Oxide Formation of Transition Metal Surfaces and Effect on Catalysis

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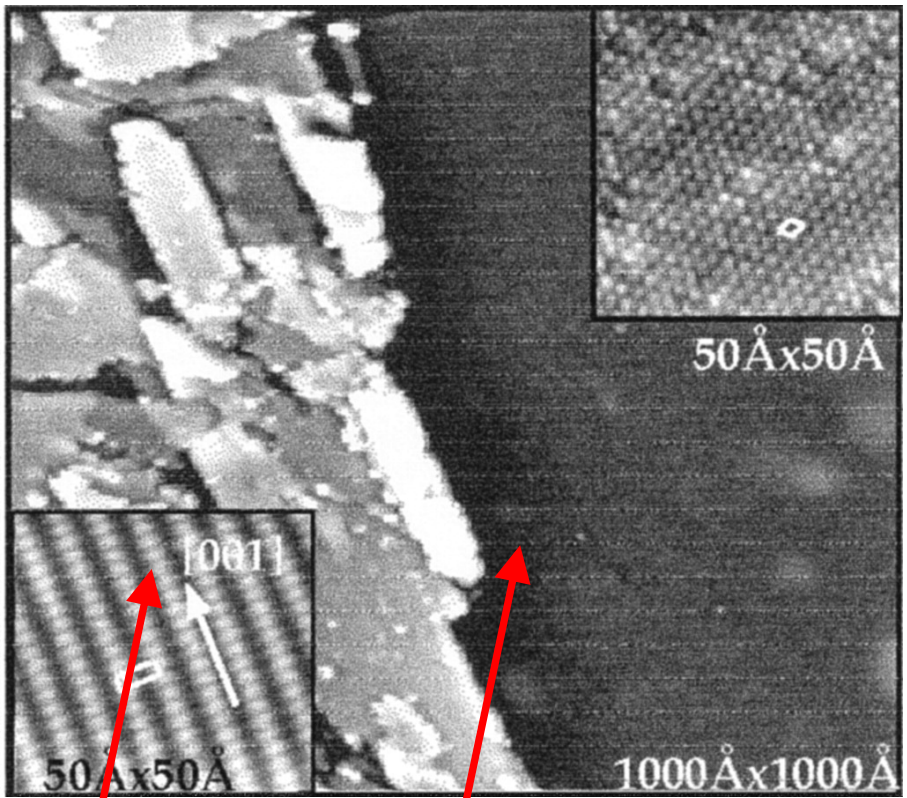
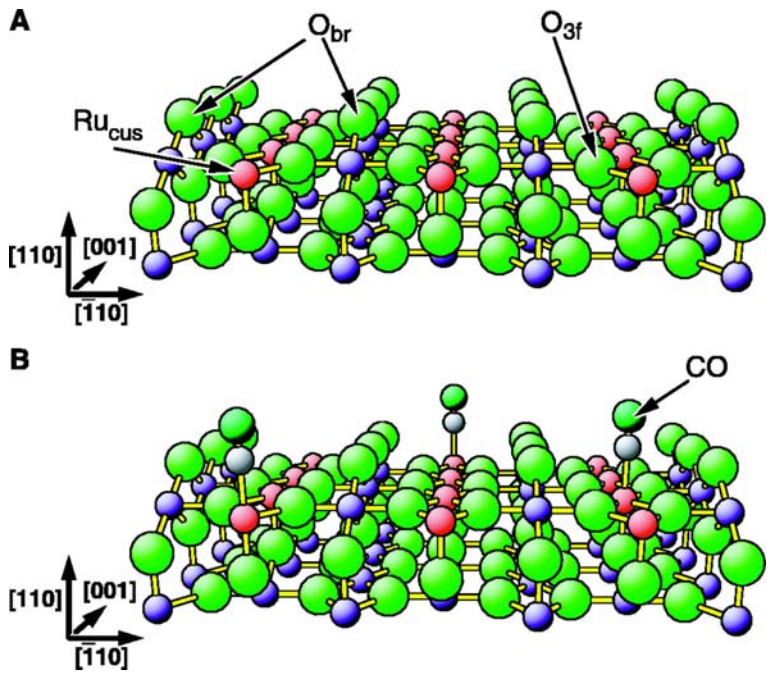
CO Oxidation on Ru(0001) versus $RuO_2(110)$

Langmuir-Hinshelwood versus Mars-Van Krevelen

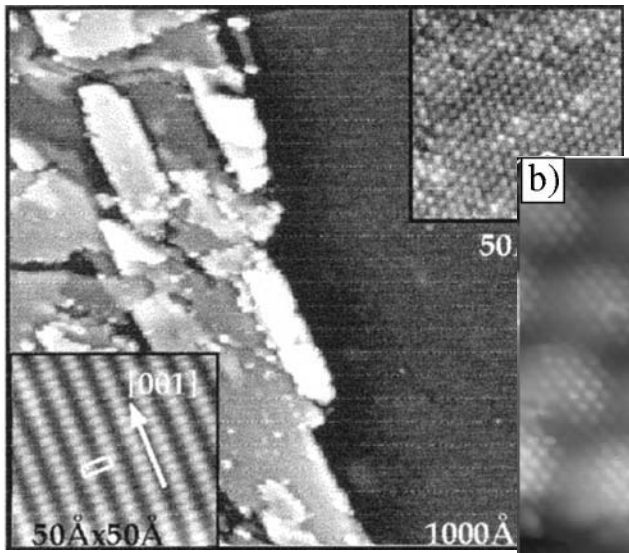


RuO_2 Ru(0001)



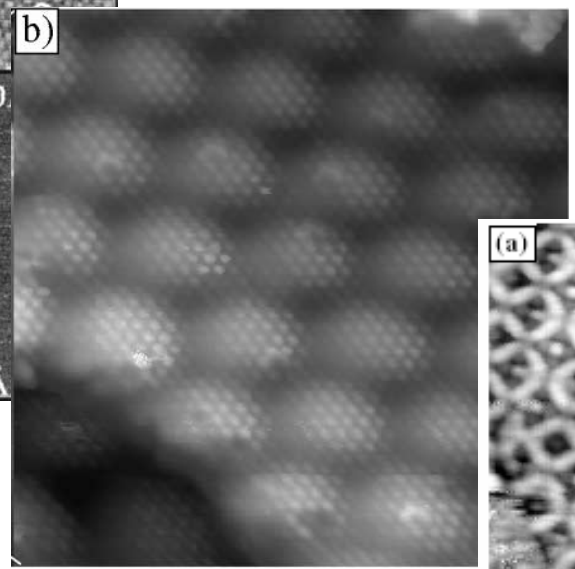
H. Over et al, Science 287, 1474 (2000)

Ru(0001)
bulk oxide



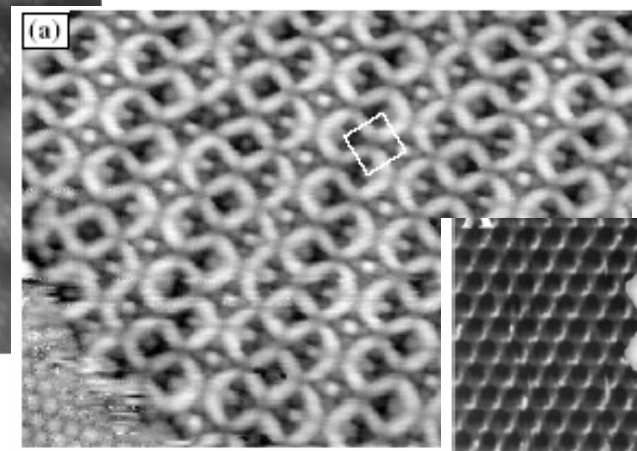
H. Over et al, Science (2000)

Rh(111)
Surface oxide
(metal stable)



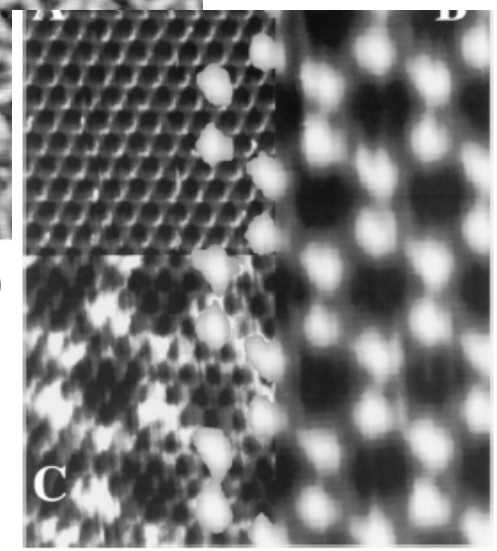
J. Gustafson et al, PRL (2004)

Pd(111)
Surface oxide



E. Lundgren et al, PRL (2002)

Ag(111)
A zoo of
surface oxide



C.I.Carlisle et al, PRL (2000)

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg

Pressures and Materials Gap

Working Conditions:
atmospheric pressures and elevated temperatures

Surface Science: Ultra high vacuum / single crystal

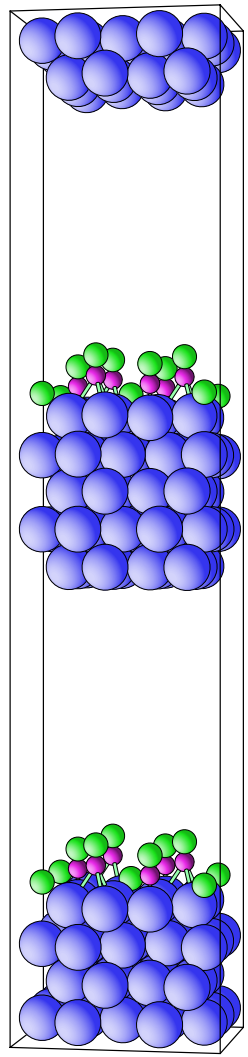
→ **``Pressure-gap'' (10^{12} magnitude difference)**

→ ``Material-gap''

Role of the atmospheric environment, *i.e.* species and gas pressure, as well as the temperature, need to be considered !

Apparatus

- Density functional theory (DACAPO, FHIMD)
  - Plane Wave Basis Set, GGA, USPP, Slab
- Transition State Theory
- Ab initio Thermodynamics
- Kinetic Monte Carlo



- Microscopy (HP-STM, TEM)
- Synchrotron (XPS, HP-SXRD)
- Vibration Spectroscopy (HREELS)
- etc

- **Oxidation of Ag(111) and ethylene epoxidation**
- Oxidation of Pt(332) and CO Oxidation
- Oxidation of Pt(110) and CO Oxidation
- Oxidation of Rh(110) and H2 Reduction

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg

Silver is unique catalyst for

oxidation of ethylene to epoxide (P=1atm, T=500-600K)

$$C_2H_4 + {}^1/_2O_2 \rightarrow C_2H_4O,$$

partial oxidation of methanol to formaldehyde (P=1atm, T=700-900K)

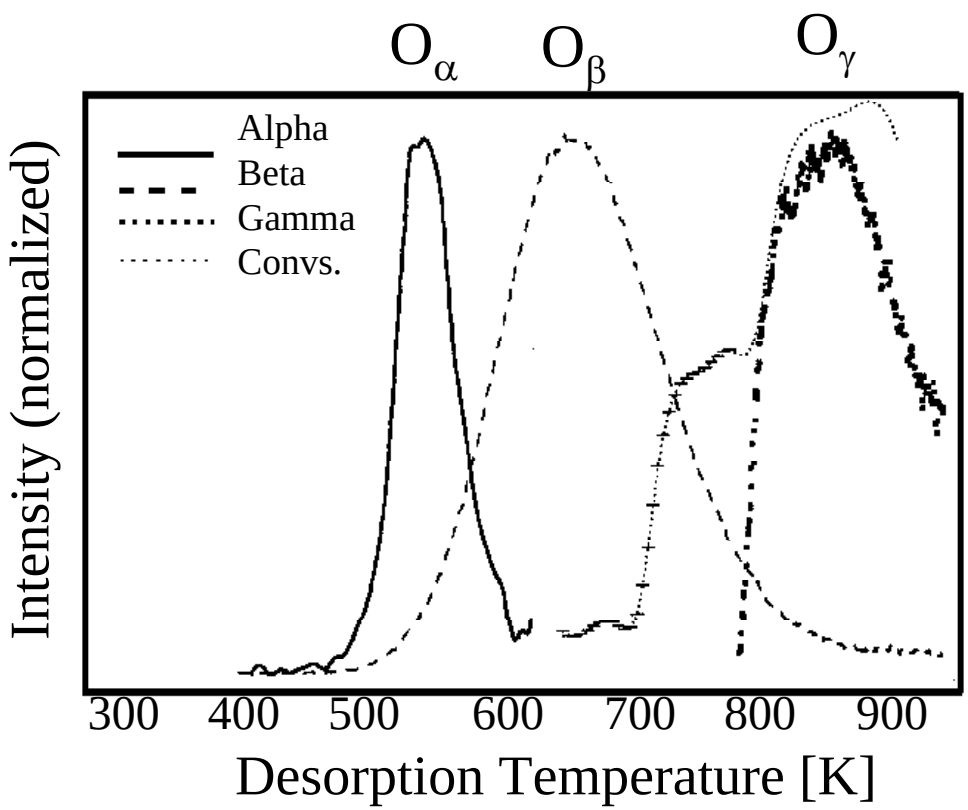
$$CH_3OH + {}^1/_2O_2 \rightarrow CH_2O + H_2O,$$

but silver is noble metal, bind particles only weakly

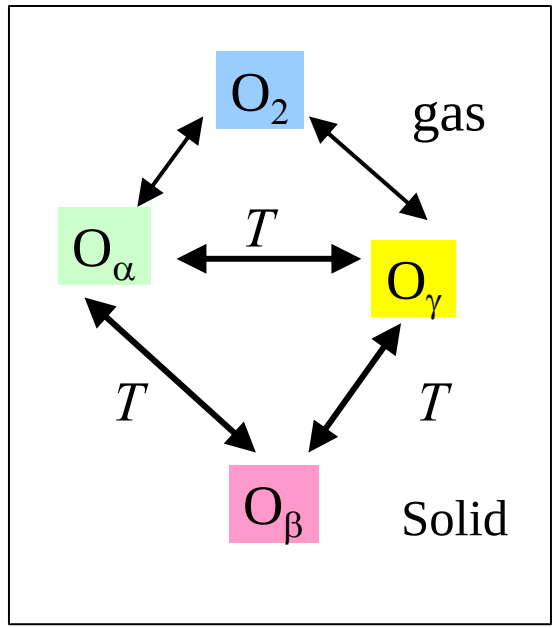
thoughts: bulk dissolved oxygen may be important

O-Ag(111) interaction, looks simple, but big challenging !

Experimental Results: (TPD)



(Herein, et al., Zeit. Phys., 1996)

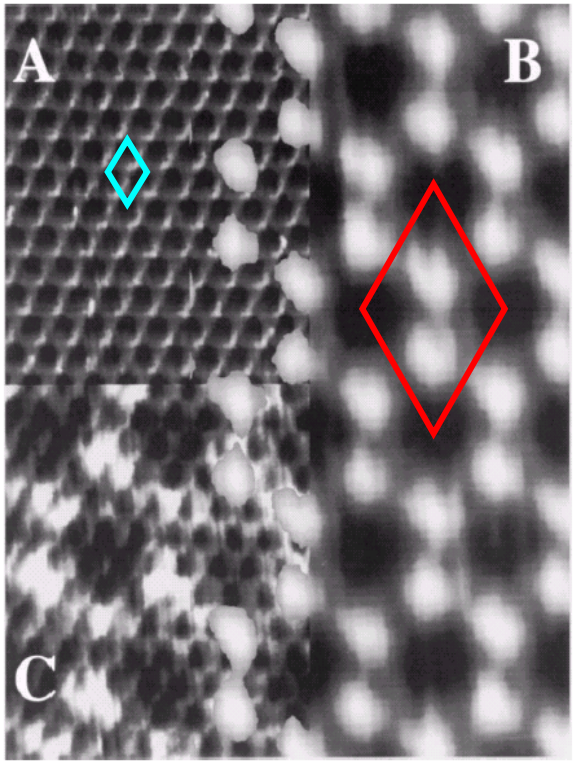


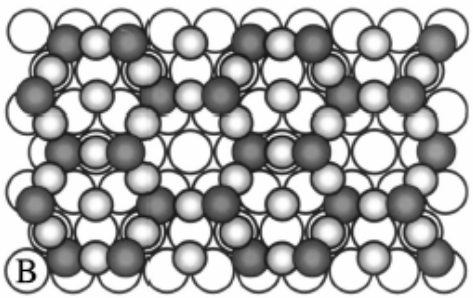
Proposed that O species Inter-change sites depending on P and T

Temperature Programmed Desorption identifies 3 O species

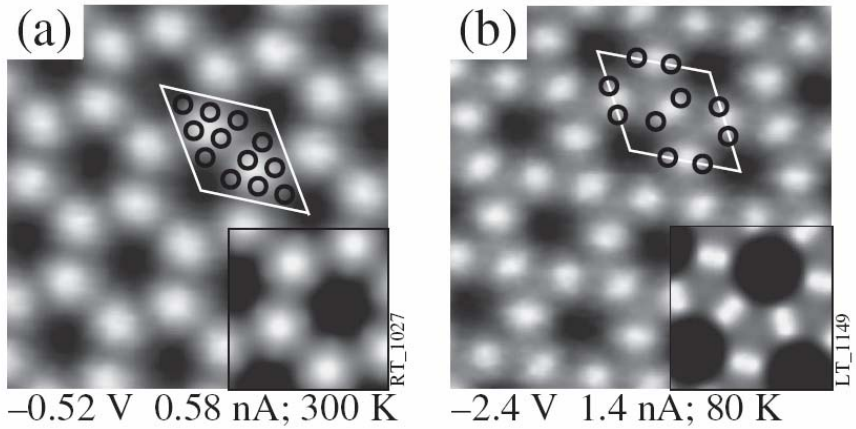
Ordered Structures: O/Ag(111)

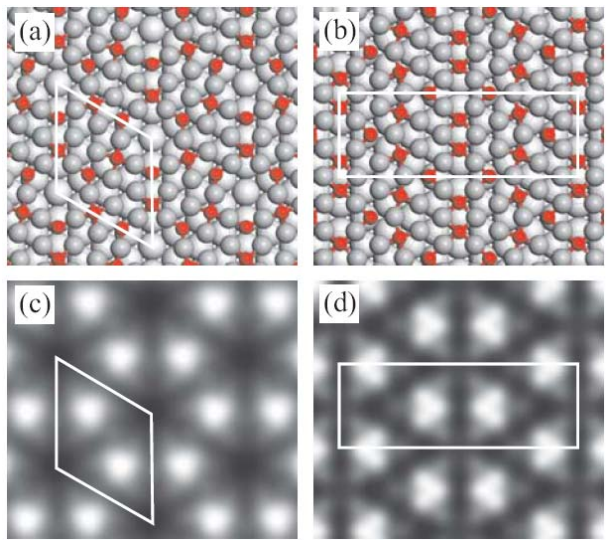
(4x4)-O *(Carlisle et al, PRL, 2000)*



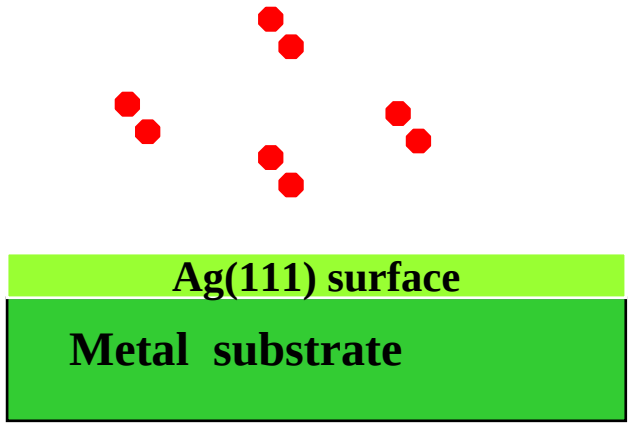


Schmid et al, Phys. Rev. Lett. 96, 146102 (2006)

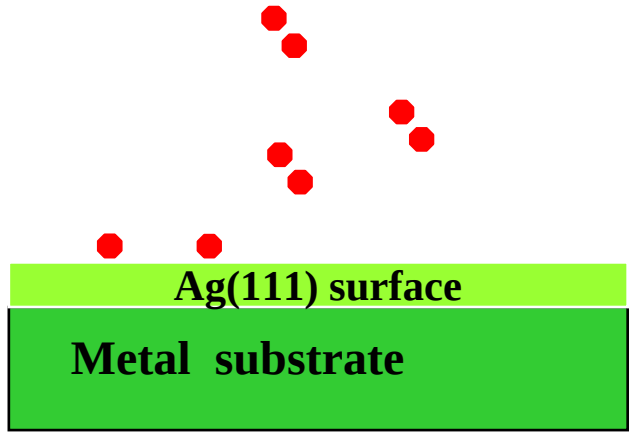




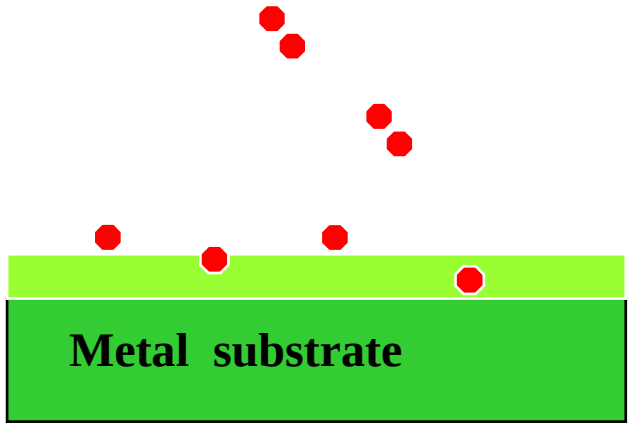
Schnadt et al, Phys. Rev. Lett. 96, 146101 (2006)



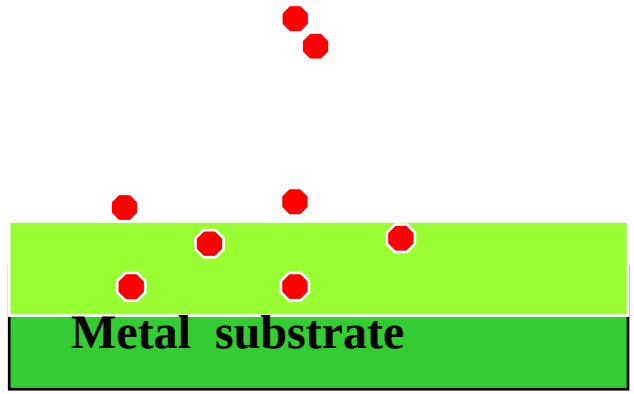
Clean Surface



Chemisorption

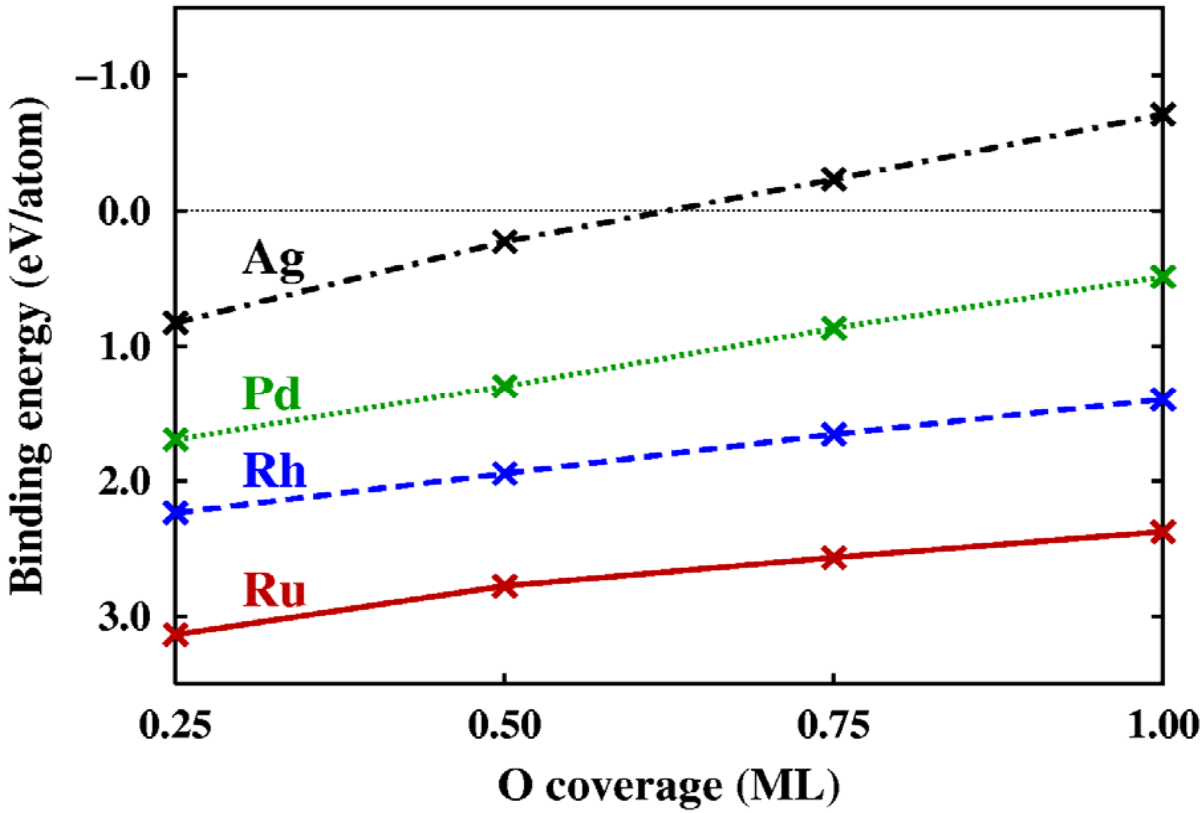


Surface Oxide



Bulk Oxide

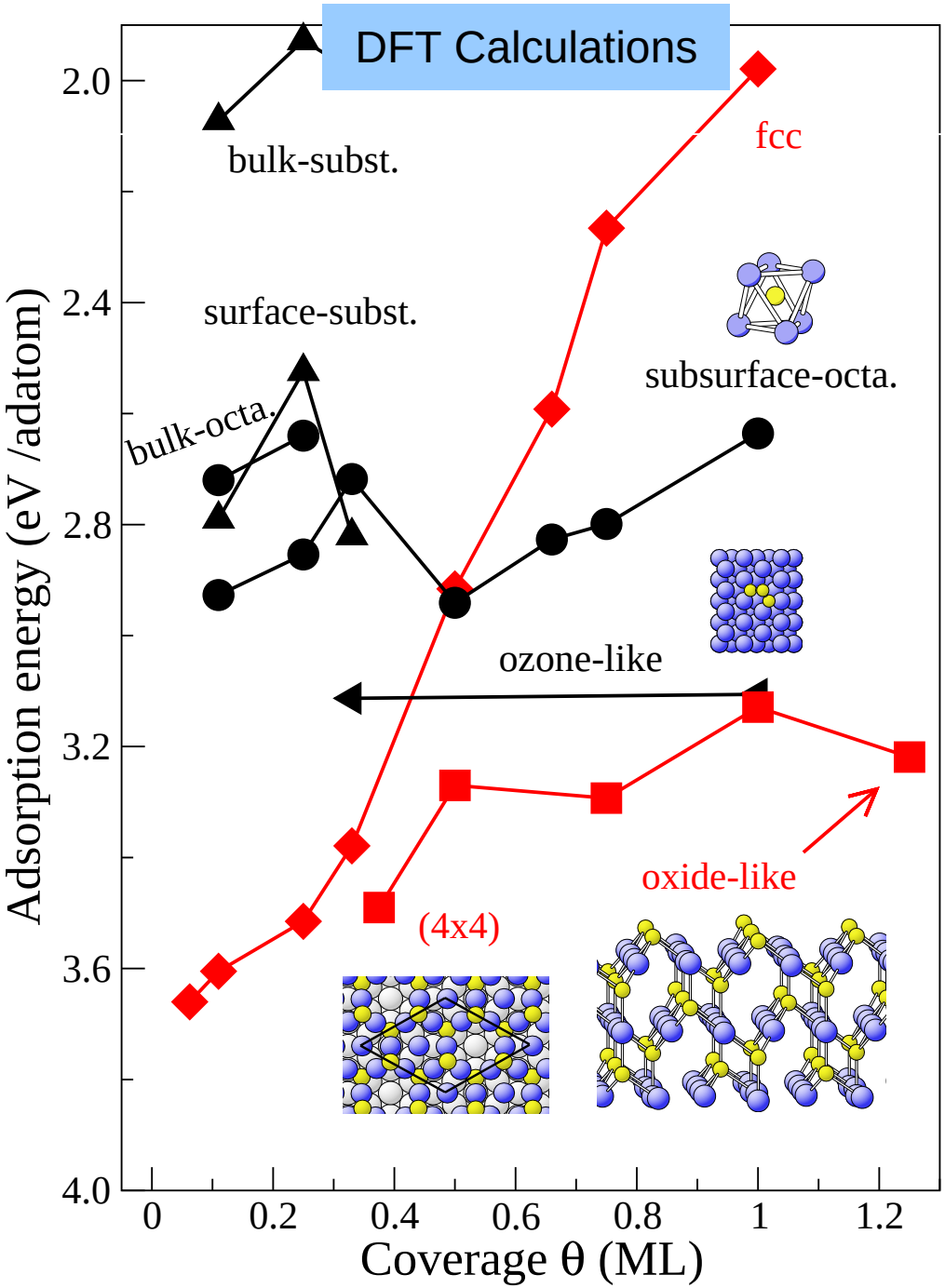
Oxygen chemisorptions on late *4d* transition metals



-Filling of *d*-band weakens substrate-adsorbate bond

- Repulsive interaction within electronegative adlayer

Todorova, Li, Pirovano, Stampfl, Reuter, Scheffler, Phys. Rev. Lett. *89, 096103* (2002)



The Role of the O-Ag Interaction in the function of Silver as an Oxidation Catalyst

Li, Stampfl, Scheffler,
Phys. Rev. B, 68, 165412 (2003),
Phys. Rev. B. 67, 045408 (2003),
Phys. Rev. B, 65, 075407 (2002)

From UHV to Real World (Theoretical Recipes)

Ab initio atomistic thermodynamics

Gibbs Formation Energy of Adsorption

$$\Delta G_{\text{Oxygen, Metal}}(T,P) = G_{\text{Oxygen,Metal}}(T,P) - G_{\text{Metal}}(T,P) - N\mu_{\text{Oxygen}}(T,P)$$

$G_{\text{O,Metal}}(T,P)$: Gibbs free energy after adsorption

Extended System: $G(T,P) = E^{tot} + F^{vib} + pV$

Molecule in Gas Phase:

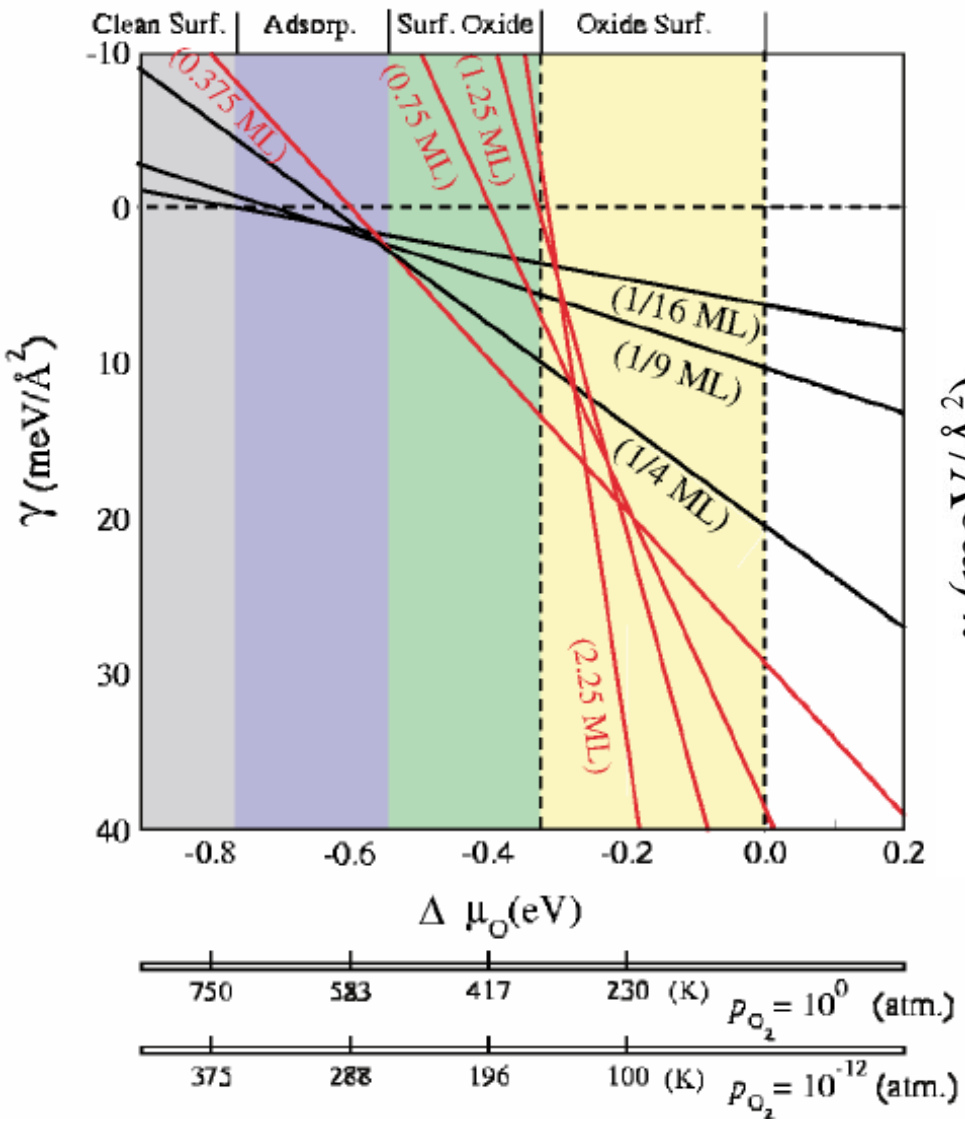
$$\mu_O(T,p) = \mu_O(T,p^0) + 1/2 k_B T \ln(p/p^0)$$

$$\Delta G_{\text{Oxygen, Metal}}(T,P) = E_{\text{Oxygen,Metal}}(DFT) - E_{\text{Metal}}(DFT) - N\mu_{\text{Oxygen}}(T,P)$$

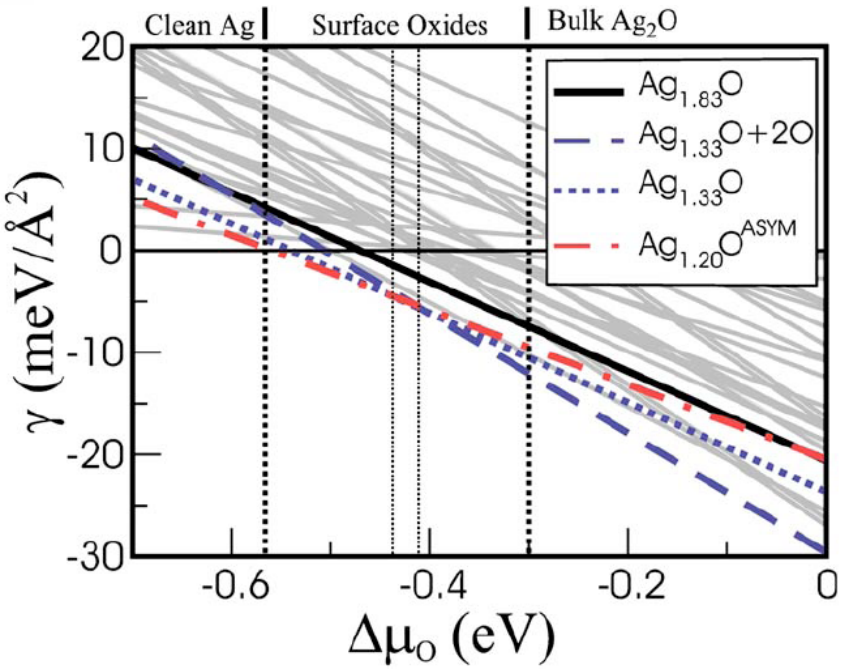
Reuter and Scheffler, Phys. Rev. B (2002)
Li, Stampfl and Scheffler, Phys. Rev. B 68, 165412 (2003)

Average Gibbs free energy of adsorption

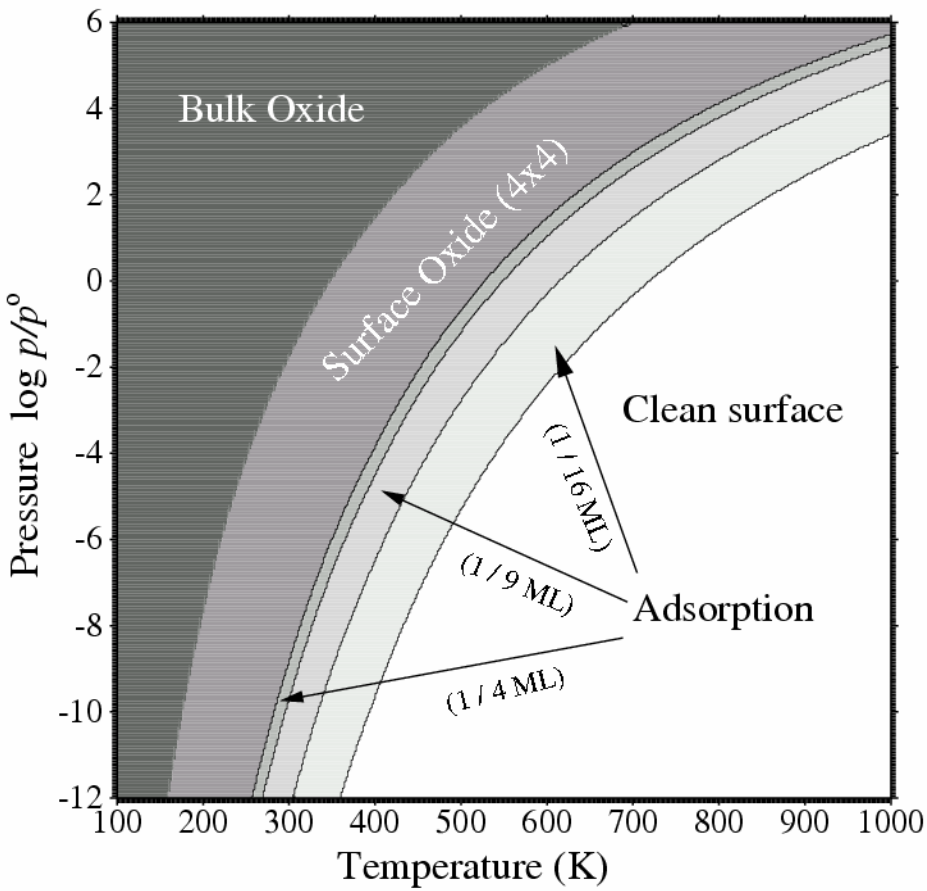
Li, Stampfl, Scheffler, Phys. Rev. Lett. 90, 256102 (2003)



Michaelide, Reuter and Scheffler, JVST(A) 23, 1487 (2005)



Pressure – Temperature Phase Diagram: O/Ag(111) bases on ab initio atomistic thermodynamics



Li, Stampfl and Scheffler, Phys. Rev. Lett. 90, 256102 (2003)

Revisiting the Structure of the $p(4 \times 4)$ Surface Oxide on Ag(111)

J. Schnadt,[1] A. Michaelides,[2] J. Knudsen,[1] R. T. Vang,[1] K. Reuter,[2] E. Lægsgaard,[1] M. Scheffler,[2] and F. Besenbacher[1]

[1]*Interdisciplinary Nanoscience Center and Department of Physics and Astronomy, University of Aarhus, Ny Munkegade, 8000 Aarhus C, Denmark*

[2]*Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany*

(Received 10 January 2006; published 10 April 2006)

Scanning tunneling microscopy (STM) and density-functional theory are used to reexamine the structure of the renowned $p(4 \times 4)$-O/Ag(111) surface oxide. The accepted structural model [C. I. Carlisle *et al.*, Phys. Rev. Lett. **84**, 3899 (2000)] is incompatible with the enhanced resolution of the current STM measurements. An "Ag_6 model" is proposed that is more stable than its predecessor and accounts for the coexistence of the $p(4 \times 4)$ and a novel $c(3 \times 5\sqrt{3})$rect phase. This coexistence is an indication of the dynamic complexity of the system that until now has not been appreciated.

Structure of Ag(111)-$p(4 \times 4)$-O: No Silver Oxide

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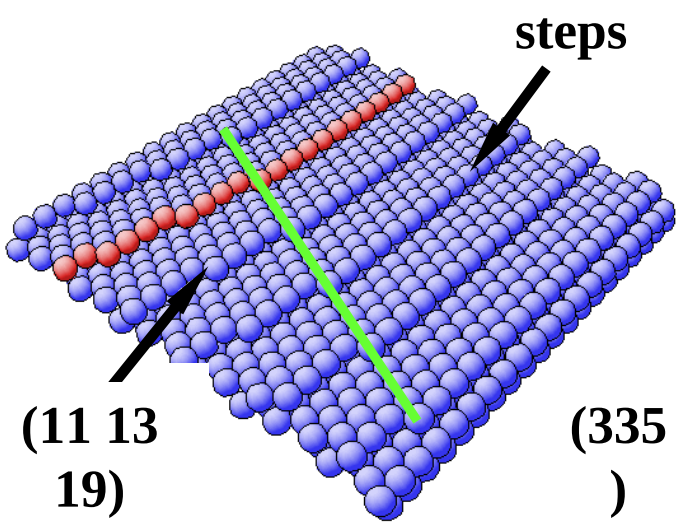
[5]*Department of Synchrotron Radiation Research, Lund University, 22100 Lund, Sweden*

(Received 12 January 2006; published 10 April 2006)

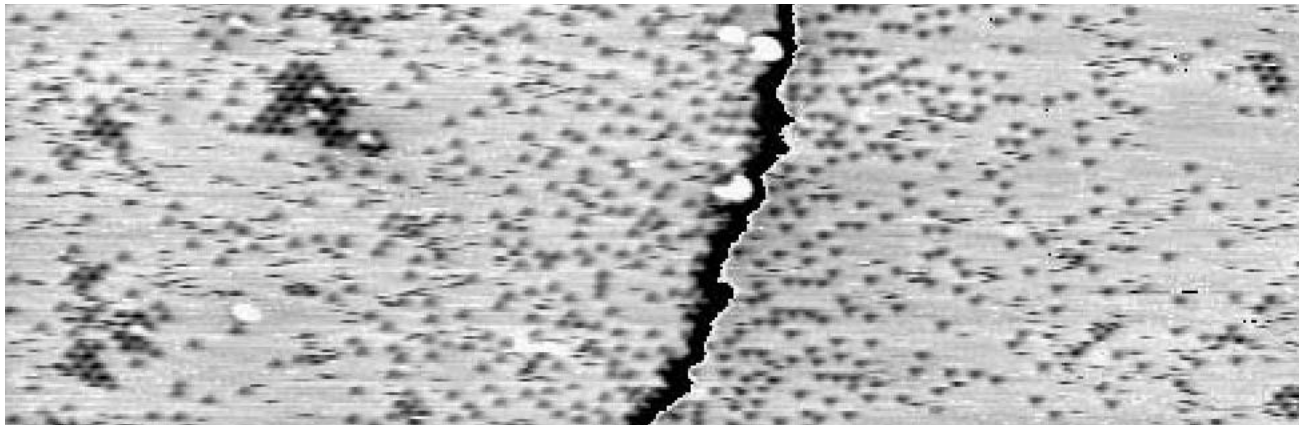
The structure of the oxygen-induced $p(4 \times 4)$ reconstruction of Ag(111) is determined by a combination of scanning tunneling microscopy, surface x-ray diffraction, core level spectroscopy, and density functional theory. We demonstrate that all previous models of this surface structure are incorrect and propose a new model which is able to explain all our experimental findings but has no resemblance to bulk silver oxide. We also shed some light on the limitations of current density functional theories and the potential role of van der Waals interactions in the stabilization of oxygen-induced surface reconstructions

- Oxidation of Ag(111) and ethylene epoxidation
- **Oxidation of Pt(332) and CO Oxidation**
- Oxidation of Pt(110) and CO Oxidation
- Oxidation of Rh(110) and H2 Reduction

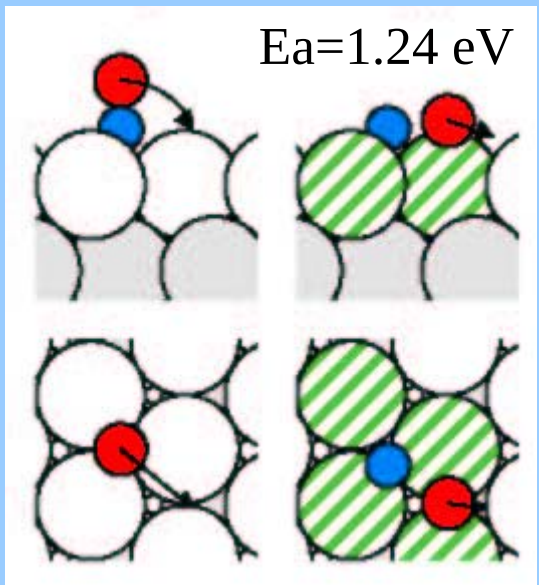


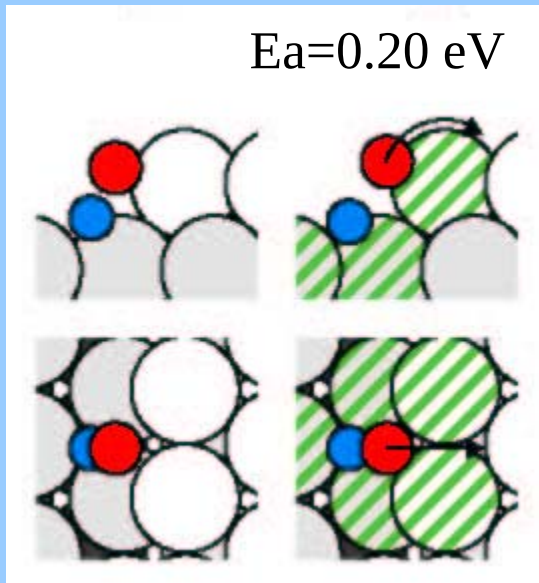
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg

NO dissociation at Ru steps



T.Zambelli, J. Wintterlin, J. Trost, G. Ertl, Science **273**, 1688 (1996).

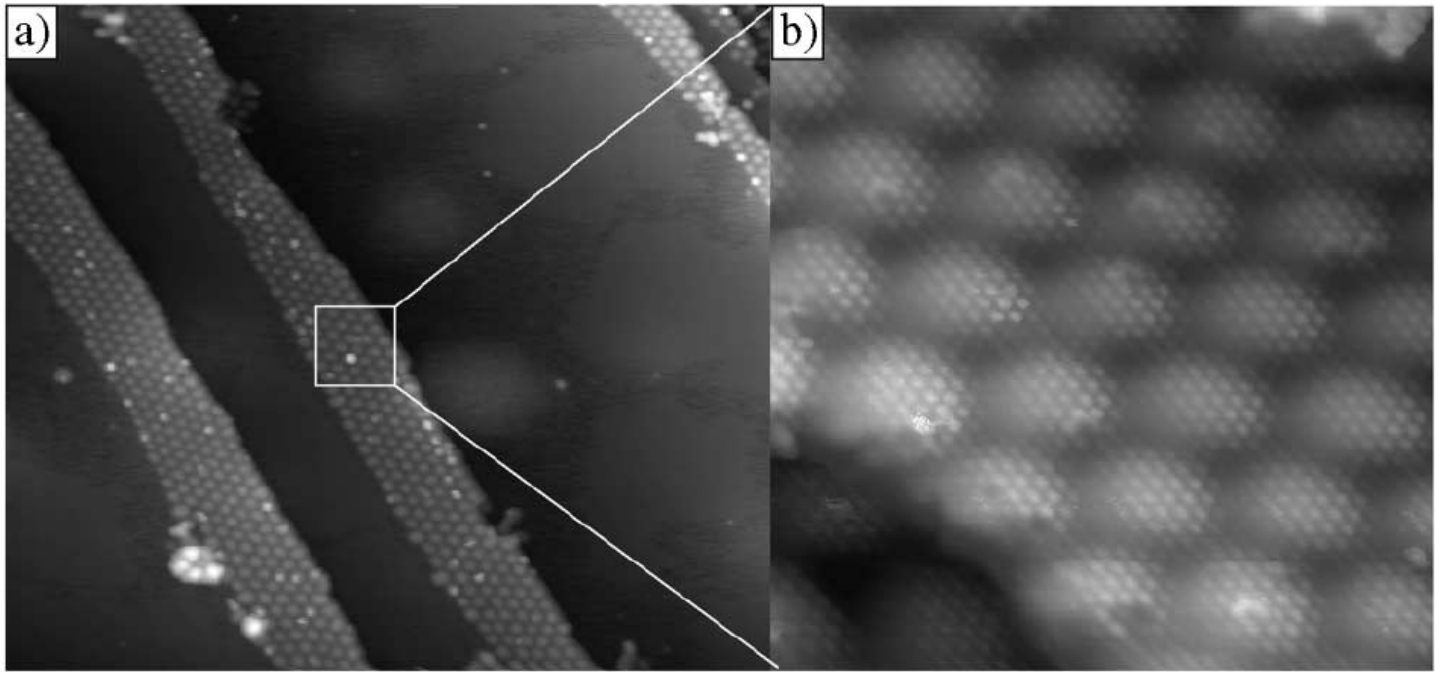




- High ε_d's at steps.
- More active metal atoms.

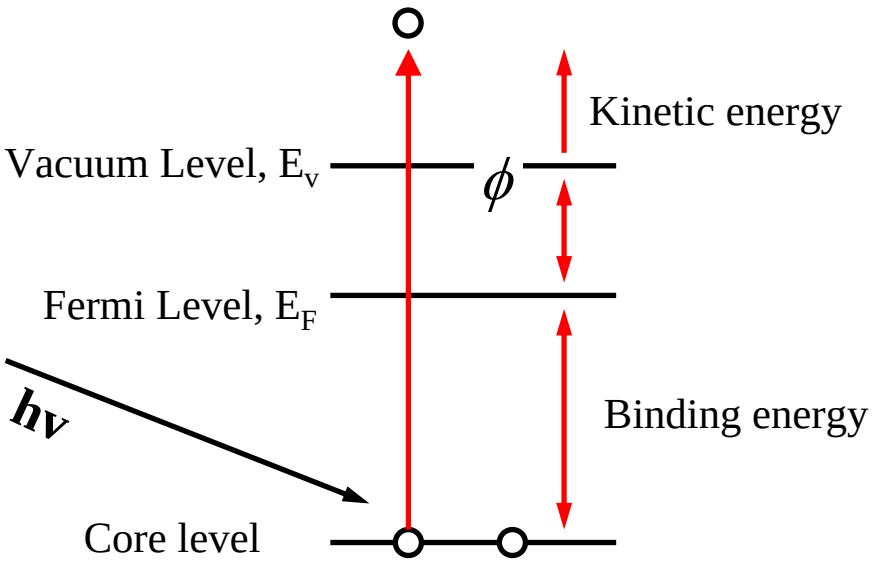
Hammer (1999).

Oxide Nucleation and Growth of Rh(111) along Step Edge



J. Gustafson et al, PRL 92, 126102 (2004)

X-ray Photoelectron Spectroscopy (XPS)



$$h\nu = E_{kin} + \phi + \varepsilon_c$$

$$\phi = \mathrm{E}_V - E_F$$

Core-electron Energy

$$\varepsilon_c = E(n-1) - E(n)$$

E(n) / E(n-1): total energy before / after core excited (frozen core approximation, valence electron relaxation included)

Surface Core Level Shift

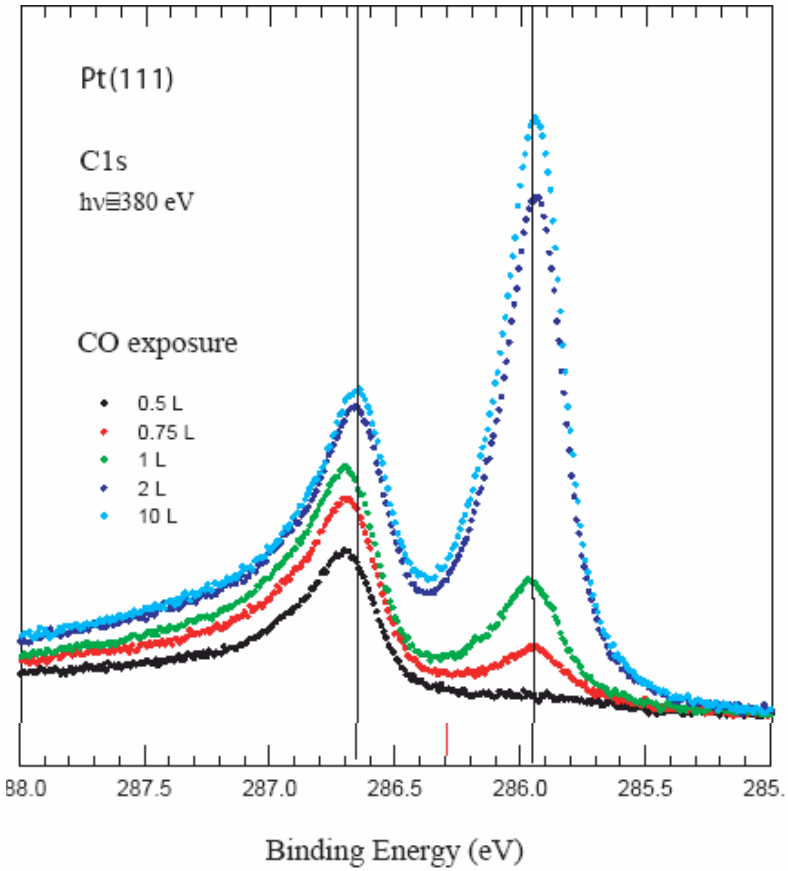
$$\Delta_{SCLS} = \varepsilon_c^{surf} - \varepsilon_c^{bulk}$$

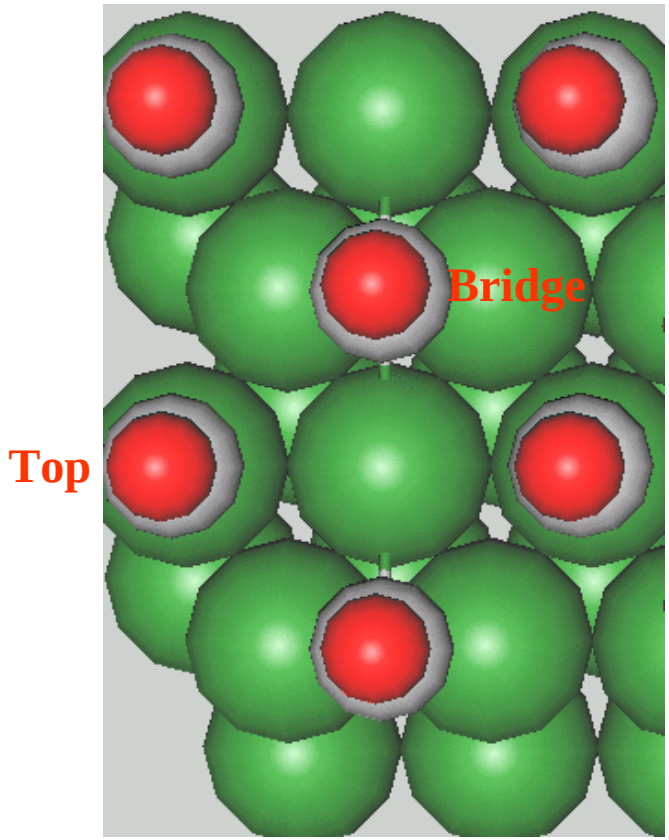
Final state effect included

Element specific and geometric sensitive
Fingerprint as adsorption site and oxidation state

CO Adsorption on Pt(111)

Top Bridge

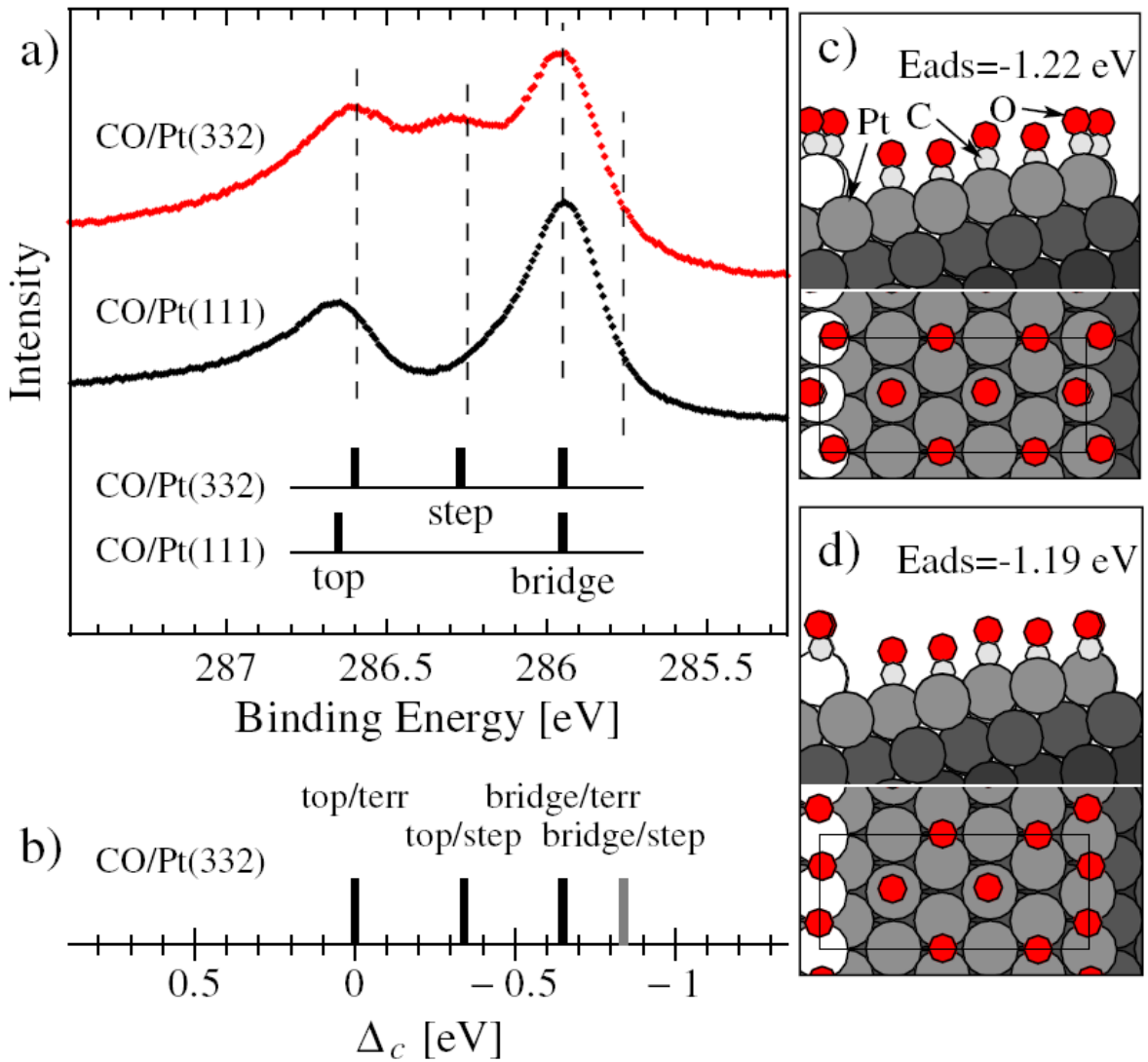




DFT Calculations

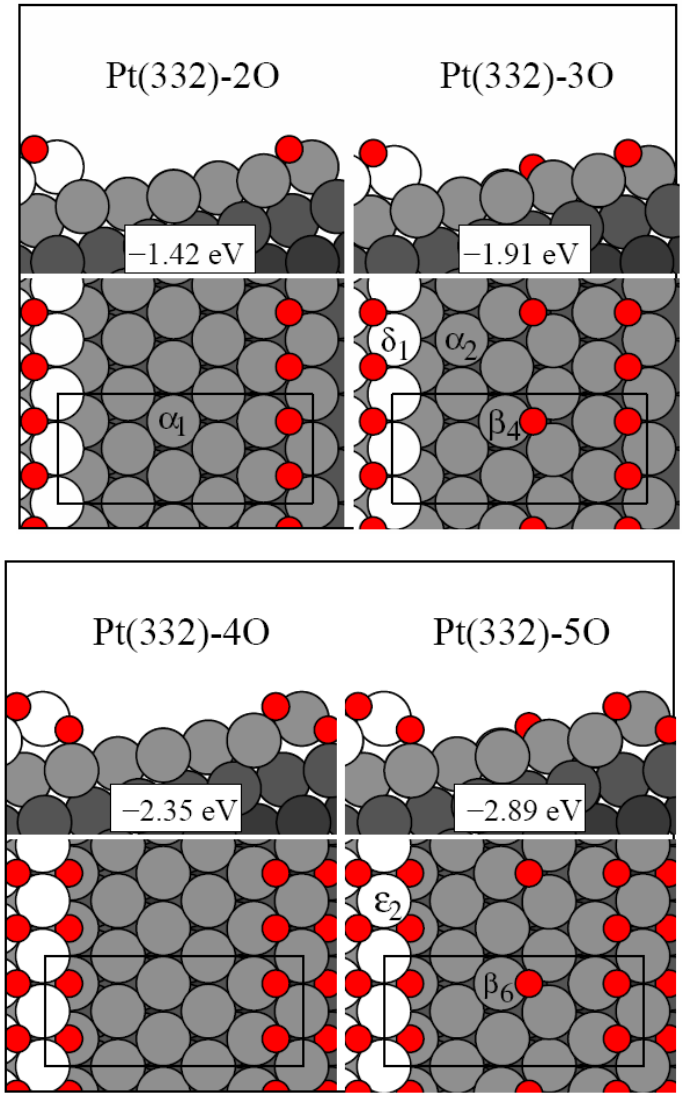
Wang, Li, Borg, Hammer and Andersen et al. Phys. Rev. Lett. 95, 256102 (2005)

CO Adsorption on Pt(332)

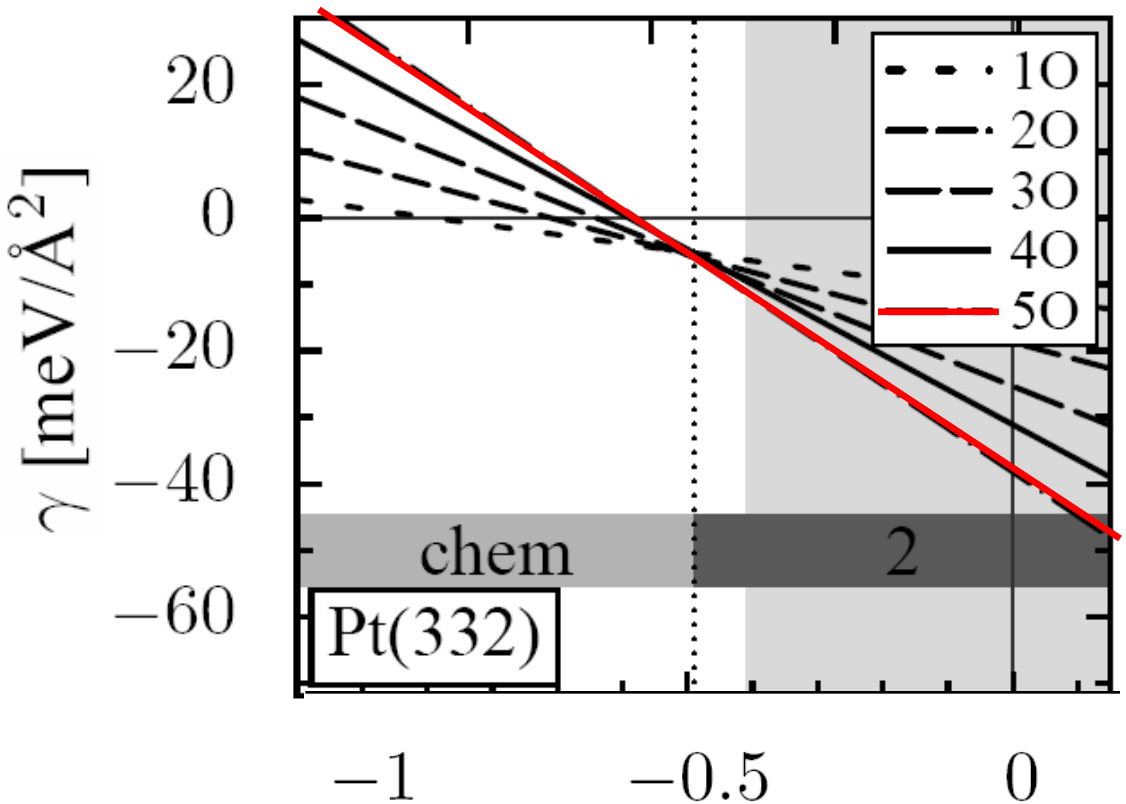


Wang, Li, Borg, Hammer and Andersen et al. Phys. Rev. Lett. 95, 256102 (2005)

Interaction between oxygen and Pt(332)

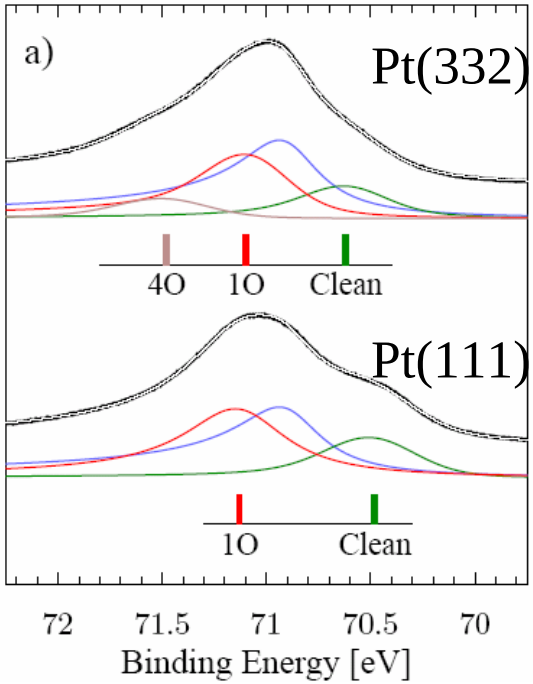


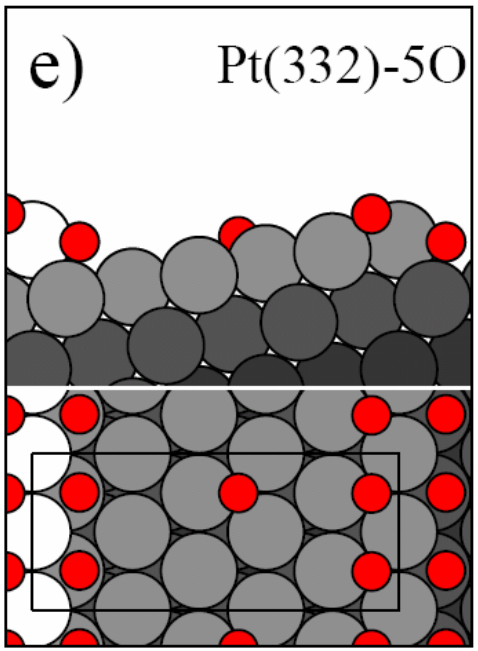
per (1x2) cell



T. M. Pedersen, J. G. Wang, W. X. Li, and B. Hammer, unpublished

1D PtO_2 along Step Edge of Pt(332)

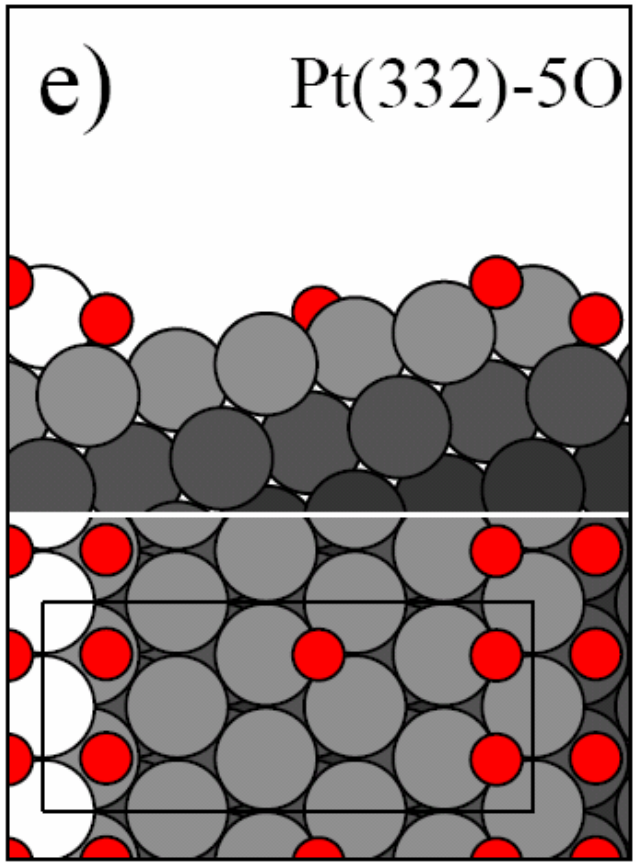




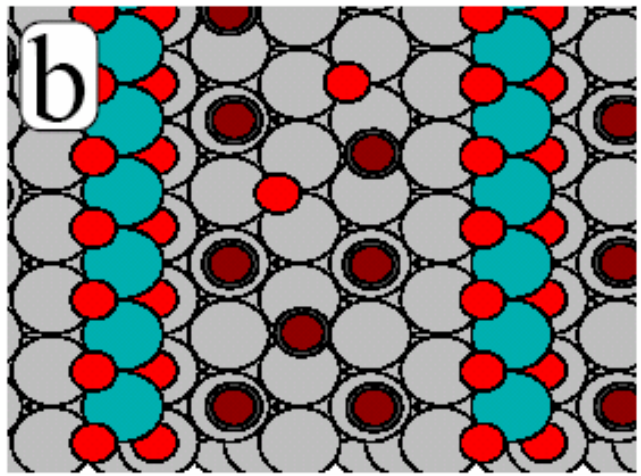
- Oxygen coverage varies from 0.37 ML to 0.46 ML without/with oxygen at terrace, which agrees with experimental 0.42 ML results
- Calculated Pt 4f binding energy of step Pt atoms coordinated with 4O oxygen atoms agree with experimental finding
- O1s binding energy for 4O (step edge) is lower 0.25 eV than 1O (terrace oxygen), which agrees with experimental findings 0.20 eV

Wang, Li, Borg, Hammer and Andersen et al.
Phys. Rev. Lett. 95, 256102 (2005)

CO Oxidation on O pre-covered Pt(332)

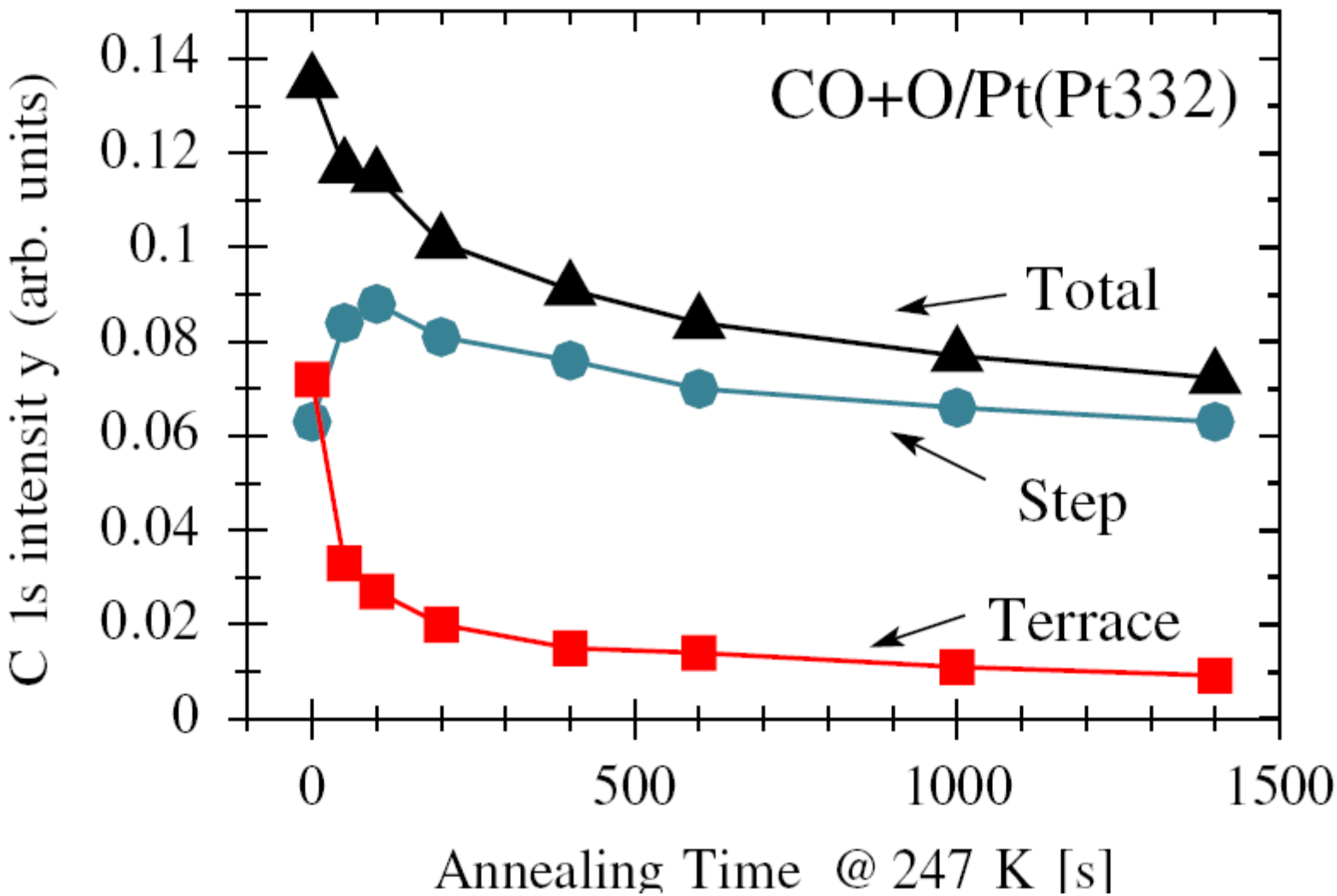


CO



reaction negligible at 220 K on Pt(332), instead of 270 K on Pt(111)

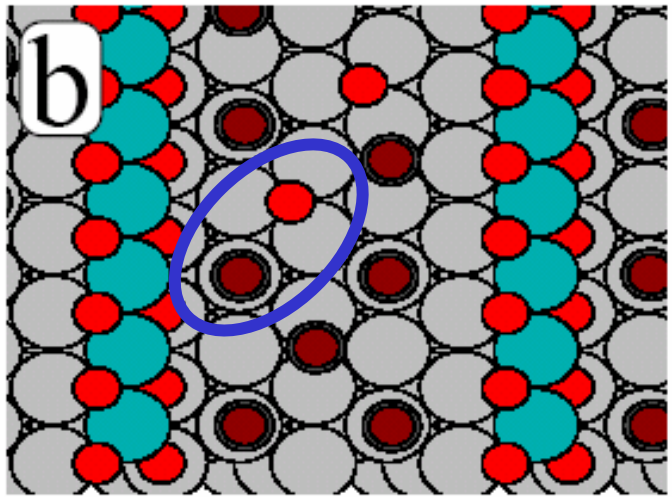
Wang, Li, Borg, Hammer and Andersen et al. Phys. Rev. Lett. 95, 256102 (2005)



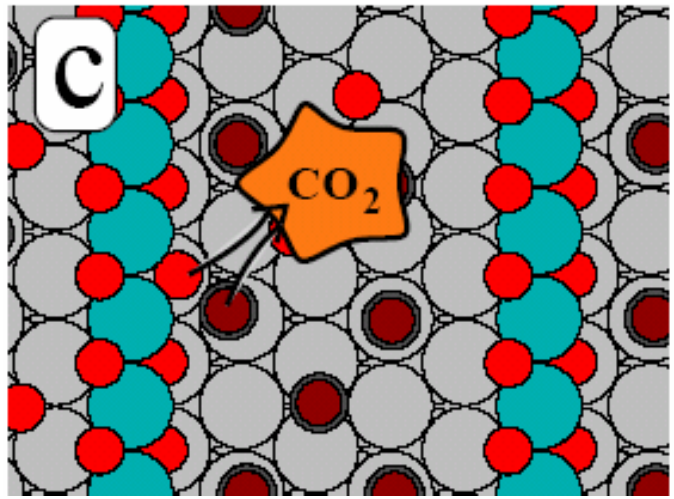
Wang, Li, Borg, Hammer and Andersen et al. Phys. Rev. Lett. 95, 256102 (2005)

CO Oxidation on Pt(332)

Initial State



TS



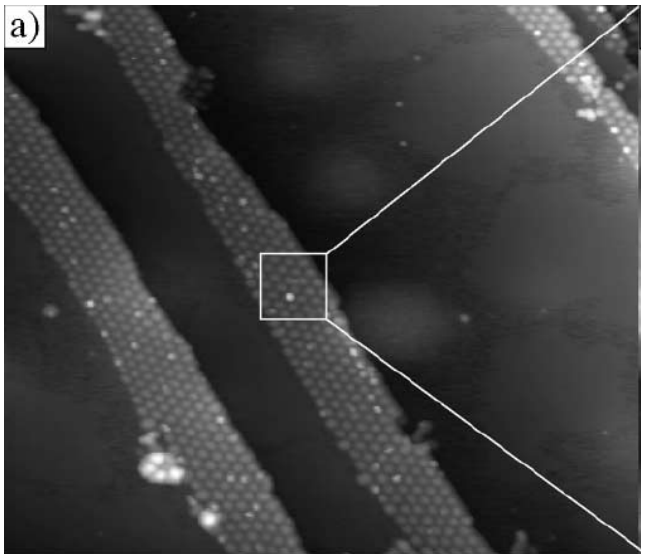
Reaction Barrier for CO oxidation:

0.60 eV for 1D PtO2 (E_b=0.77 eV for step oxygen)

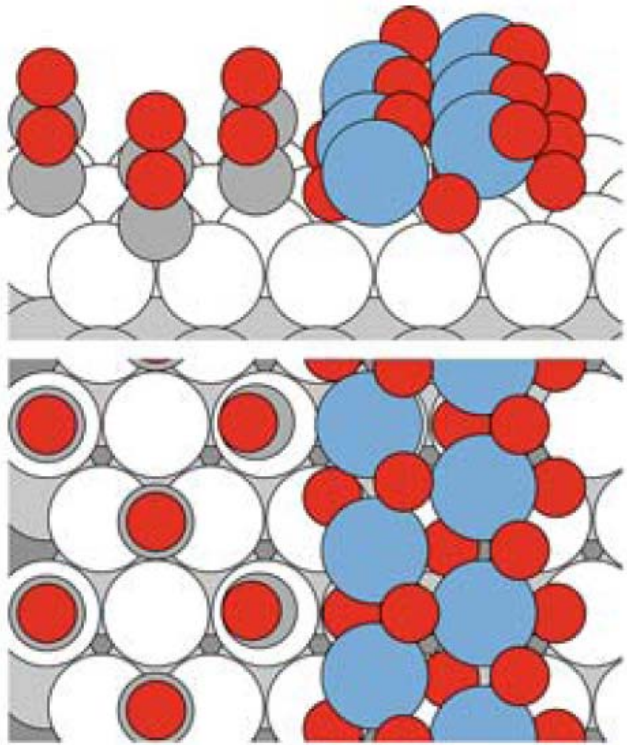
0.71 eV for terrace oxygen (E_b =0.54 eV for terrace oxygen)

Wang, Li, Borg, Hammer and Andersen et al. Phys. Rev. Lett. 95, 256102 (2005)

Reactivity of a gas/metal/metal-oxide three-phase boundary



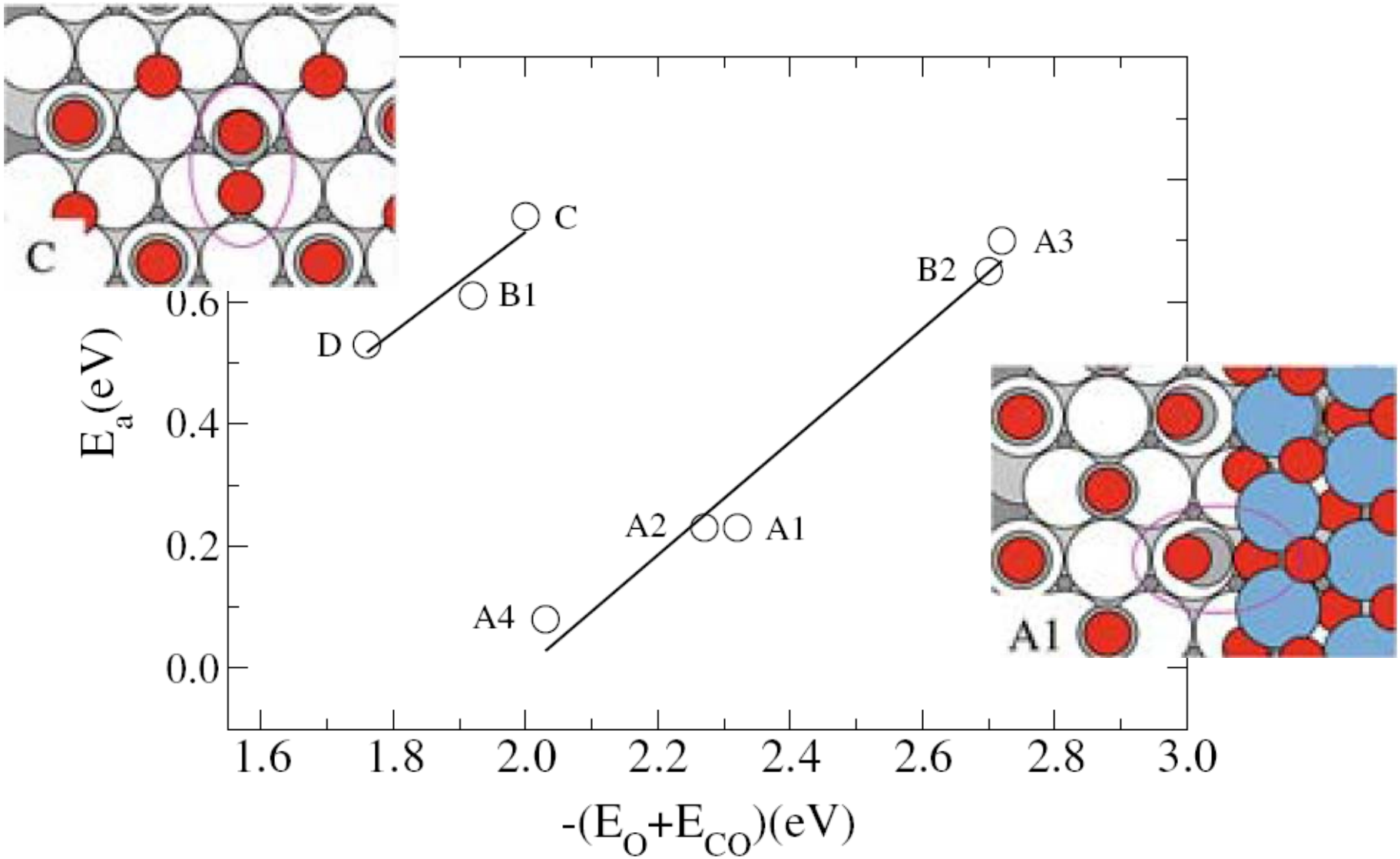
Oxidation of Rh(111) Surface
J. Gustafson et al, PRL (2004)



CO Oxidation on oxidized Pt surfaces

W. X. Li and B. Hammer, Chem. Phys. Lett. (409) 1, 2005

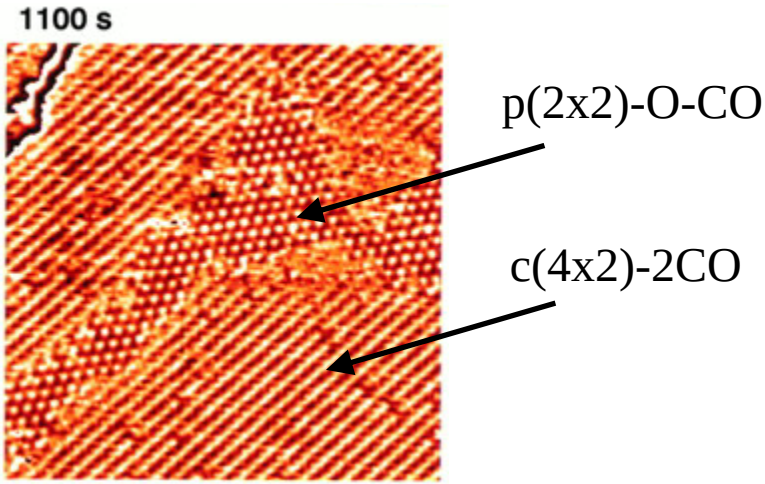
Reactivity at gas/metal/metal oxide three phases boundary



W. X. Li and B. Hammer,
Chem. Phys. Lett. (409) 1, 2005

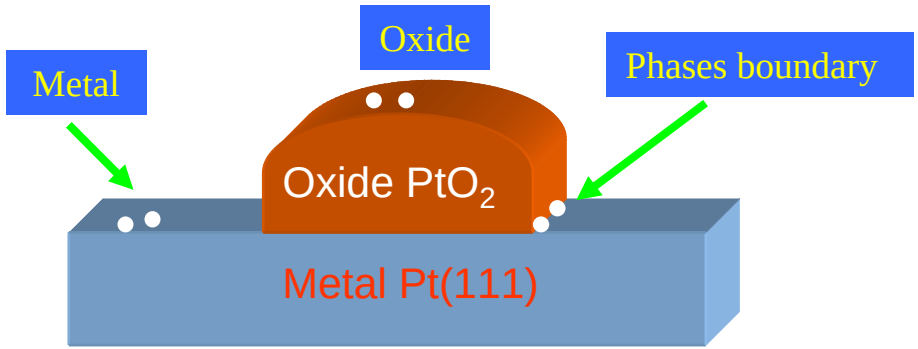
Enhanced Reactivity at phases boundary

Pt(111)



J. Wintterlin et al,
Science 278, 1931 (1997)

Pt(111)-PtO_2(0001)



A "Reverse" Model Catalyst

<u>Calculated Barrier for CO Oxidation</u>

- Inside p(2x2)-O-CO: 0.74 eV
- Phases boundary: 0.53 eV

<u>Calculated Barrier for CO Oxidation</u>

- Oxide: > 2 eV
- Metal: 0.78 eV
- Phases boundary: 0.1-0.65 eV

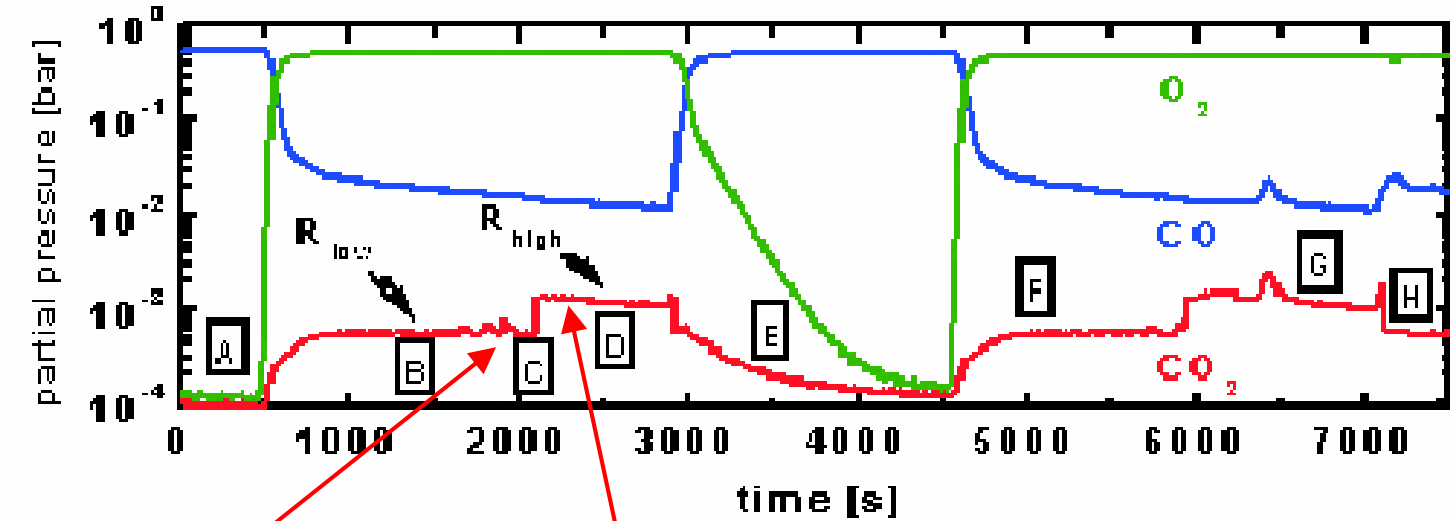
W. X. Li and B. Hammer, Chem. Phys. Lett. 409, 1 (2005)

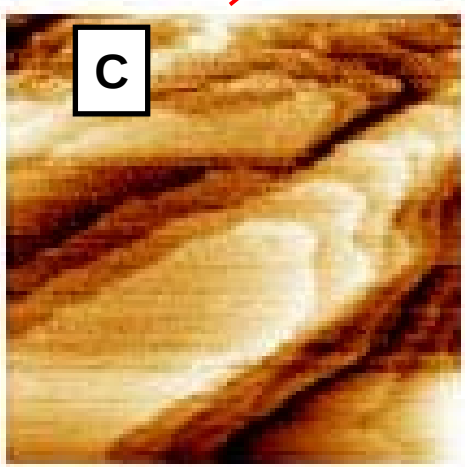
- Oxidation of Ag(111) and ethylene epoxidation
- Oxidation of Pt(332) and CO Oxidation
- **Oxidation of Pt(110) and CO Oxidation**
- Oxidation of Rh(110) and H2 Reduction

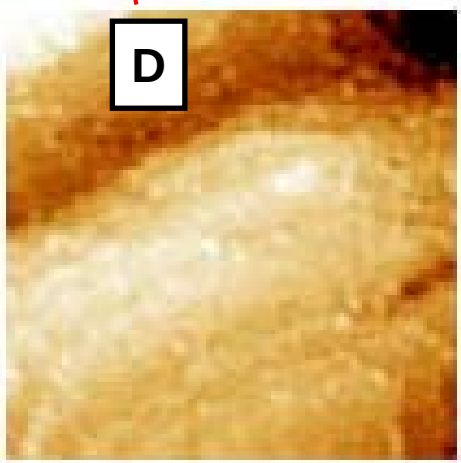
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg

CO oxidation on Pt(110)

STM tip zoom in Reactor



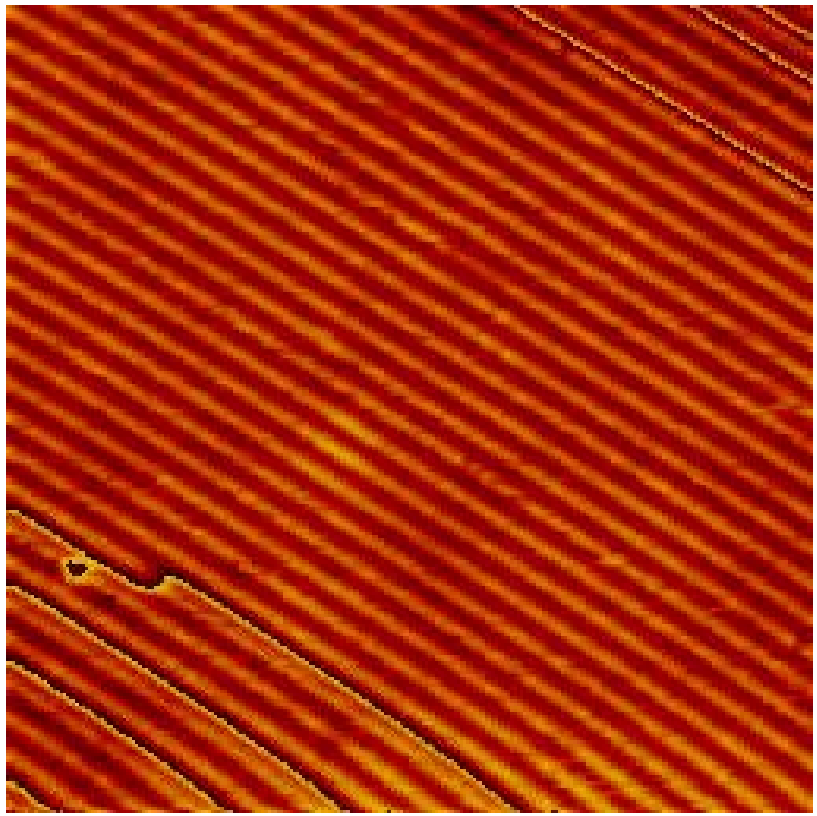




Langmuir Mechanism (metal)
Or
Mars Van Krevelen Mechanism
(Metal Oxide)

B. Hendriksen and J. Frenken
Phys. Rev. Lett. 89, 046104 (2002)

Low Oxygen Exposure on Pt(110)

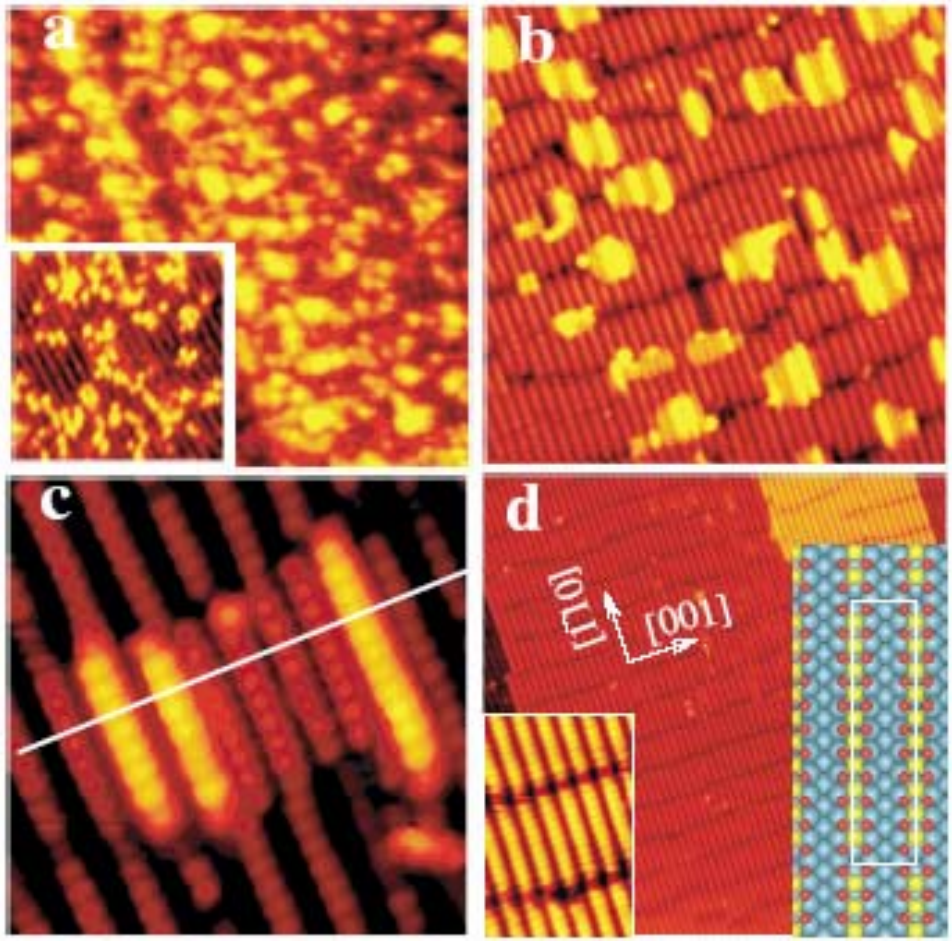


T=357 K
O dosage up to 205 L
Frame rate: 0.12/sec.
20.8nm x 22.6 nm

Helveg, Li, Bartelt, Hammer, Besenbacher et al., submitted to Phys. Rev. Lett.

Oxidation of Pt(110)

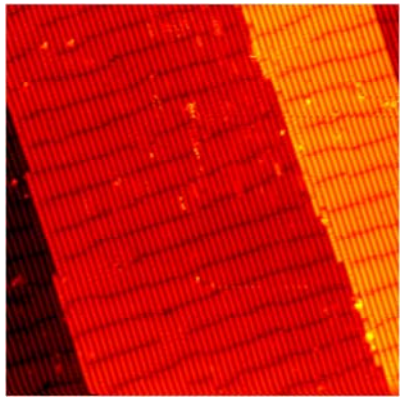
298K 30x30nm^2 500K 30x30nm^2



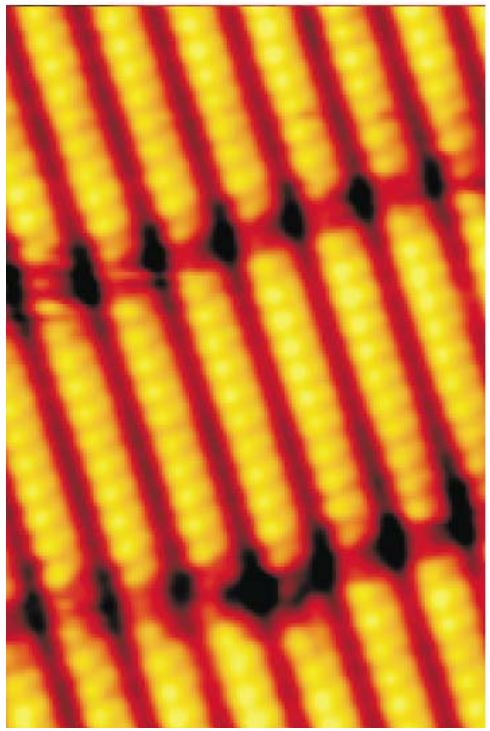
500K 6x6nm^2 600K 50x50nm^2

Li, Osterlund, Vestergaard, Hammer, Besenbacher et al., Phys. Rev. Lett. 93, 146103 (2004)

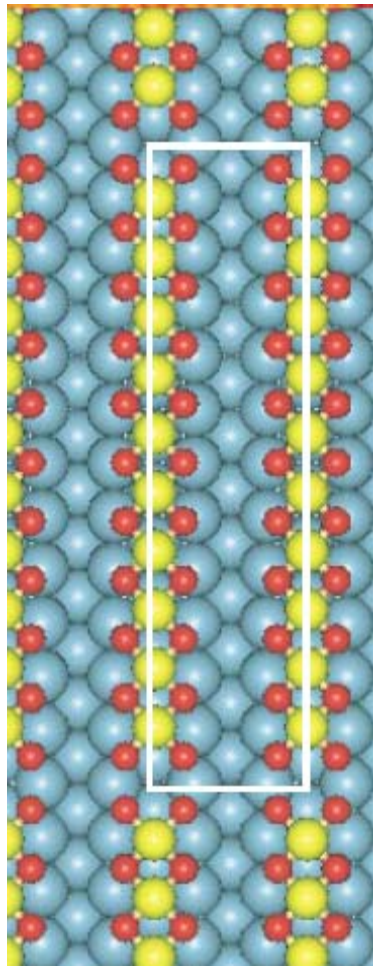
Strained (12x2) Reconstruction



600K, 50x50nm^2



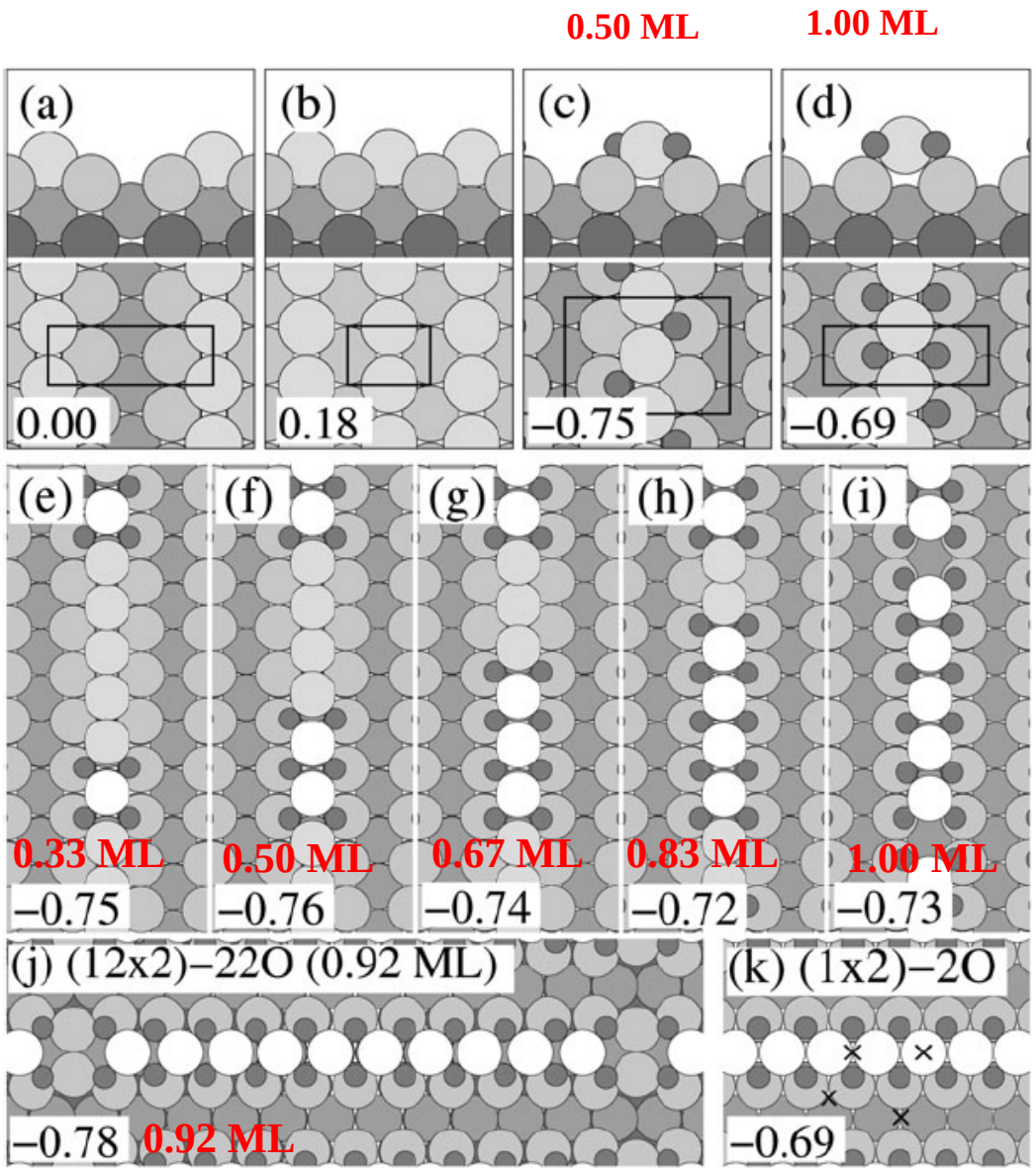
600K, 4.6x7.7nm^2



Surface Oxide

- strained nanostructure (12x2) reconstruction underneath
  increased Pt-Pt dist. along [110] (expansion 14 %)
  2 Pt atoms out of 12 ejected

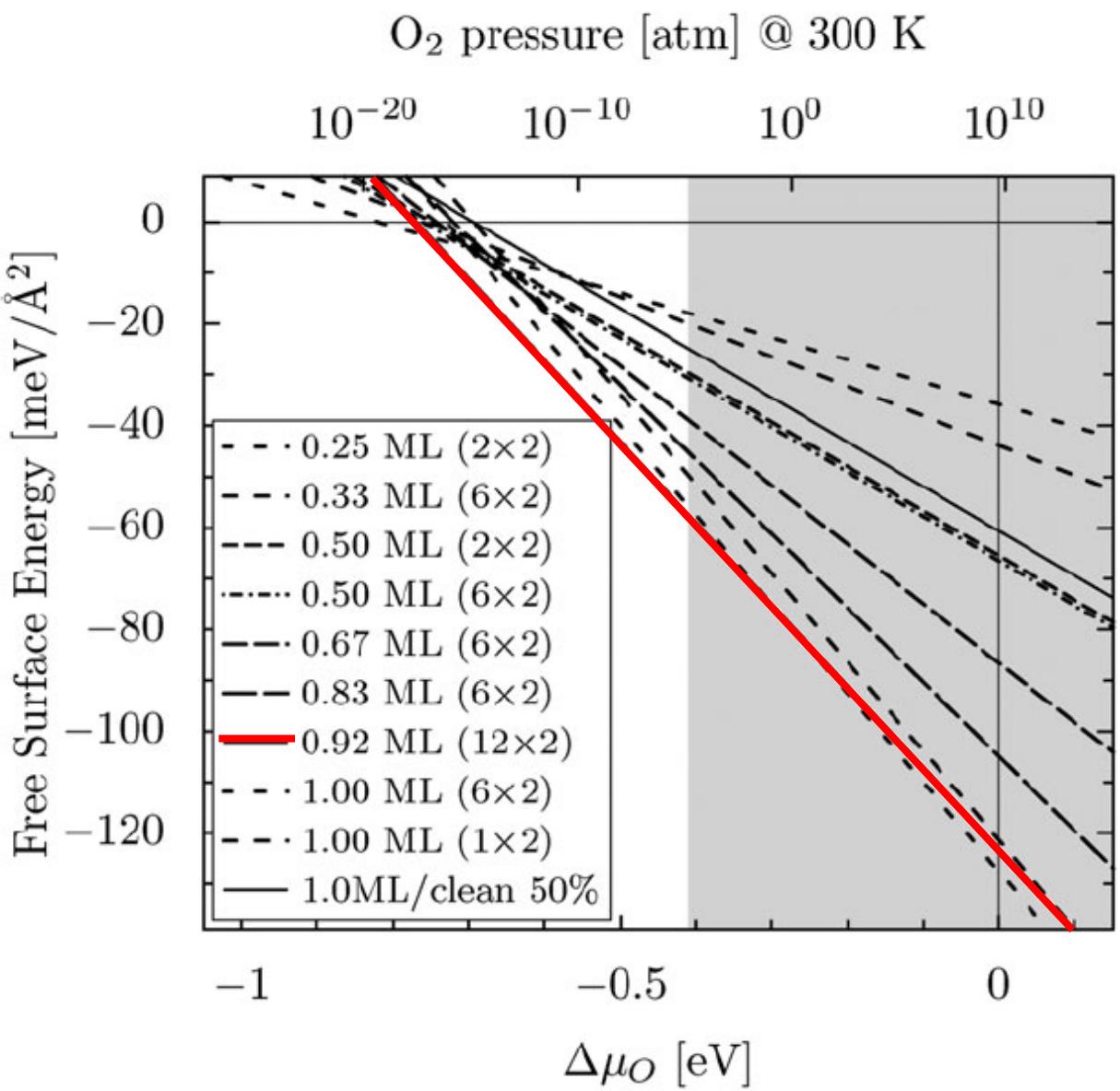
Interaction between oxygen and Pt(110)



(eV / O atom)

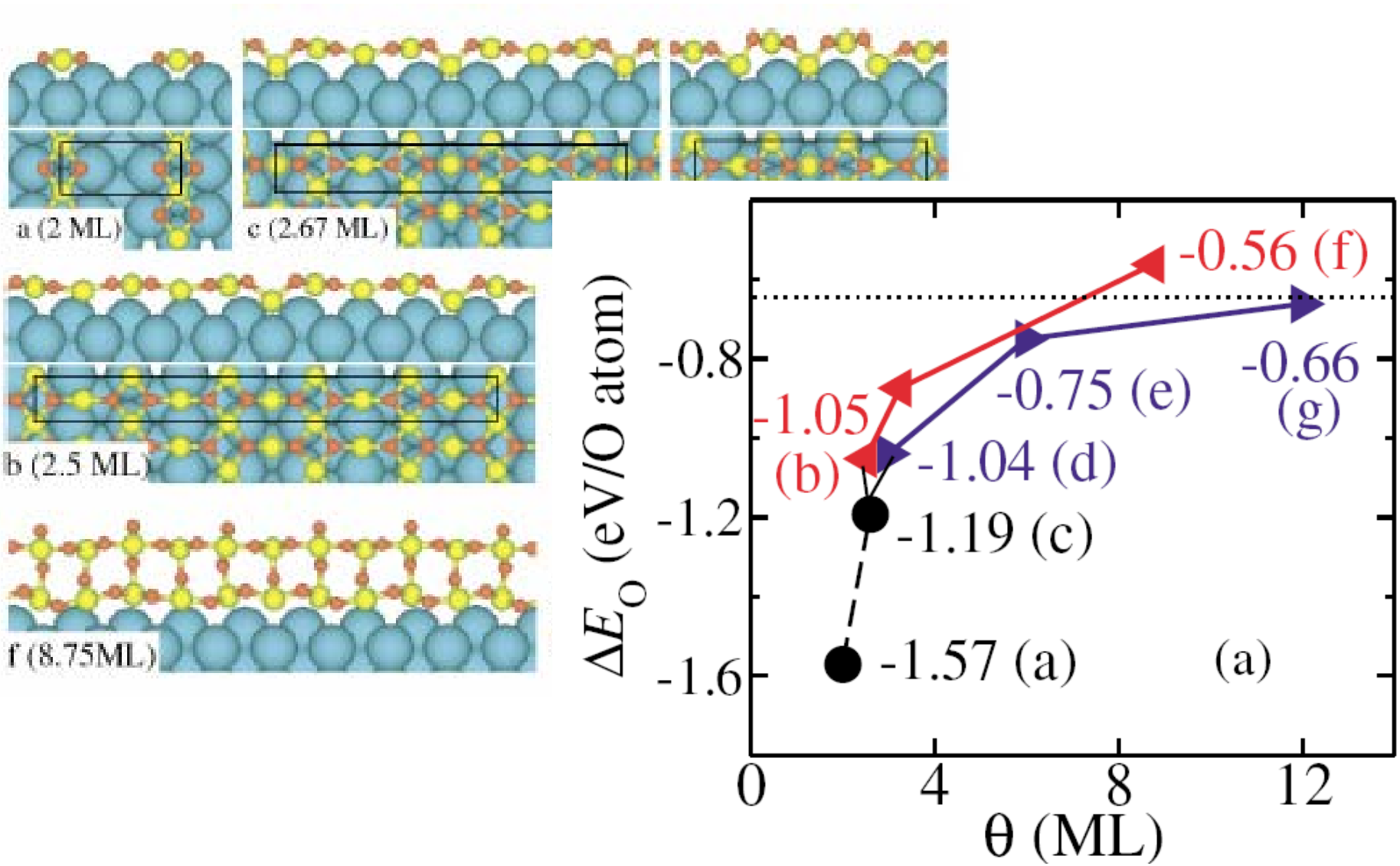
Surface Oxide

Pederson, Li and Hammer, PCCP 8, 1566 (2006)



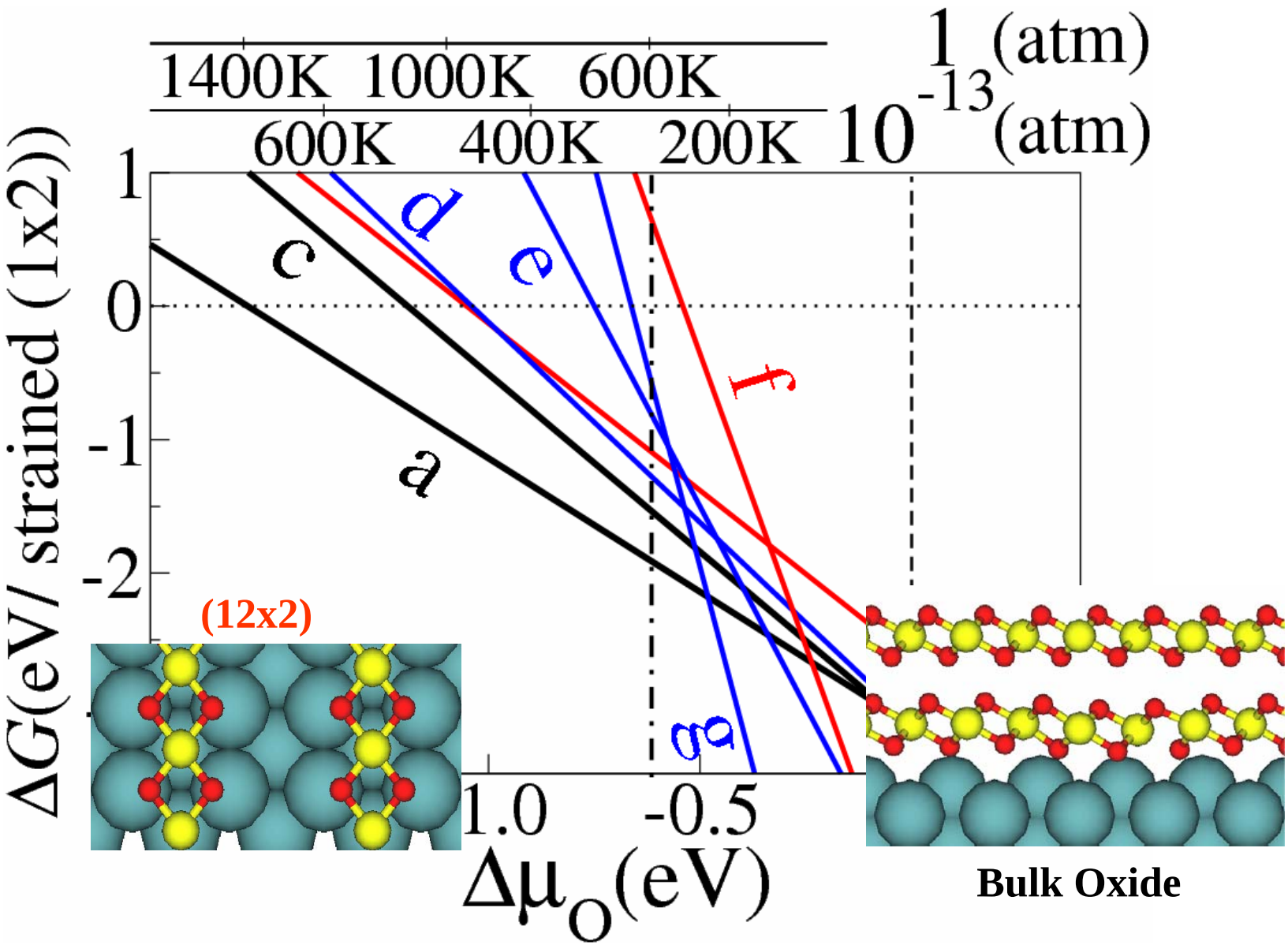
T. M. Pederson, W. X. Li and B. Hammer, PCCP 8, 1566 (2006)

Oxidation of Pt(110)



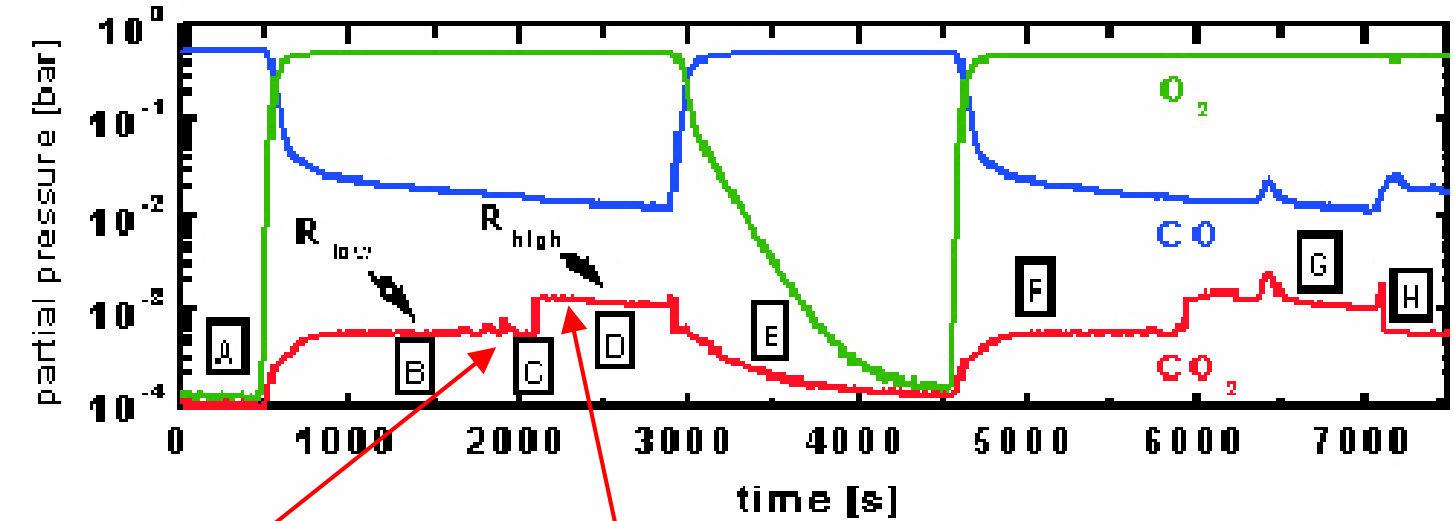
Li, Osterlund, Vestergaard, Hammer, Besenbacher et al., Phys. Rev. Lett. 93, 146103 (2004)

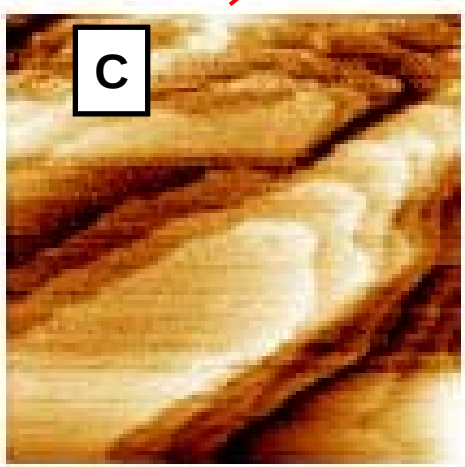
Phase Diagram of O/Pt(110) Surfaces

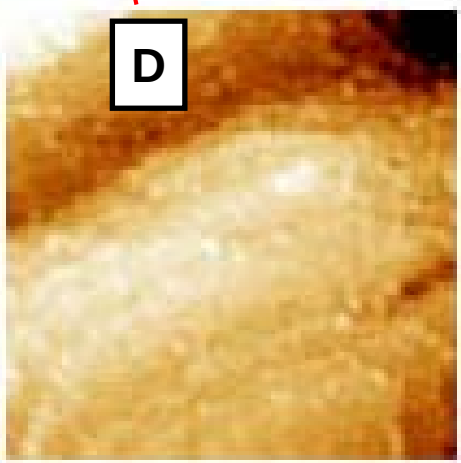


CO oxidation on Pt(110)

STM tip zoom in Reactor







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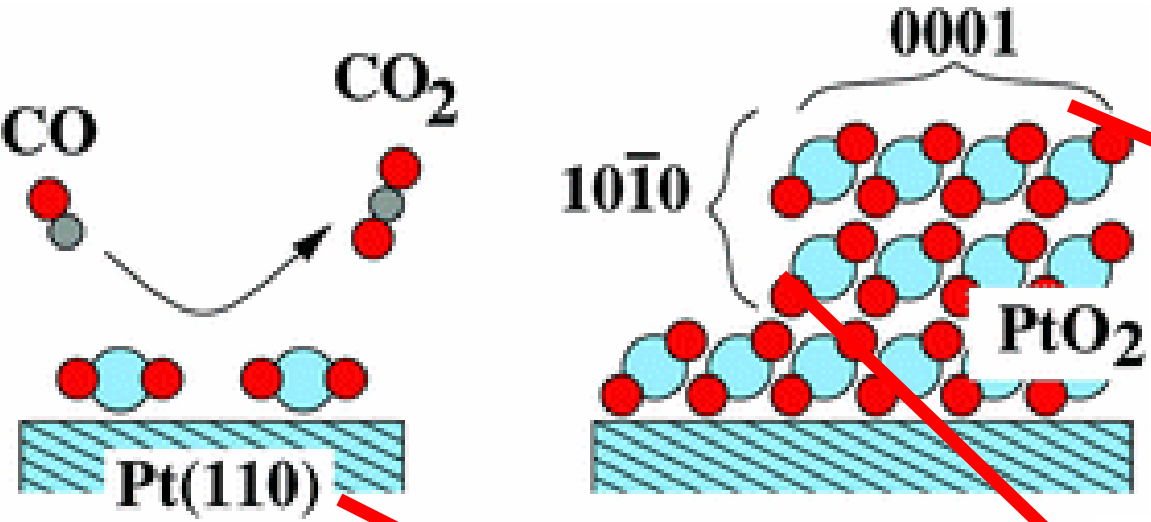
Or
Mars Van Krevelen Mechanism
(Metal Oxide)

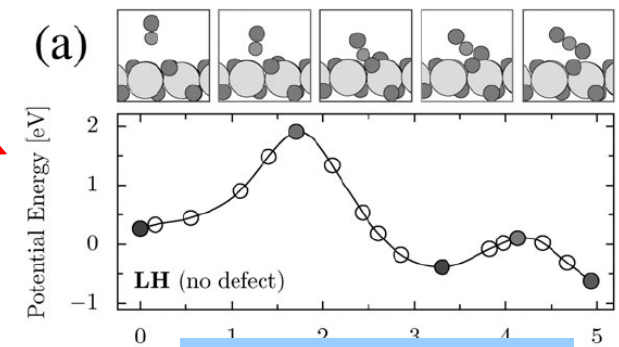
B. Hendriksen and J. Frenken
Phys. Rev. Lett. 89, 046104 (2002)

Oxidation and Reaction of Pt(110) with CO

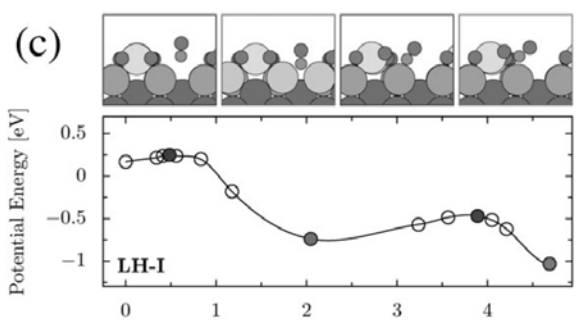
Surface Oxide

Bulk PtO2

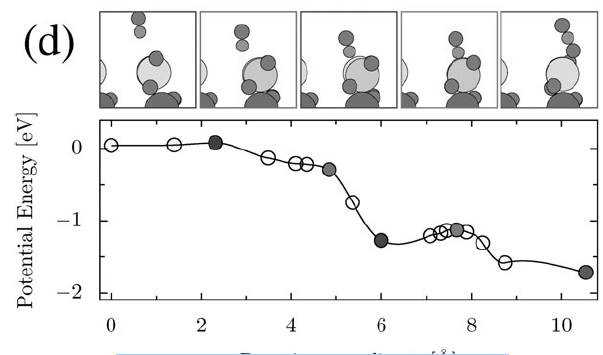




Barrier: ~ 2 eV



Barrier: 0.3 eV



Barrier: 0.2 eV

T. M. Pederson, W. X. Li and B. Hammer, PCCP 8, 1566 (2006)

Structure and Reactivity of Surface Oxides on Pt(110) during Catalytic CO Oxidation

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[1]*ESRF, 6, rue Jules Horowitz, F-38043 Grenoble cedex, France*
[2]*Kamerlingh Onnes Laboratory, Leiden University, P.O. Box 9504, 2300 RA Leiden, The Netherlands*
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[4]*CEA-Grenoble DRFMC/SI3M/PCM17, rue des Martyrs, 38054 Grenoble cedex 9, France*
[5]*Departamento de Física, Faculdad de Ciencias, Universidad de Oviedo, Avda. Calvo Sotelo, s/n, 33007 Oviedo, Spain*
[6]*CELLS - ALBA, Edifici Ciències Nord. Mòdul C-3 centra, Campus Universitari de Bellaterra, Universita Autònoma de Barcelona, 08193 Bellaterra, Spain*

(Received 1 July 2005; published 16 December 2005)

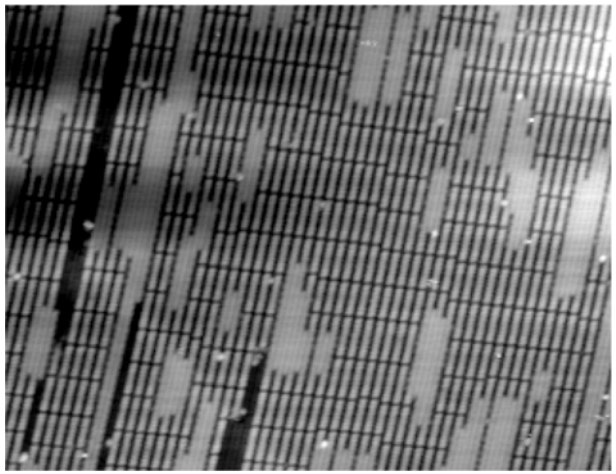
We present the first structure determination by surface x-ray diffraction during the restructuring of a model catalyst under reaction conditions, i.e., at high pressure and high temperature, and correlate the restructuring with a change in catalytic activity. We have analyzed the Pt(110) surface during CO oxidation at pressures up to 0.5 bar and temperatures up to 625 K. Depending on the O_2/CO pressure ratio, we find three well-defined structures: namely, (i) the bulk-terminated Pt(110) surface, (ii) a thin, commensurate oxide, and (iii) a thin, incommensurate oxide. The commensurate oxide only appears under reaction conditions, i.e., when both O_2 and CO are present and at sufficiently high temperatures. Density functional theory calculations indicate that the commensurate oxide is stabilized by carbonate ions (CO_3^{2-}). Both oxides have a substantially higher catalytic activity than the bulk-terminated Pt surface.

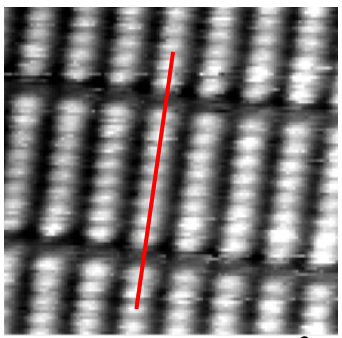
- Oxidation of Ag(111) and ethylene epoxidation
- Oxidation of Pt(332) and CO Oxidation
- Oxidation of Pt(110) and CO Oxidation
- **Oxidation of Rh(110) and H2 Reduction**

high local oxygen coverage
strained
nanostructured

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg

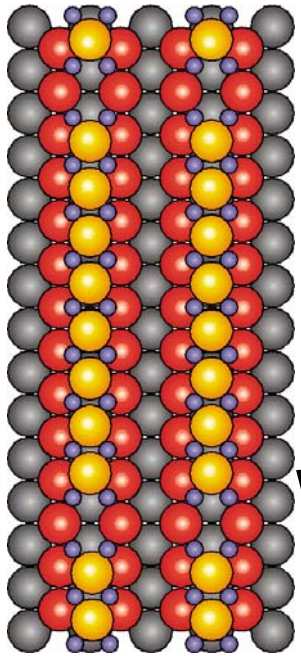
Characteristics of the (10×2) structure





53×53 Å^2

(10×2)

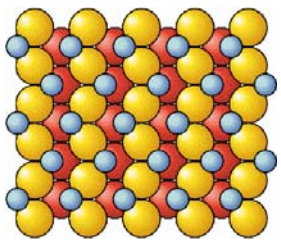


- ***strained nanostructure***

  increased Rh-Rh dist. (11%)

  2 Rh atoms out of 10 ejected

- reconstructed areas
  +
  unreconstructed areas
  covered by (2×1)p2mg-O

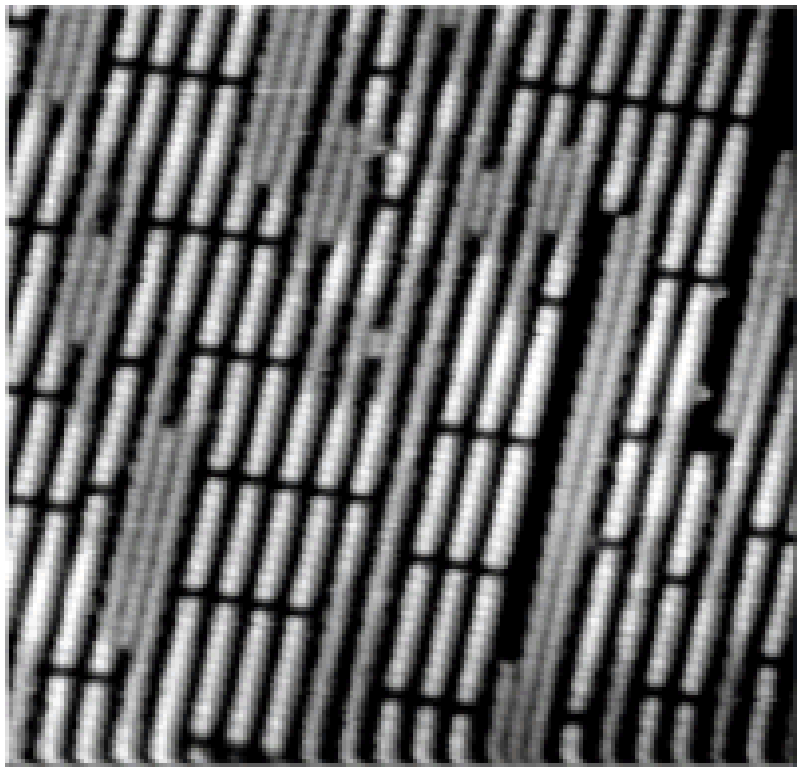


(2×1)p2mg

Africh, Esch, Li, Corso, Hammer, Rosei, and Comelli, Phys. Rev. Lett. 93, 126104 (2004)

H2 Reduction: Two-Step Reaction

Room temperature, partial pressure of H_2: 10^{-8} mbar



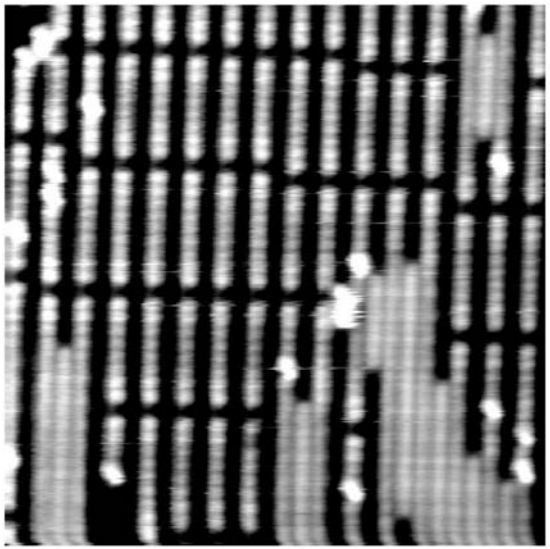
40x30nm^2

Acquisition time: 35 s per image

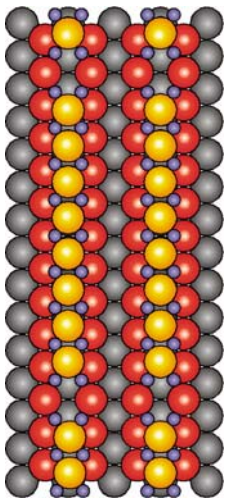
Africh, Esch, Li, Corso, Hammer, Rosei, and Comelli, Phys. Rev. Lett. 93, 126104 (2004)

1st-step reaction

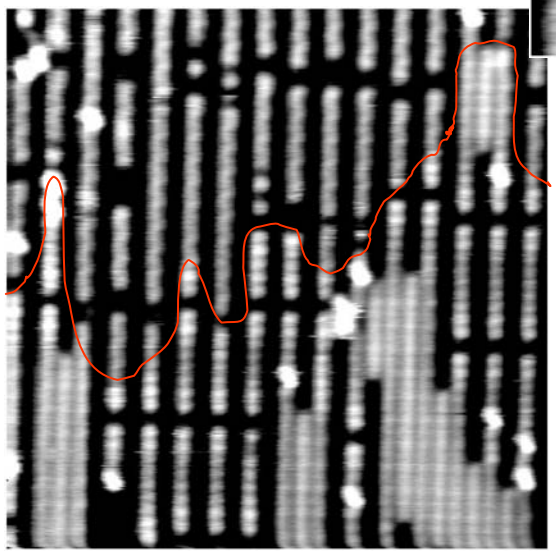
Initial surface: (10x2)



150 x 150 Å^2



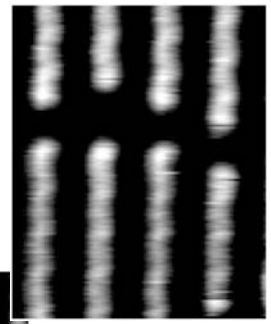
Distance between the segments increased: no more strain!



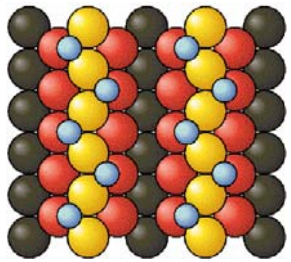
1st oxygen removal:

- reaction front
- zig-zag oxygen left
- strain removal

40 x 50 Å^2



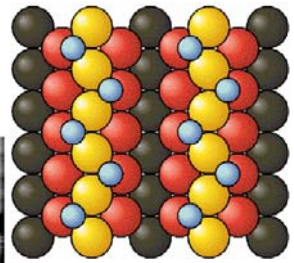
Zig-zaged appearance due to oxygen in threefold sites

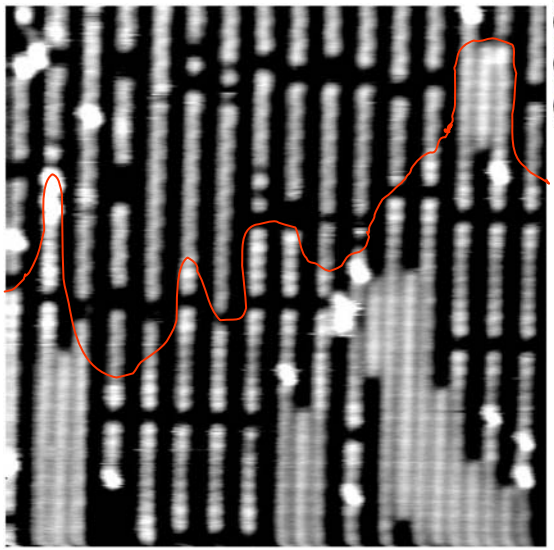


(2×2)p2mg segmented

2nd-step reaction

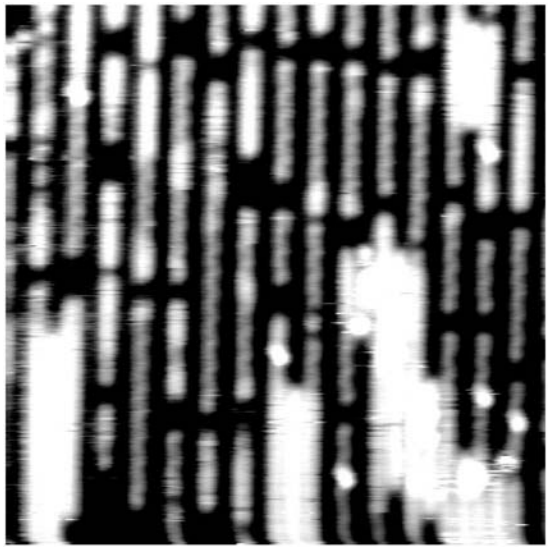
(2×2)p2mg
segmented





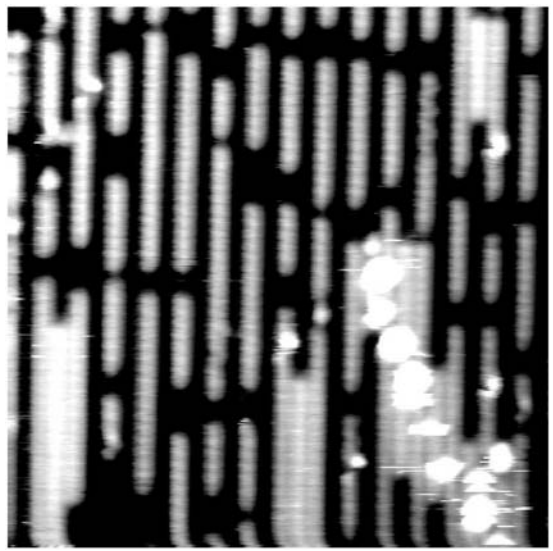
1st oxygen removal:
- reaction front
- zig-zag oxygen left
- strain removal

Brighter areas
where zig-zag
oxygen reacted
off



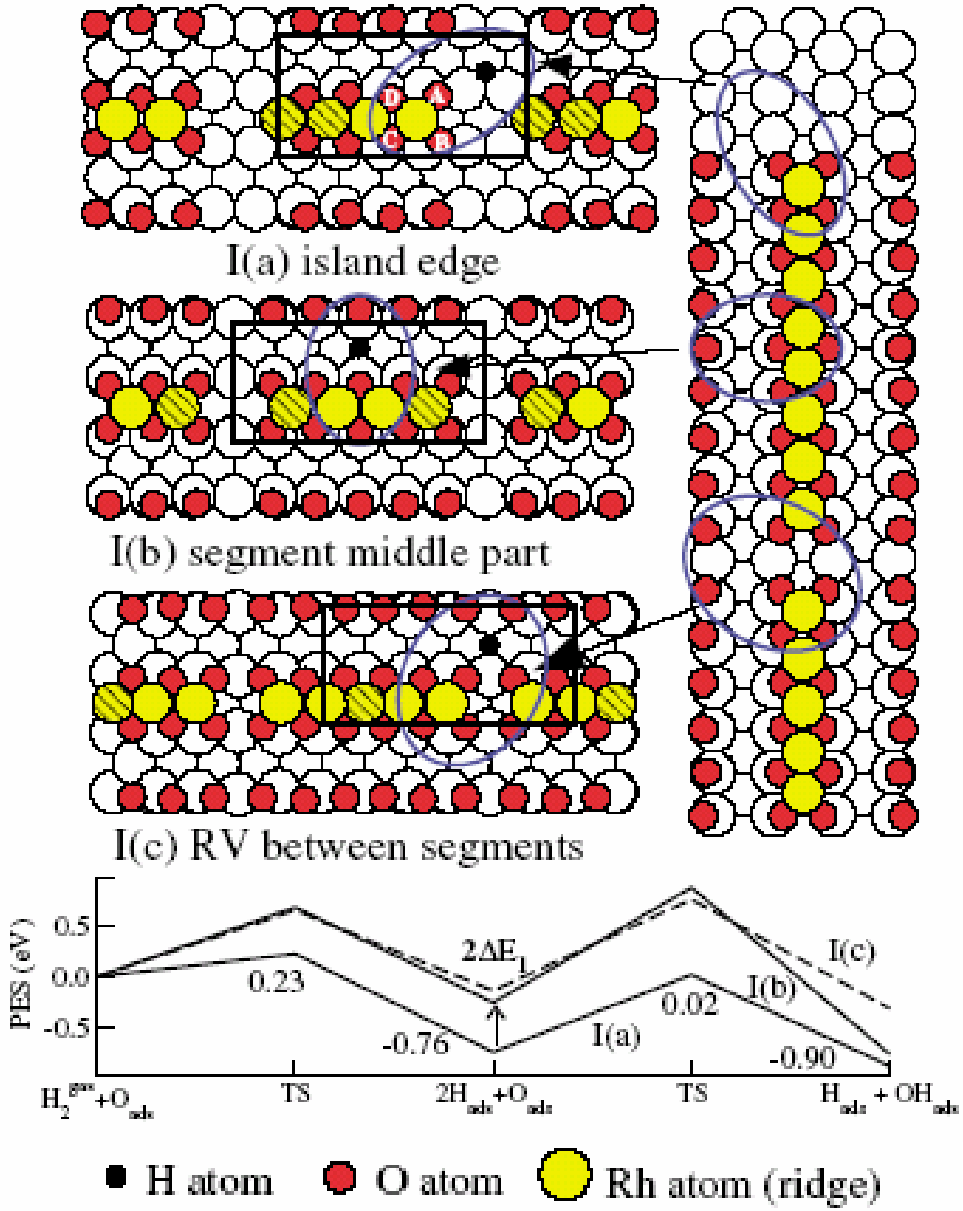
2nd oxygen removal:
- homogeneous
nucleation

150 x 150 Å^2



Final surface: clean,
segmented (1x2)

1st Step reaction



H_2 dissociation barrier:

- island edge: 0.23 eV
- middle part and RV between segments: larger than 0.67 eV

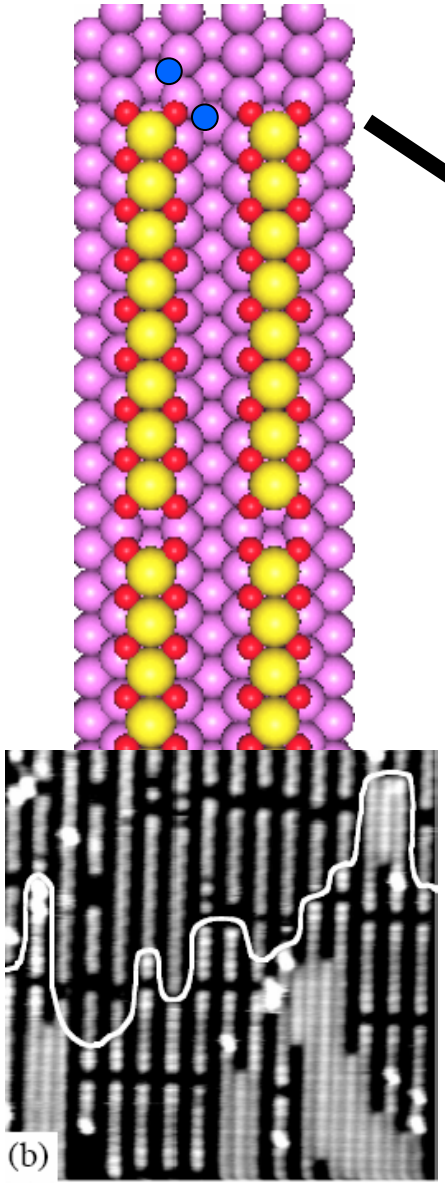
OH formation barrier:

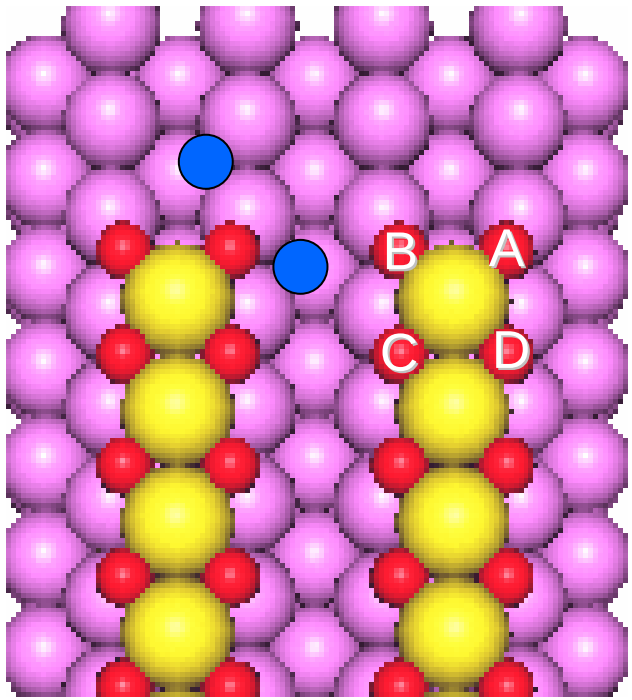
- island edge: 0.78 eV
- middle part and RV between segments: 0.92 eV and 1.16 eV

H2 Dissociation barrier on Rh(110)-(1x2) less than 0.1 eV

Africh, Esch, Li, Corso, Hammer, Rosei, and Comelli, Phys. Rev. Lett. 93, 126104 (2004)

Wavefront Formation



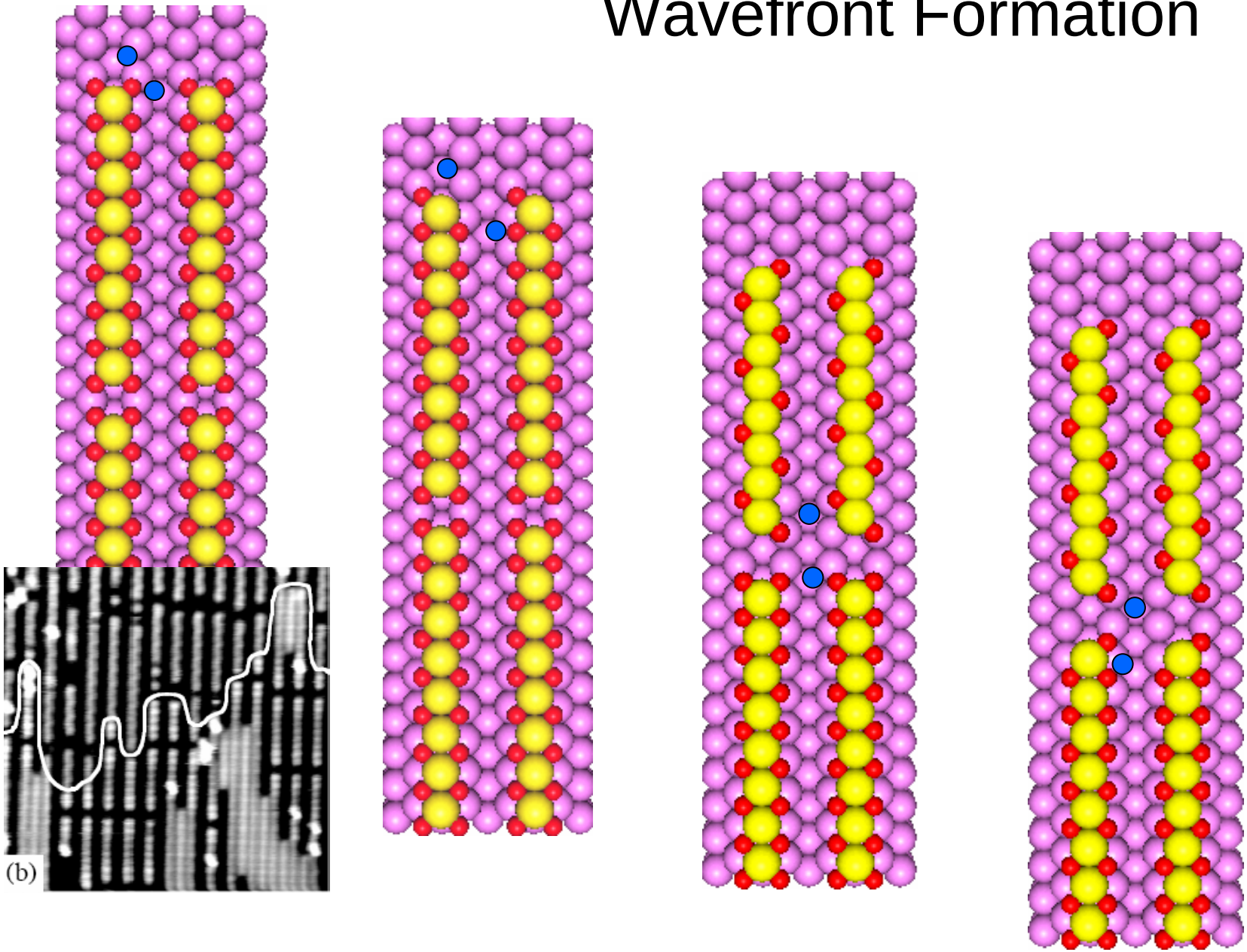


O's Stability:

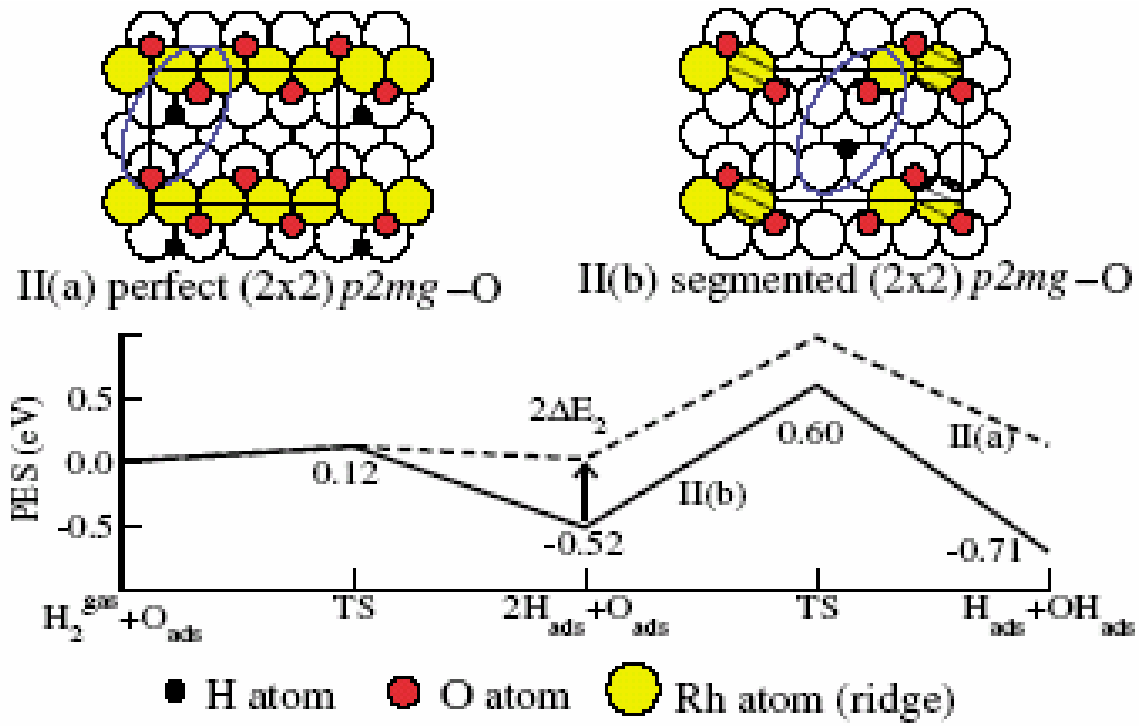
- Site A: 1.85 eV
- Site B: 1.85 eV
- Site C: 1.36 eV
- Site D: 1.98 eV

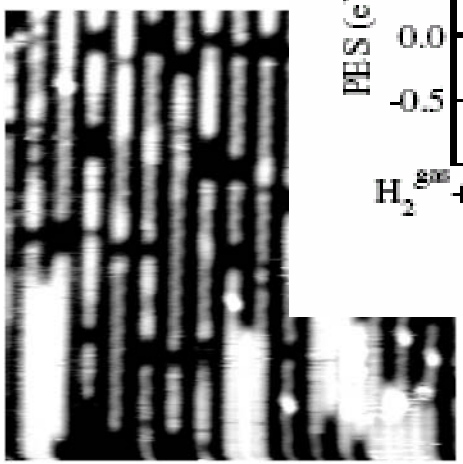
zig-zag structure preferred

Wavefront Formation



2nd Step Reaction





2nd oxygen removal:
- homogeneous nucleation

H2 dissociates barrier: 0.12 eV
H atom can only adsorb between the ridge

Conclusion

- It is mandatory to study the catalytic reaction under realistic condition by various experimental and theoretical apparatus, which have to be applied simultaneously, to unravel the active sites, structures and reaction mechanism.

- To do so, in situ facilities and theoretical simulation including temperature and pressure as well as statistics mechanics (KMC) have to be applied or developed.

- Defects (step) and surface orientations has significant impact to the formation of (surface) oxide, reaction mechanism, materials dependent, and therefore has to be studied case by case, in term of bridging so-called pressure and materials gap.

Xinghai Square, Dalian

Acknowledgments

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