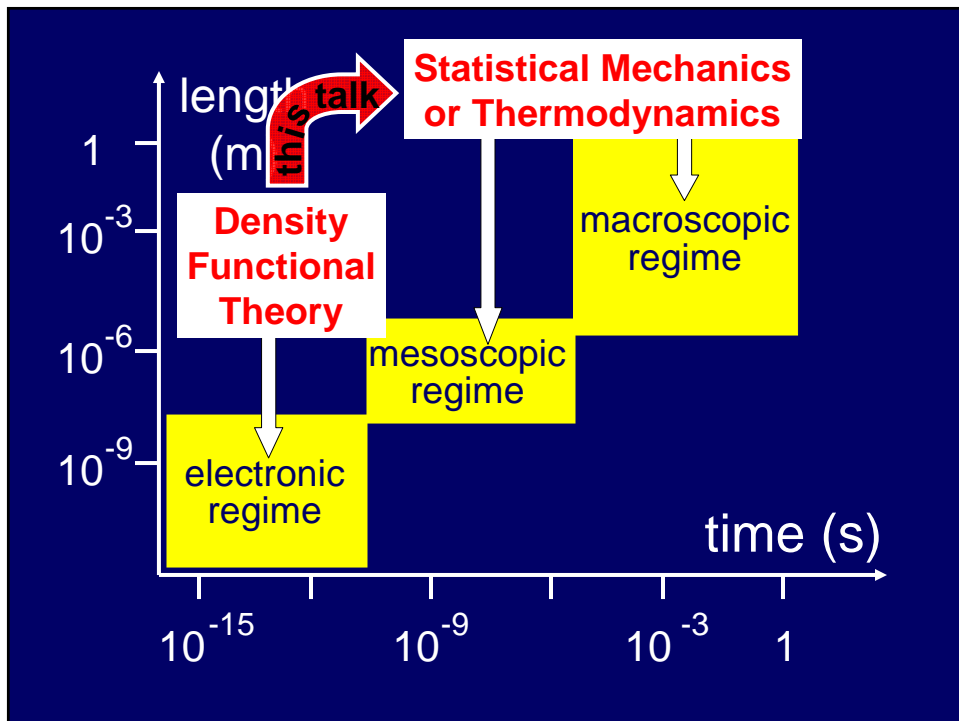
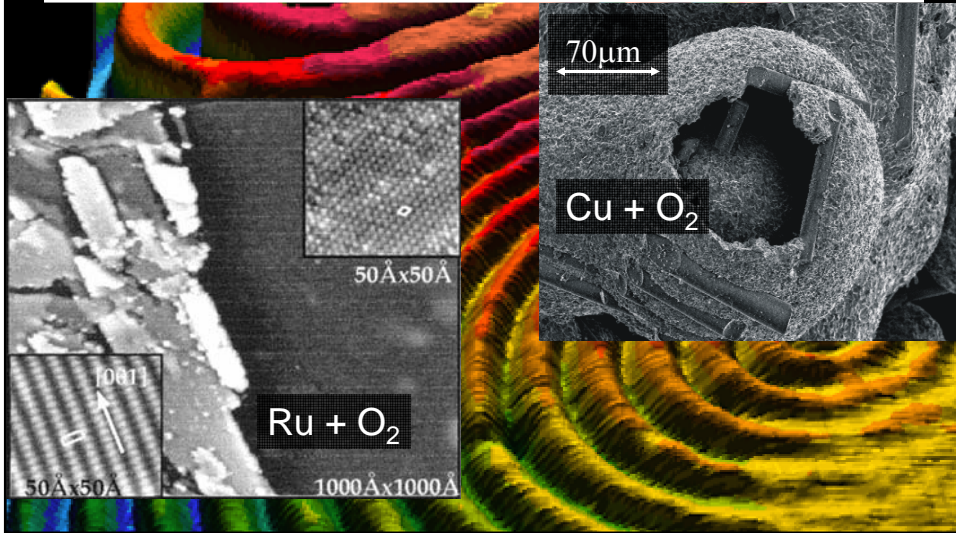


The Function of Heterogeneous Catalysts: New Insights by First-Principles Statistical Mechanics



Density-Functional Theory

The energy of the ground state of a many-electron system :

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

Hohenberg and Kohn (1964): The functional

$$n(\mathbf{r}) = n[\Phi] = \langle \Phi | \sum_i \delta(\mathbf{r} - \mathbf{r}_i) | \Phi \rangle$$

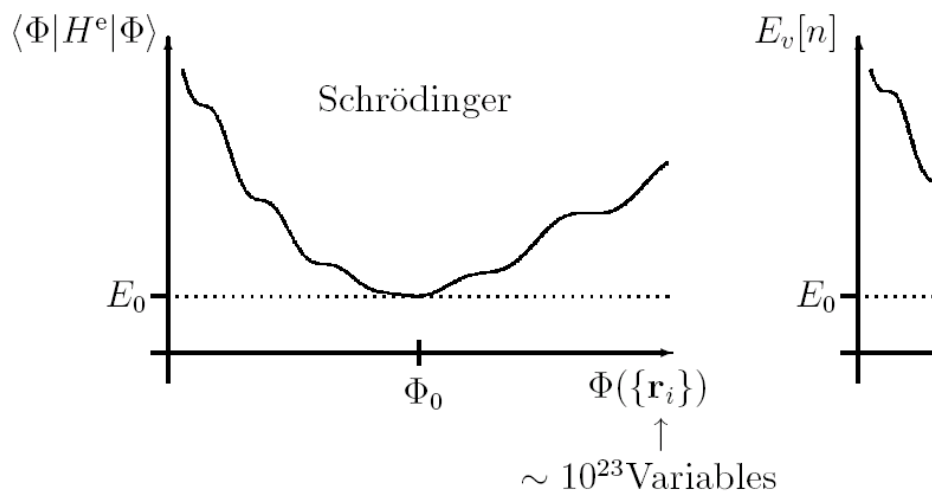
can be inverted, *i.e.*,

$$\Phi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \Phi[n(\mathbf{r})] .$$

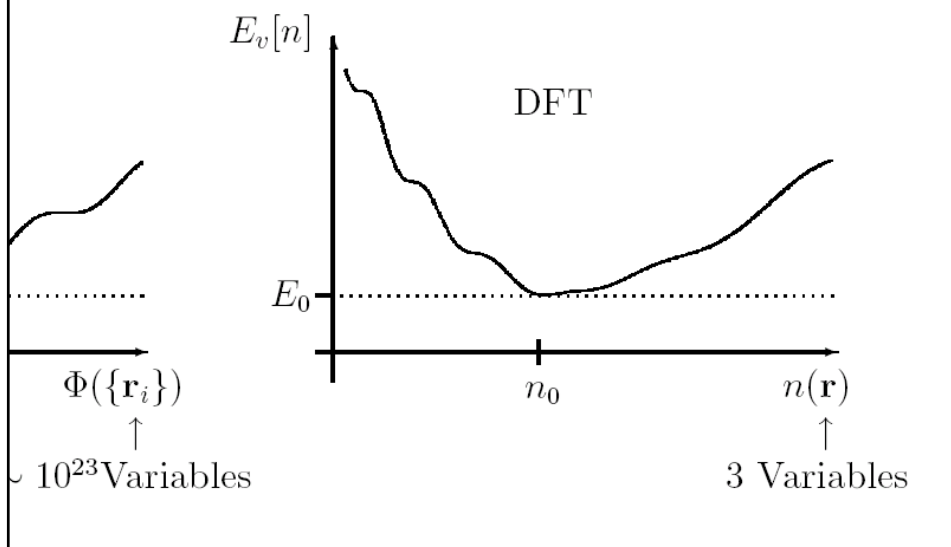
This implies:

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

Comparison of Wave-Function and Density-Functional theory



Comparison of Wave-Function and Density-Functional theory



The Kohn-Sham Ansatz

- **Kohn-Sham** (1965) – **Replace** the original many-body problem with an **independent electron problem that can be solved!**
- Only the **ground state density** and the **ground state energy** are required to be the same as in the original many-body problem.

$$E_v[n] = T_s[n] + \int v(\mathbf{r})n(\mathbf{r})d^3\mathbf{r} + E^{\text{Hartree}}[n] + E^{\text{xc}}[n]$$

- Maybe the exact $E^{\text{xc}}[n]$ functional cannot be written as a closed mathematical expression. Maybe we have to take a detour similar to that taken for $T_s[n]$? **The challenge is to find useful, approximate xc functionals.**

Most-Cited Papers in APS Journals

11 papers published in APS journals since 1893 with
>1000 citations in APS journals (~5 times as many
references in all science journals)

Table 1. Physical Review Articles with more than 1000 Citations Through June 2003

Publication	# cites	Av. age	Title	Author(s)
PR 140, A1133 (1965)	3227	26.7	Self-Consistent Equations Including Exchange and Correlation Effects	W. Kohn, L. J. Sham
PR 136, B864 (1964)	2460	28.7	Inhomogeneous Electron Gas	P. Hohenberg, W. Kohn
PRB 23, 5048 (1981)	2079	14.4	Self-Interaction Correction to Density-Functional Approximations for Many-Electron Systems	J. P. Perdew, A. Zunger
PRL 45, 566 (1980)	1781	15.4	Ground State of the Electron Gas by a Stochastic Method	D. M. Ceperley, B. J. Alder
PR 108, 1175 (1957)	1364	20.2	Theory of Superconductivity	J. Bardeen, L. N. Cooper, J. R. Schrieffer
PRL 19, 1264 (1967)	1306	15.5	A Model of Leptons	S. Weinberg
PRB 12, 3060 (1975)	1259	18.4	Linear Methods in Band Theory	O. K. Anderson
PR 124, 1866 (1961)	1178	28.0	Effects of Configuration Interaction of Intensities and Phase Shifts	U. Fano
RMP 57, 287 (1985)	1055	9.2	Disordered Electronic Systems	P. A. Lee, T. V. Ramakrishnan
RMP 54, 437 (1982)	1045	10.8	Electronic Properties of Two-Dimensional Systems	T. Ando, A. B. Fowler, F. Stern
PRB 13, 5188 (1976)	1023	20.8	Special Points for Brillouin-Zone Integrations	H. J. Monkhorst, J. D. Pack

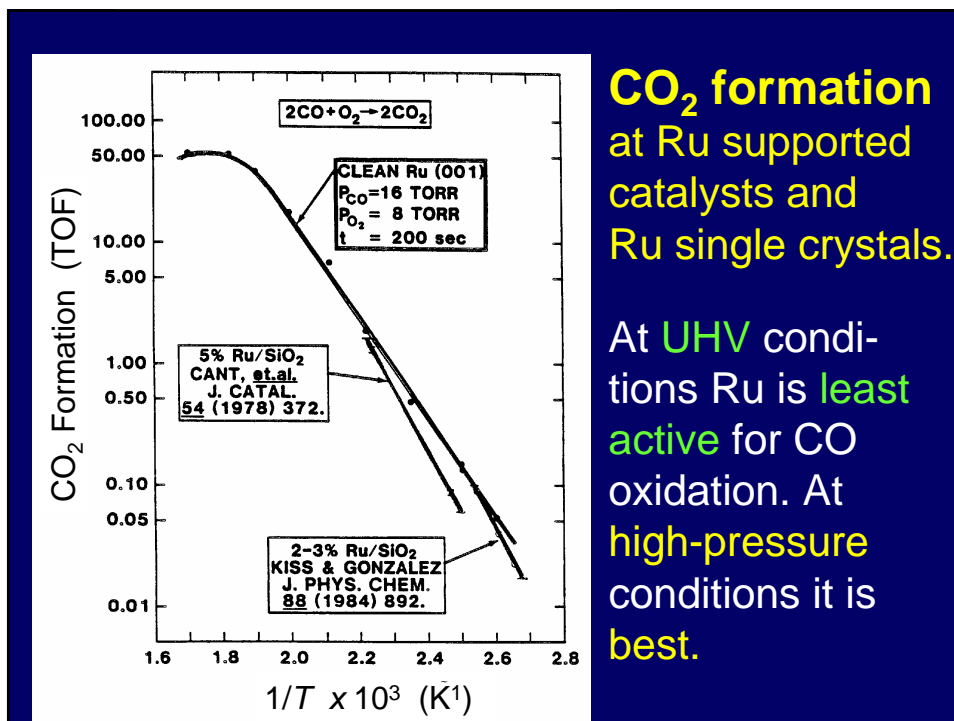
PR, Physical Review; PRB, Physical Review B; PRL, Physical Review Letters; RMP, Reviews of Modern Physics.

From Physics Today, June, 2005

Oxidation catalysis, e.g.:



A "simple", prototypical surface chemical reaction



Oxidation catalysis, e.g.:

$$\text{CO} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2$$

A "simple", prototypical surface chemical reaction

at Ru(0001)

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

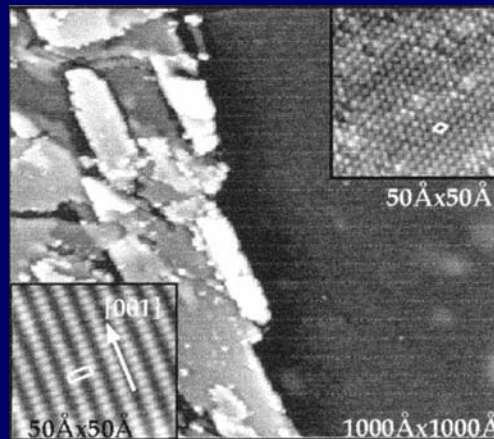
Transition-metals/oxides as oxidation catalysts ? !

Catalytic activity of Ru(0001) is due to RuO₂(110) domains (1-2 nm thin films), that form in the reactive environment.

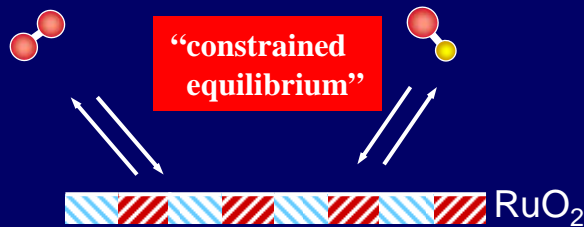
Also:

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

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



Ab initio atomistic thermodynamics



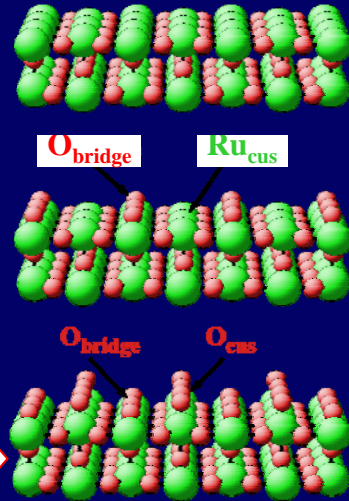
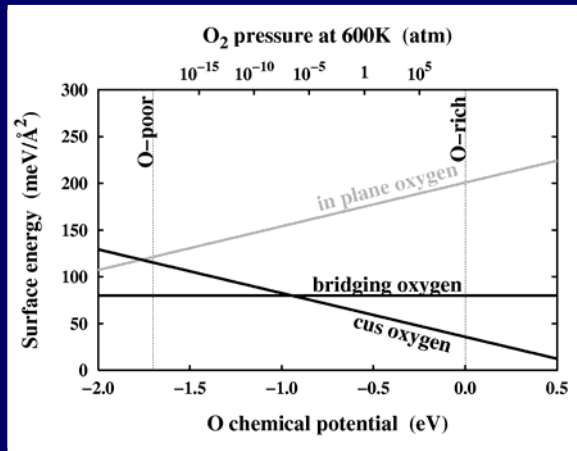
$$G(T, p) = E^{\text{tot}} + F^{\text{vib}} - TS^{\text{conf}} + pV$$

DFT (FP-LAPW; GGA)

$$\mu_{\text{O}}(T, p) = \frac{1}{2} \mu_{\text{O}_2}(T, p^0) + \frac{1}{2} kT \ln(p/p^0)$$

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

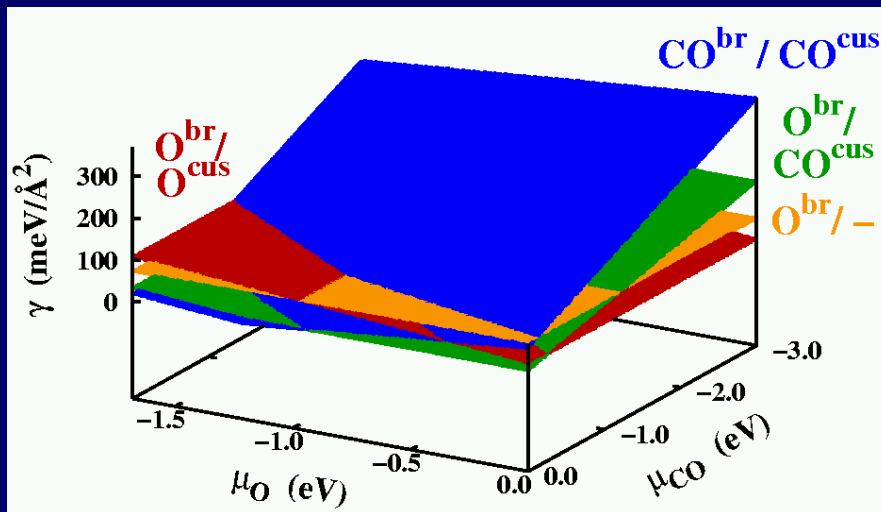
RuO₂(110) surface terminations



high pressure termination →

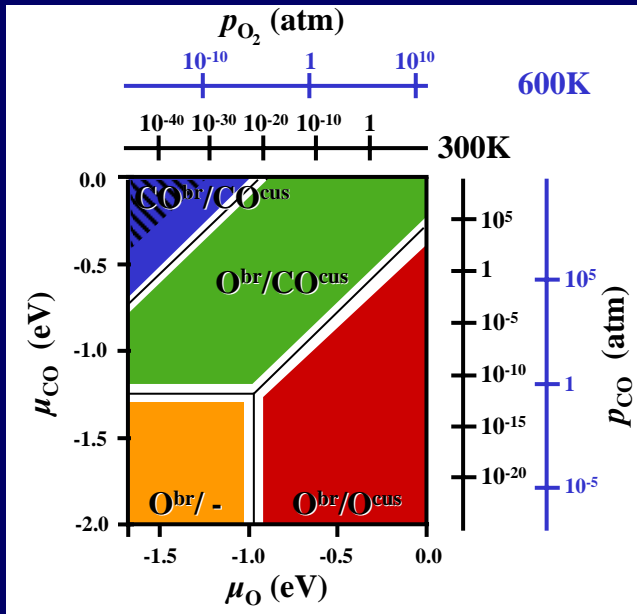
K. Reuter et al., PRB 65 (2001)

RuO₂ (110) surface structures with O₂ and CO in the gas phase

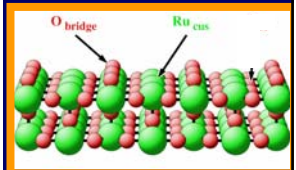


K. Reuter & M.S., PRL 90, 046103 (2003)

RuO₂ (110) stability regions in (T, p) space



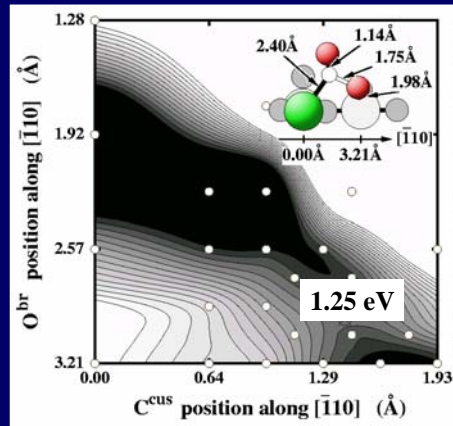
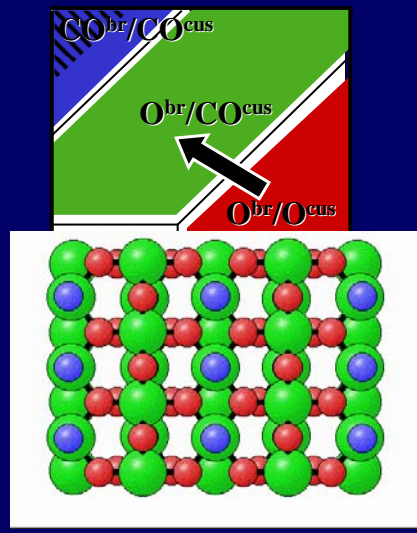
Ab initio thermodynamics for a "constrained equilibrium"



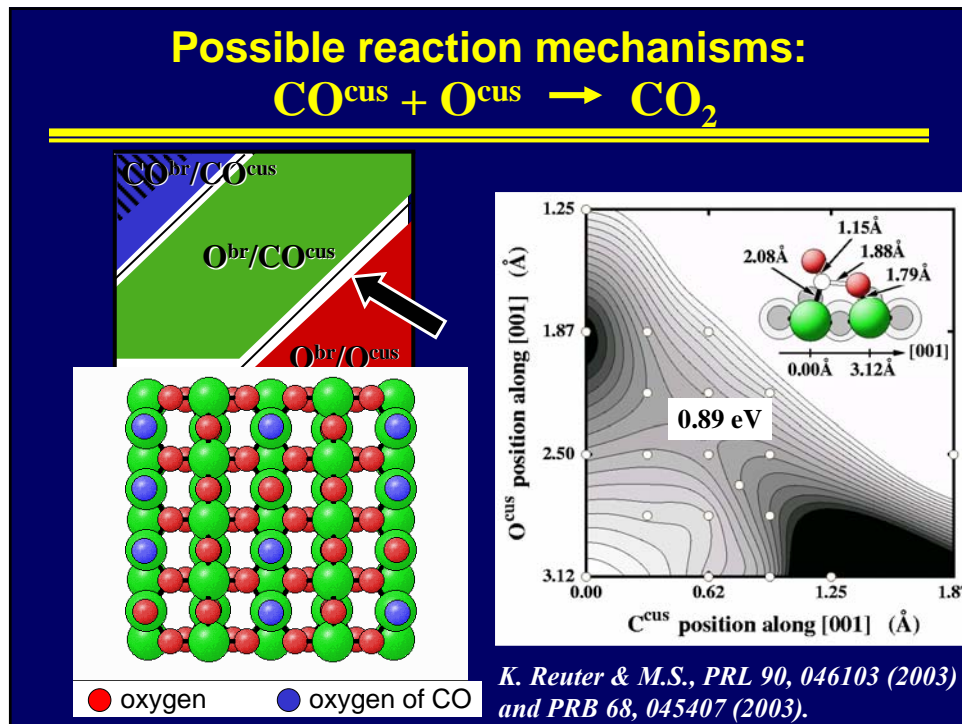
UHV surface termination

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

Possible reaction mechanisms:



K. Reuter & M.S., PRL 90, 046103 (2003) and PRB 68, 045407 (2003).



Kinetics of catalysis from first principles

-- **example: $\text{CO} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2$** --

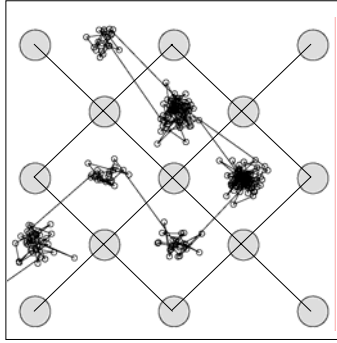
- 1) Analysis of all *possibly relevant* processes using **density-functional theory**
- 2) Calculate the rates of all important processes

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

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

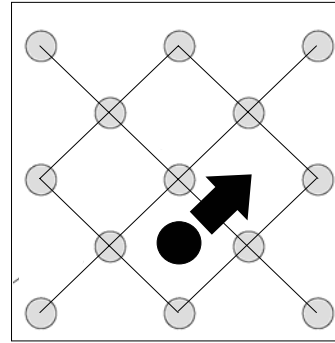
➔ **extended kinetic Monte Carlo**

Kinetic Monte Carlo: Coarse-Graining Molecular Dynamics



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

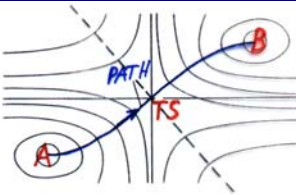
ab initio MD:
up to 50 ps



Kinetic Monte Carlo simulation: Coarse-grained hops.

ab initio kMC:
up to minutes

Transition State Theory



Transition state theory

$$\Gamma = \frac{k_B T}{h} \exp\left(\frac{-\Delta F}{k_B T}\right)$$

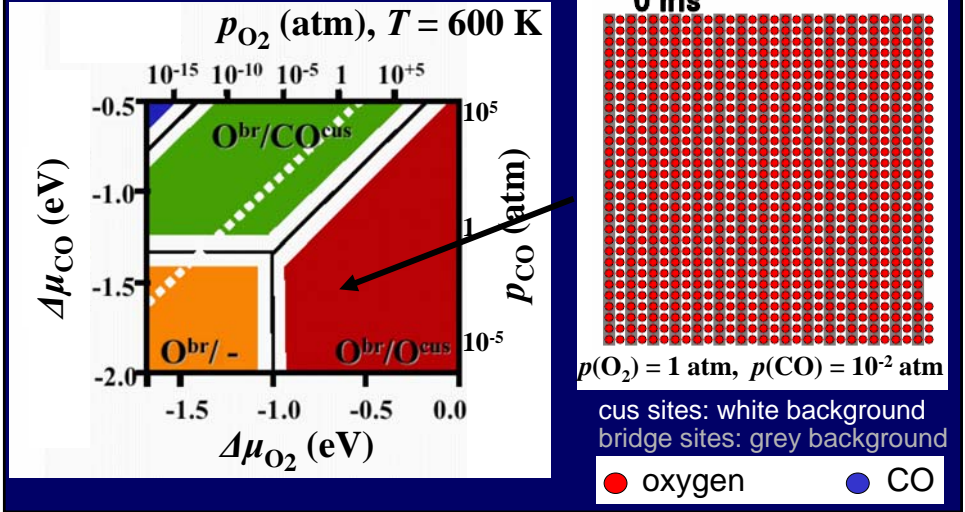
$$\Delta F = -k_B T \ln Z_{TS} + k_B T \ln Z_A$$

$$\Gamma = \Gamma_0 \exp\left(\frac{-\Delta E}{k_B T}\right)$$

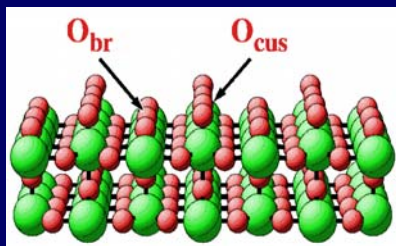
$$\Gamma_0 = \frac{k_B T}{h} \exp\left(\frac{\Delta S^{\text{vib}}}{k_B} - \frac{\Delta U^{\text{vib}}}{k_B T}\right)$$

RuO₂ (110) stability regions in (T, p) space

K. Reuter and M.S., PRB in print.

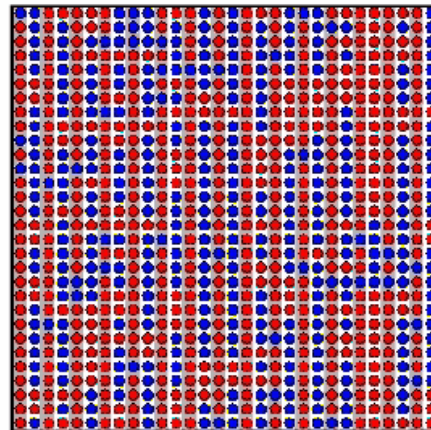


Oxidation catalysis at RuO₂ (110)



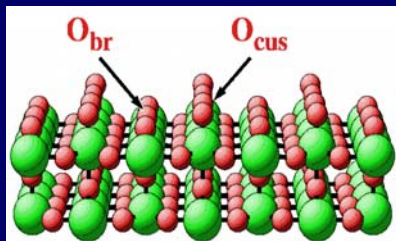
$p(O_2) = 1$ atm, $p(CO) = 10$ atm

$T = 600$ K $t = 5$ mscc



K. Reuter, D. Frenkel, M.S.,
PRL 93, 116105 (2004).

Oxidation catalysis at RuO₂ (110)



termination for high O₂ pressure

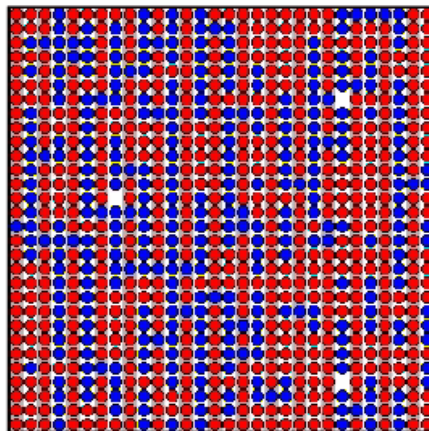
● oxygen ● CO

cus sites: white background
bridge sites: grey background

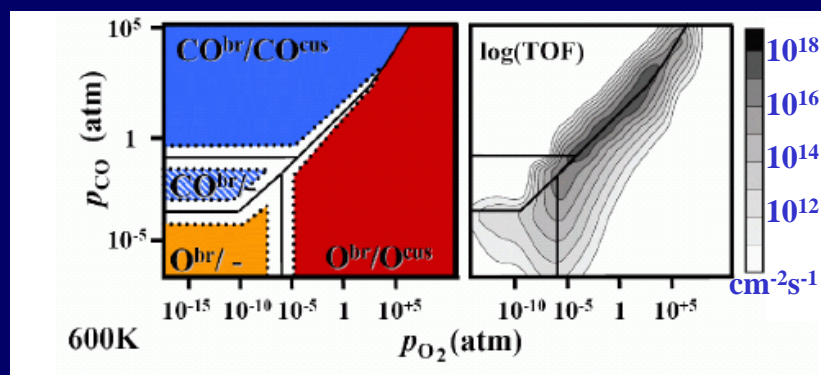
*K. Reuter, D. Frenkel, M.S.,
PRL 93, 116105 (2004).*

$p(\text{O}_2) = 1 \text{ atm}$, $p(\text{CO}) = 10 \text{ atm}$

$T = 600 \text{ K}$ $t = 2 \text{ nsec}$



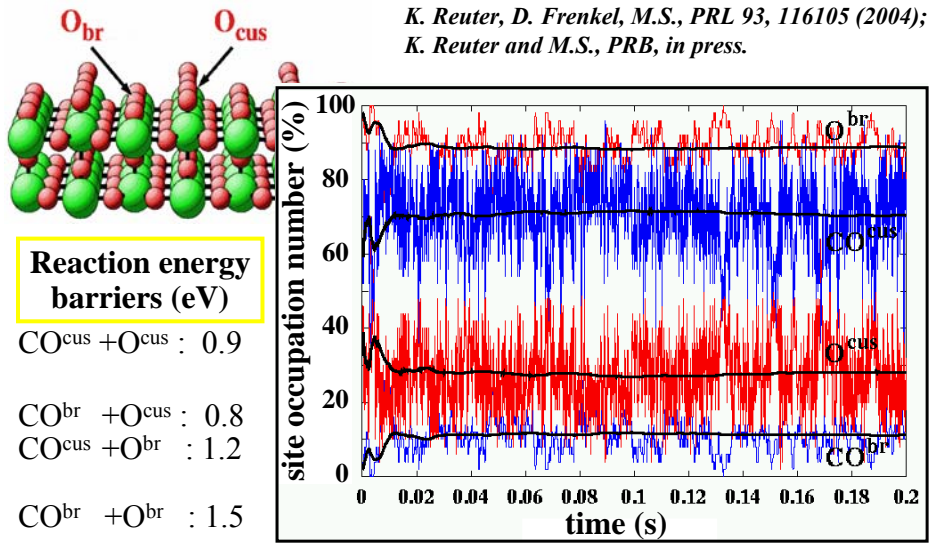
RuO₂ (110) high reactivity regions (bridging the pressure gap)



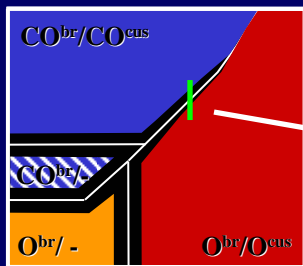
The measured rate is $r_{\text{CO}_2} = 10^{18} \text{ cm}^{-2} \text{ s}^{-1}$

*C.H.F. Peden, D.W. Goodman, D.S. Blair, P.J. Berlowitz, G.B. Fisher, S.H. Oh,
J. Phys. Chem. 92, 1563 (1988)*

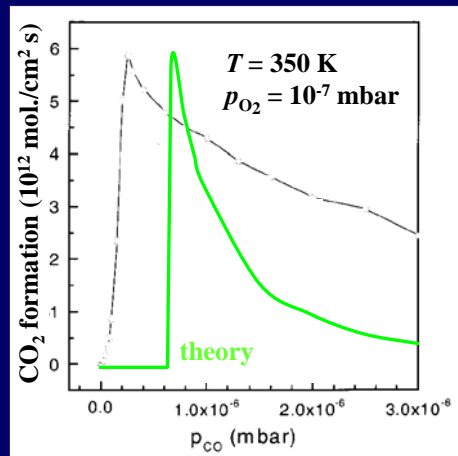
Site occupation statistics at the steady state (strong fluctuations)



Comparison with experimental results

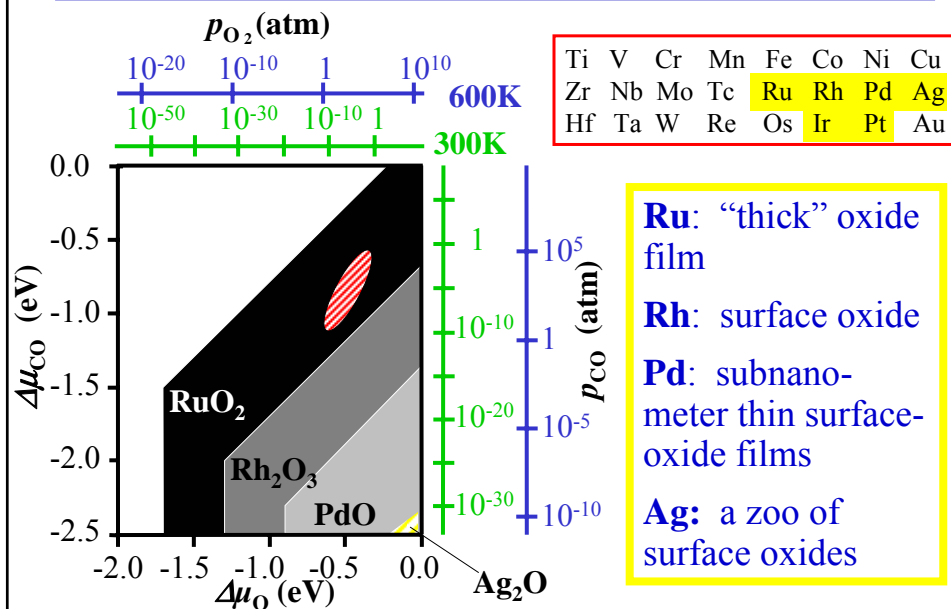


*J. Wang, C.Y. Fan,
K. Jacobi, and G. Ertl,
J. Phys. Chem. B 106,
3422 (2002)*

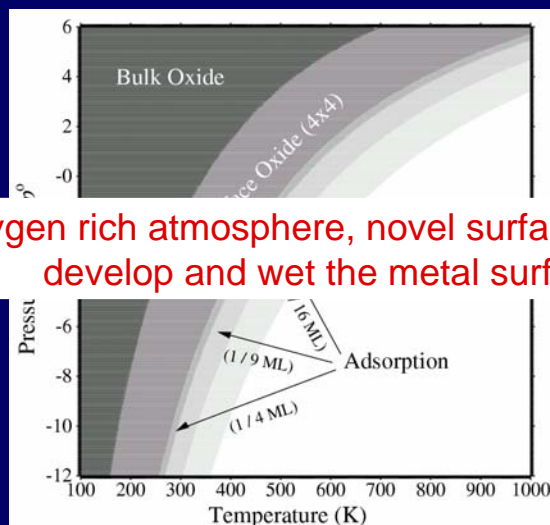


... what can we tell about other systems?

Stability of bulk oxides in CO oxidation catalysis



O on 4d metals (Ru - Ag): here Ag(111)



In an oxygen rich atmosphere, novel surface oxides develop and wet the metal surface

*W.X. Li, C. Stampfl, and M.S., PRL 90 (2003); and PRB (2003);
M. Todorova, et al., PRL 89 (2002); A. Michaelides et al. J.Phys. Chem (2003)*

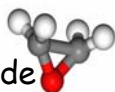
O on Ag (111):

When seeing is not believing

Why O on Silver ?

Partial oxidation catalyst:

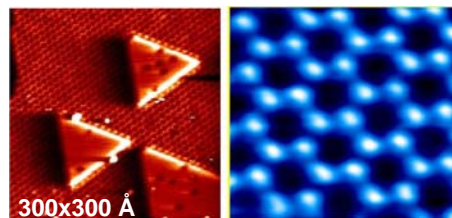
- methanol to formaldehyde
- ethylene to ethylene epoxide



US ethylene epoxide production in 2000:
~ Billion kg⁽¹⁾

A noble-metal catalyst

Moderate exposures of O to Ag(111) leads a characteristic (4x4) superstructure.



C.I. Carlisle et al. Surf. Sci. 470 (2000): "The structure of the O/Ag surface oxide resembles that of bulk Ag₂O."

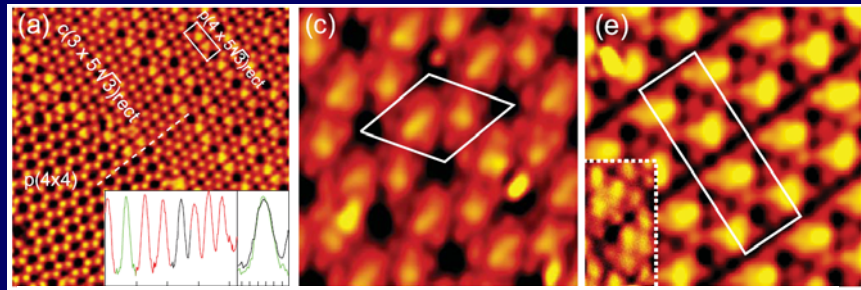
¹Chem. & Eng. News, June 24, 2002

The "old" understanding of $(4 \times 4)O/Ag$:
The structure resembles that of bulk Ag_2O .

DFT calculations questioned this interpretation:

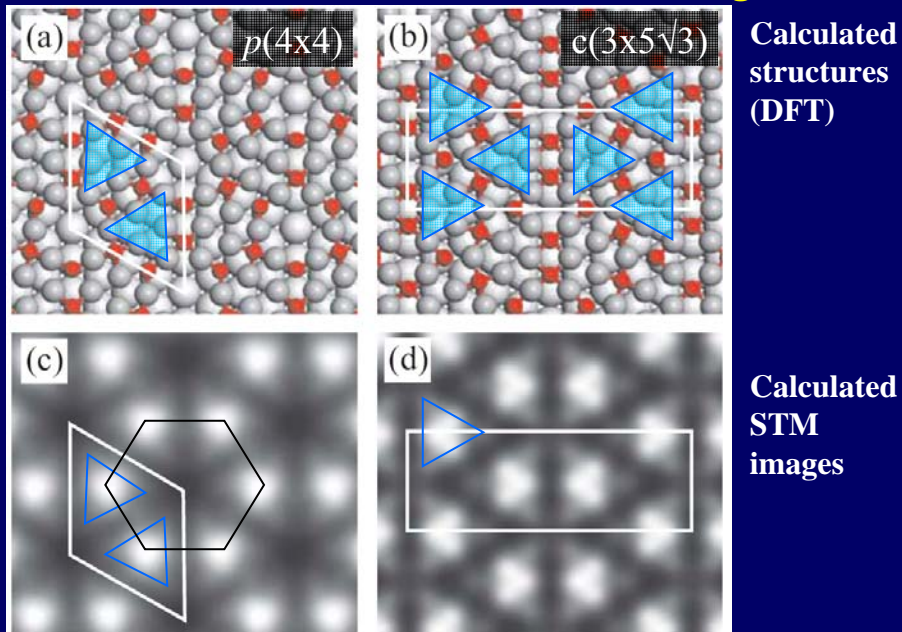
A. Michaelides, K. Reuter, and M.S., J. Vac. Sci. Technol. A 23 (2005).

Several structures have the same or even lower energy!



New STM data by J. Schnadt, F. Besenbacher, et al.

Theoretical results for O/Ag



The Ag-oxide "Nano-Lego"

The "seen" $p(4 \times 4)\text{-O}/\text{Ag}(111)$ structure does NOT resemble Ag_2O , and it may not be very relevant. There are many structures of nearly the same energy. At realistic conditions all these structures will be present (law of mass action; kinetics).

Many (all?) low-energy oxide overlayers on $\text{Ag}(111)$ are comprised of Ag_6O_x building blocks: A "Nano-Lego"

J. Schnadt, A. Michaelides, J. Knudsen, R. T. Vang, K. Reuter, E. Lægsgaard, M. Scheffler, and F. Besenbacher, submitted to PRL.

On the $p(4 \times 4)$ structure M. Schmid, A. Stierle, et al., recently arrived at exactly the same "Ag₆" model.

Towards an exact treatment of exchange and correlation in materials

Examples:

1. Surface structure, adsorption energies, reaction energy barriers for H_2 at $\text{Si}(001)$
2. CO adsorption at transition metal surfaces:

LDA and GGA xc functionals dramatically fail to predict the correct adsorption site. For low coverage the theory gives the hollow site, but experimentally CO adsorbs on top. E.g.: For $\text{CO}/\text{Cu}(111)$ the LDA error is ≥ 0.4 eV, and the GGA error is ≥ 0.15 eV.



How to correct the xc error of DFT-LDA

1. Do super-cell calculations using DFT-LDA
2. Do cluster calculations with DFT-LDA and with xc-better = B3LYP, HF-MP2, or QMC using the same geometry as in 1.

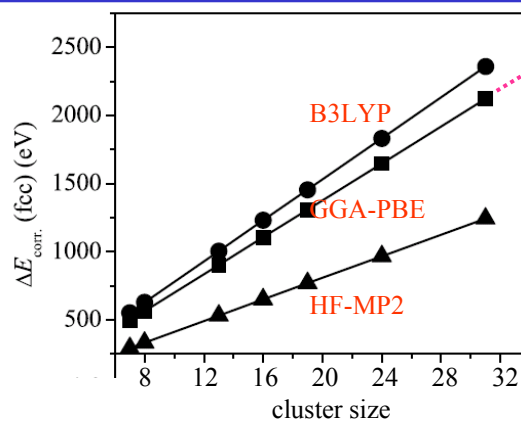
3. Evaluate the correction of the DFT-LDA result:

$$\Delta E_{\text{corr.}} = E_{\text{cluster}}(\text{xc-better}) - E_{\text{cluster}}(\text{LDA})$$

How does $\Delta E_{\text{corr.}}$ change with cluster size?

We need the correction for the limit
cluster size $\rightarrow \infty$

$$\Delta E_{\text{corr.}} = E_{\text{cluster}}(\text{xc-better}) - E_{\text{cluster}}(\text{LDA})$$

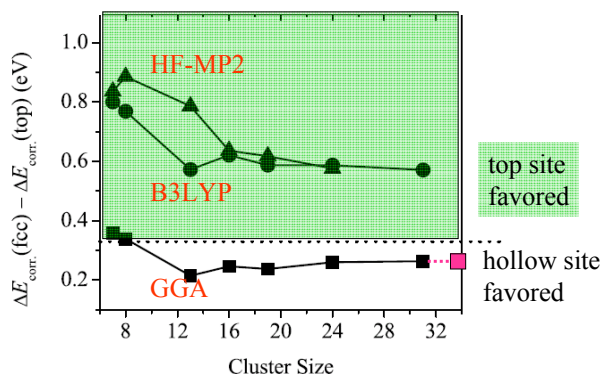


example:
CO adsorption
in the fcc-hollow
site of Cu (111)

$\Delta E_{\text{corr.}}$ increases as $a + b \cdot V^{2/3} + c \cdot V$.

For the clean surface and for other adsorption sites
the scaling is the same.

Towards an exact treatment of exchange and correlation in materials -- CO at Cu (111): The correction for fcc-hollow and atop adsorption site



A 16-atom cluster is sufficiently big to evaluate the LDA error.

Note: The adsorption energy (and other quantities) is NOT described properly by a 16-atom cluster.

Conclusions

- The described techniques are applicable to a wide variety of **gas-phase and solution-phase chemistry, crystal growth, heterogeneous catalysis, etc.**
- **In an oxygen rich atmosphere, novel surface oxides develop and wet the metal surface.**
- The active phase present under realistic conditions is not the bulk phase introduced as “the catalyst”, but **a different (sometimes novel) material** with different composition and different structure. Recent examples include: **hematite, Ru, Rh, Pd, Ag.**
- Complexity is essential for understanding **the function of materials.**

The people behind the work



Cathy Stampfl



Karsten Reuter



Wei-Xue Li



A. Michaelides



et al. ...

<http://www.fhi-berlin.mpg.de/th/th.html>