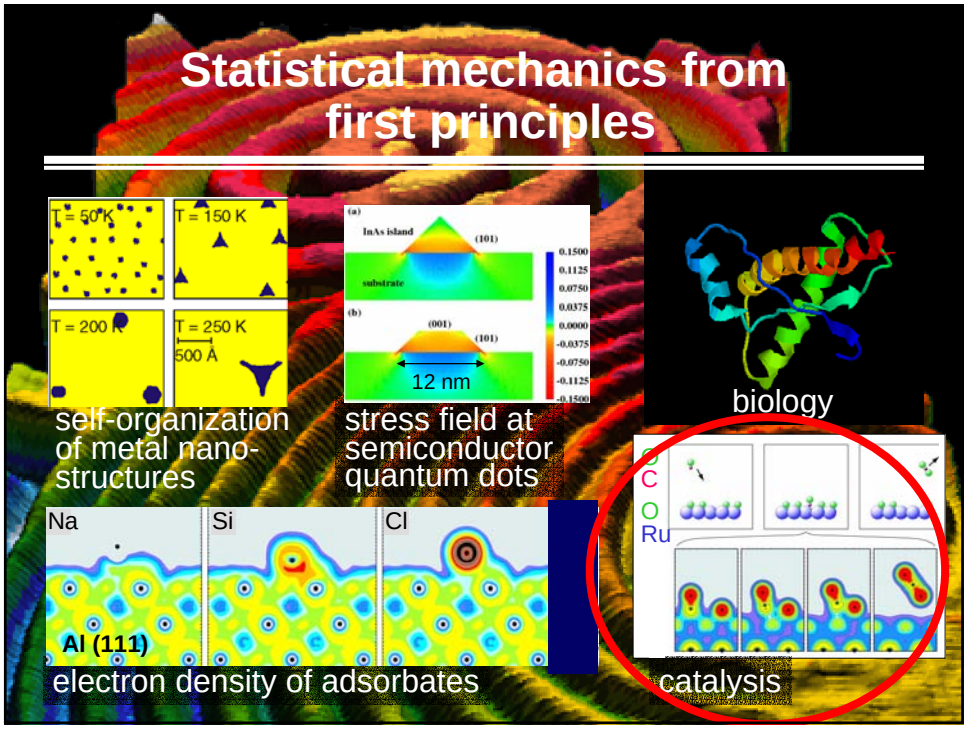
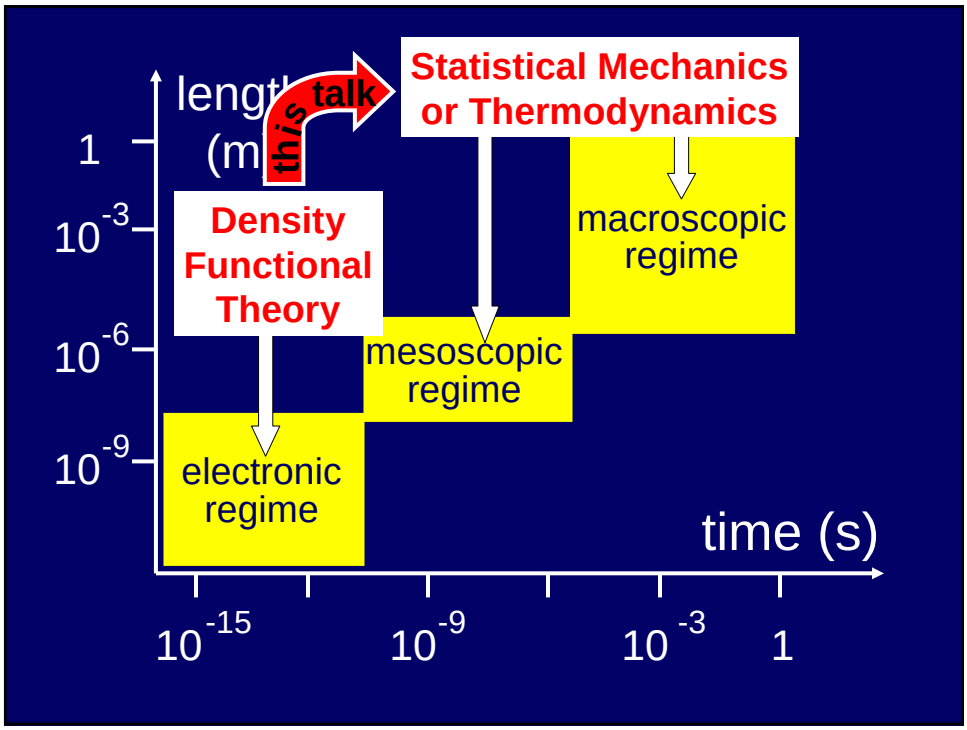
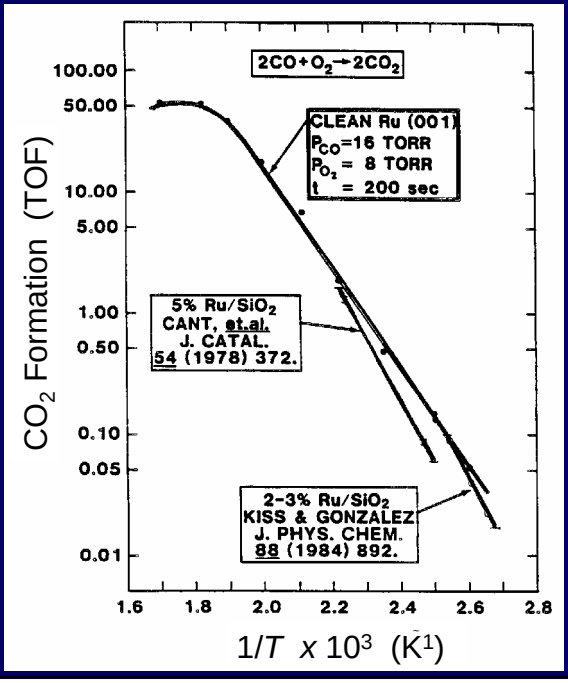

Statistical mechanics from first principles
T = 50 K
T = 150 K
T = 200 K
T = 250 K
500 Å
self-organization of metal nano-structures
InAs island
substrate
(101)
(001)
12 nm
stress field at semiconductor quantum dots
biology
Na
Si
Cl
Al (111)
electron density of adsorbates
O
C
O
Ru
catalysis


this talk
Statistical Mechanics or Thermodynamics
Density Functional Theory
macroscopic regime
mesoscopic regime
electronic regime
1
10^{-3}
10^{-6}
10^{-9}
time (s)
10^{-15}
10^{-9}
10^{-3}
1

Oxidation catalysis, e.g.:

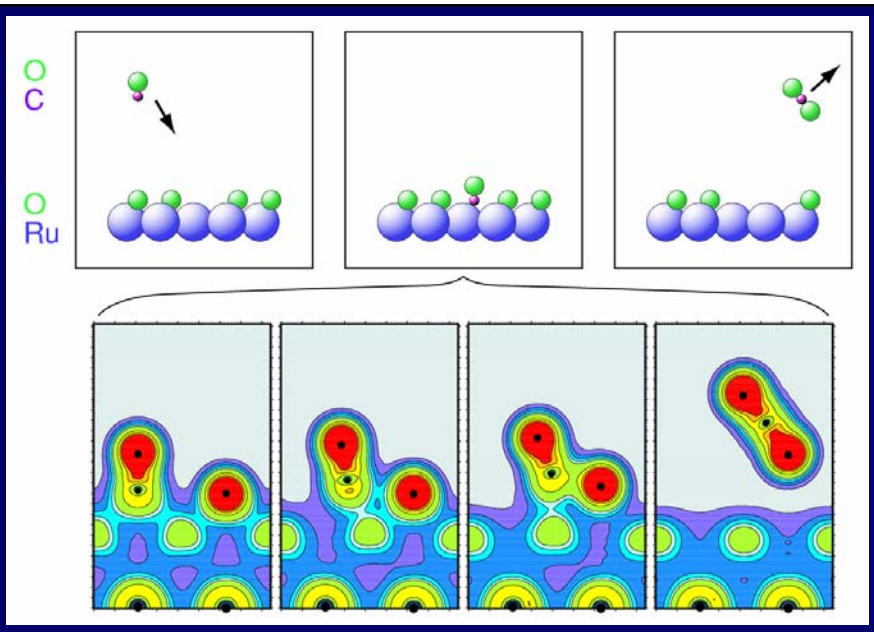
$$CO + \tfrac{1}{2}\, O_2 \rightarrow CO_2$$

A "simple", prototypical surface chemical reaction



CO_2 formation at Ru supported catalysts and Ru single crystals.

At UHV conditions Ru is least active for CO oxidation. At high-pressure conditions it is best.

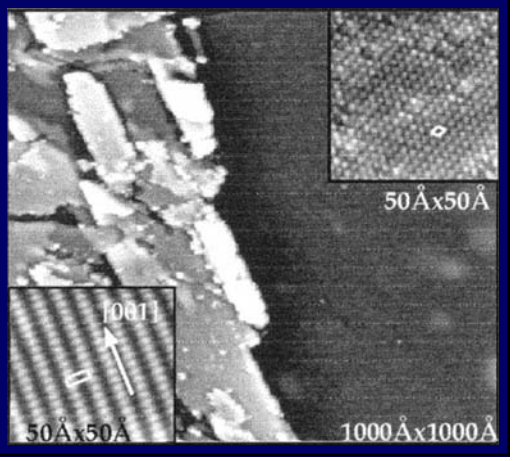


C. Stampfl, M.Scheffler, Surf. Sci. 433-435, 119 (1999),
M. Scheffler and C. Stampfl, in Handbook of Surface Science (2000)

Transition-metals oxides as oxidation catalysts ? !

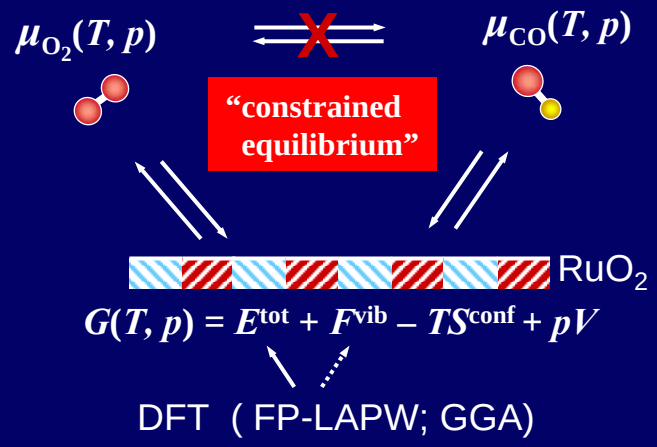
Catalytic activity of Ru(0001) is due to RuO_2(110) domains (1-2 nm thin films), that form in the re-active environment.

H. Over, Y.D. Kim, A.P. Seitsonen, S. Wendt, A. Morgante, E. Lundgren, M. Schmid, P. Varga, and G. Ertl, Science 287 (2000)



Also:
A. Böttcher, et al.,
Surf. Sci. 466, L811 (2000) ;
L. Zang and H. Kisch,
Angew. Chem. 112, 4075 (2000)

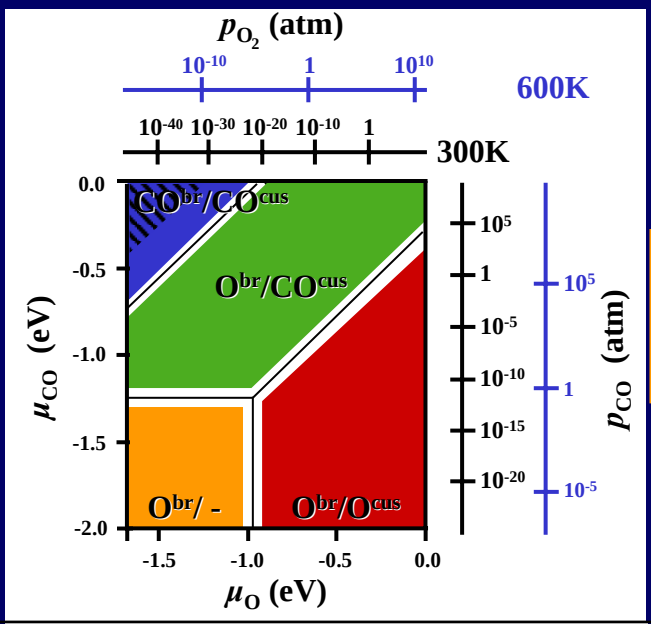
Ab initio atomistic thermodynamics



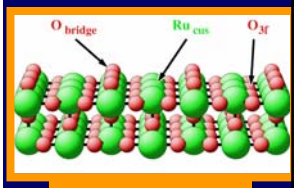
$$\mu_O(T, p) = \tfrac{1}{2}\,\mu_{O_2}(T, p^0) + \tfrac{1}{2}\,kT\ln(p/p^0)$$

C.M. Weinert and M.S., Mat. Sci. Forum 10-12, 25 (1986).
Reuter and M. S., PRL 90, 046103 (2003).

RuO_2 (110) stability regions in (*T*,*p*) space



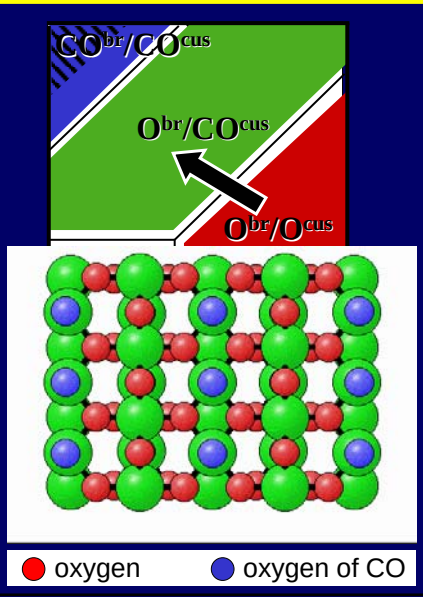
For a "constrained equilibrium"

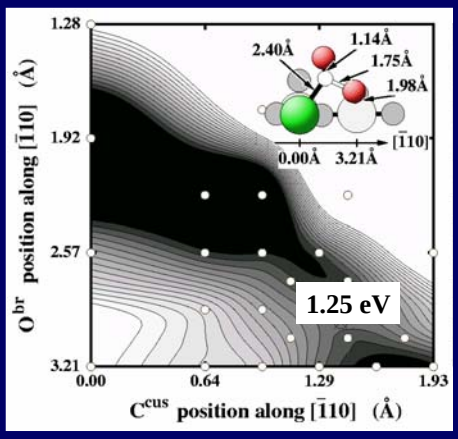


UHV surface termination

K. Reuter & M.S., PRL 90, 046103 (2003)

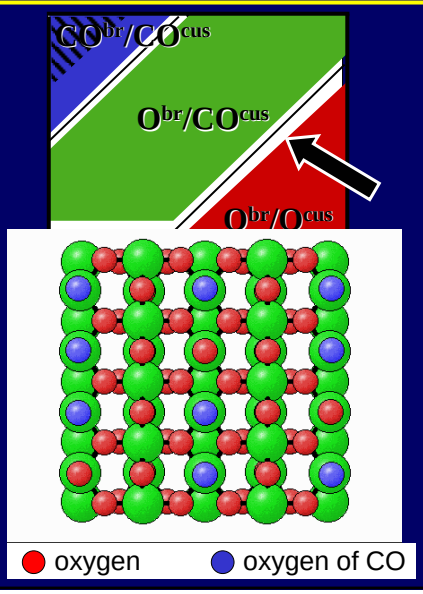
Possible reaction mechanisms:
$CO^{cus} + O^{br} \rightarrow CO_2$

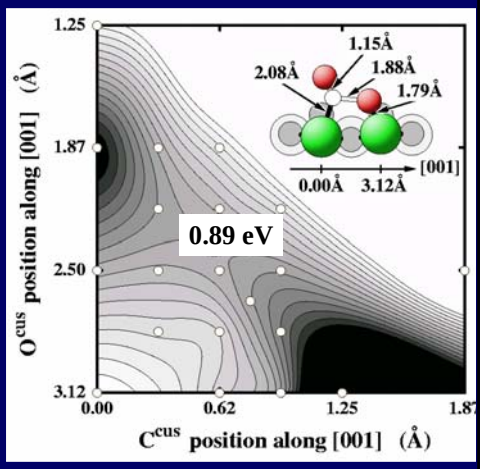




K. Reuter & M.S., PRL 90, 046103 (2003) and PRB in print

Possible reaction mechanisms:
$CO^{cus} + O^{cus} \rightarrow CO_2$





K. Reuter & M.S., PRL 90, 046103 (2003) and PRB in print

Kinetics of catalysis from first principles
-- *example*: CO + ½ O_2 ⟶ CO_2 --

1) Analysis of all possibly relevant processes using density-functional theory
2) Calculate the rates of all important processes

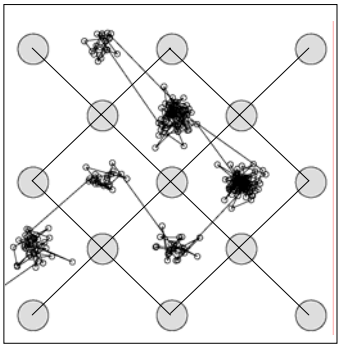
$$\Gamma^{(i)} = \Gamma_0^{(i)} \exp(\Delta E^{(i)} / k_B T)$$

3) Statistical approach to describe
   - dissociation, adsorption, desorption
   - diffusion
   - reaction (CO_2 formation)
   - desorption of the product

➡ **kinetic Monte Carlo method**

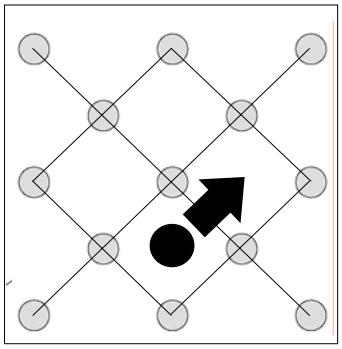
movies

Kinetic Monte Carlo: Coarse-Graining MD



Molecular Dynamics of Co on Cu(001): The whole trajectory.

ab initio MD: up to 50 ps

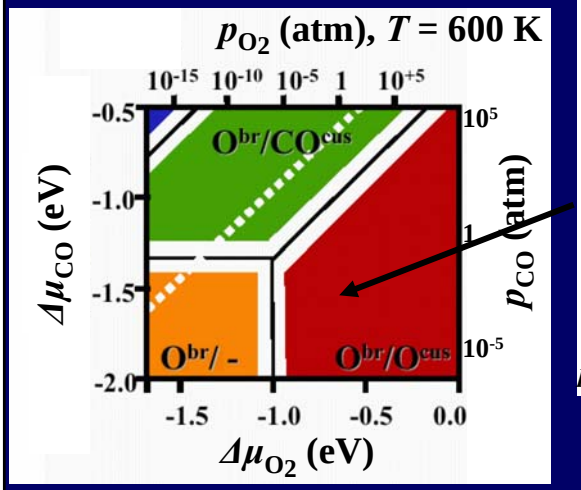


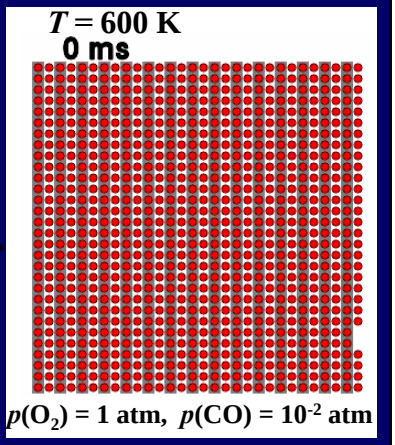
Kinetic Monte Carlo simulation: Coarse-grained hops.

ab initio kMC: up to minutes

RuO_2 (110) stability regions in (T, p) space

K. Reuter and M.S., PRL to be published.

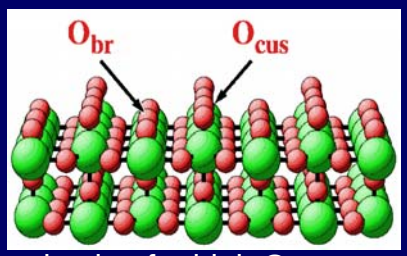




cus sites: white background
bridge sites: grey background

oxygen CO

Oxidation catalysis at RuO_2 (110)

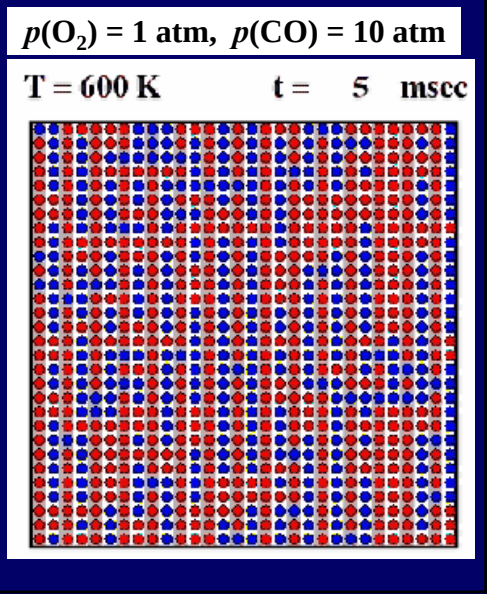


termination for high O_2 pressure

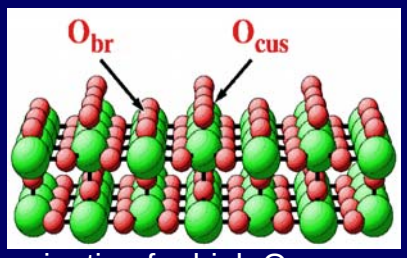
oxygen CO

cus sites: white background
bridge sites: grey background

K. Reuter, D. Frenkel, M.S., PRL to be published.



Oxidation catalysis at RuO_2 (110)



termination for high O_2 pressure

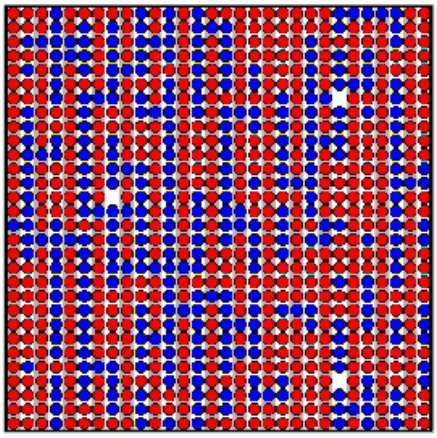
oxygen CO

cus sites: white background
bridge sites: grey background

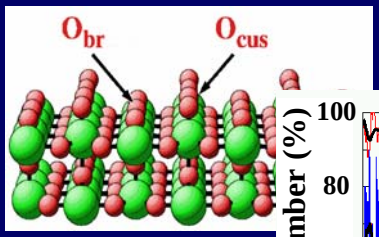
The rate is $r_{CO2} = 10^{18}$ cm^{-2} s^{-1} .

$p(O_2)$ = 1 atm, p(CO) = 10 atm

T = 600 K t = 2 nsec



Site occupation statistics at the steady state (strong fluctuations)



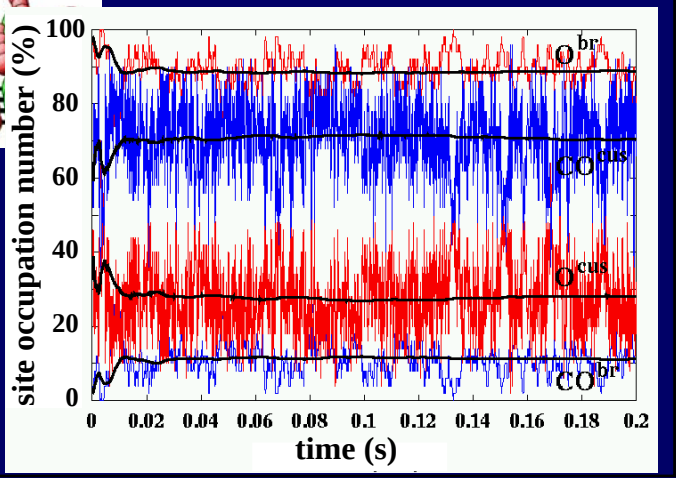
K. Reuter, D. Frenkel, and M.S., PRL to be published.

Reaction energy barriers (eV)

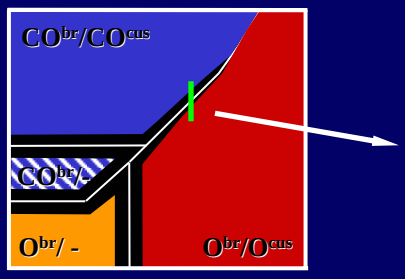
$CO^{cus} + O^{cus}$: 0.9

$CO^{br} + O^{cus}$: 0.8
$CO^{cus} + O^{br}$: 1.2

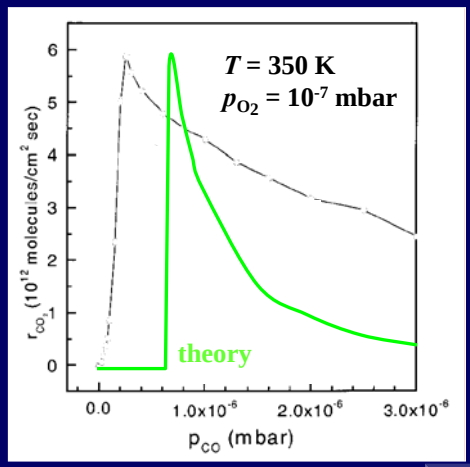
$CO^{br} + O^{br}$: 1.5



Comparison with experimental results



J. Wang, C.Y. Fan, K. Jacobi, and G. Ertl, J. Phys. Chem. B 106, 3422 (2002)



Conclusions

- Combining DFT and Statistical Mechanics is essential for understanding the function of materials (e.g. realistic T, p, t, l).
- The accuracy of the method is (even) better than its reputation (compensation of DFT-LDA/GGA errors due to the statistical interplay of many processes).
- The described techniques are applicable to a wide variety of gas-phase and solution-phase chemistry, surface phase transitions, crystal growth, heterogeneous catalysis, etc.

The people behind the work

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Karsten Reuter

et al. …

Institute for Pure & Applied Mathematics

I P A M

University of California, Los Angeles

UCLA

Bridging Time and Length Scales in Materials Science and Bio-Physics

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