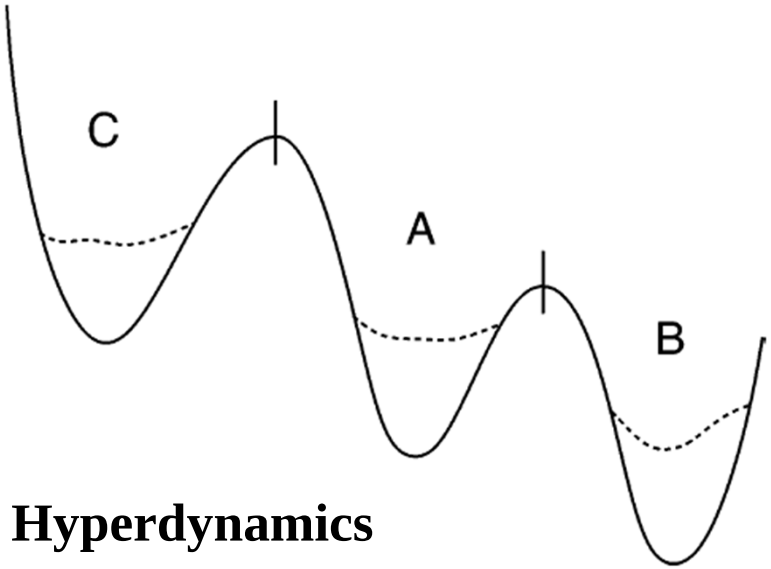
Exchange mechanism

Ag(100) ΔE **= 0.73 eV**
Au(100) ΔE **= 0.65 eV**

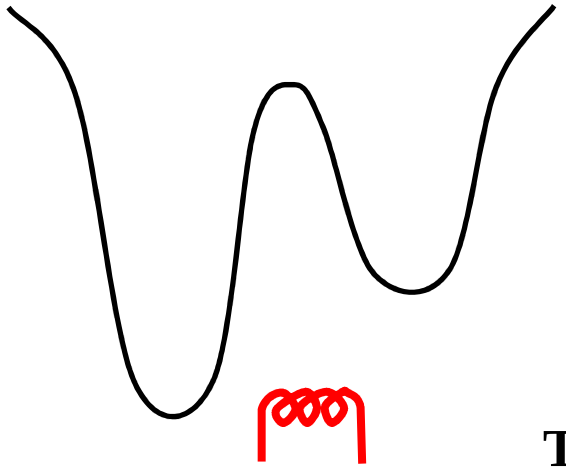
B.D. Yu and M. Scheffler, Phys. Rev. B 56, R15569 (1997)

Automatized process identification

Accelerated molecular dynamics:



Hyperdynamics



TAD

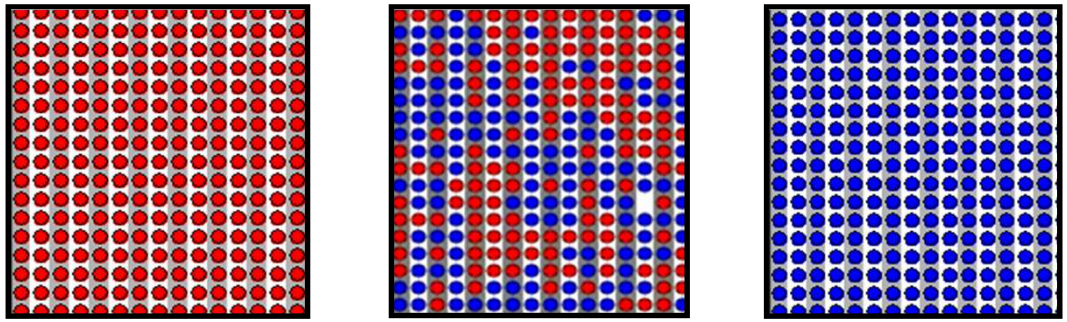
Other approaches:

- 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 $RuO_2(110)$

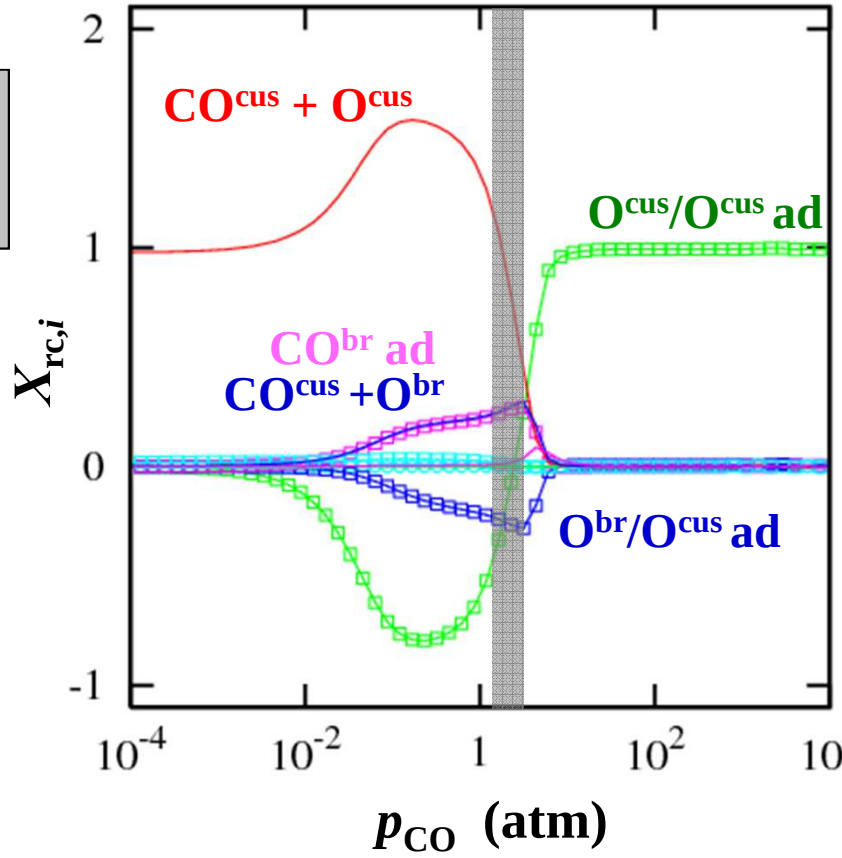


O-poisoned **CO-poisoned**

Sensitivity analysis:

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

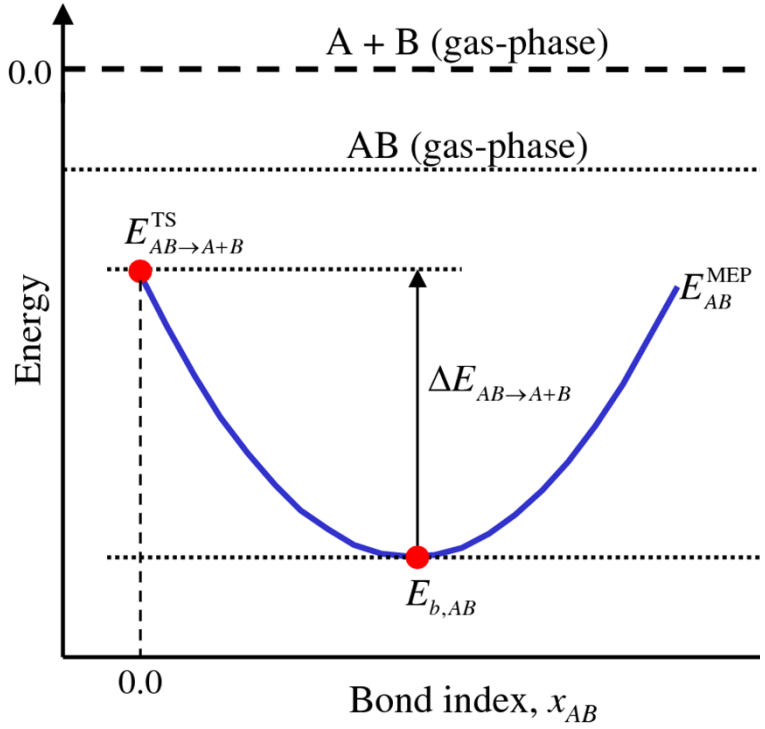
C.T. Campbell,
J. Catal. 204, 520 (2001);
Nature 432, 282 (2004)

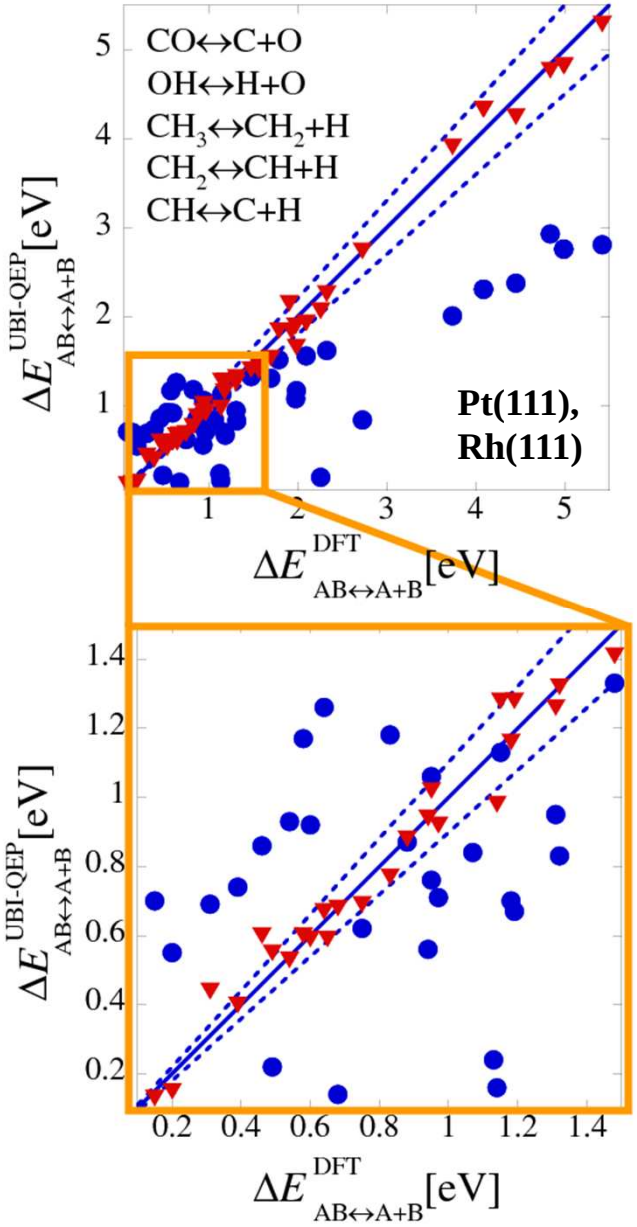


p_{O_2} = 1 atm
T = 600 K

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

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





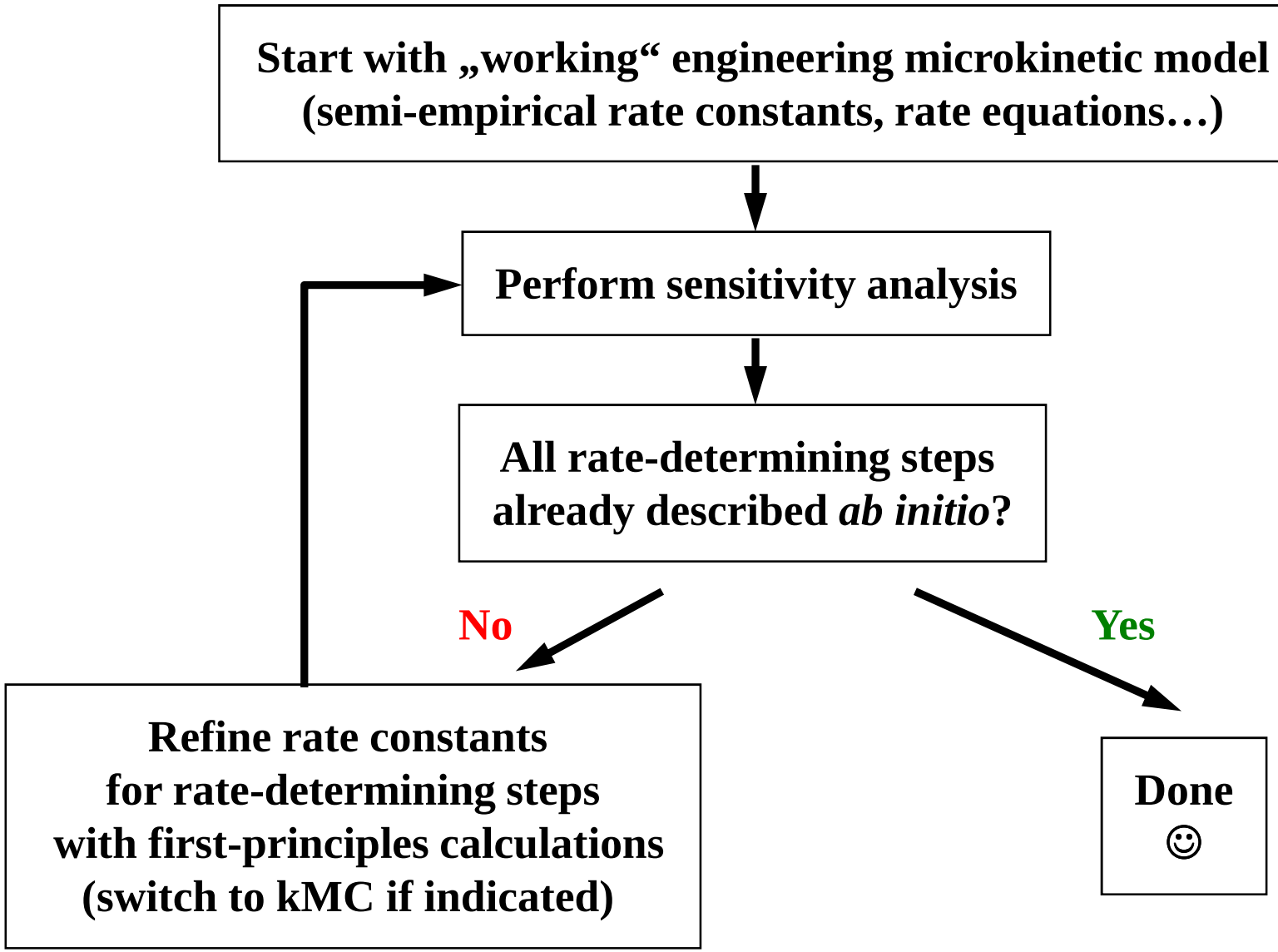
Unity Bond-Index Quadratic Exponential Potential

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

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

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

Tackling complexity: Bottom-up meets top-down



C1 microkinetic model for methane conversion to syngas on Rh/Al_2O_3

	No.	Reaction	A (unitless or s^{-1})	beta	Bond index	Activation Energy [kcal/mol]
H_2 oxidation	1	$H_2 + 2^* \rightarrow 2H^*$	7.73E-01	0.9387	0.50	0.0
	2	$2H^* \rightarrow H_2 + 2^*$	5.56E+11	-0.4347	0.50	$20.5+f(T)$
	3	$O_2 + 2^* \rightarrow 2O^*$	4.81E-02	1.9965	0.50	0.0
	4	$2O^* \rightarrow O_2 + 2^*$	4.31E+12	1.1995	0.50	$81.0 - 52.0\theta_O + f(T)$
	5	$OH^* + ^* \rightarrow H^* + O^*$	5.20E+12	-0.2659	0.30	$24.2 + f(\theta_O, \theta_H, \theta_{CO}, \theta_{H2O}, T)$
	6	$H^* + O^* \rightarrow OH^* + ^*$	4.69E+12	-0.8196	0.30	$14.2 + f(\theta_O, \theta_H, \theta_{CO}, \theta_{H2O}, T)$
	7	$H_2O^* + ^* \rightarrow H^* + OH^*$	5.74E+11	0.0281	0.55	$24.6 + f(\theta_O, \theta_{OH}, \theta_H, \theta_{CO}, \theta_{H2O}, T)$
	8	$H^* + OH^* \rightarrow H_2O^* + ^*$	1.80E+09	1.2972	0.55	$26.8 + f(\theta_O, \theta_{OH}, \theta_H, \theta_{CO}, \theta_{H2O}, T)$
	9	$H_2O^* + O^* \rightarrow 2OH^*$	2.08E+13	-2.1130	0.30	$11.4 + f(\theta_O, \theta_{OH}, \theta_{H2O}, T)$
	10	$2OH^* \rightarrow H_2O^* + O^*$	7.22E+10	-0.2902	0.30	$23.6 + f(\theta_O, \theta_{OH}, \theta_{H2O}, T)$
	11	$OH + ^* \rightarrow OH^*$	2.66E-01	-0.2891	0.50	0.0
	12	$OH^* \rightarrow OH + ^*$	1.14E+13	-0.9500	0.50	$70.0 - 33.0\theta_O - 25.0\theta_{H2O} + f(T)$
	13	$H_2O + ^* \rightarrow H_2O^*$	7.72E-02	1.4067	0.50	0.0
	14	$H_2O^* \rightarrow H_2O + ^*$	2.06E+13	-1.8613	0.50	$10.8 - 25.0\theta_{OH} - 4.5\theta_{H2O} + f(T)$
	15	$H + ^* \rightarrow H^*$	1.93E-01	1.6313	0.50	0.0
	16	$H^* \rightarrow H + ^*$	2.40E+12	1.3208	0.50	$62.3 - 2.5\theta_H - 3.7\theta_{CO} + f(T)$
	17	$O + ^* \rightarrow O^*$	4.46E-02	-1.9236	0.50	0.0
CO oxidation	18	$O^* \rightarrow O + ^*$	9.74E+12	-1.9701	0.50	$100.0 - 26.0\theta_O + f(T)$
	19	$CO + ^* \rightarrow CO^*$	5.00E-01	-2.0000	0.50	0.0
	20	$CO^* \rightarrow CO + ^*$	5.65E+12	1.9879	0.50	$38.5 - 3.7\theta_H - 15.0\ \theta_{CO} + f(T)$
	21	$CO_2 + ^* \rightarrow CO_2^*$	3.67E-01	-2.3294	0.50	0.0
	22	$CO_2^* \rightarrow CO_2 + ^*$	7.54E+10	2.1831	0.50	$5.2 + f(T)$
	23	$CO_2^* + ^* \rightarrow CO^* + O^*$	4.12E+09	1.9698	0.90	$19.5 + f(\theta_O, \theta_H, \theta_{CO}, T)$
	24	$CO^* + O^* \rightarrow CO_2^* + ^*$	3.27E+09	1.3560	0.90	$25.6 + f(\theta_O, \theta_H, \theta_{CO}, T)$
coupling H_2 & CO	25	$COOH + ^* \rightarrow COOH^*$	5.34E-01	-1.0767	0.50	0.0
	26	$COOH^* \rightarrow COOH + ^*$	1.12E+11	1.6803	0.50	$62.2+f(T)$
	27	$HCOO + 2^* \rightarrow HCOO^{**}$	1.89E-02	-0.5548	0.50	0.0
	28	$HCOO^{**} \rightarrow HCOO + 2^*$	3.74E+13	0.5548	0.50	$69.2+f(T)$
	29	$CO_2^* + H^* \rightarrow CO^* + OH^*$	1.60E+13	0.0301	0.70	$6.1 + f(\theta_O, \theta_H, \theta_{CO}, \theta_{H2O}, T)$
	30	$CO^* + OH^* \rightarrow CO_2^* + H^*$	1.40E+13	-0.0301	0.70	$22.2 + f(\theta_O, \theta_H, \theta_{CO}, \theta_{H2O}, T)$

M. Maestri *et al.*, AIChE J. 55, 993 (2009)

C1 microkinetic model for methane conversion to syngas on Rh/Al_2O_3

coupling H_2 & CO

CH_4 pyro-lisis

No.	Reaction	A (unitless or s^{-1})	beta	Bond index	Activation Energy [kcal/mol]
31	$COOH^*+^* \rightarrow CO^*+OH^*$	1.07E+12	-0.4123	0.50	$6.2 + f(\theta_O, \theta_H, \theta_{CO}, \theta_{H2O}, T)$
32	$CO^*+OH^* \rightarrow COOH^*+^*$	9.37E+11	0.4123	0.50	$18.6 + f(\theta_O, \theta_H, \theta_{CO}, \theta_{H2O}, T)$
33	$COOH^*+^* \rightarrow CO_2^*+H^*$	1.00E+10	-0.4424	0.80	$6.8 + f(\theta_H, \theta_{CO}, T)$
34	$CO_2^*+H^* \rightarrow COOH^*+^*$	9.99E+09	0.4424	0.80	$3.1 + f(\theta_H, \theta_{CO}, T)$
35	$CO^* + H_2O^* \rightarrow COOH^* + H^*$	3.34E+11	-0.2222	0.80	$33.1 + f(\theta_{OH}, \theta_H, \theta_{CO}, \theta_{H2O}, T)$
36	$COOH^* + H^* \rightarrow CO^* + H_2O^*$	1.20E+09	0.2223	0.80	$22.9 + f(\theta_{OH}, \theta_H, \theta_{CO}, \theta_{H2O}, T)$
37	$CO_2^* + OH^* \rightarrow COOH^* + O^*$	1.05E+11	0.7192	0.50	$22.3 + f(\theta_O, \theta_{H2O}, T)$
38	$COOH^* + O^* \rightarrow CO_2^* + OH^*$	9.51E+10	-0.7192	0.50	$16.0 + f(\theta_O, \theta_{H2O}, T)$
39	$CO_2^* + H_2O^* \rightarrow COOH^* + OH^*$	1.78E+12	-0.1922	0.50	$13.5 + f(\theta_O, \theta_{OH}, \theta_{H2O}, T)$
40	$COOH^* + OH^* \rightarrow CO_2^* + H_2O^*$	5.60E+09	0.1922	0.50	$19.4 + f(\theta_O, \theta_{OH}, \theta_{H2O}, T)$
41	$CO_2^*+H^* \rightarrow HCOO^{**}$	1.04E+09	1.1254	0.50	$4.3 + f(\theta_H, \theta_{CO}, T)$
42	$HCOO^{**} \rightarrow CO_2^*+H^*$	3.86E+13	-1.1253	0.50	$0.0 + f(\theta_H, \theta_{CO}, T)$
43	$CO_2^* + OH^* + ^* \rightarrow HCOO^{**} + O^*$	1.09E+09	1.4022	0.50	$27.6 + f(\theta_O, \theta_{H2O}, T)$
44	$HCOO^{**} + O^* \rightarrow CO_2^* + OH^* + ^*$	3.67E+13	-1.4022	0.50	$13.4 + f(\theta_O, \theta_{H2O}, T)$
45	$CO_2^* + H_2O^* + ^* \rightarrow HCOO^{**} + OH^*$	9.24E+09	0.4908	0.50	$18.4 + f(\theta_O, \theta_{OH}, \theta_{H2O}, T)$
46	$HCOO^{**} + OH^* \rightarrow CO_2^* + H_2O^* + ^*$	1.08E+12	-0.4908	0.50	$16.4 + f(\theta_O, \theta_{OH}, \theta_{H2O}, T)$
48	$C^* \rightarrow C + ^*$	3.54E+04	1.8618	0.50	$159.0 + f(T)$
49	$CH + ^* \rightarrow CH^*$	2.29E-02	-1.0798	0.50	0.0
50	$CH^* \rightarrow CH + ^*$	3.08E+13	1.0798	0.50	$151.2 + f(T)$
51	$CH_2 + ^* \rightarrow CH_2^*$	4.09E-02	-0.4265	0.50	0.0
52	$CH_2^* \rightarrow CH_2 + ^*$	1.73E+13	0.4265	0.50	$109.3 + f(T)$

M. Maestri *et al.*, AIChE J. 55, 993 (2009)

C1 microkinetic model for methane conversion to syngas on Rh/Al_2O_3

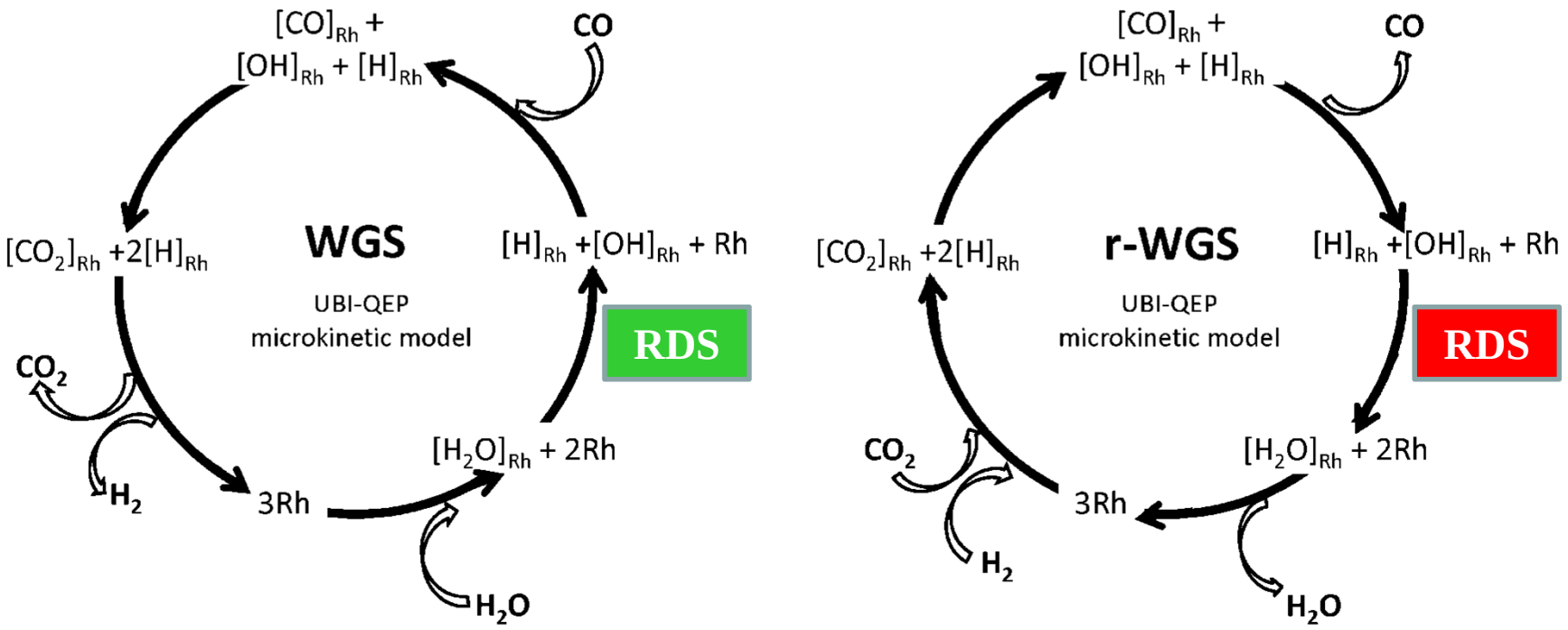
CH_4 pyrolisis

CH_4 oxidation

No.	Reaction	A (unitless or s^{-1})	beta	Bond index	Activation Energy [kcal/mol]
53	$CH_3 + * \rightarrow CH_3*$	1.35E-01	0.0326	0.50	0.0
54	$CH_3* \rightarrow CH_3 + *$	5.22E+12	-0.0325	0.50	42.4+$f(T)$
55	$CH_4 + 2* \rightarrow CH_3* + H*$	5.72E-01	0.7883	0.50	9.7 + $f(\theta_H, \theta_{CO}, T)$
56	$CH_3* + H* \rightarrow CH_4 + 2*$	7.72E+10	-0.7883	0.50	9.5 + $f(\theta_H, \theta_{CO}, T)$
57	$CH_3* + * \rightarrow CH_2* + H*$	2.49E+10	0.0862	0.50	10.6 + $f(\theta_H, \theta_{CO}, T)$
58	$CH_2* + H* \rightarrow CH_3* + *$	2.57E+09	-0.0862	0.50	29.1 + $f(\theta_H, \theta_{CO}, T)$
59	$CH_2* + * \rightarrow CH* + H*$	5.50E+10	-0.1312	0.50	20.5 + $f(\theta_H, \theta_{CO}, T)$
60	$CH* + H* \rightarrow CH_2* + *$	7.27E+09	0.1312	0.50	23.6 + $f(\theta_H, \theta_{CO}, T)$
61	$CH* + * \rightarrow C* + H*$	4.58E+12	-0.2464	0.50	27.6 + $f(\theta_H, \theta_{CO}, T)$
62	$C* + H* \rightarrow CH* + *$	2.18E+11	0.2464	0.50	17.1 + $f(\theta_H, \theta_{CO}, T)$
63	$CH_3* + O* \rightarrow CH_2* + OH*$	2.86E+11	-0.1906	0.70	10.0 + $f(\theta_O, \theta_{H2O}, T)$
64	$CH_2* + OH* \rightarrow CH_3* + O*$	3.38E+10	0.1906	0.70	38.4 + $f(\theta_O, \theta_{H2O}, T)$
65	$CH* + OH* \rightarrow CH_2* + O*$	3.83E+10	0.4081	0.70	45.7 + $f(\theta_O, \theta_{H2O}, T)$
66	$CH_2* + O* \rightarrow CH* + OH*$	2.61E+11	-0.4081	0.70	32.6 + $f(\theta_O, \theta_{H2O}, T)$
67	$C* + OH* \rightarrow CH* + O*$	2.30E+10	0.5232	0.50	29.8 + $f(\theta_O, \theta_{H2O}, T)$
68	$CH* + O* \rightarrow C* + OH*$	4.35E+11	-0.5232	0.50	30.4 + $f(\theta_O, \theta_{H2O}, T)$
69	$CH_2* + H_2O* \rightarrow CH_3* + OH*$	5.73E+10	-0.7208	0.70	29.9 + $f(\theta_O, \theta_{OH}, \theta_{H2O}, T)$
70	$CH_3* + OH* \rightarrow CH_2* + H_2O*$	1.74E+09	0.7208	0.70	13.6 + $f(\theta_O, \theta_{OH}, \theta_{H2O}, T)$
71	$CH* + H_2O* \rightarrow CH_2* + OH*$	6.49E+11	-0.5033	0.70	21.8 + $f(\theta_O, \theta_{OH}, \theta_{H2O}, T)$
72	$CH_2* + OH* \rightarrow CH* + H_2O*$	1.54E+10	0.5033	0.70	20.9 + $f(\theta_O, \theta_{OH}, \theta_{H2O}, T)$
73	$C* + H_2O* \rightarrow CH* + OH*$	9.74E+11	-0.3882	0.50	10.5 + $f(\theta_O, \theta_{OH}, \theta_{H2O}, T)$
74	$CH* + OH* \rightarrow C* + H_2O*$	6.41E+10	0.3882	0.50	23.3 + $f(\theta_O, \theta_{OH}, \theta_{H2O}, T)$
75	$CO* + * \rightarrow C* + O*$	1.25E+09	0.5712	0.50	49.1 + $f(\theta_O, \theta_H, \theta_{CO}, T)$
76	$C* + O* \rightarrow CO* + *$	7.22E+09	-0.5712	0.50	12.3 + $f(\theta_O, \theta_H, \theta_{CO}, T)$
77	$CO* + H* \rightarrow CH* + O*$	9.07E+09	0.8176	0.80	69.1 + $f(\theta_O, \theta_H, \theta_{CO}, T)$
78	$CH* + O* \rightarrow CO* + H*$	1.10E+12	-0.8176	0.80	42.9 + $f(\theta_O, \theta_H, \theta_{CO}, T)$
79	$CO* + H* \rightarrow C* + OH*$	1.18E+12	0.2944	0.15	26.8 + $f(\theta_O, \theta_H, \theta_{CO}, \theta_{H2O}, T)$
80	$C* + OH* \rightarrow CO* + H*$	7.60E+12	-0.2944	0.15	0.0 + $f(\theta_O, \theta_H, \theta_{CO}, \theta_{H2O}, T)$
81	$2CO* \rightarrow C* + CO_2*$	1.11E+09	0.2644	0.50	42.9 + $f(\theta_H, \theta_{CO}, T)$
82	$C* + CO_2* \rightarrow 2CO*$	8.10E+09	-0.2644	0.50	0.0 + $f(\theta_H, \theta_{CO}, T)$

M. Maestri *et al.*, AIChE J. 55, 993 (2009)

Identified key issues: Water-gas shift and r-WGS

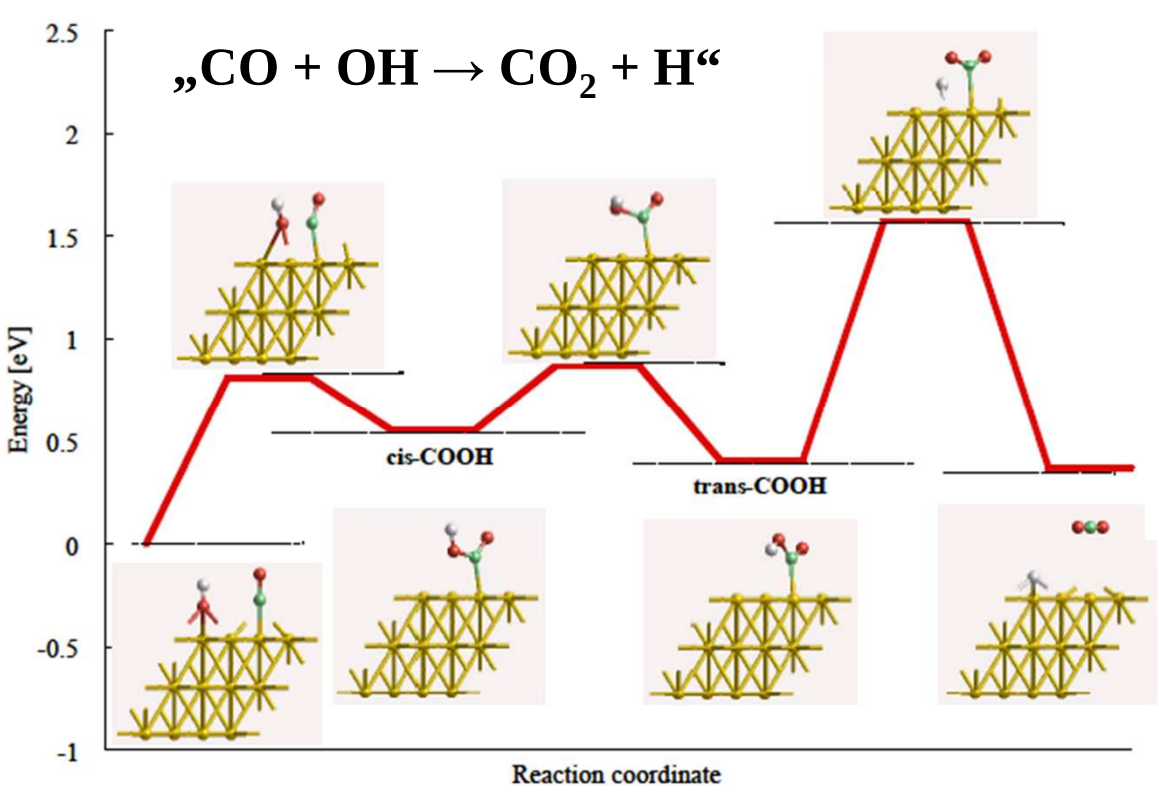


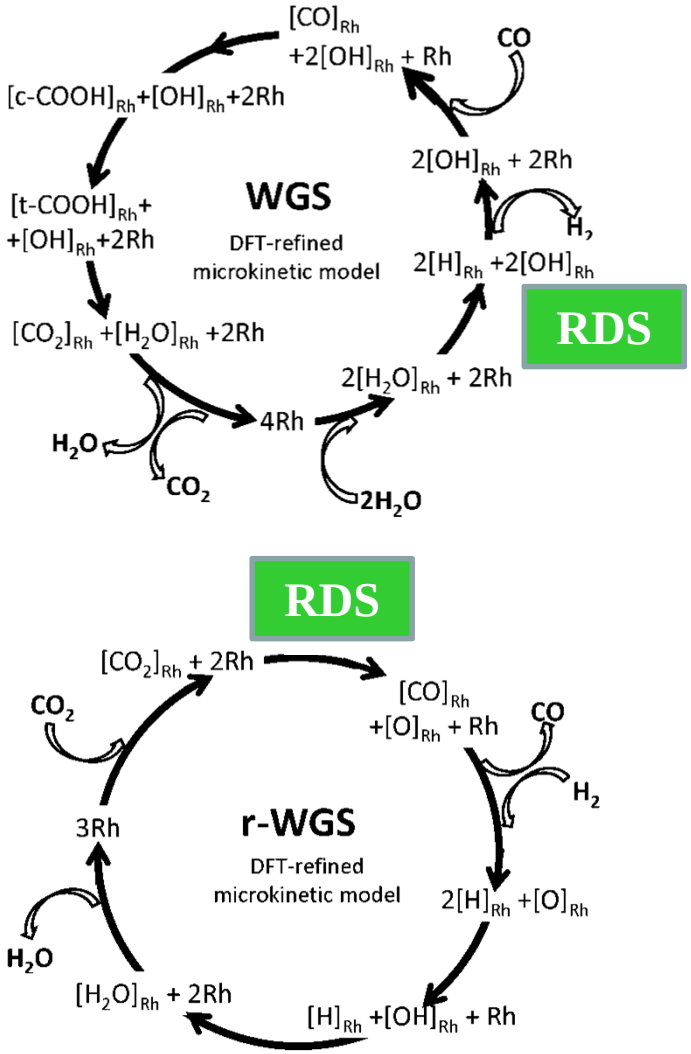
CO_2/CO ratio not well captured by the model, pointing at an incorrect description of WGS pathways

Same RDS for WGS/r-WGS inconsistent with experimental data

M. Maestri *et al.*, Topics Catal. 52, 1983 (2009)

First-principles refinement:
When an „elementary step“ is not elementary…





WGS proceeds through carboxyl mechanism

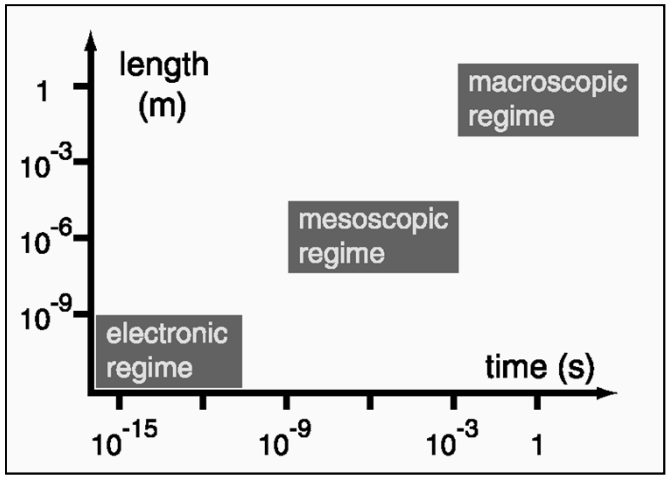
New RDS consistent with all experimental data

M. Maestri and K. Reuter (submitted)

Multiscale catalysis modeling: From hype to reality

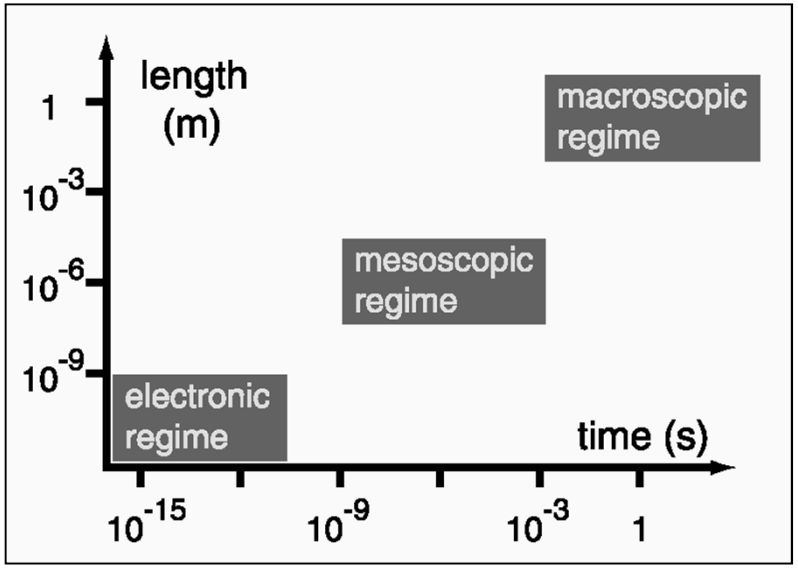
State-of-the-art in catalysis modeling:

- **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* dual-scale modeling**
  first-principles kinetic Monte Carlo simulations for heterogeneous catalysis



Steps towards a predictive character multiscale catalysis modeling:

- **Replace effective parameters by first-principles data**
  fitted vs. DFT-based rate constants
- **Refined modeling at each individual level**
  necessity to resolve spatial arrangement at surface
  integrate first-principles surface chemistry into reactor models
- **Robust links between theories that enable reverse-mapping**
  sensitivity analysis to control flow of error across scales



www.th4.ch.tum.de