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**2145-14**

**Spring College on Computational Nanoscience**

*17 - 28 May 2010*

**From Supported Clusters to Nanocatalysis**
**Part I**

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*Dipt. Scienze dei Materiali*
*Univ. Milano Bicocca*
*Italy*

Spring College on Computational Nanoscience, Trieste, May 18, 2010

# FROM SUPPORTED CLUSTERS TO NANOCATALYSIS

## Nanocatalysis: supported clusters, particles, and model systems


Gianfranco Pacchioni

*Dipartimento di Scienza dei Materiali*

*Università Milano-Bicocca*


Part I – Nanocatalysis: supported clusters, particles, and model systems

Part II - CO on MgO: lessons from 25 years of interplay between theory and experiment

Part III – New phenomena: metal clusters on ultra-thin oxide films

# CATALYSIS: OLD BUT FUNDAMENTAL TECHNOLOGY

1909

Fritz Haber develops the industrial process of ammonia synthesis on Fe catalysts: $3H_2 + N_2 \rightarrow 2NH_3$

$$H_2 \rightleftharpoons 2\,H_{ad}$$

$$N_2 \rightleftharpoons N_{2,ad} \rightleftharpoons 2\,N_s$$

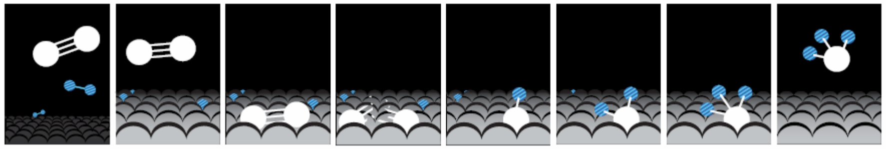
$$N_s + H_{ad} \rightleftharpoons NH_{ad}$$

$$NH_{ad} + H_{ad} \rightleftharpoons NH_{2,ad}$$

$$NH_{2,ad} + H_{ad} \rightleftharpoons NH_{3,ad}$$

$$NH_{3,ad} \rightleftharpoons NH_3$$

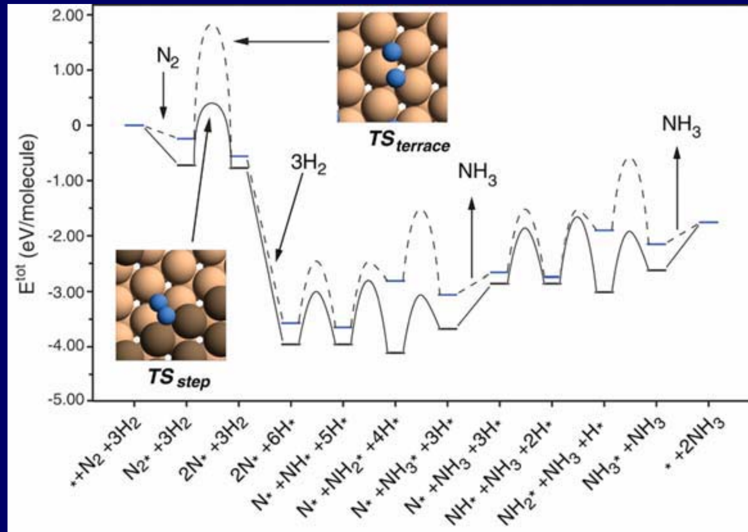
The Haber-Bosch process step-by-step



*In the Haber-Bosch process nitrogen (white) reacts with hyrogen (striped) on an iron surface to then form molecules of ammonia which are released from the surface. This reaction, which extracts nitrogen from air, is an important step in the production of artificial fertilizer.*

**Ammonia Synthesis from First-Principles Calculations**

K. Honkala,[1,2] A. Hellman,[4] I. N. Remediakis,[1,2] A. Logadottir,[1,2] A. Carlsson,[4] S. Dahl,[4] C. H. Christensen,[1,3] J. K. Nørskov[1,2*]

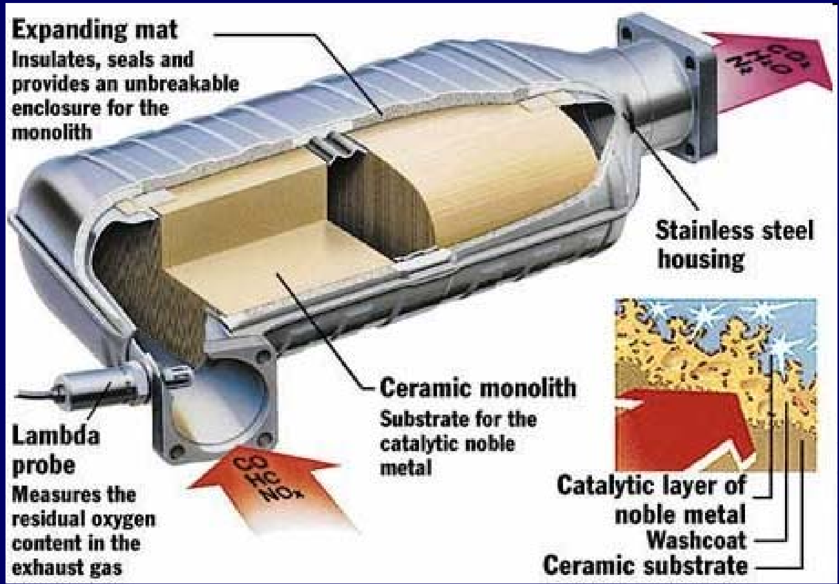


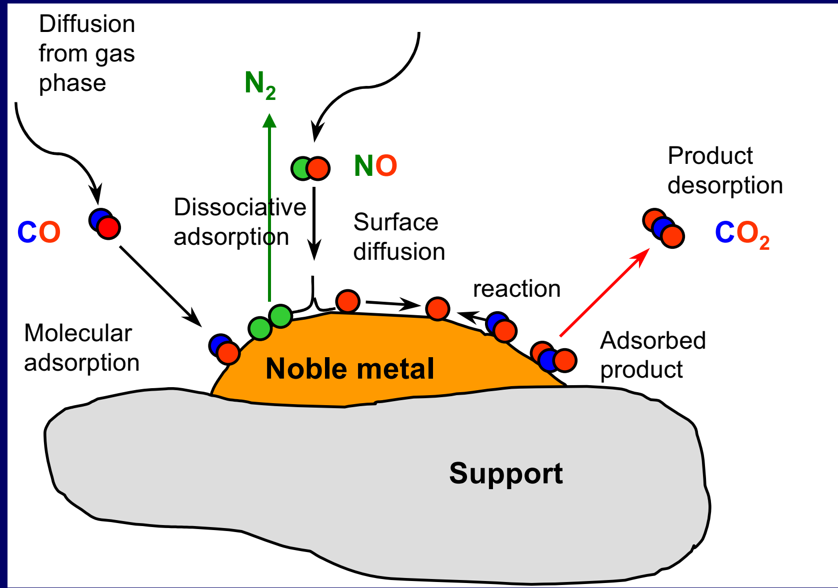

SCIENCE VOL 307 28 JANUARY 2005

2005

The process is completely elucidated at a first-principles level of theory

# ENVIRONMENT: AUTOMOBILE CATALYTIC CONVERTERS




**Car exhaust catalyst: monolithic backbone covered internally with alumina+ceria+zirconia. Support for metal particles (Rh, Pt) of nanometer size**

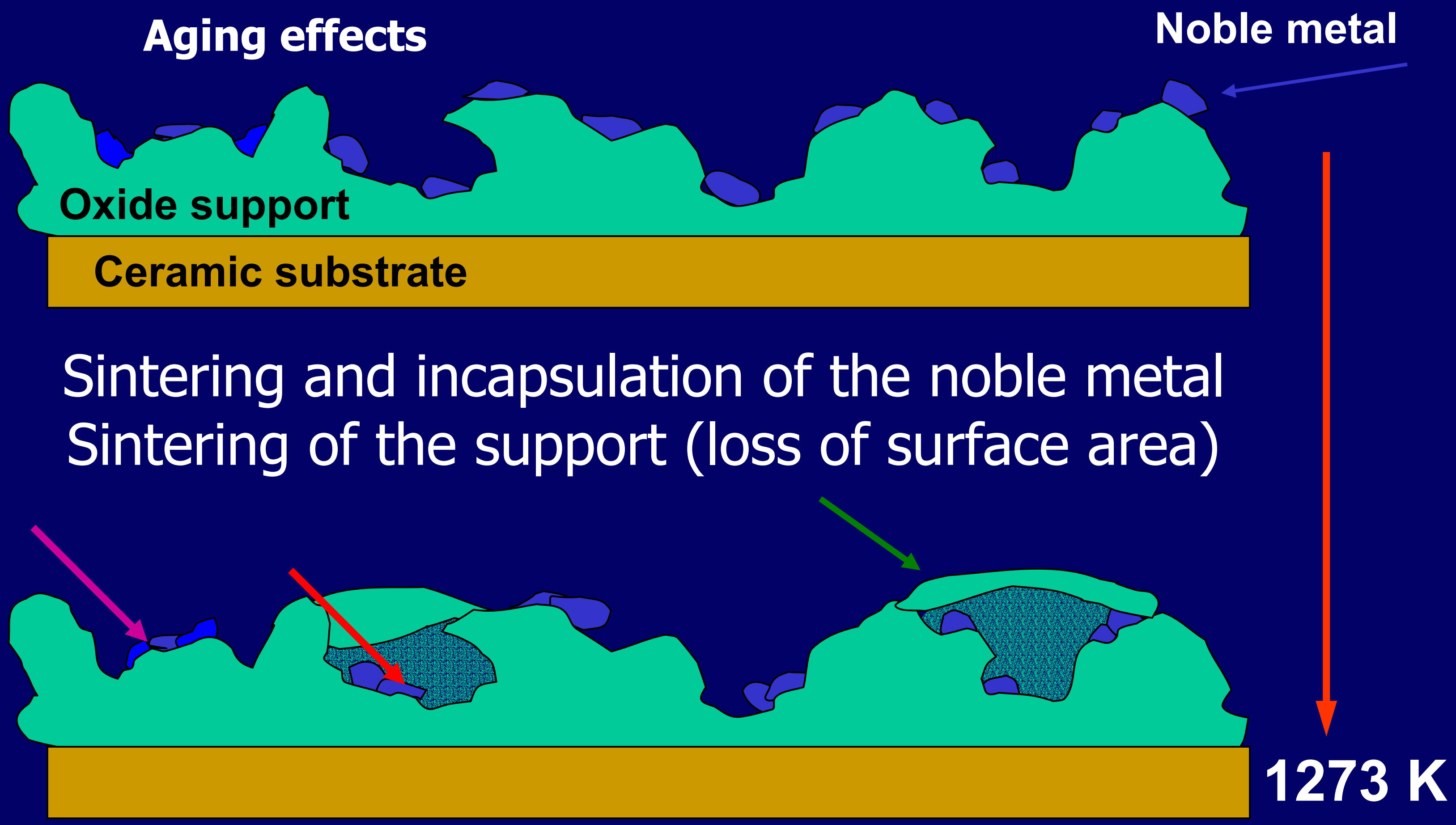
**CO converted to $CO_2$,**

**$C_nH_{2n+2}$ converted to $CO_2$,**

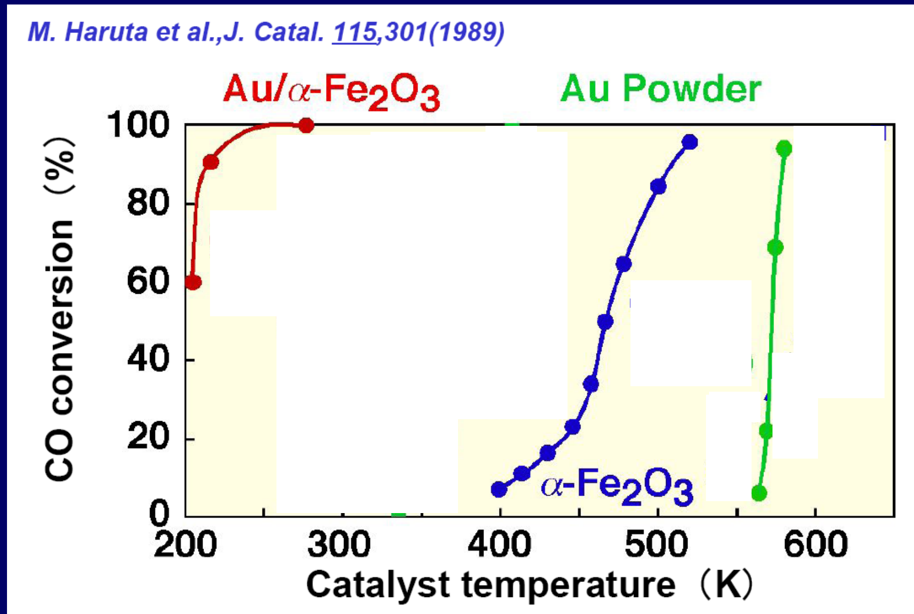
**$NO_x$ converted to $N_2$**

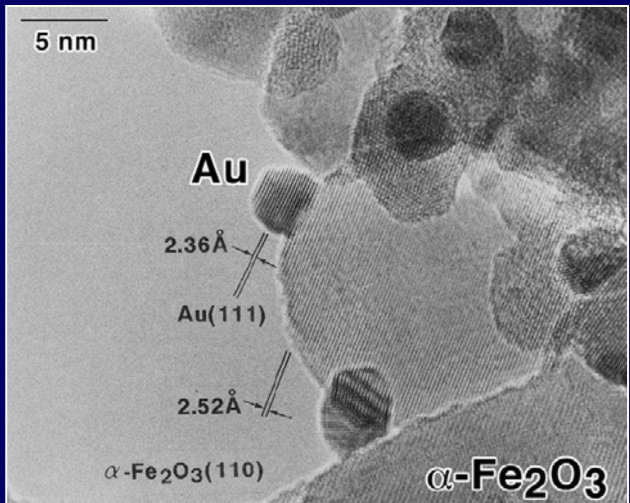
**THE IMPORTANT ROLE OF NANOSIZED METAL PARTICLES ON OXIDE SUPPORTS**

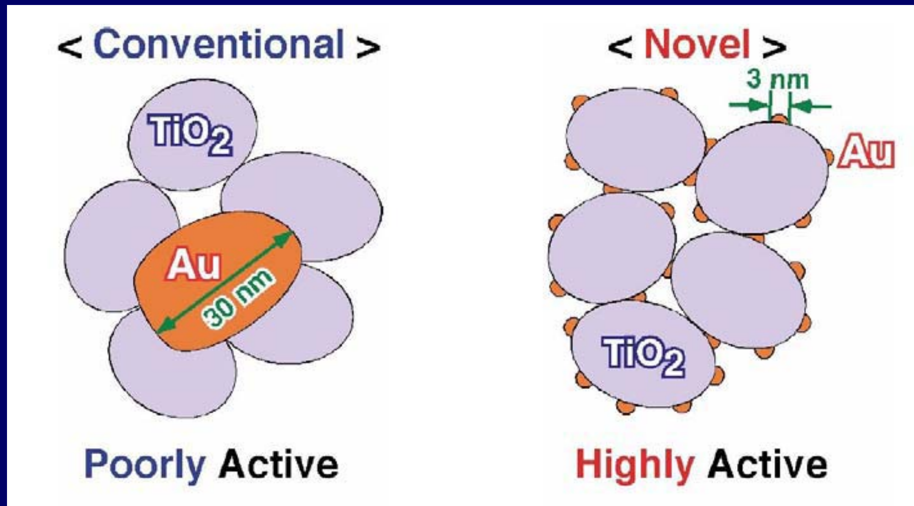
# TRADITIONAL HETEROGENEOUS CATALYST: SUPPORTED METAL PARTICLES



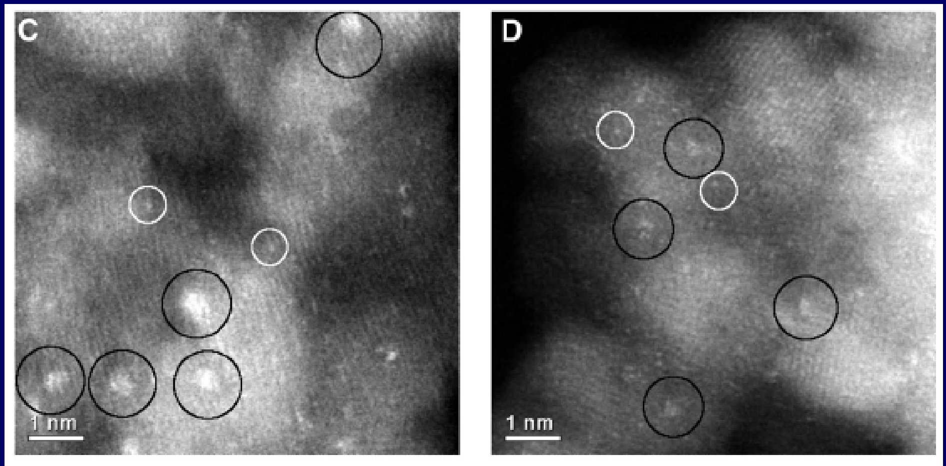
# CATALYSIS BY GOLD: PARTICLE SIZE COUNTS!



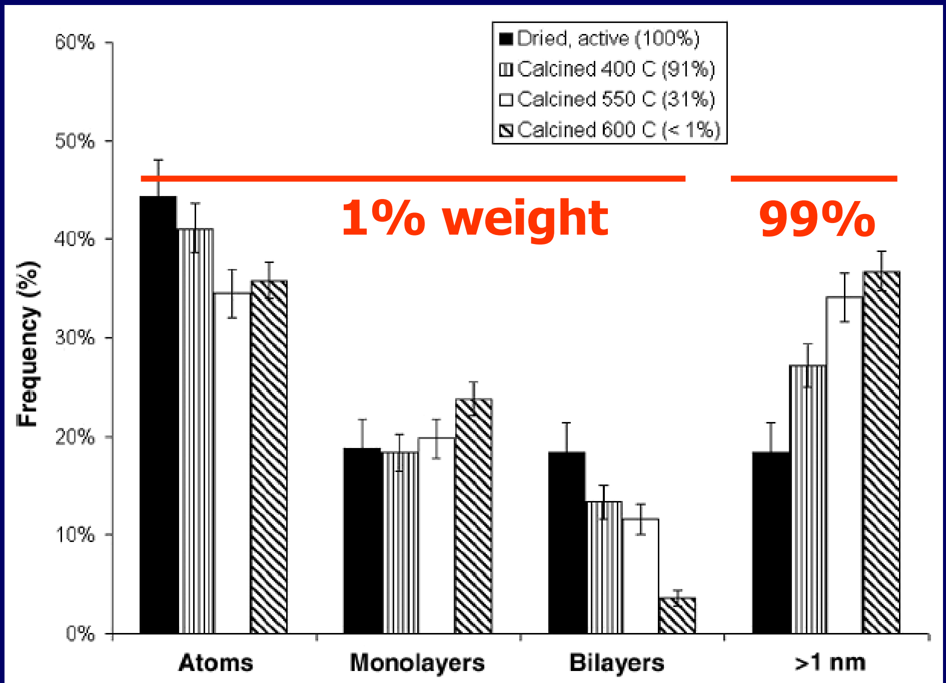
# SUBNANOMETER GOLD IN CATALYSIS




**Identification of Active Gold Nanoclusters on Iron Oxide Supports for CO Oxidation**

Andrew A. Herzing,[1,2] Christopher J. Kiely,[1*] Albert F. Carley,[3] Philip Landon,[3] Graham J. Hutchings[3*]

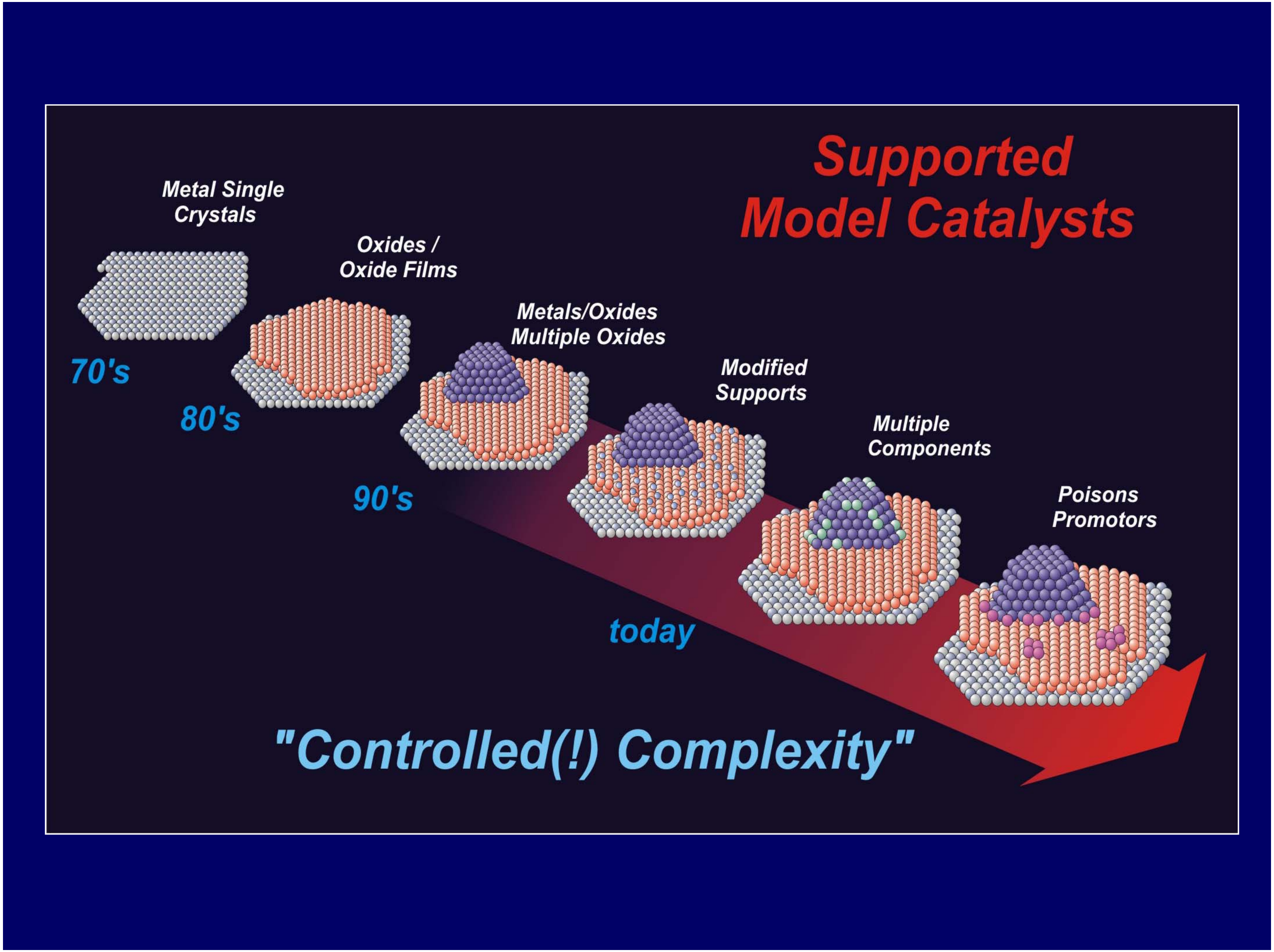
**Science, 321, 1331 (2008)**

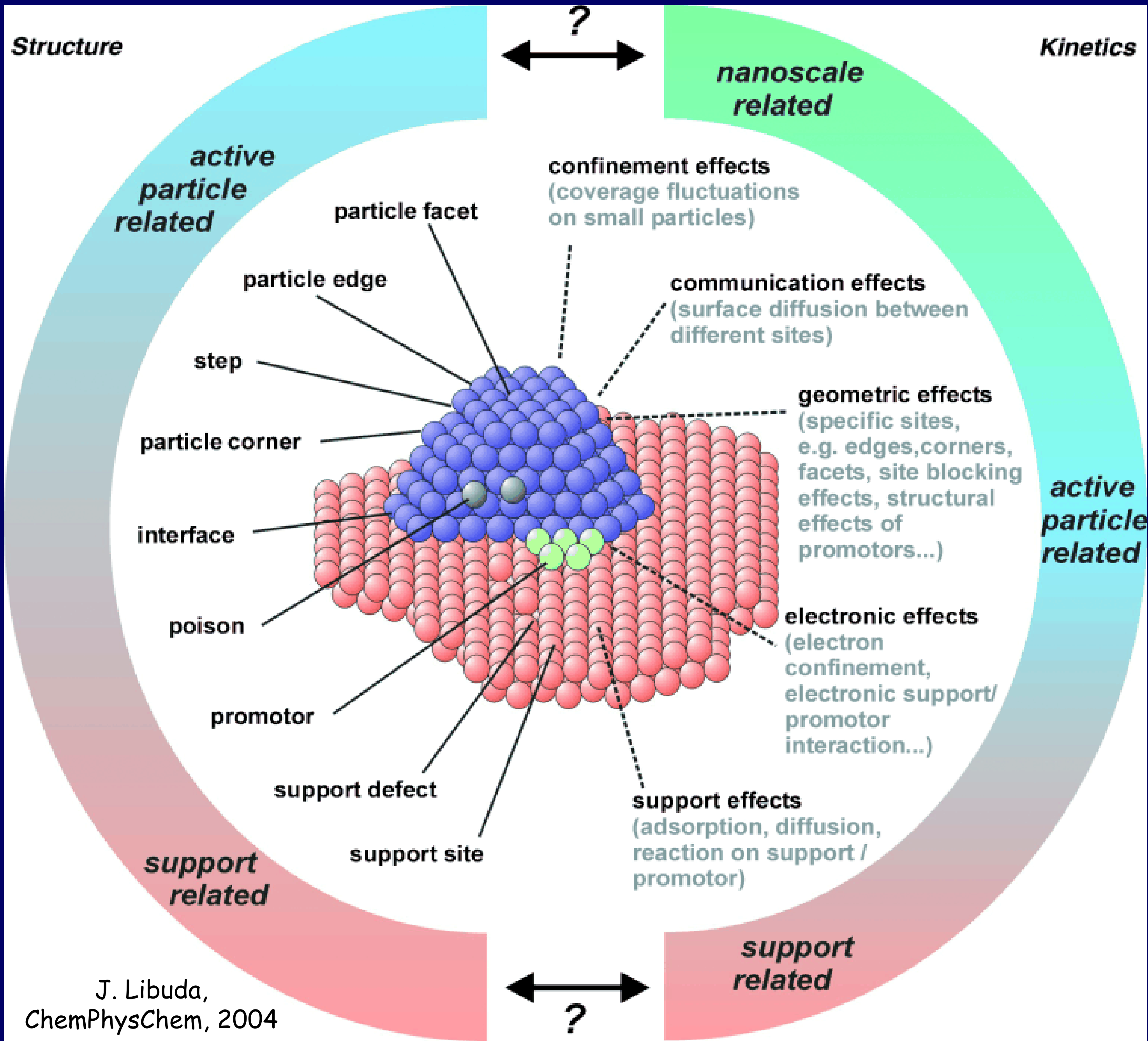



High resolution TEM (aberration correction): Au atoms & Au nanoclusters (0.2-0.5 nm) present on active $Au/Fe_2O_3$ catalyst

0.5 nm two-layer Au clusters (<10 atoms) responsible for catalyst activity

Active Au <1% of total Au. Not detectable with normal spectroscopies!

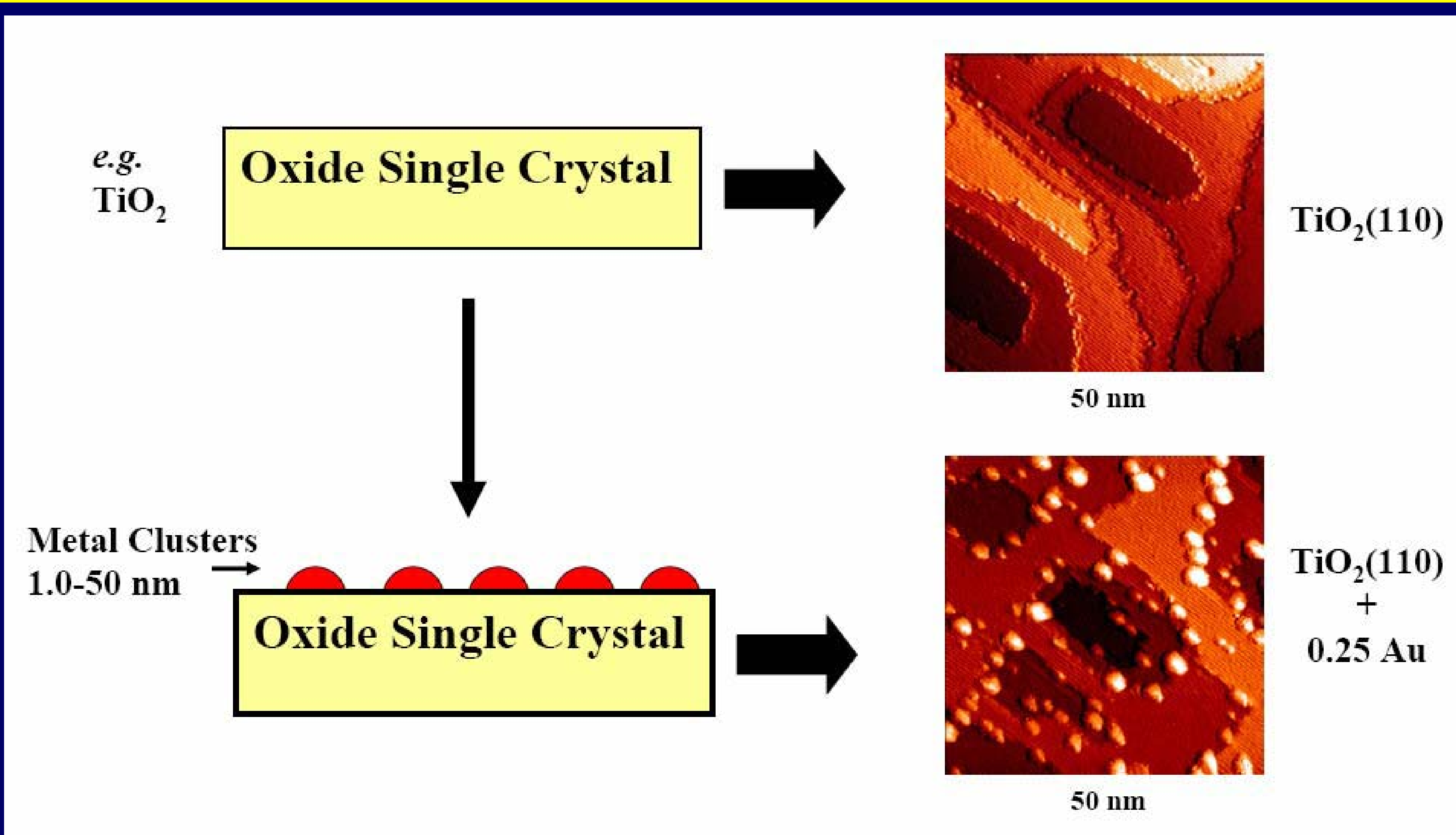

Supported
Model Catalysts
Metal Single
Crystals
Oxides /
Oxide Films
Metals/Oxides
Multiple Oxides
Modified
Supports
Multiple
Components
Poisons
Promotors
70's
80's
90's
today
"Controlled(!) Complexity"




J. Libuda, ChemPhysChem, 2004

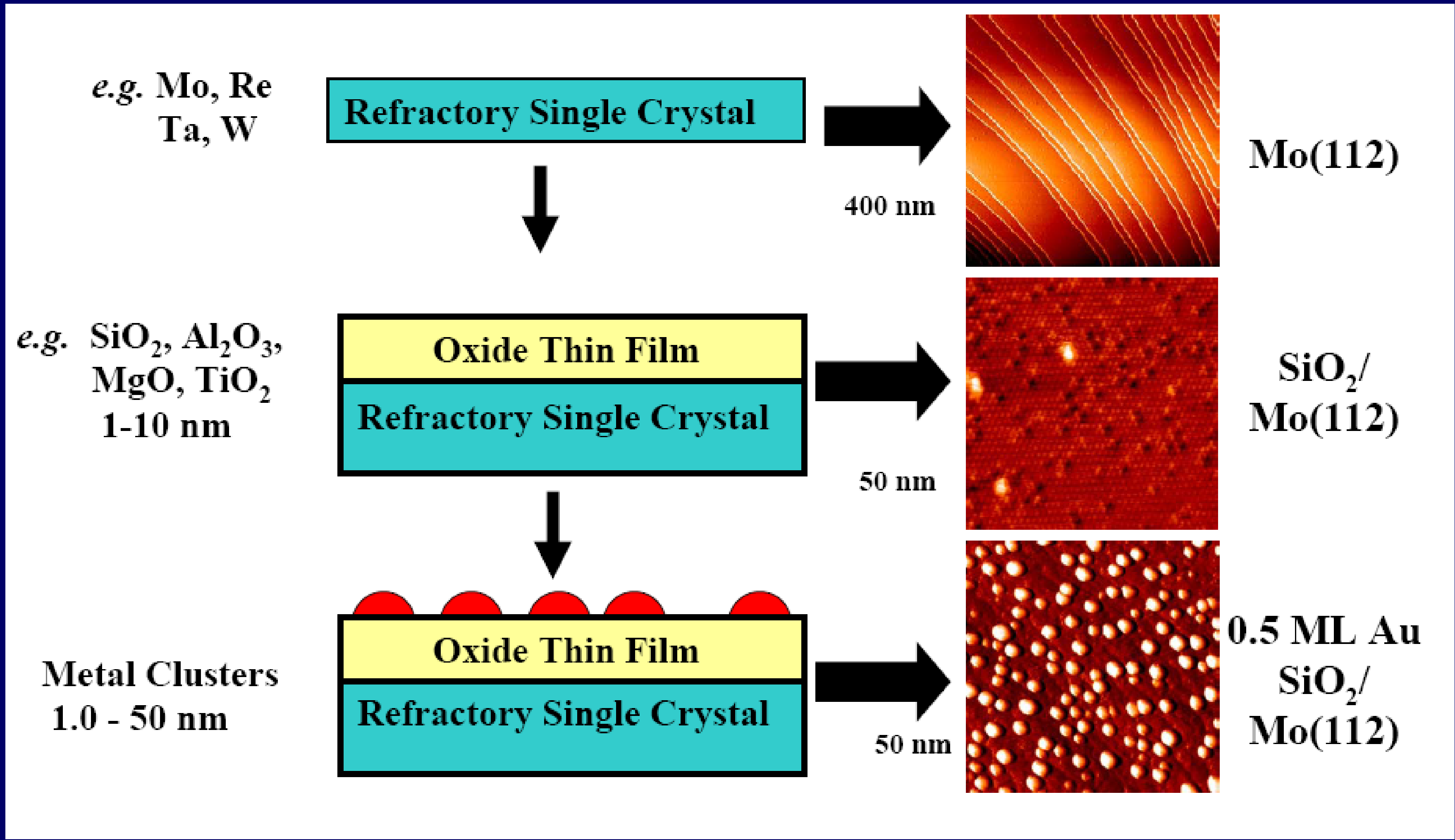
# SUPPORTED METAL NANOCATALYSTS:

# OXIDE SINGLE CRYSTAL SUPPORTS



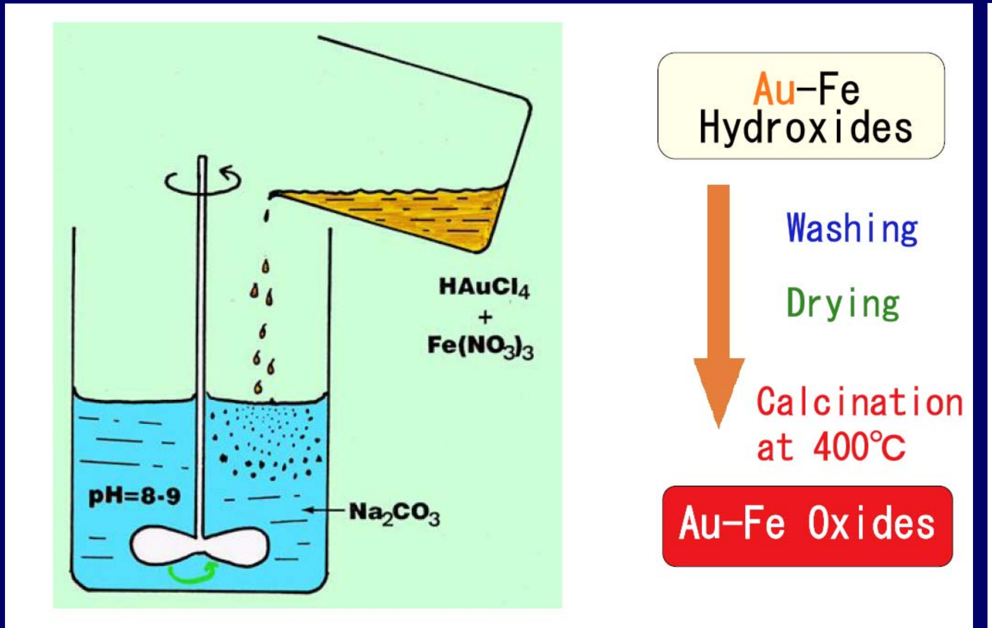
# SUPPORTED METAL NANOCATALYSTS:

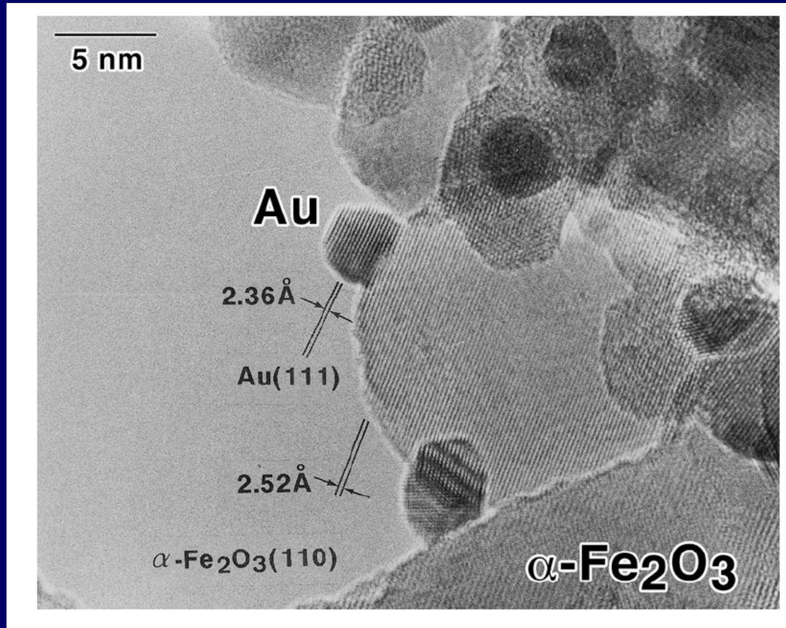
# OXIDE THIN FILM SUPPORTS



# Supported metal nanoparticles: preparation

# CATALYST PREPARATION: COPRECITATION (WET CHEMISTRY)



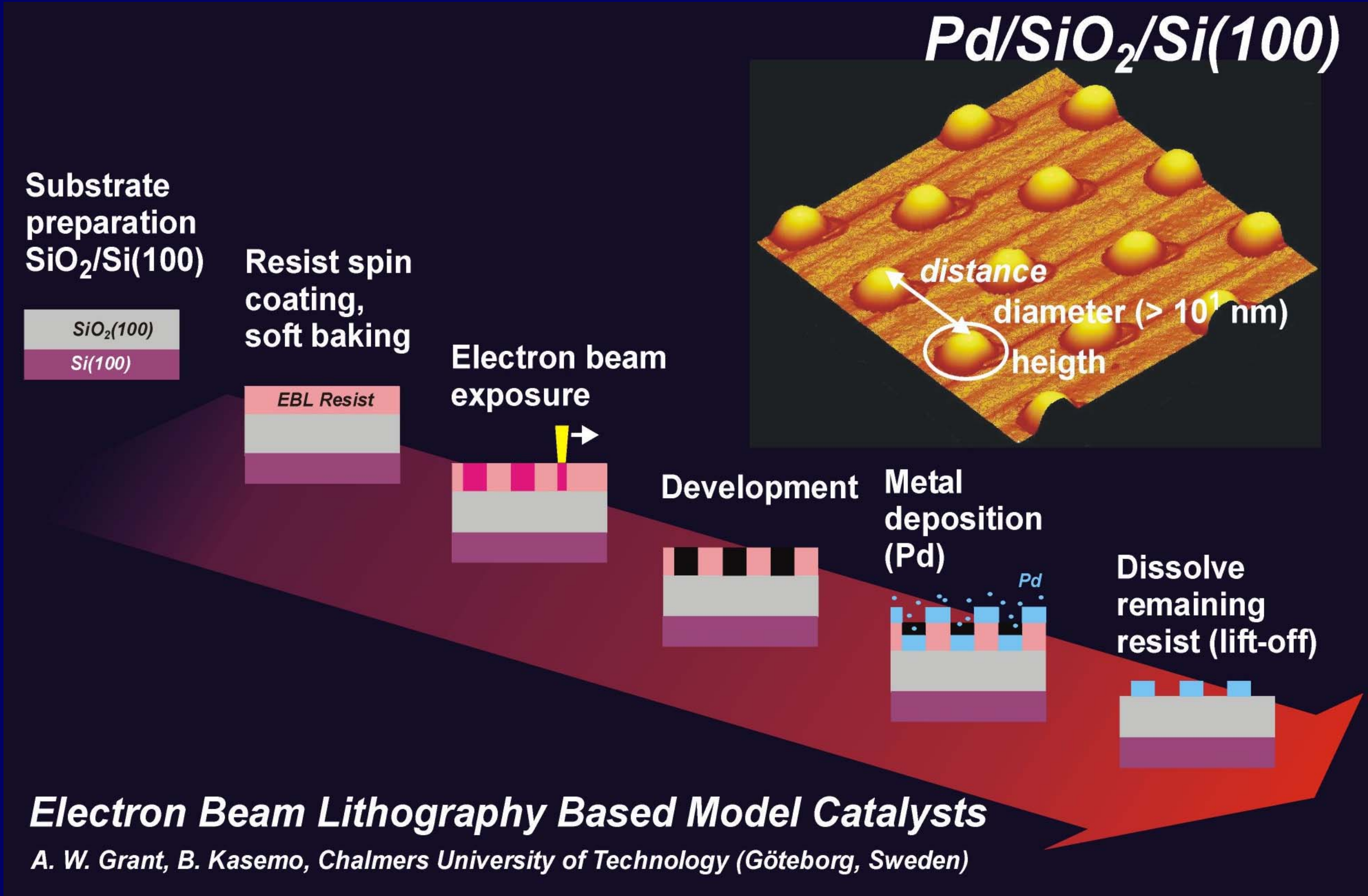




**Precipitation from solution followed by calcination**

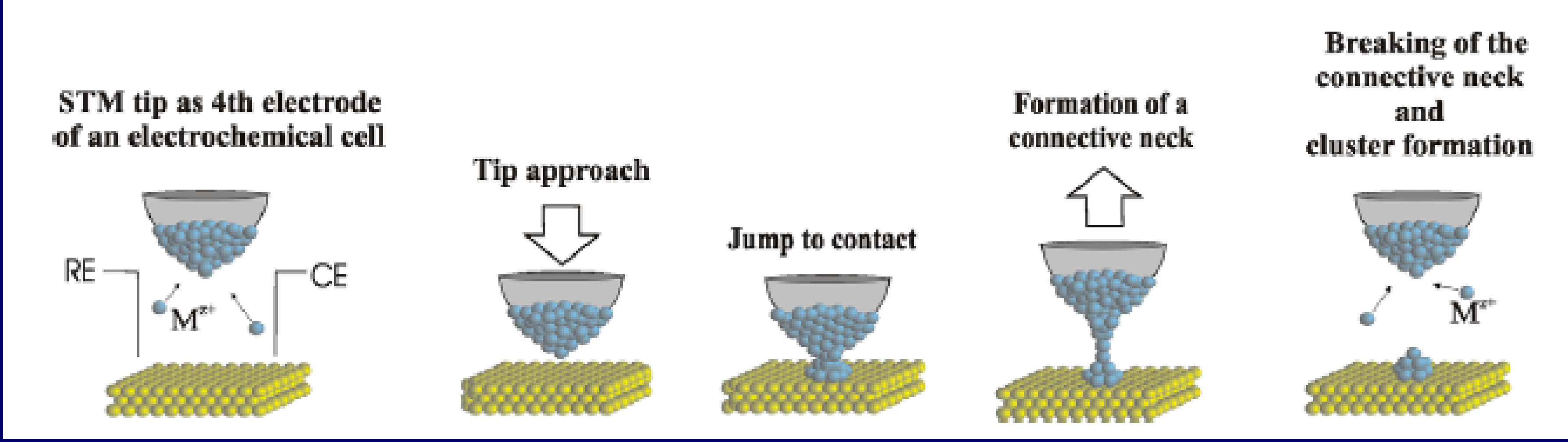
**Little or no control on particle size and particle size distribution**

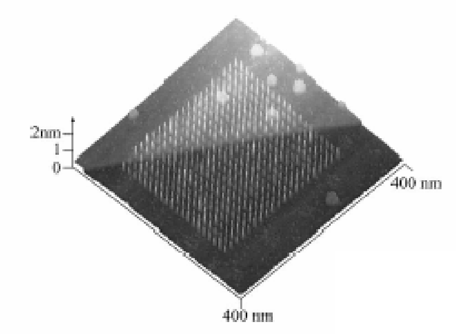
**CAN WE PREPARE METAL NANOPARTICLES OF CONTROLLED SIZE ?**

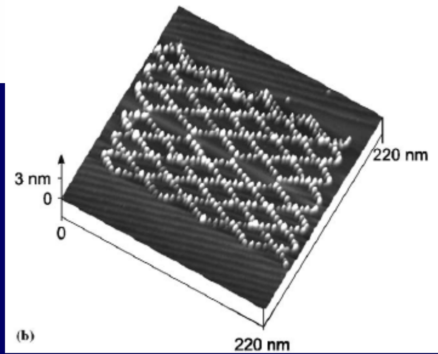
# NANOLITOGRAPHY



# ELECTROCHEMICAL NANOSTRUCTURING




**Tip-induced cluster formation**

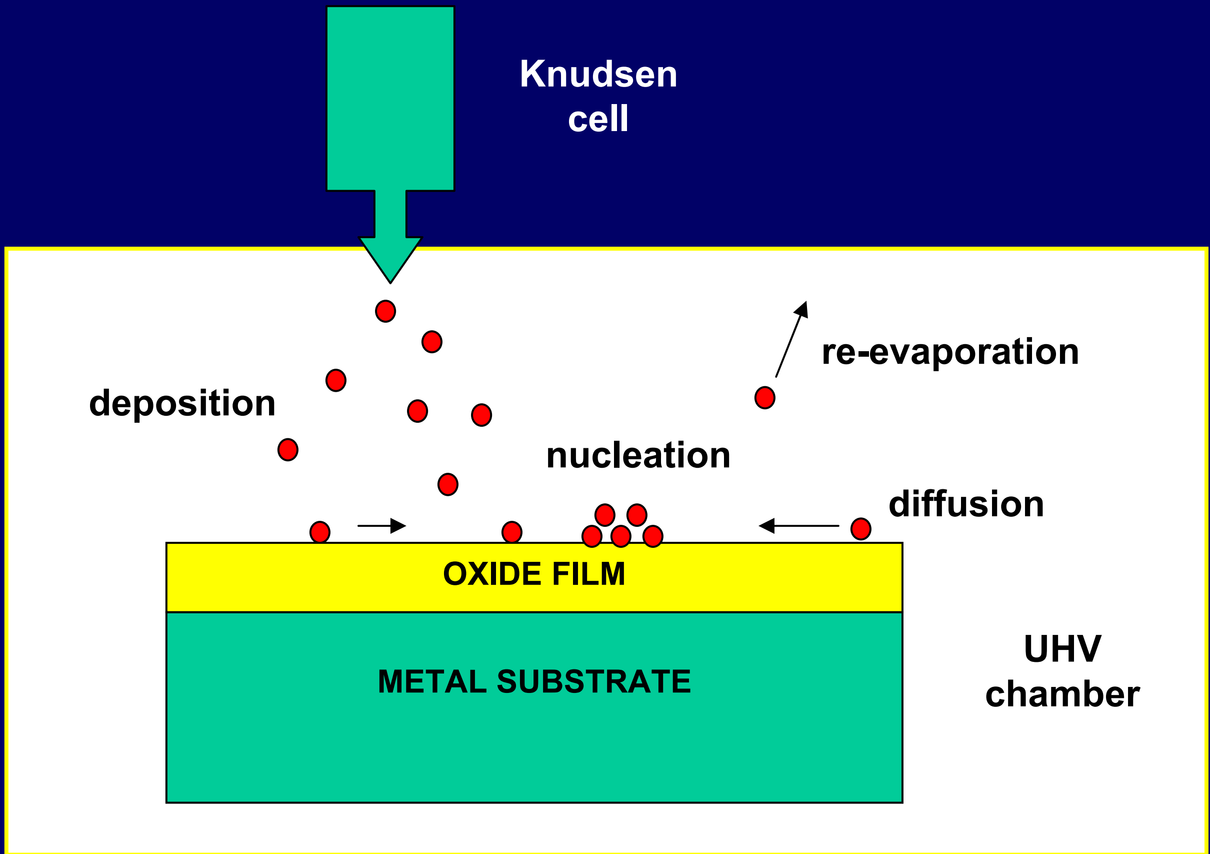
**Metal is deposited onto the tip**

**The metal-loaded tip approaches the surface for a short time depositing small amounts of material**

**Left: array of 400 Cu clusters on Au(111); the Cu clusters are about 0.6 nm in height**

Kolb et al. Science 275 (1997) 1097

# SELF-ASSEMBLY OF METAL CLUSTERS FROM GAS-PHASE




**Metal clusters on oxide thin films in UHV**

**Metal clusters formed on oxide thin films from vapor deposition**

**ultra-thin oxide films grown on a metal substrate in UHV allow use of electron spectroscopies, STM, etc.**

# WELL-DEFINED SUPPORTED METAL PARTICLES

## Rh clusters on $Al_2O_3$

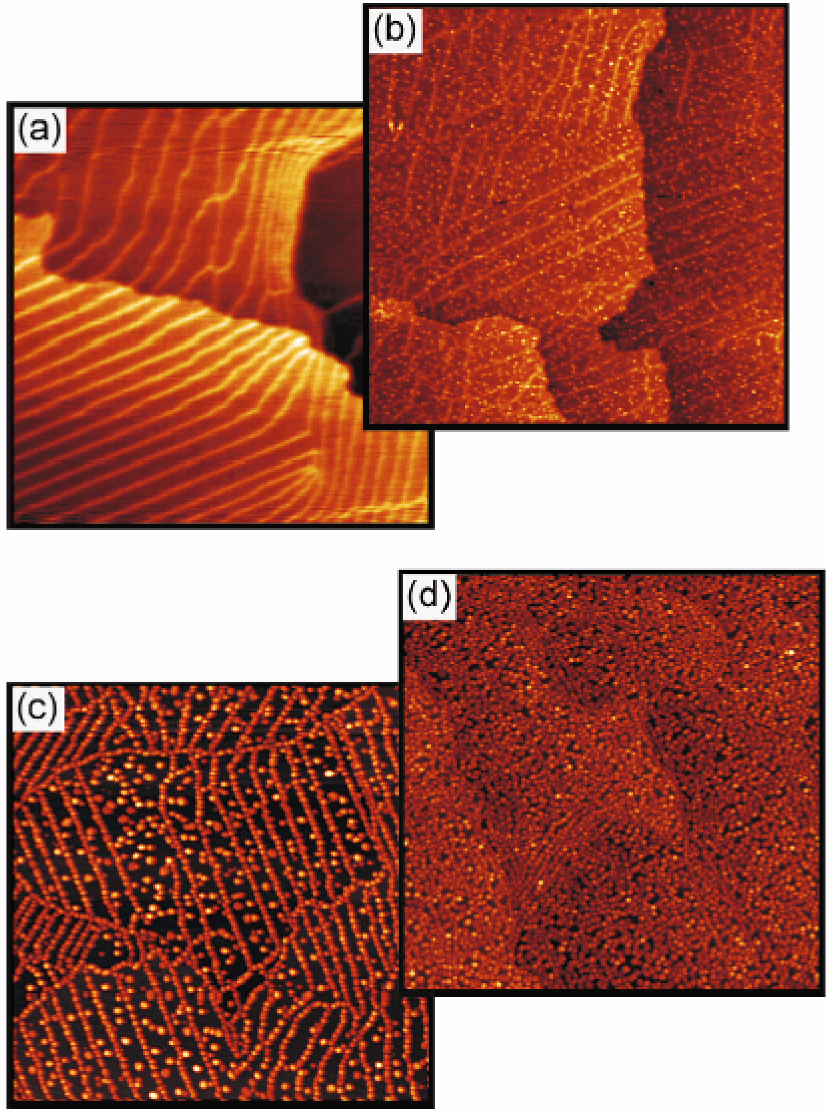
**Metal deposited from vapor on $Al_2O_3$ ultra-thin films grown on a metal in UHV: allows use of Scanning Tunneling Microscopy (STM).**

**STM images of:**

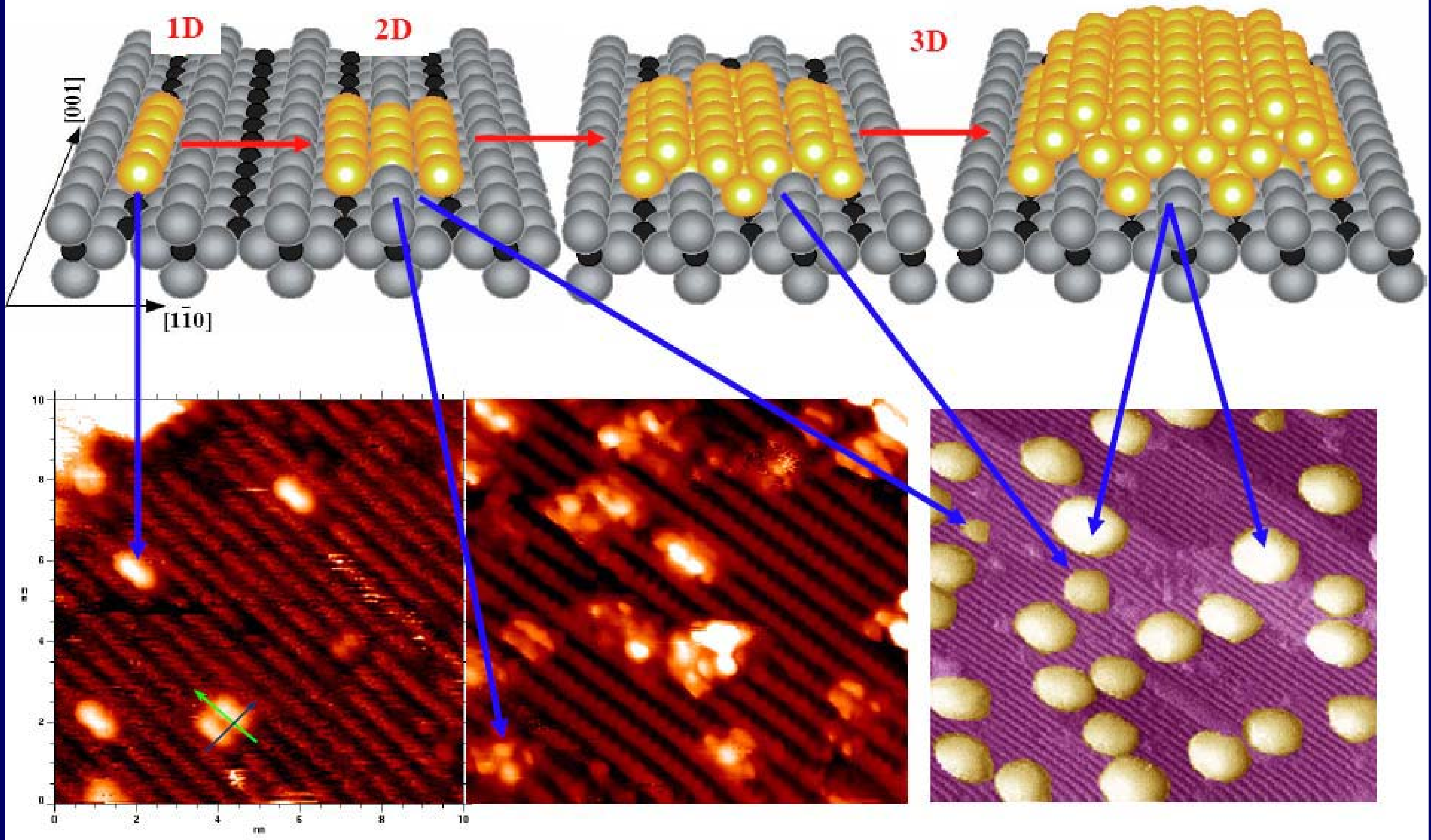
**(a) clean $Al_2O_3$ thin film surface (b) deposition of Rh at 90 K (c) deposition of Rh at 300 K (d) deposition of Rh at 300 K on hydroxylated surface**

**Nucleation occurs at steps and defects; the particles have a nearly uniform size (few nm).**

Bäumer, Freund, Progr. Surf. Sci. 61 (1999) 127.

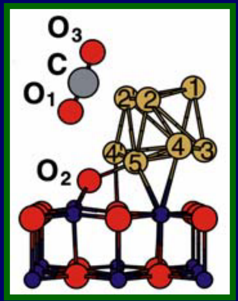


# Au/$TiO_2$(110): 1D → 2D → 3D

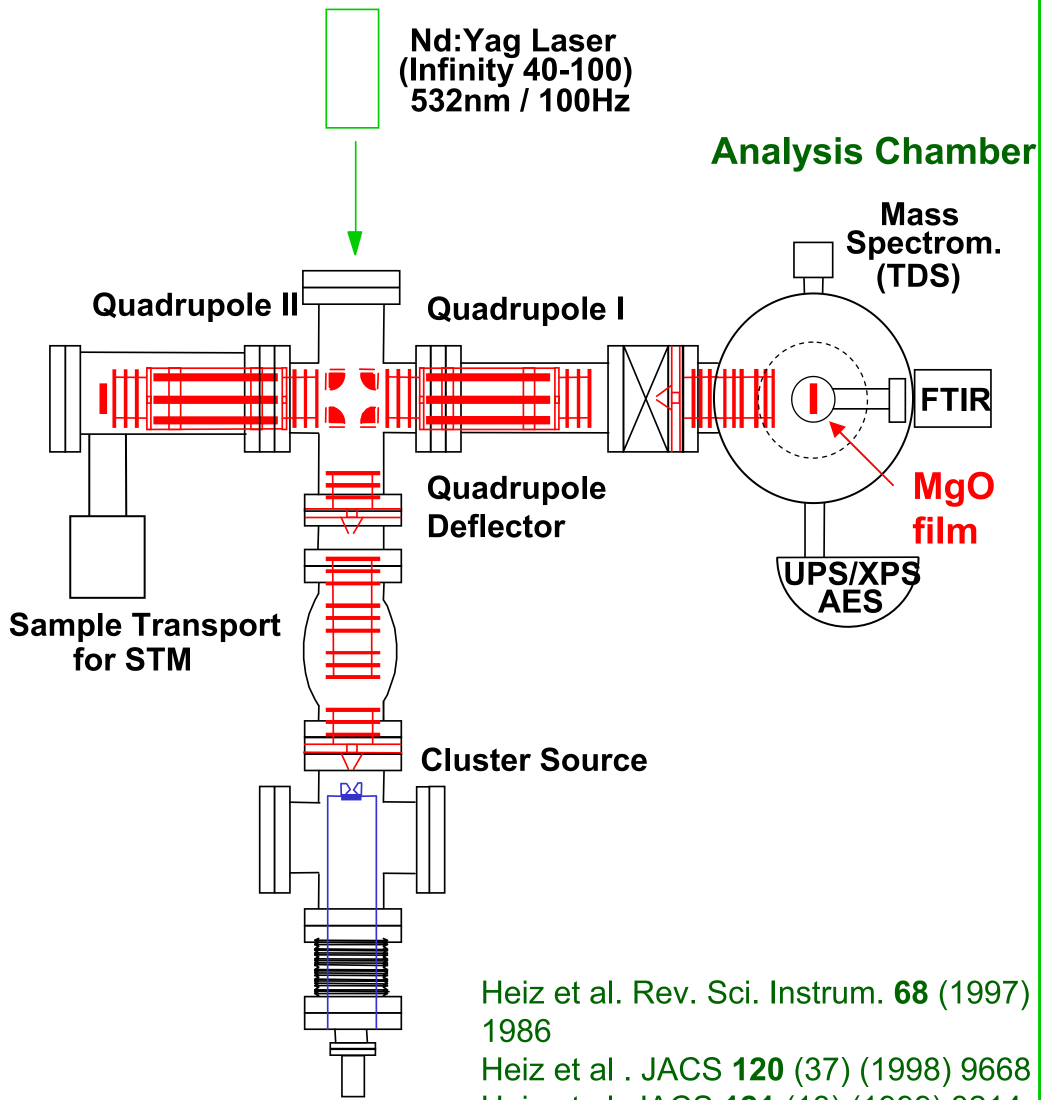



*M. Valden, X. Lai, and D. W. Goodman, Science 281, 1647 (1998)*

# FABRICATION OF NANO-CATALYSTS ATOM BY ATOM




- Epitaxial MgO thin films on Mo(100) grown by vaporizing Mg in $O_2$ atmosphere
- Gas-phase metal clusters generated by laser vaporization
- Clusters are ionized, mass-selected and deposited at low kinetic energy (<0.2 eV/atom) (soft landing)
- Low cluster concentration (<0.1 mono-layer) and low substrate temperature (90 K) to prevent cluster diffusion and aggregation




Heiz et al. Rev. Sci. Instrum. **68** (1997) 1986
Heiz et al . JACS **120** (37) (1998) 9668
Heiz et al. JACS **121** (13) (1999) 3214

# Supported metal nanoparticles: characterization

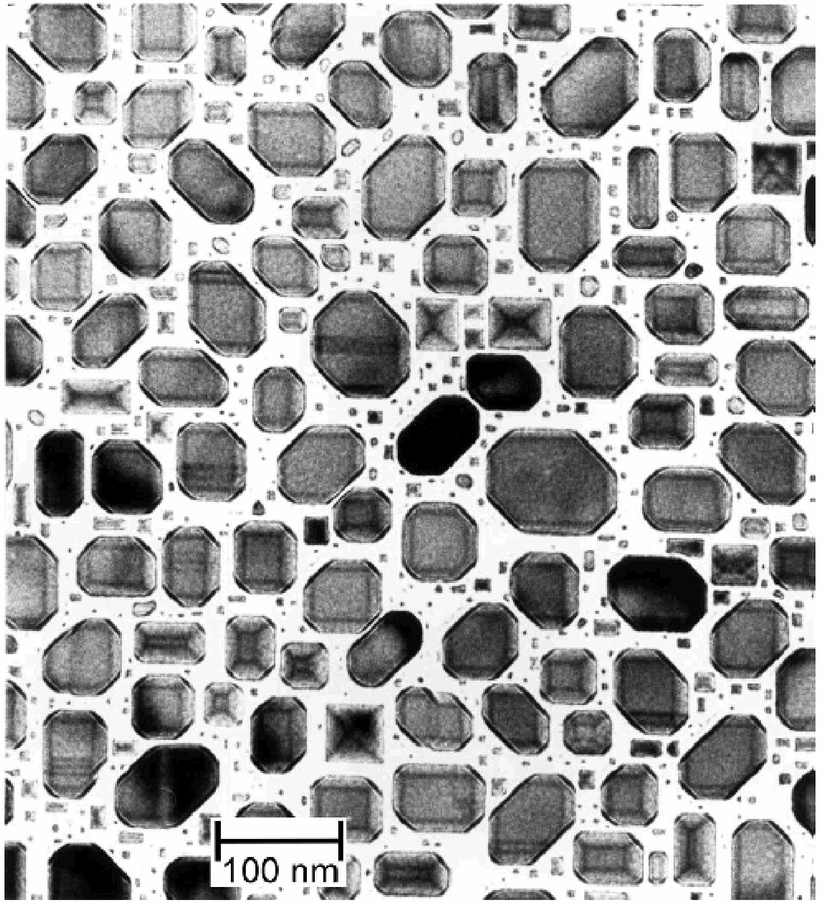
# PARTICLES SIZE, SHAPE, MORPHOLOGY AND DISPERSION

**Pd particles on MgO**

**Transmission Electron Microscopy (TEM) of Pd particles grown on MgO single crystal generated by metal deposition on the oxide surface in ultra-high vacuum (UHV)**

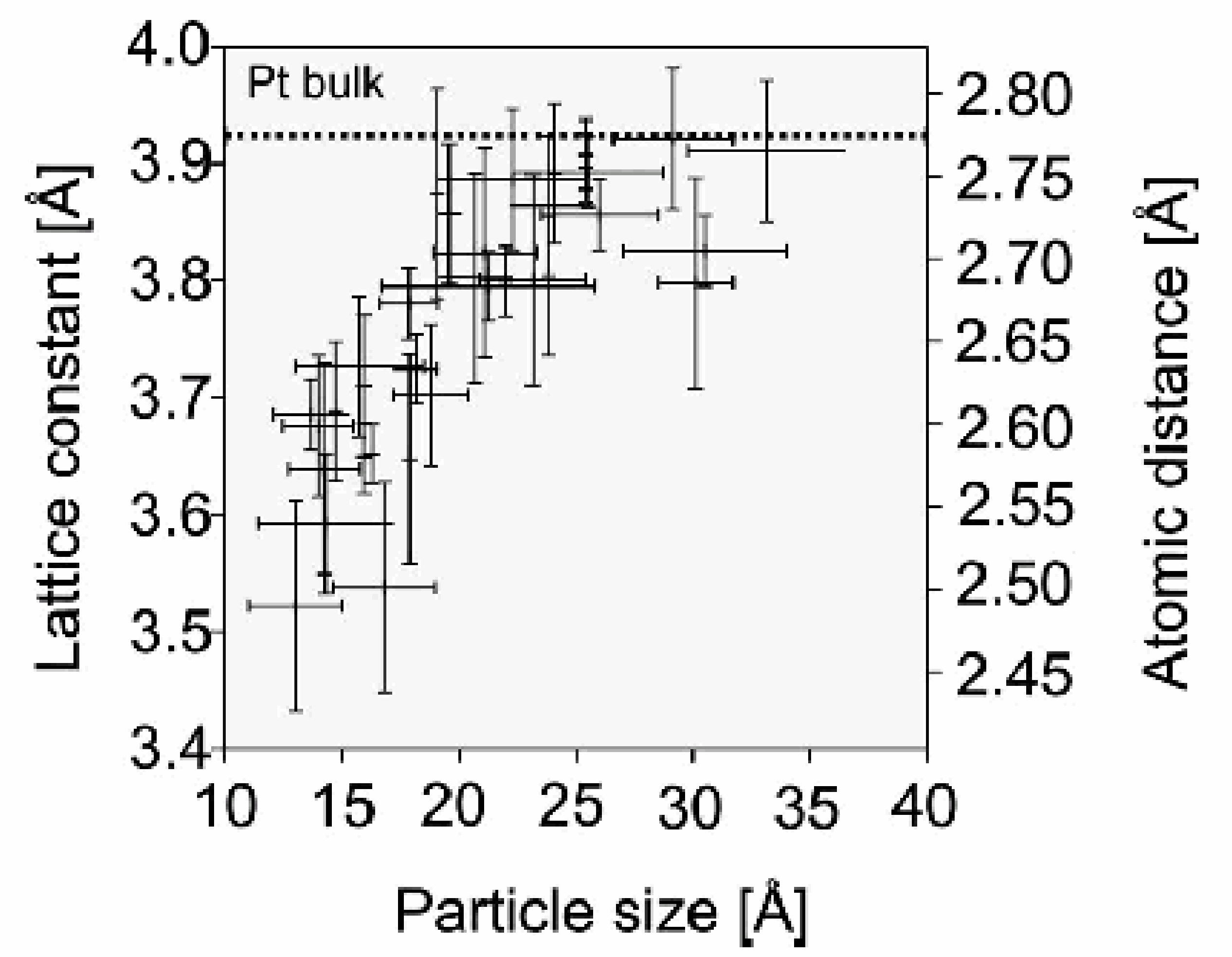
**Various sizes of nano-crystals can be identified; average size 150x150 $nm^2$**

Goyenex, Henry, Urban, Phil. Mag. A 69 (1994) 1073




**High-resolution TEM required to identify very small particles**

# METAL-METAL DISTANCES IN NANOCLUSTERS



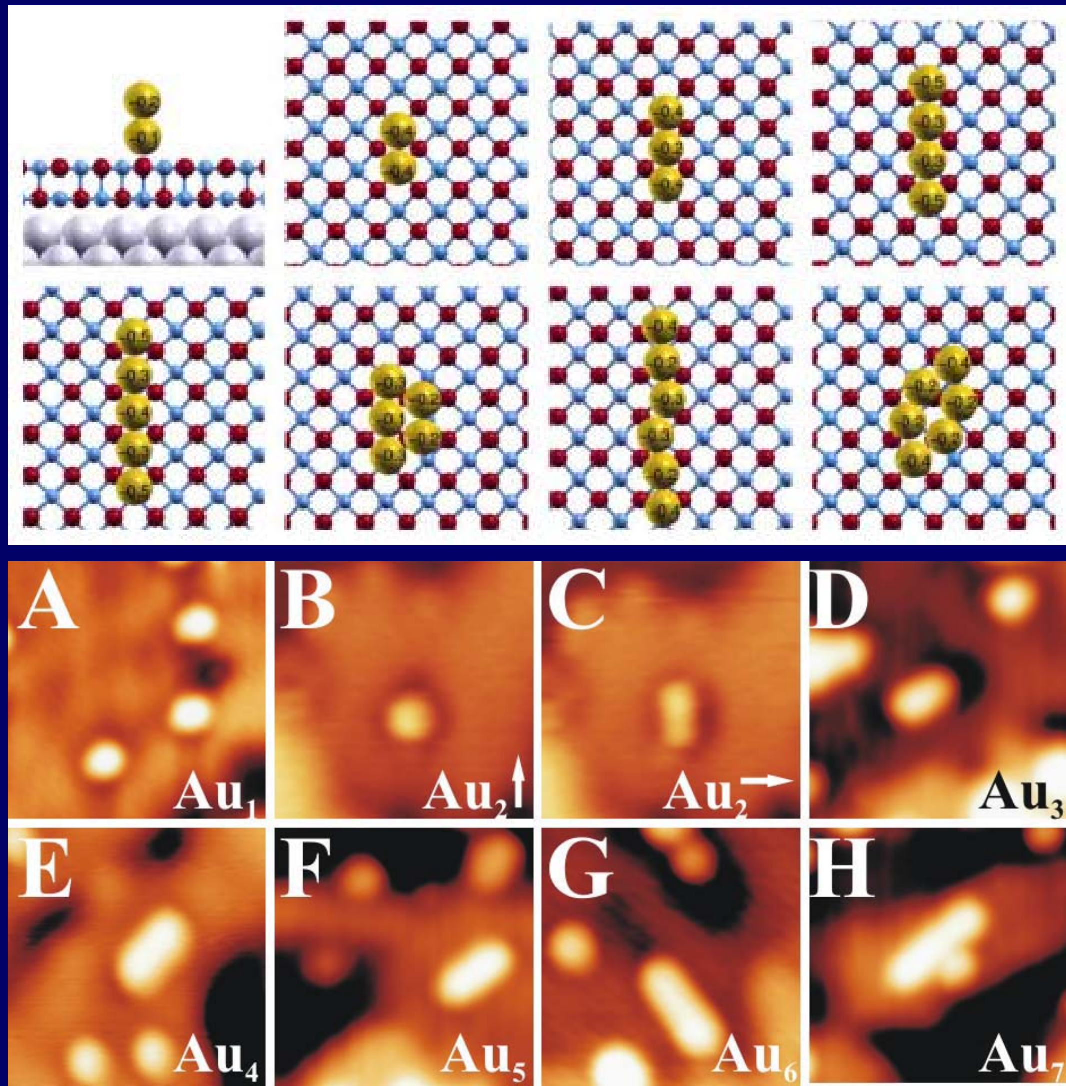

Lattice constants (from HRTEM) and interatomic distances of Pt particles grown on $Al_2O_3$/NiAl(110) as function of their size (horizontal bars represent the difference of the widths and the lengths of the clusters, vertical bars represent error bars)

# Au NANOCLUSTERS ON MgO FILMS: STM

STM: possible on conducting substrates (e.g. thin oxid films on metals)

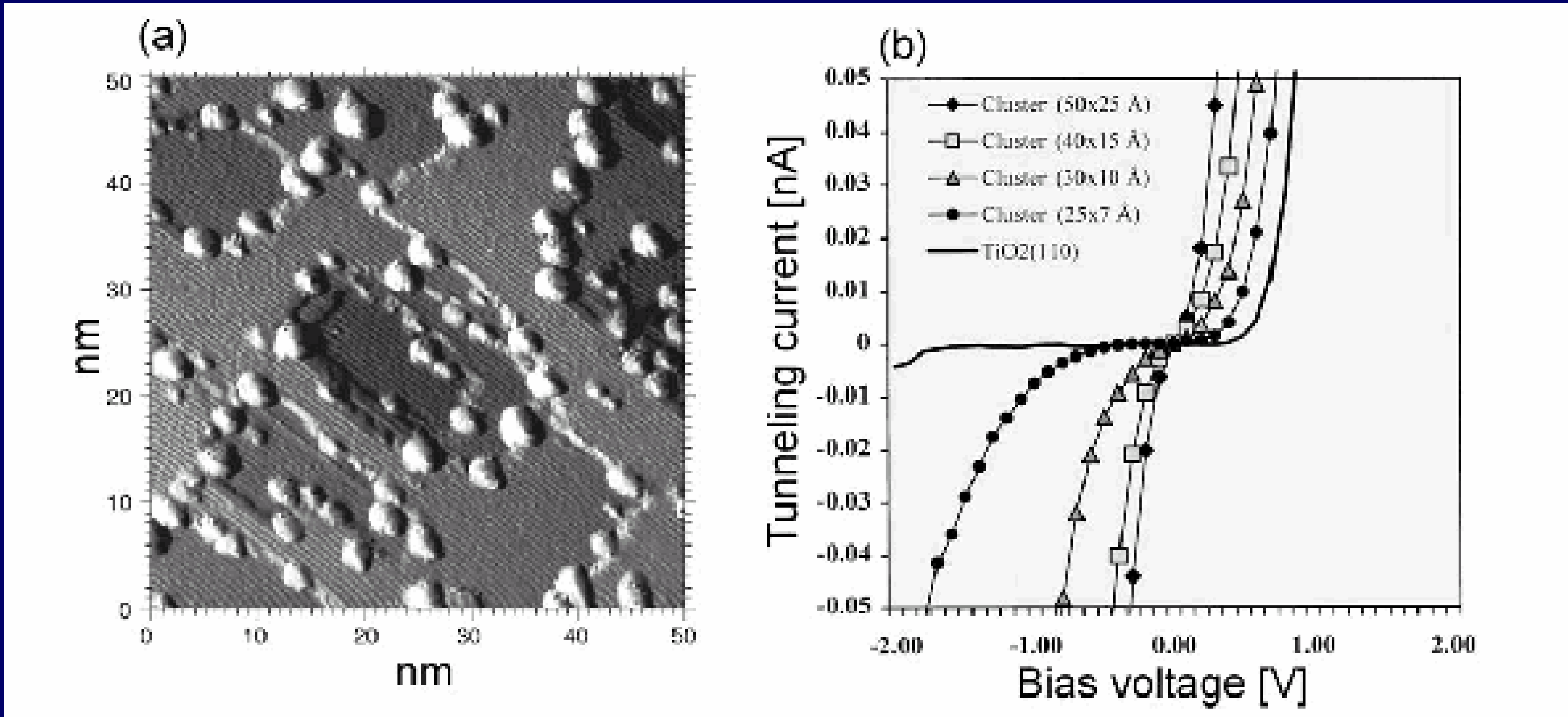
Structure of small gold clusters different in gas-phase, on MgO(100) crystal and on MgO/Ag(100) thin films

Simic-Milosevic, Heyde, Lin, König, Rust, Sterrer, Risse, Nilius, Freund, Giordano, GP, Phys. Rev. B, 78, 235429 (2008)
Frondelius, Hakkinen, Honkala, Phys. Rev. B 76, 073406 (2007)



# Supported metal nanoparticles: properties

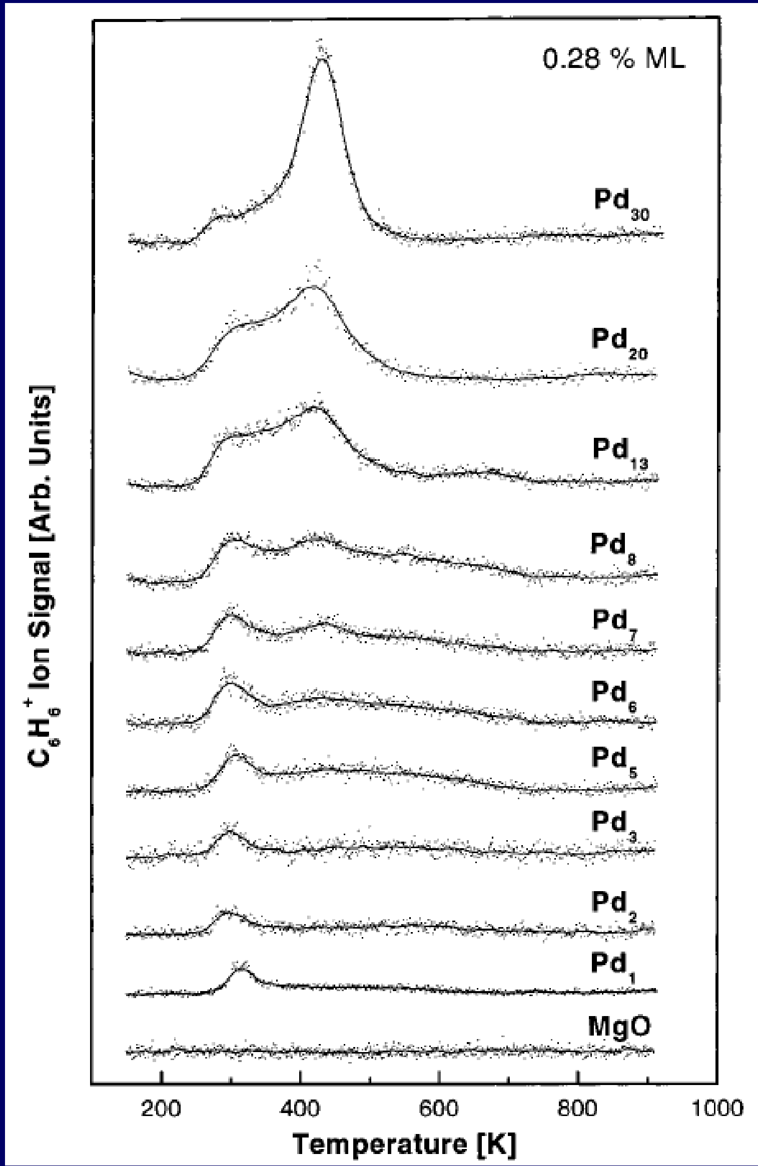
# INSULATOR TO METAL TRANSITION: HOW MANY ATOMS ARE REQUIRED? LOCAL MEASURE OF PARTICLE GAP FROM STS




**Scanning tunneling spectroscopy (STS) of single Au clusters deposited on $TiO_2$(110); recording of current-voltage curves (I-V).**

**Large particles do not exhibit a plateu near I = V = 0, smaller clusters do show the behaviour expected for a system with a gap**

# CHEMISTRY ON SIZE-SELECTED CLUSTERS




**Acetylene trimerization to form benzene on MgO supported Pd clusters**

$$3\ C_2H_2 \rightarrow C_6H_6$$

**up to $Pd_6$ benzene produced at T ≈ 300K from $Pd_7$ to $Pd_{30}$ additional peak bserved at 430 K**

**different mechanisms for small- and medium-siize clusters**

Abbet, Sanchez, Heiz, Schneider, Ferrari, GP, Rösch, J. Am. Chem. Soc. 122, 3453 (2000)

temperature programmed reaction (TPR) for $Pd_1$ to $Pd_{30}$; peak in TPR corresponds to benzene formation

one Pd atom is enough to catalyze the reaction!

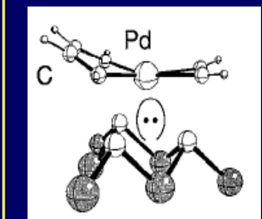
# ROLE OF SUBSTRATE IN CATALYTIC REACTIONS

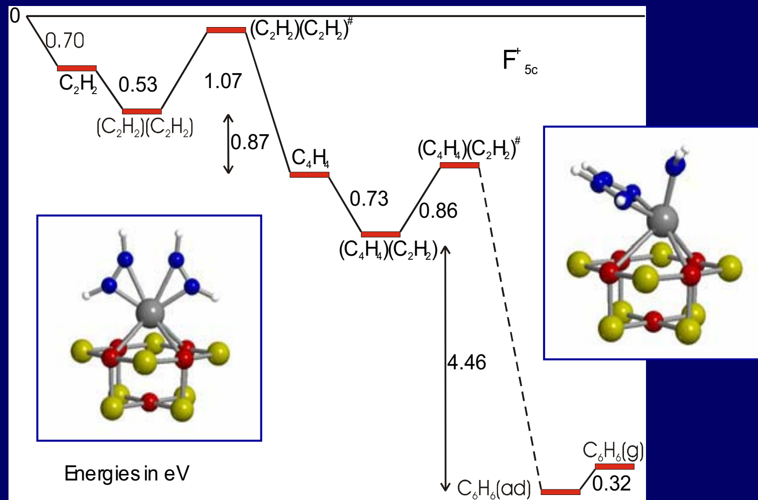
- Pd atoms deposited on MgO films, then exposed to acetylene; benzene forms and desorbs at 300 K.
- Reaction: $3\ C_2H_2 \rightarrow C_6H_6$
- Pd acts as catalyst (MgO inactive)

- Gas-phase Pd atom is inactive because there is not enough electron density
- Pd is active when charged $Pd^{\delta-}$ (DFT B3LYP calculations)

# Pd ATOMS ADSORBED ON F CENTERS OF MgO

- **Reaction path: only on oxygen vacancies centers activation energy of ≈1 eV, compatible with measured desorption barrier ($T_{des}$ ≈300 K)**
- **All other MgO sites (terraces, low-coordinated ions, etc.) not active because Pd is neutral**



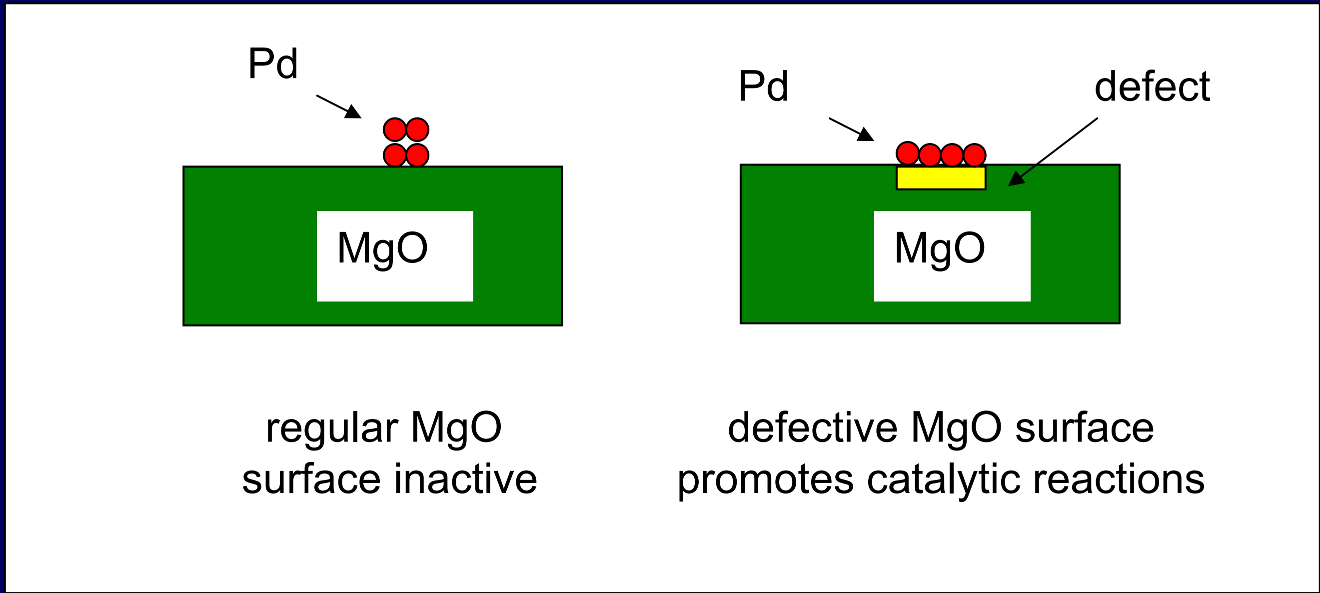




Abbet, Sanchez,Heiz, Schneider, Ferrari, GP, Rösch, *J. Am. Chem. Soc.* 122 3453 (2000)

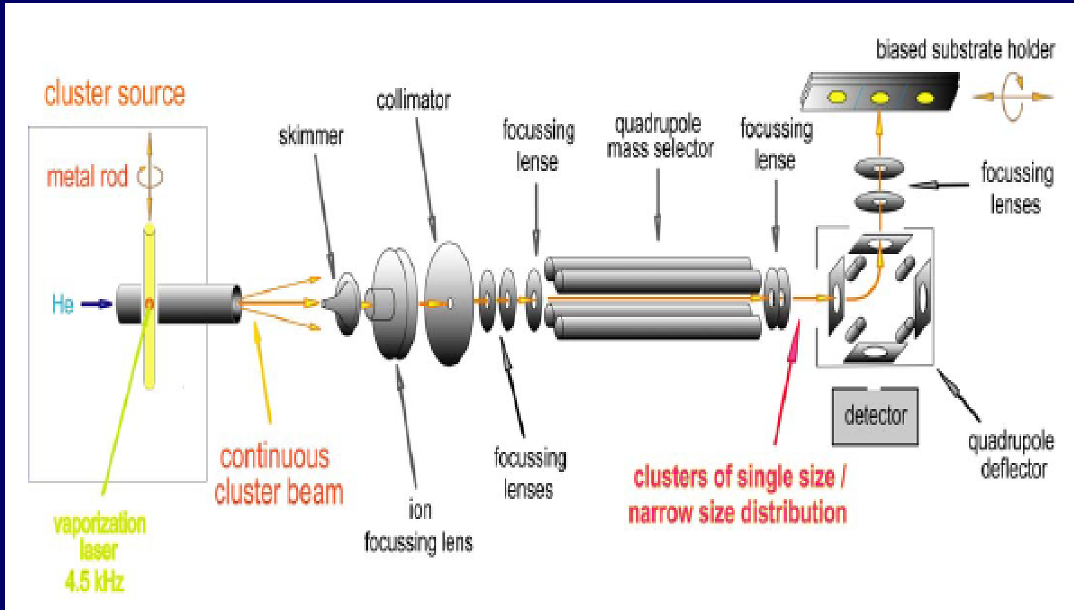
**Charging is essential to turn inactive Pd atoms into active catalysts**

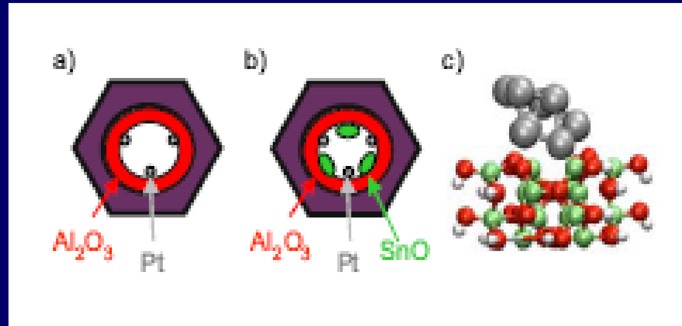
# DEFECTS AND SURFACE IRREGULARITIES

- role of surface defects: they act as nucleation centers where cluster grow begins
- they can alter the properties of nano-size metal clusters deposited on the surface



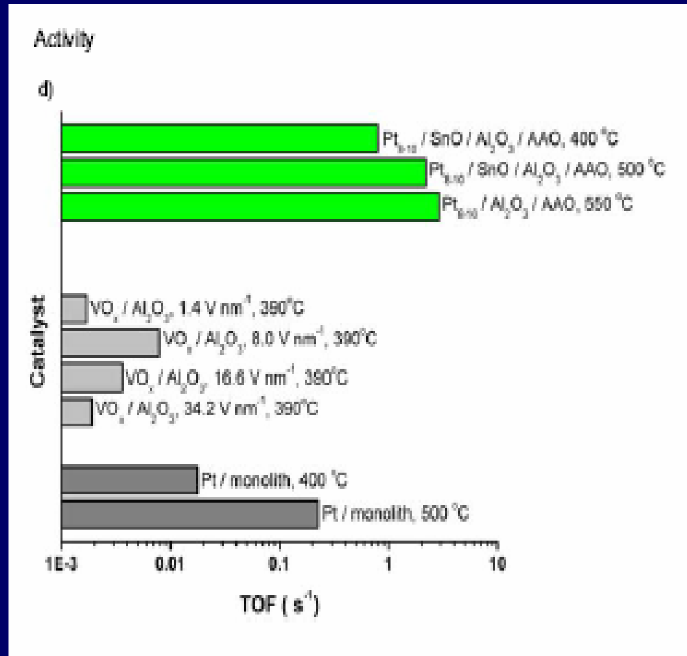
# STABLE (AND VERY ACTIVE!) NANOCATALYSTS




**$Pt_{8\text{-}10}$ clusters on alumina**

- **Mass selected, soft-landing deposition**
- **Thermally stable up to 500 °C**
- **100-400 times more active than conventional catalysts in alkane dehydro-genation**




Vajda et al. Nature Materials 8, 213, 2009

# Oxide surfaces in nanocatalysis: not only an inert support (role of morphology, defects, etc.)

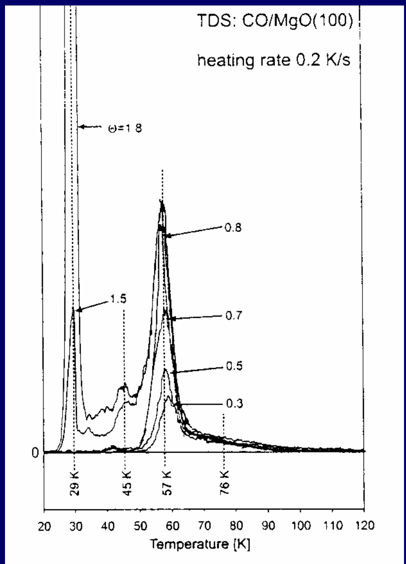
# VARIOUS FORMS OF OXIDE SURFACES

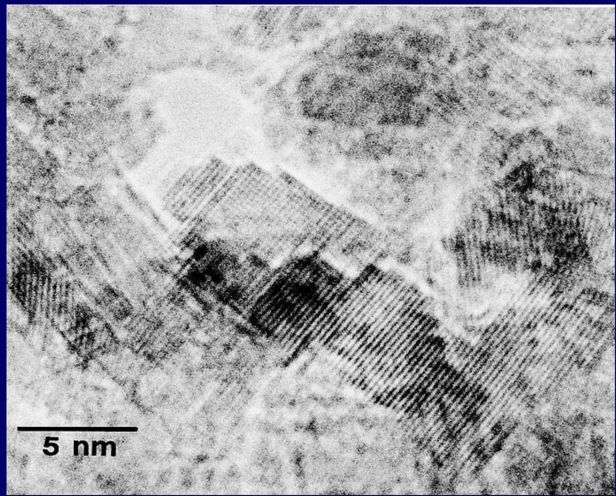
| | |
|---|---|
| **Single crystals** | **Advantages: almost defect free**<br>**Disadvantages: brittle and insulating, difficult to prepare, low surface area** |
| **Powders, polycrystals** | **Advantages: high surface area, easy to prepare by chemical synthesis (decomposition, CVD, etc.)**<br>**Disadvantages: surface heterogeneity, complex morphology, impurities** |
| **Amorphous (porous) structures** | **Advantages: easy to prepare (sol-gel, etc.)**<br>**Disadvantages: surface heterogeneity, complex morphology, local structure undefined** |
| **Epitaxial thin films (1-100 layers)** | **Advantages: low-dimensionality, nanostructure**<br>**Disadvantages: difficult to prepare, thermal stability** |

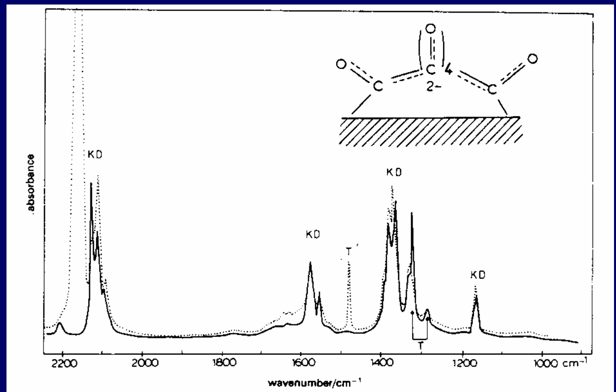
# Different reactivity of oxide surfaces with different morphologies: CO on MgO

**CO on single crystal MgO, no reactivity at all and adsorption occurs only below 57 K**

**(Freund 1998)**

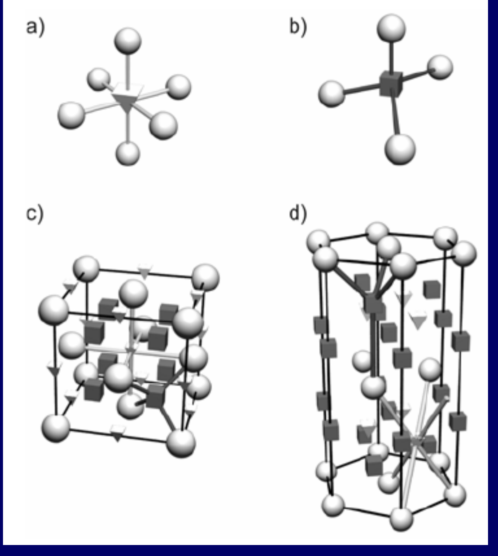


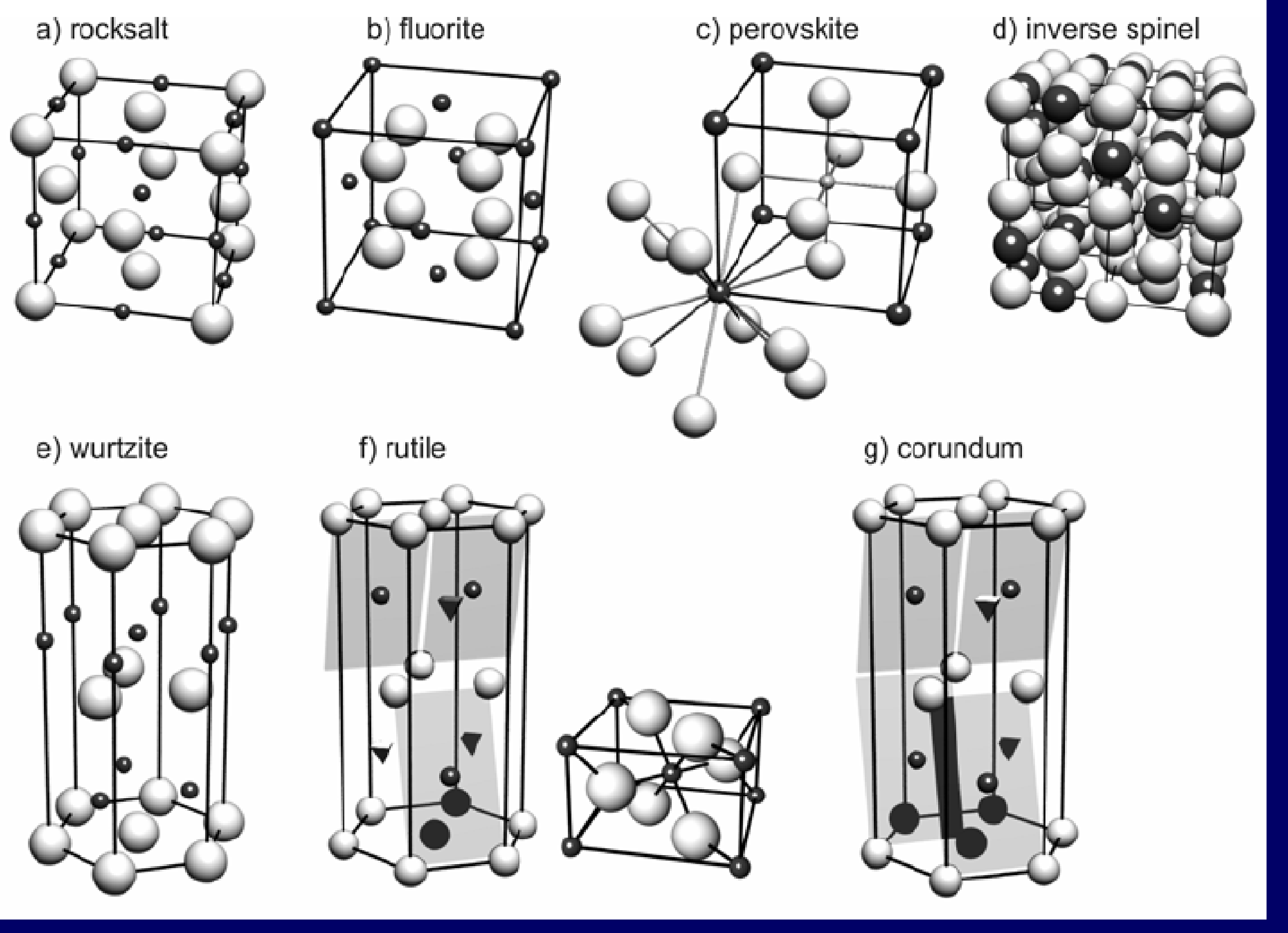




**CO on polycrystalline MgO, complex radical anions form at 60 K! (Zecchina 2004)**

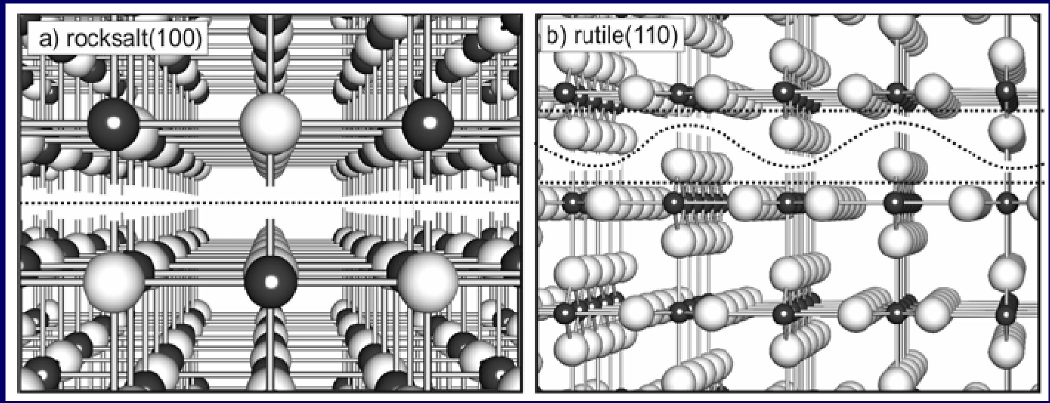
# OXIDES CRYSTAL STRUCTURES



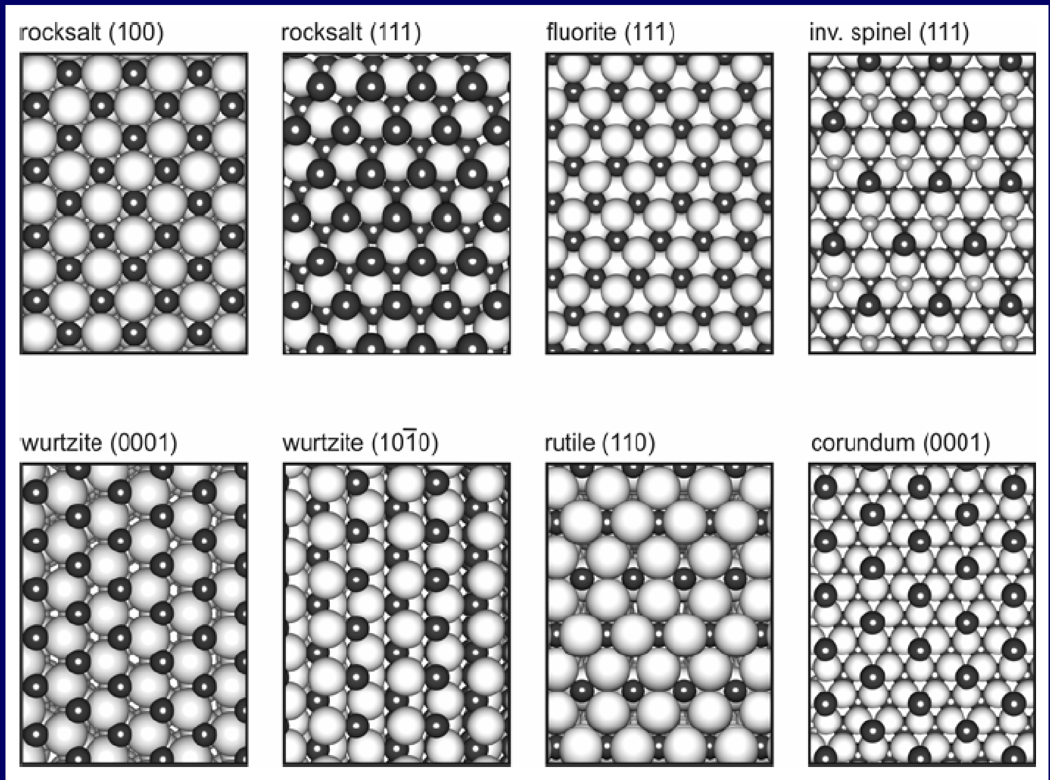

| Name | Examples |
|---|---|
| rocksalt | MgO, NiO, MnO, CoO, FeO |
| fluorite | $CeO_2$, $ZrO_2$ |
| spinel | $Al_2MgO_4$, $Fe_3O_4$ (inverse) |
| perovskite | $SrTiO_3$, $BaTiO_3$, $NaWO_3$ |
| wurtzite | ZnO, BeO |
| rutile | $TiO_2$, $RuO_2$, $SnO_2$ |
| corundum | $Al_2O_3$, $Fe_2O_3$, $Cr_2O_3$, $V_2O_3$, $Ti_2O_3$ |

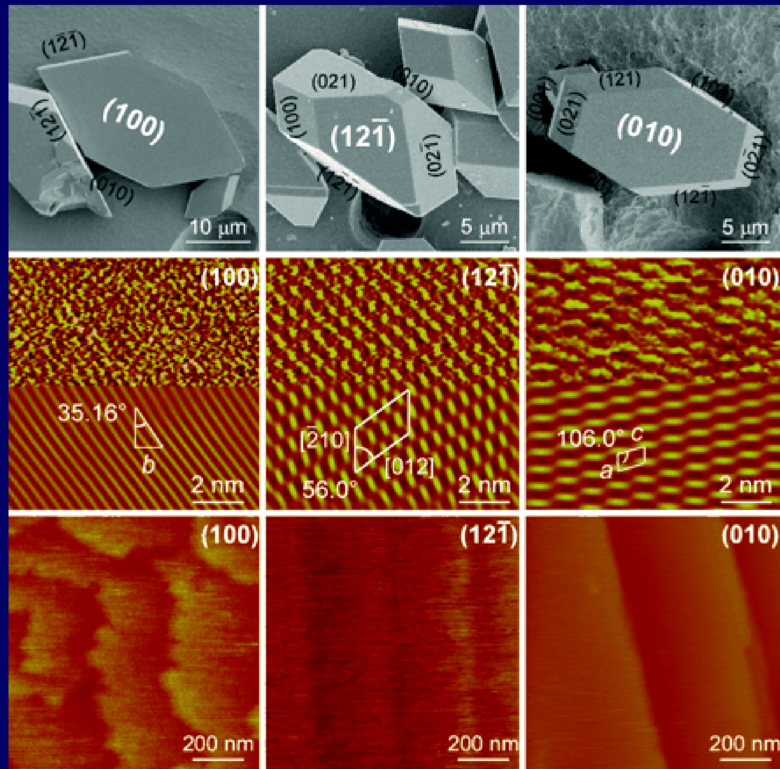


# OXIDES SURFACE PLANES

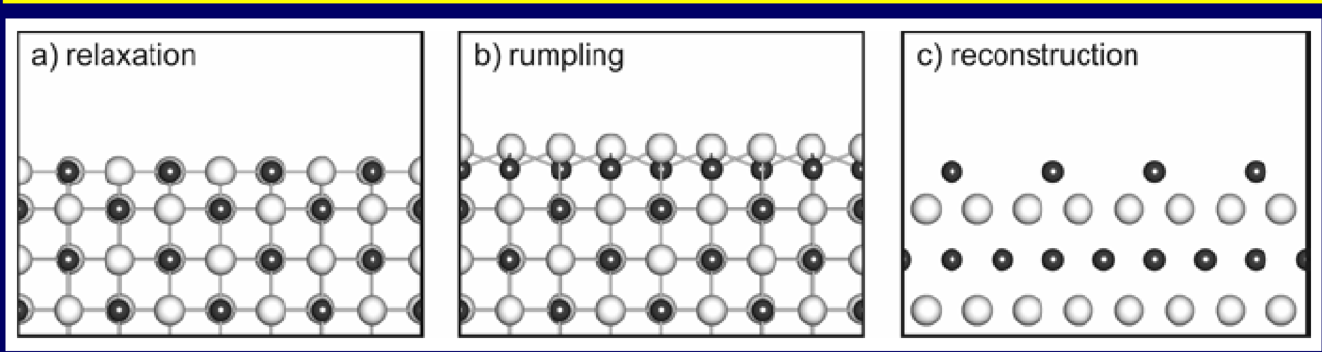


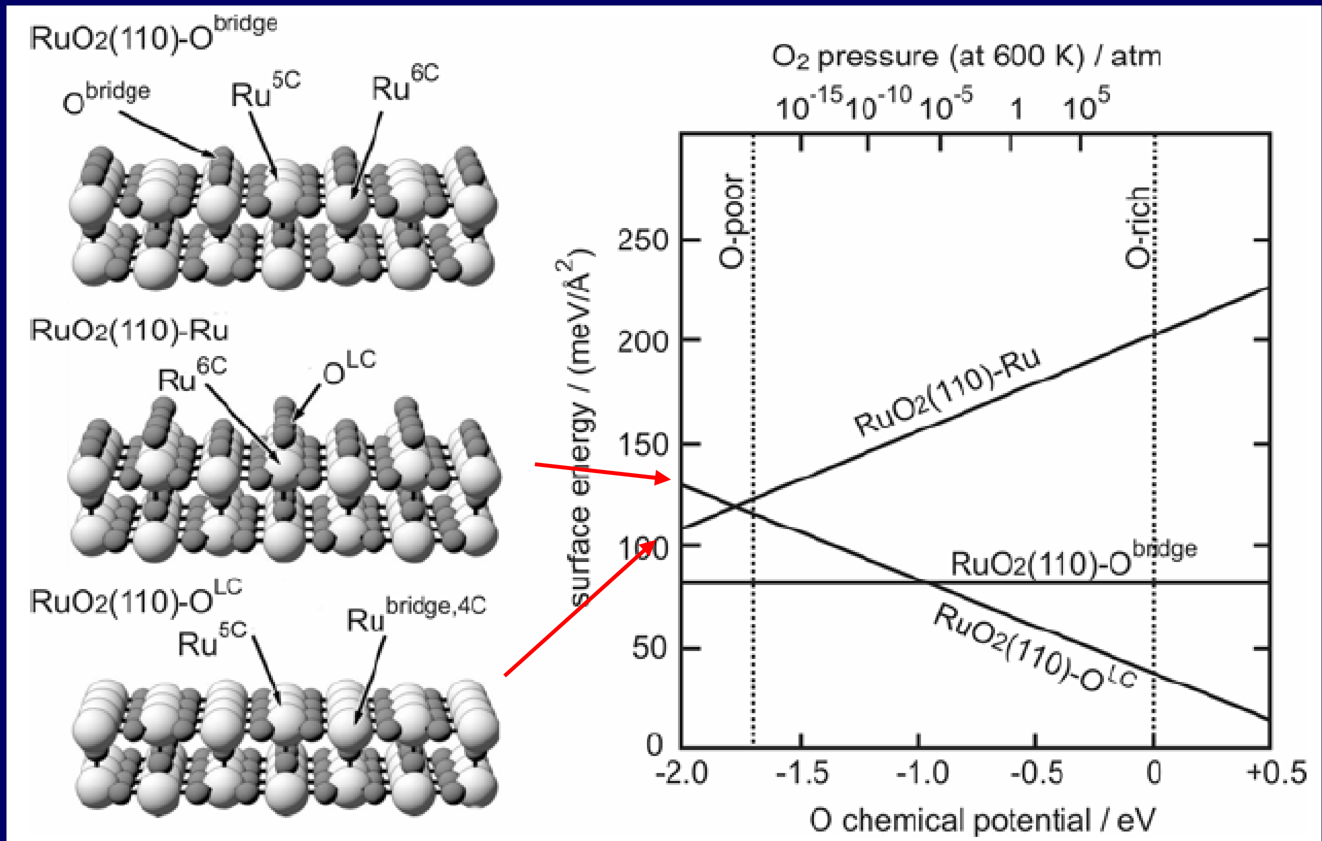

Calcium oxalate crystal surfaces. (*Top*) Scanning electron microscopy images viewed perpendicular to the (100), (12-1), and (010) faces. (*Middle*) AFM lattice images. (*Bottom*) Topographical images of the three crystal faces



# SURFACE RELAXATION & COMPOSITION



# DEFECTS IN OXIDE SURFACES

low-coordinated cations

low-coordinated anions

anion vacancies (F centers)

cation vacancies

divacancies

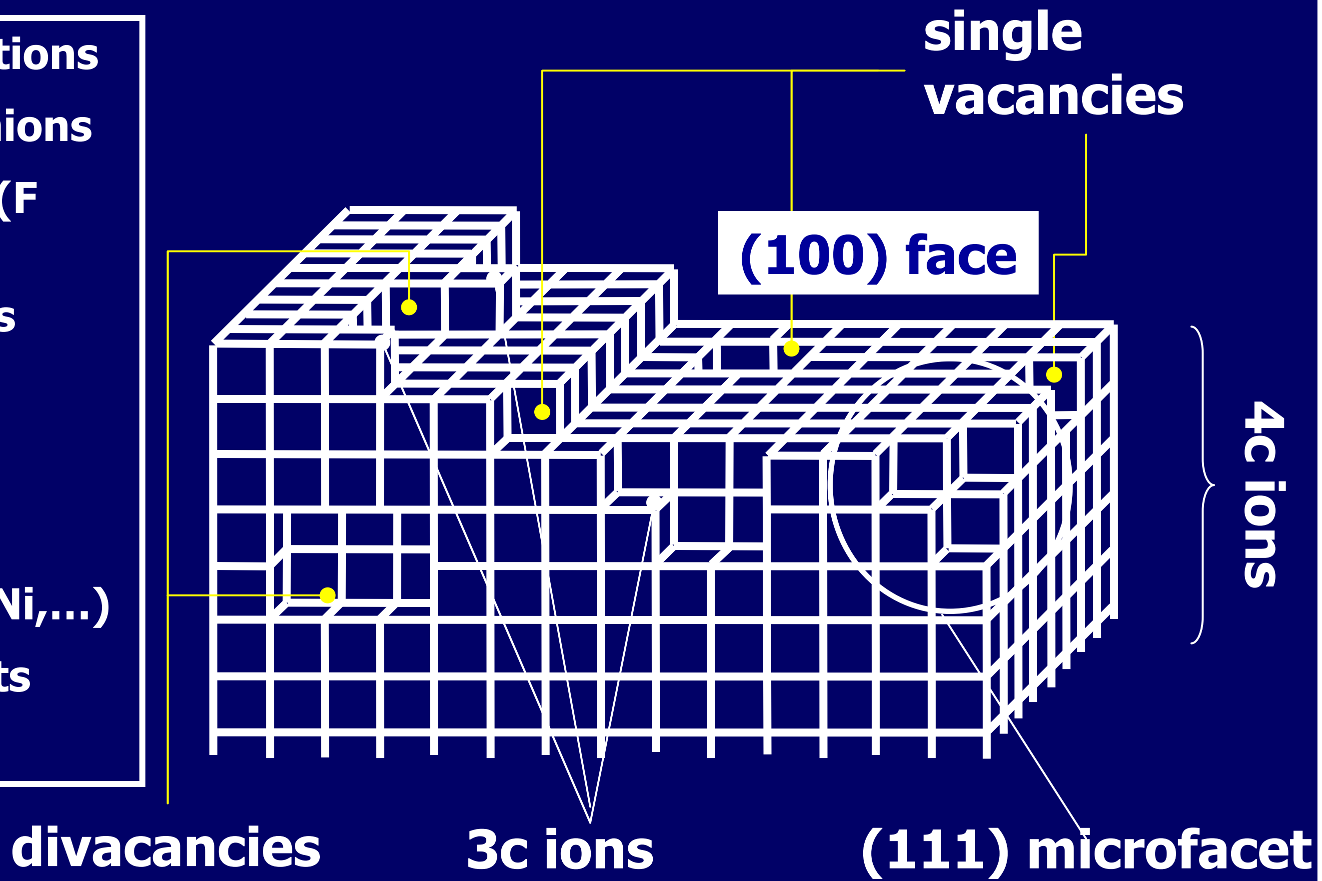
$O^-$ radical ions

OH groups

impurity atoms (Li, Ni,...)

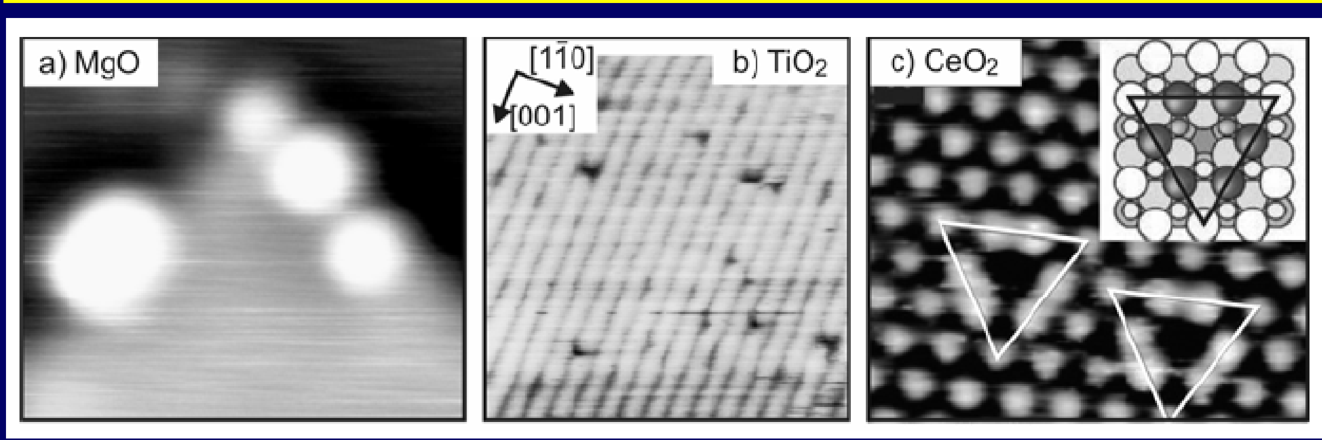
(111) microfacets

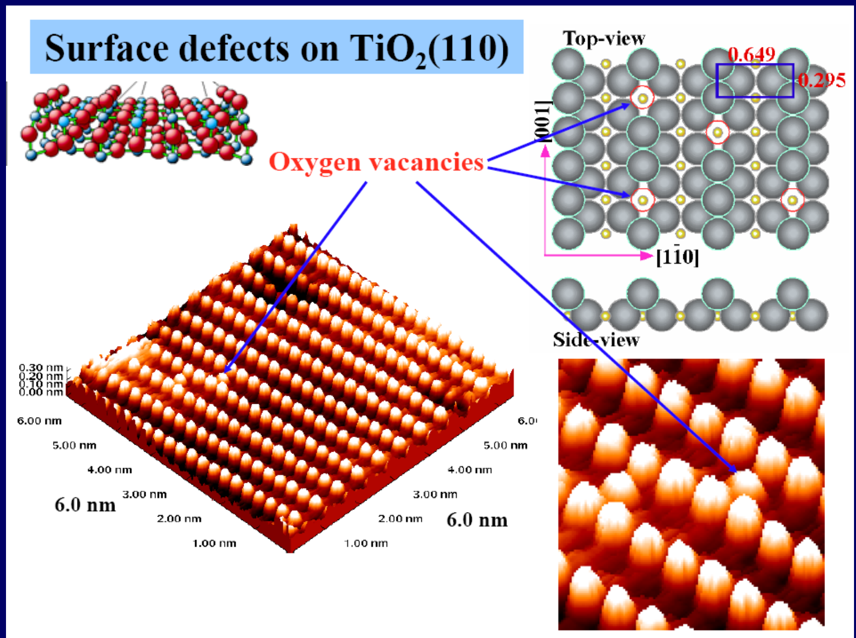
electon traps




**ROLE OF ATOMIC PROBES AND THEORY IN IDENTIFYING POINT DEFECTS IN OXIDES**

# POINT DEFECTS: VACANCIES (STM IMAGES)

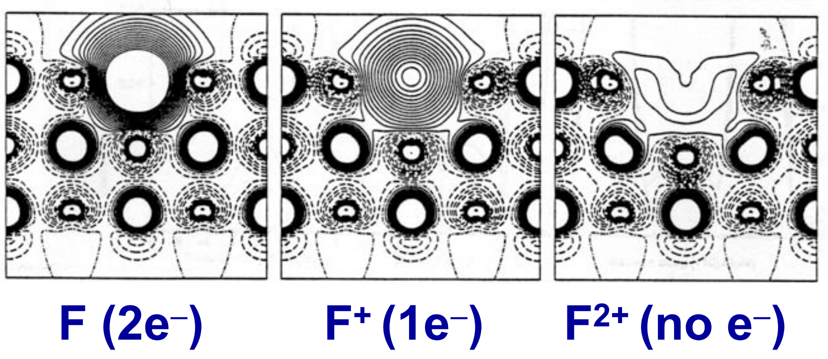



**STM possible only on conducting substrates, not on insulating oxides (unless thin films).**

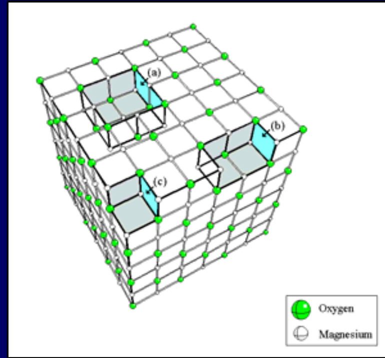
**STM needs theoretical interpretation**

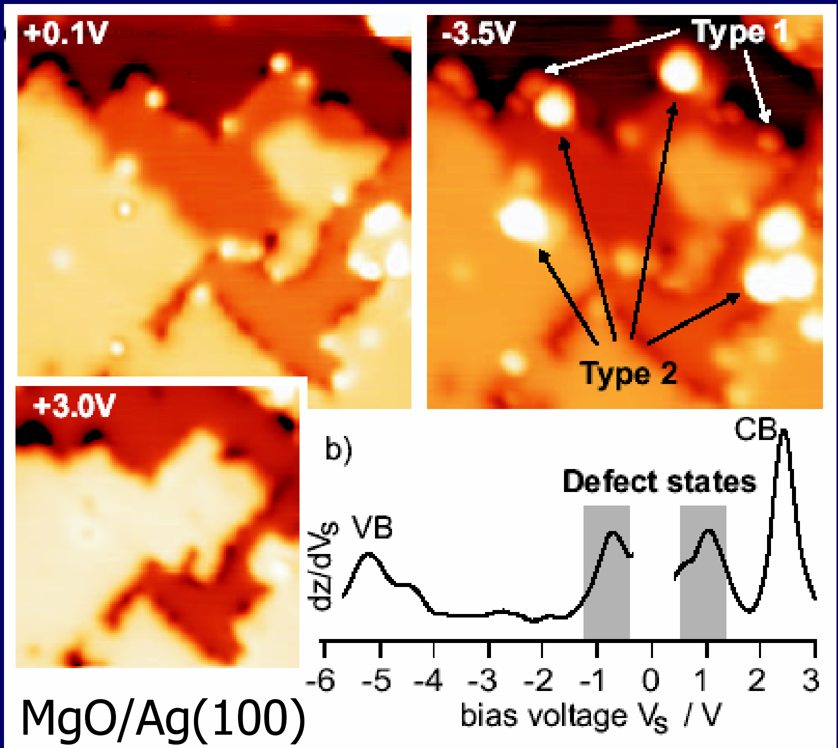
# STS OF F CENTERS (O VACANCIES) ON MgO THIN FILMS

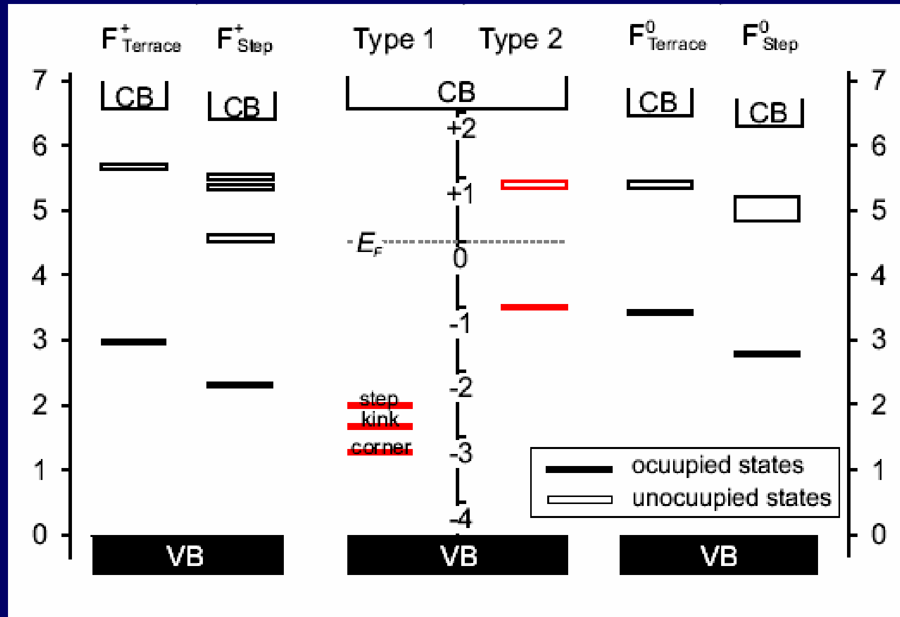



**F centers form more easily on low-coordinated sites**

GP, Pescarmona, Surf. Sci. 412/413 (1998) 657

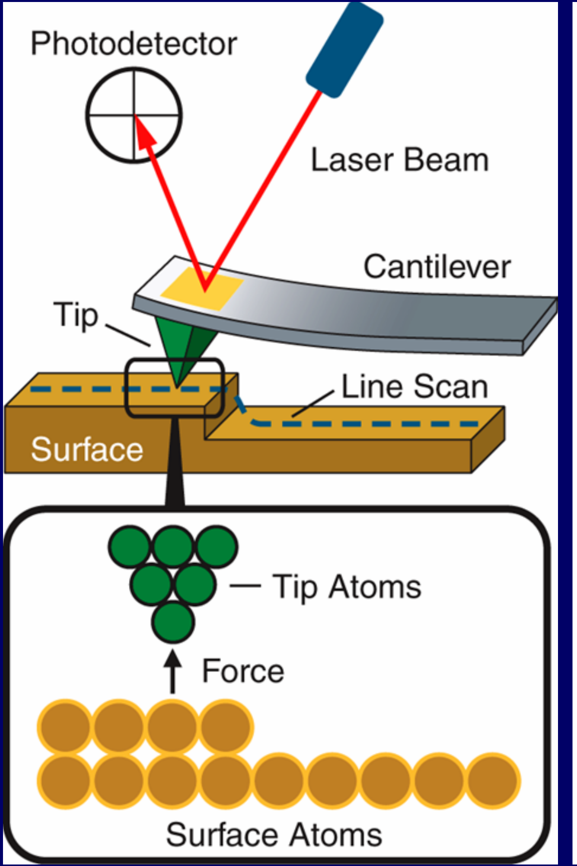


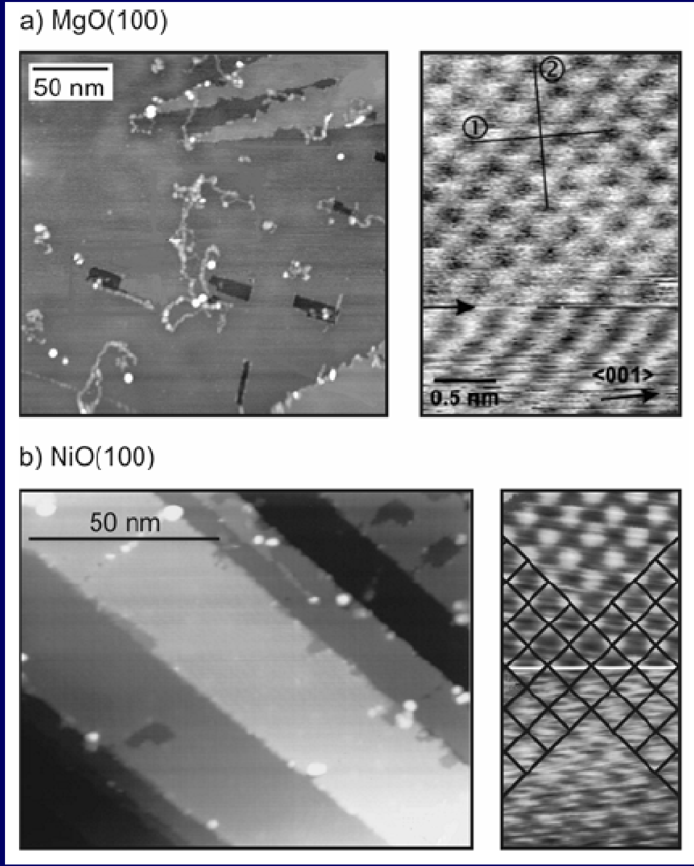



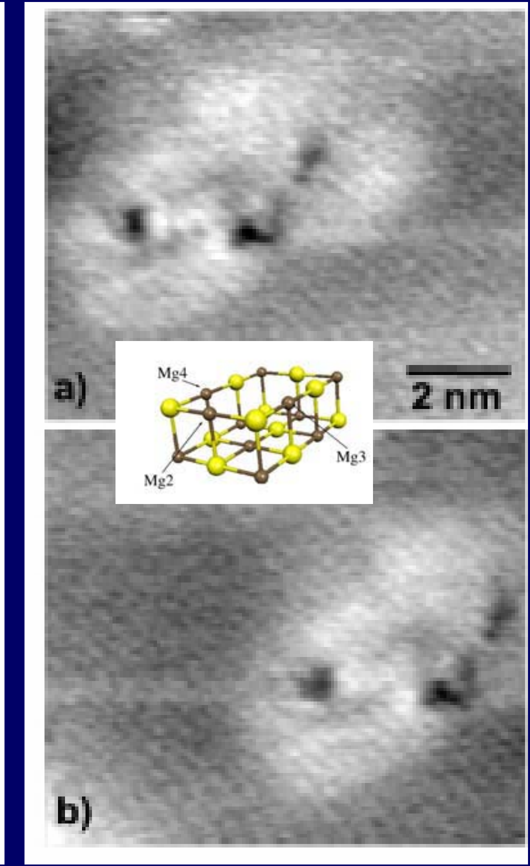




Sterrer, Heyde, Novicki, Nilius, Risse, Rust, GP, Freund, J. Phys. Chem. B 110, 46 (2006)

# ATOMIC FORCE MICROSCOPY (AFM)



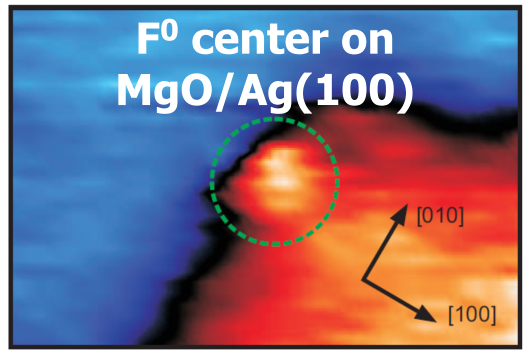



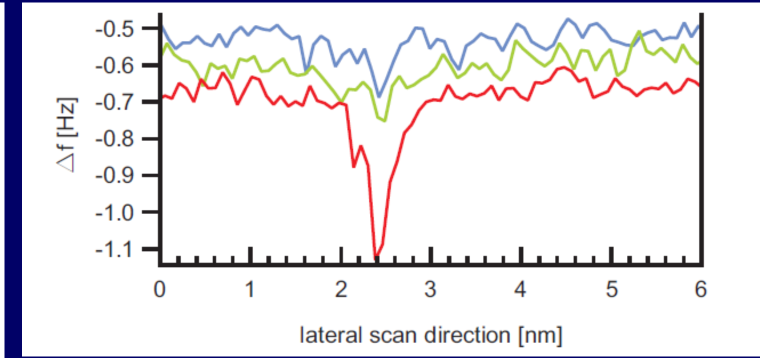



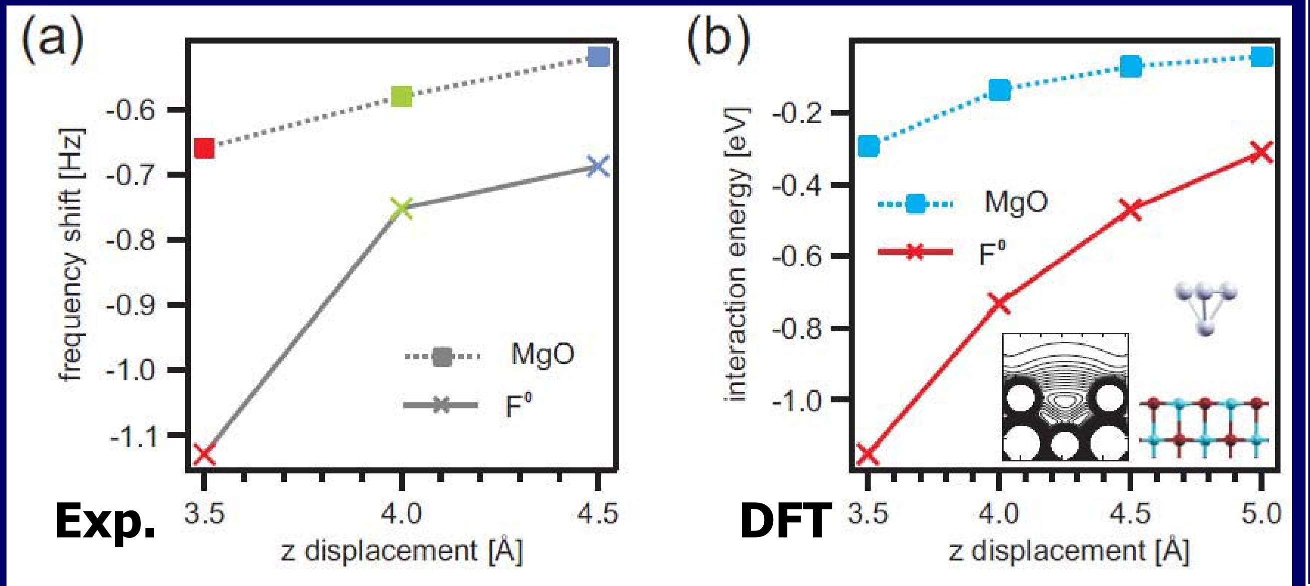

**AFM of MgO single crystal show point defects with atomic resolution (divacancies?)**

C. Barth & C. Henry, Phys. Rev. Lett. 91 (2003) 196102

# AFM: MEASURING INTERACTION STRENGTH WITH DEFECTS



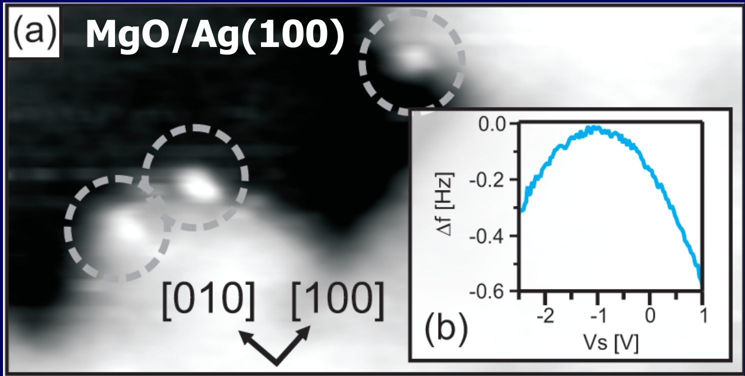

**Dynamic Force Microscope (non-contact AFM): direct measure of force between tip and point defect**

**Different interaction of Pt tip with MgO and an oxygen vacancy ($F^0$)**

**Compare to DFT interaction energy curves**

**König, Simon, Martinez, Giordano, GP, Heyde, Freund, ACS Nano, in press (2010)**

# DFM: MEASURING CHARGE STATE OF POINT DEFECTS

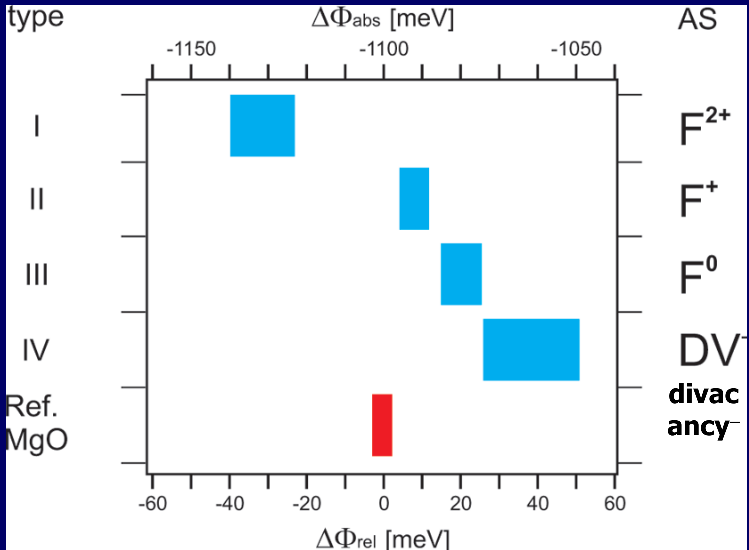


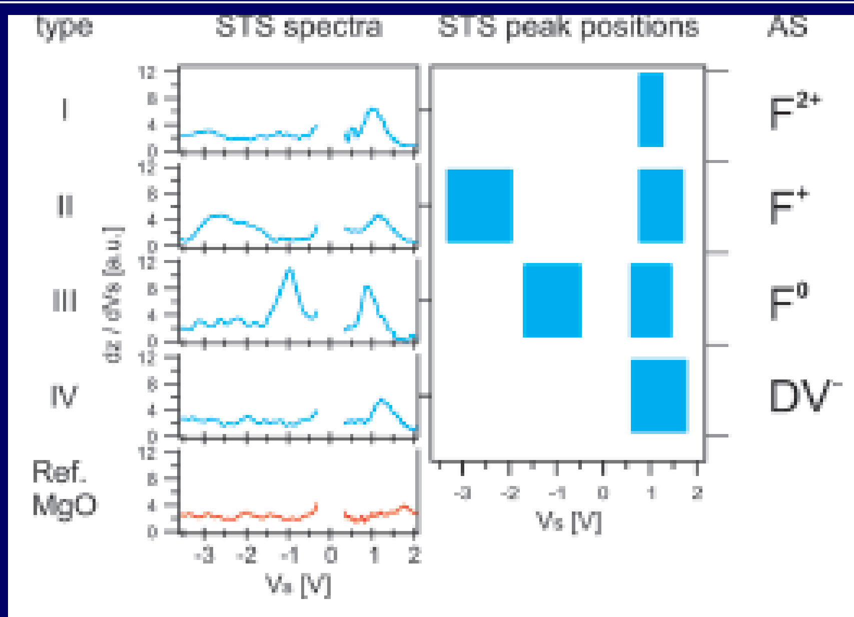

**DFM: measure frequency shift vs bias**

**Maximum determined by charge q and local work function $\Delta\Phi$**

**Different defects on MgO/Ag films result in different frequency shifts**

$$F_{el} = \frac{1}{2C_\Sigma^2}\frac{\partial C_1}{\partial z}\left(nq + C_2\left(V_S - \frac{\Delta\Phi_{loc}}{|q|}\right)\right)^2$$

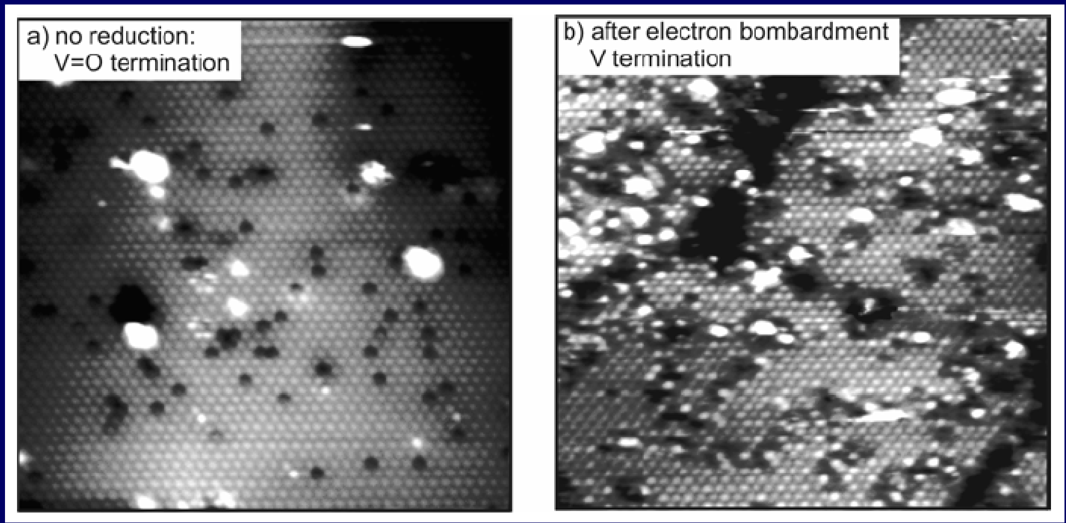


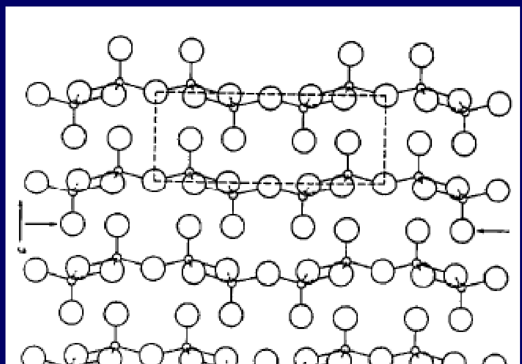



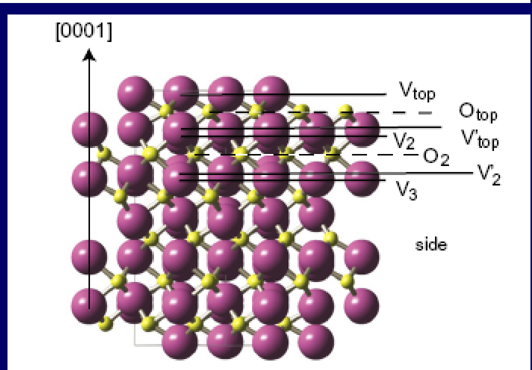

**König, Simon, Rust, GP, Heyde, Freund, J. Am. Chem. Soc. 131, 17544 (2009)**

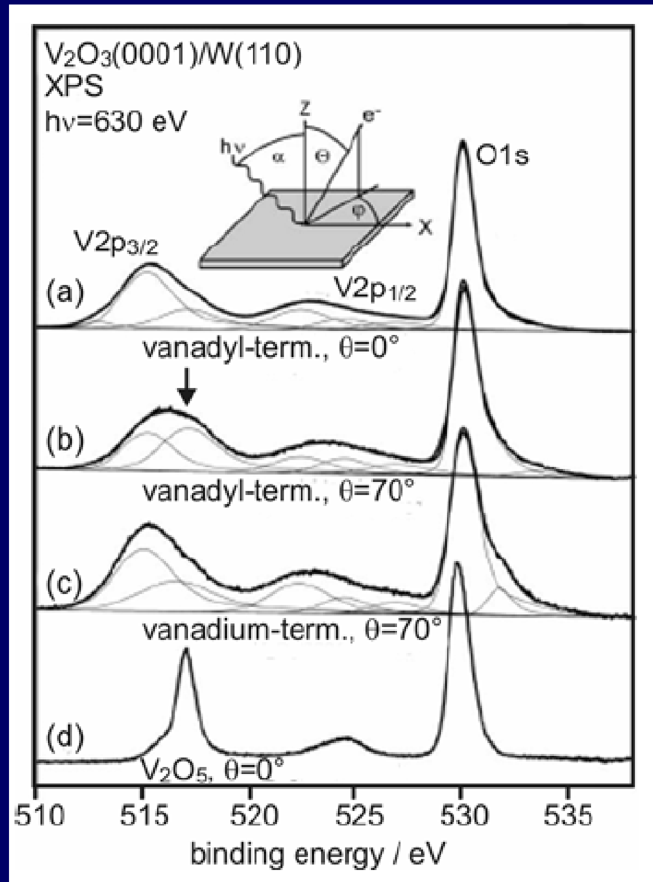
END OF
LECTURE 1

# OXIDES ELECTRONIC STRUCTURE: CORE LEVELS

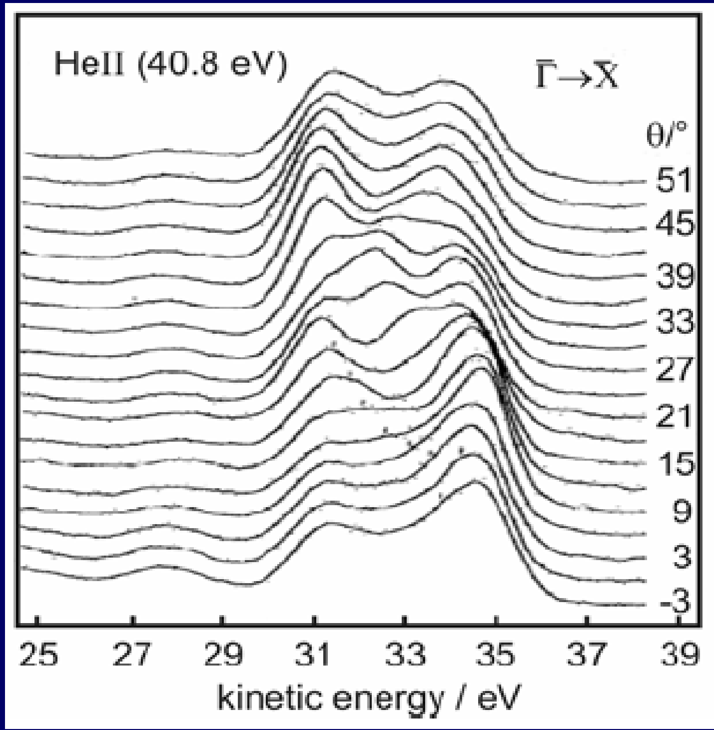


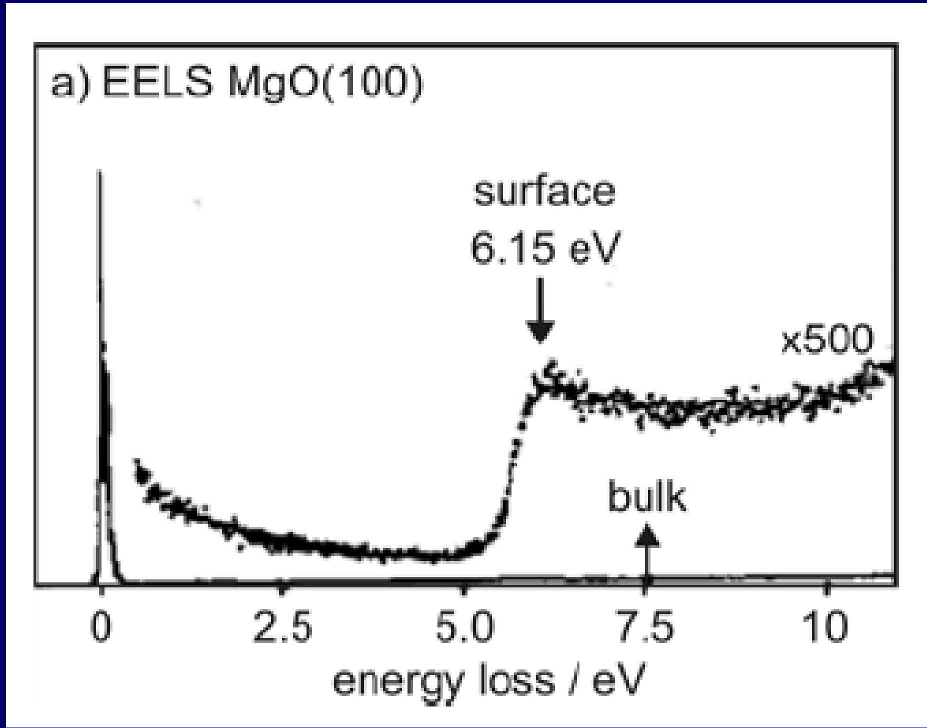





# OXIDES ELECTRONIC STRUCTURE: VALENCE BAND



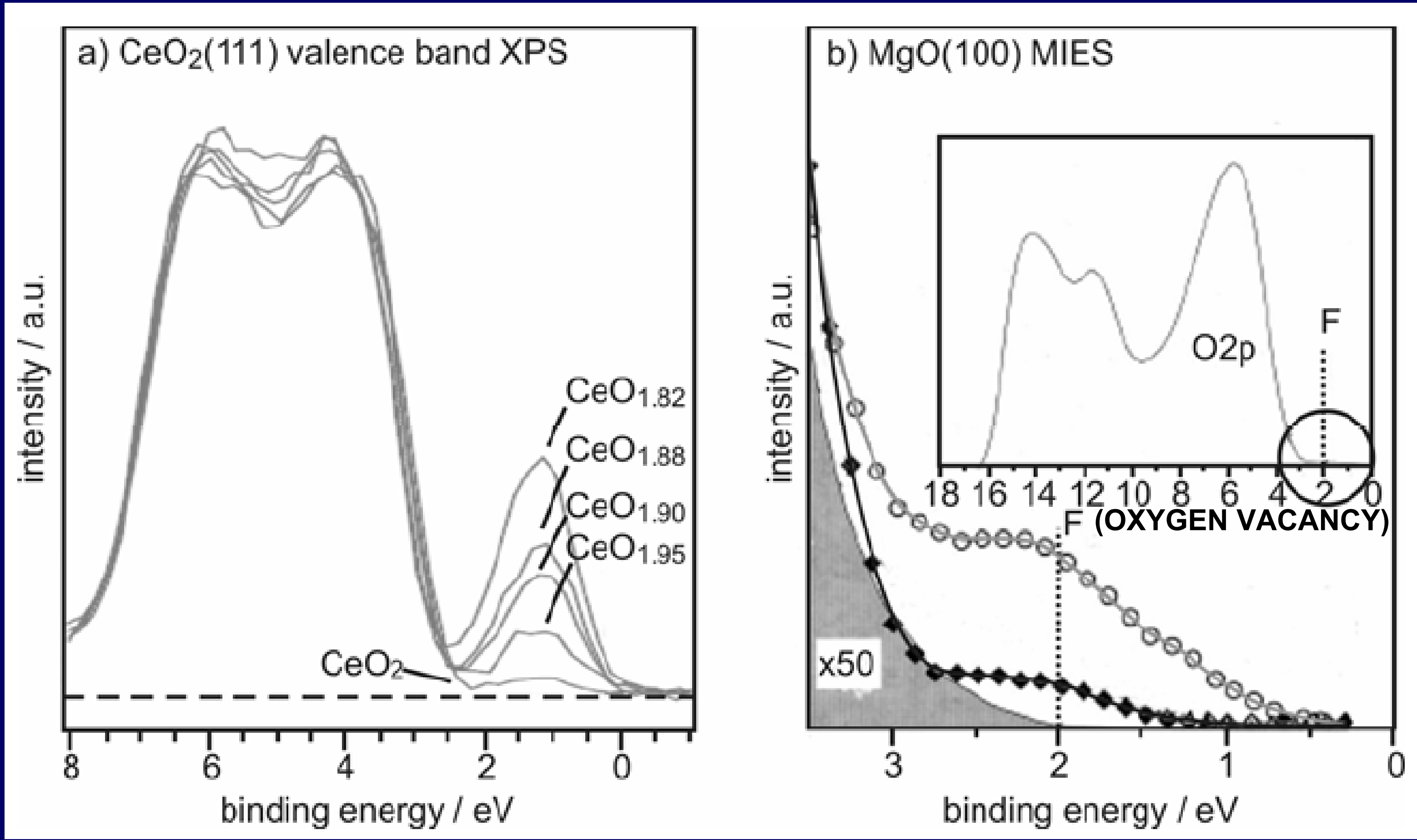




**Angular resolved Ultraviolet Photoemission Spectroscopy (UPS): valence band structure**

**Electron Energy Loss Spectroscopy (EELS): band gap**

**Surface gap smaller than bulk gap**

# OXIDES ELECTRONIC STRUCTURE: DEFECTS



# DEFECTS AND MORPHOLOGY OF OXIDE SURFACES

## Bulk defects

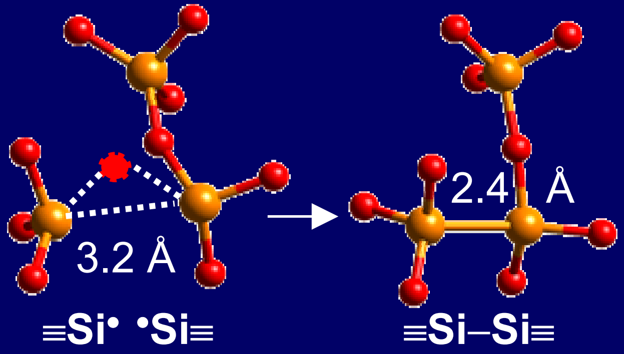
- electrical, optical, electronic properties
- ion conductivity
- superconductivity
- insulator-to-metal transition

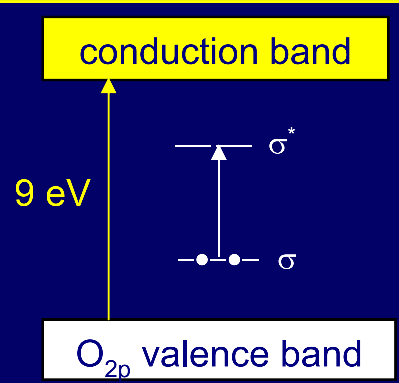
## Surface defects

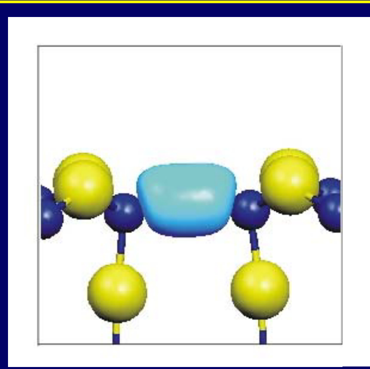
- chemical reactivity (catalysis)
- corrosion
- nucleation and growth of supported metal particles
- chemical properties of nano-clusters

# THE OXYGEN VACANCY IN METAL OXIDES

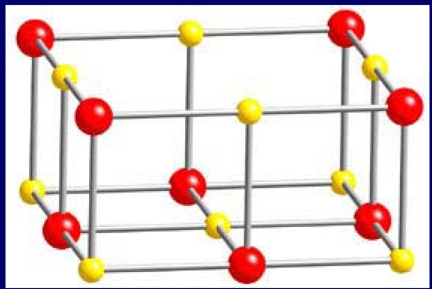
**$SiO_2$: covalent polar**

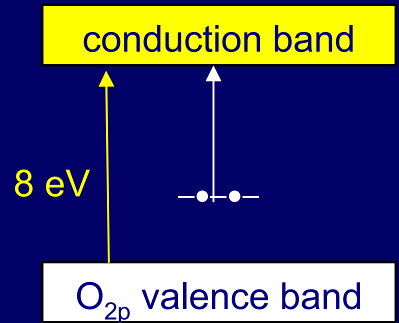


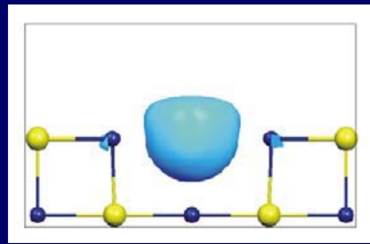



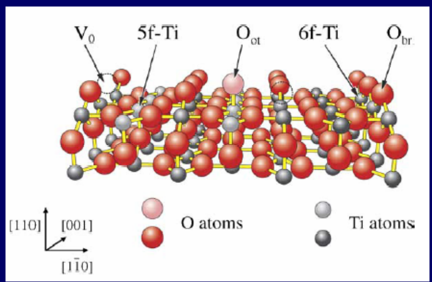
**MgO: largely ionic**

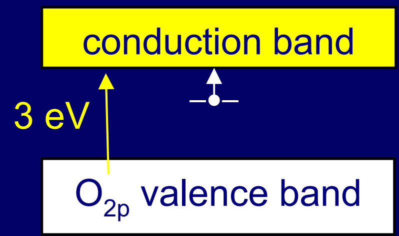


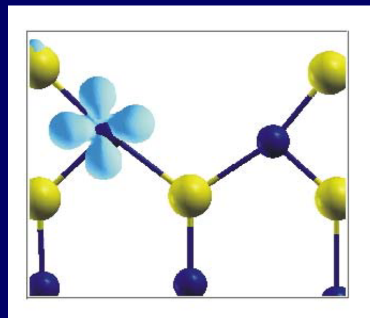


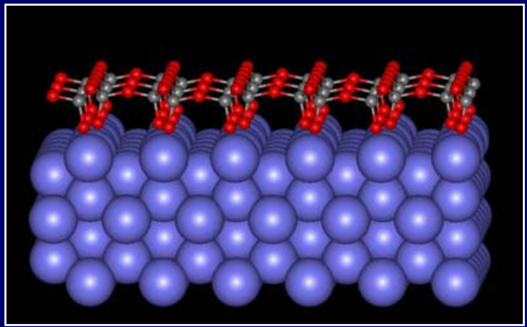
**$TiO_2$: mixed**

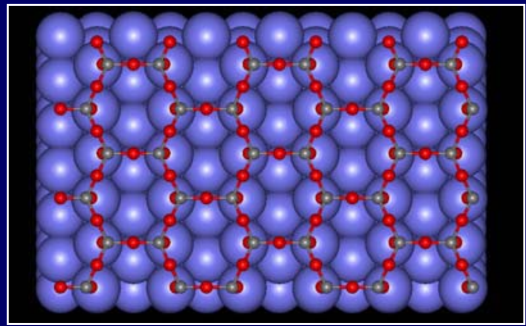


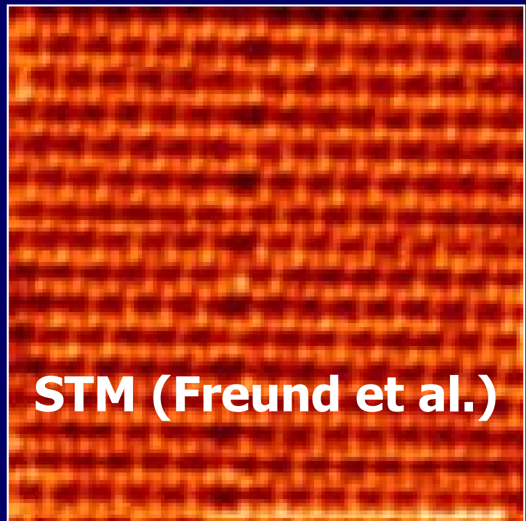



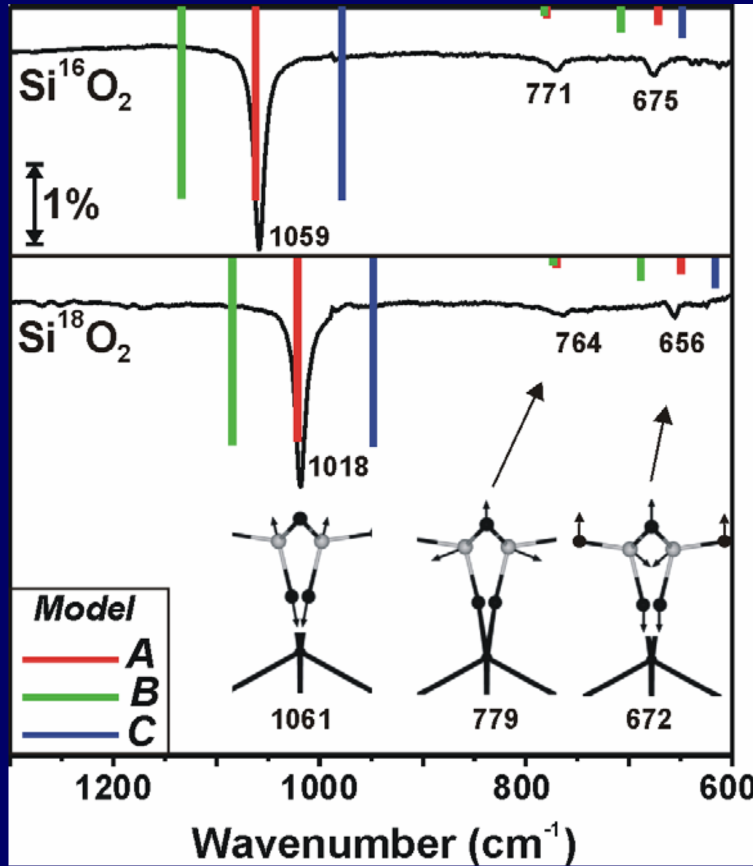
# SURFACE PHONONS: $SiO_2$/Mo(112) FILMS





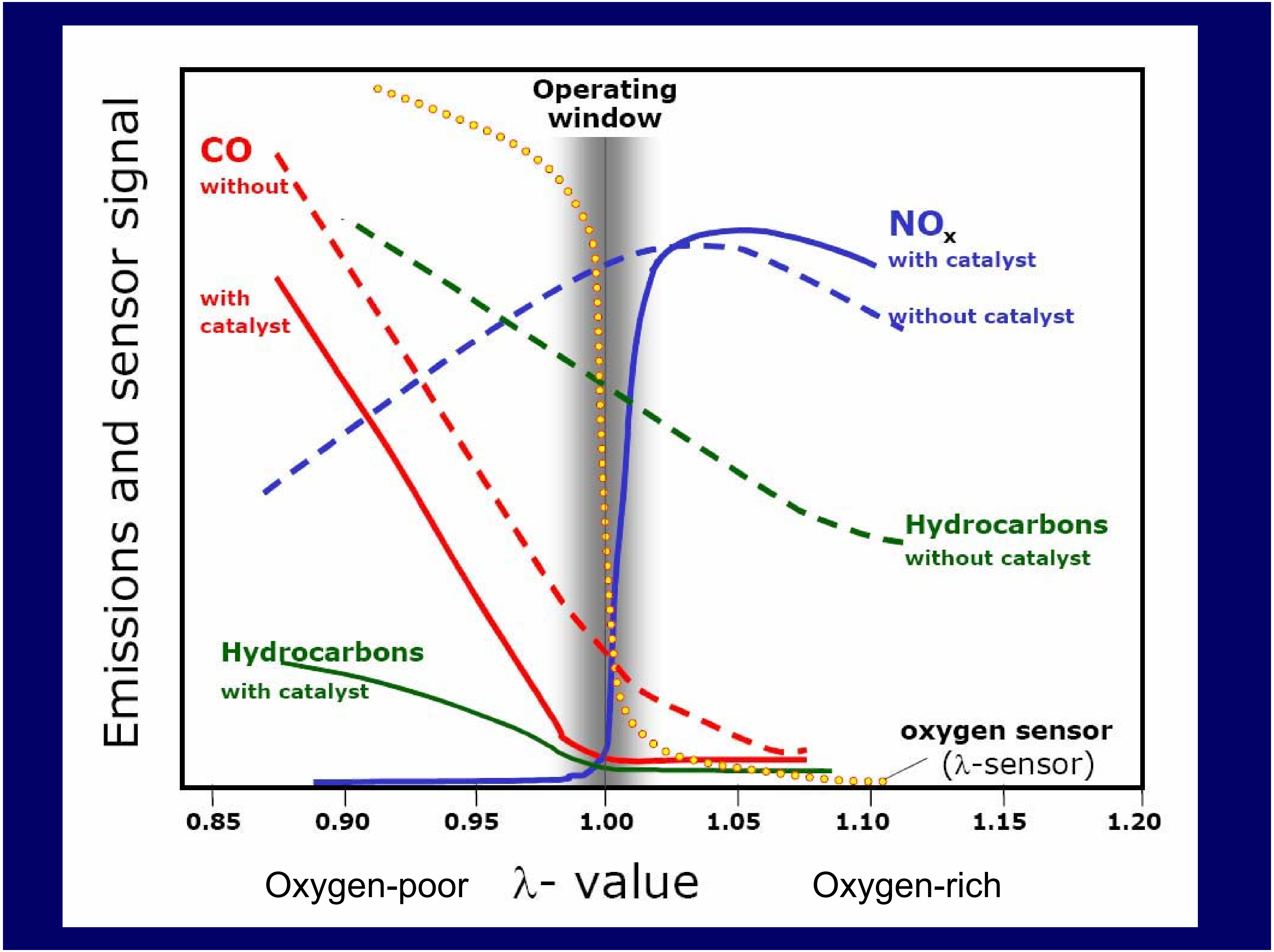
- **1 layer film 3 Å thick with $SiO_{2.5}$ stoichiometry; hexagonal pattern**
- **Computed phonons reproduce IR and HREELS spectra**




**Preparation**: Schroeder, Giorgi, Bäumer, Freund, *Phys. Rev. B* 66 (2002) 165422

**Structure**: Giordano, Ricci, Pacchioni, Ugliengo, *Surf. Sci.* 584 (2005) 225; Weissenrieder, Kaya, Lu, Gao, Shaikhutdinov, Freund, Sierka, Todorova, Sauer, *Phys. Rev. Lett.* 95 (2005) 076103



Operating window
CO
without
with catalyst
NO$_x$
with catalyst
without catalyst
Hydrocarbons
without catalyst
Hydrocarbons
with catalyst
oxygen sensor
(λ-sensor)
Emissions and sensor signal
0.85
0.90
0.95
1.00
1.05
1.10
1.15
1.20
Oxygen-poor
λ- value
Oxygen-rich

# EXTENDED DEFECTS: STEPS, DISLOCATIONS (STM)