# 3D Electron Microscopy of Nanocatalysts with Single Atom Sensitivity


**Microscopy:**

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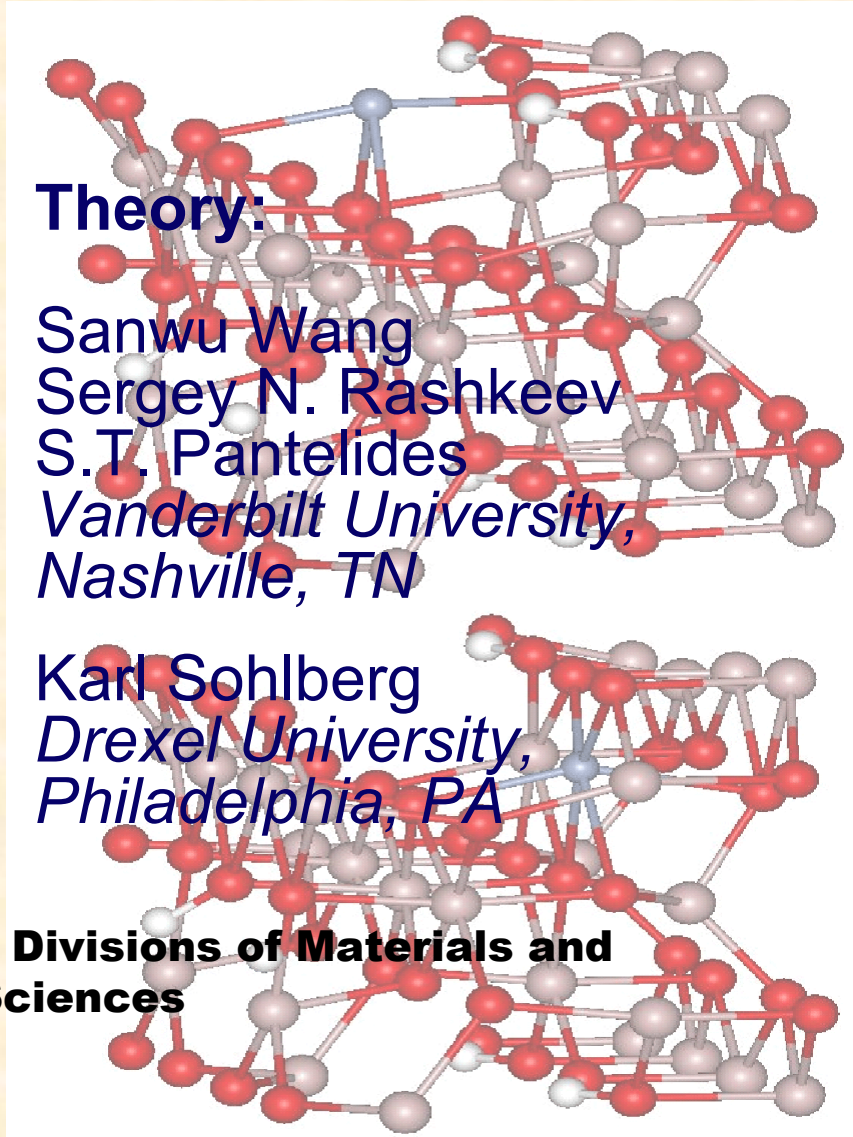


**Theory:**

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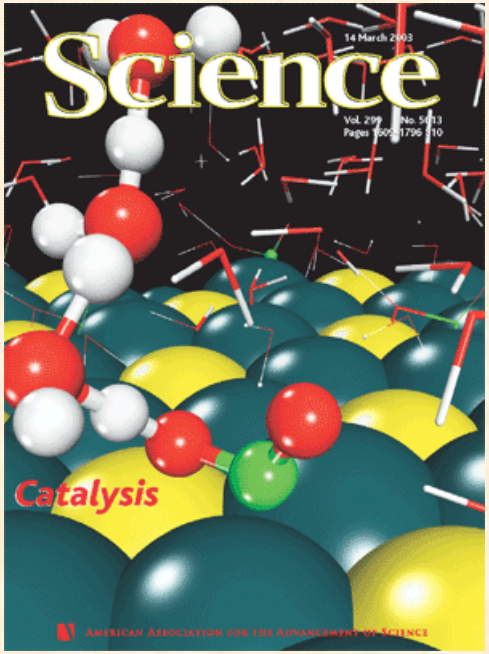
Sergey N. Rashkeev
S.T. Pantelides
*Vanderbilt University, Nashville, TN*

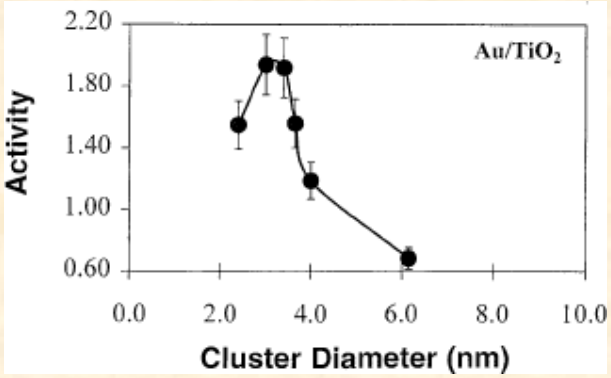
Karl Sohlberg
*Drexel University, Philadelphia, PA*



**Research funded by DOE BES Divisions of Materials and Chemical Sciences**

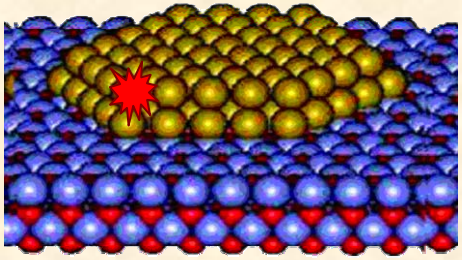
# Catalysis and High-Resolution Imaging





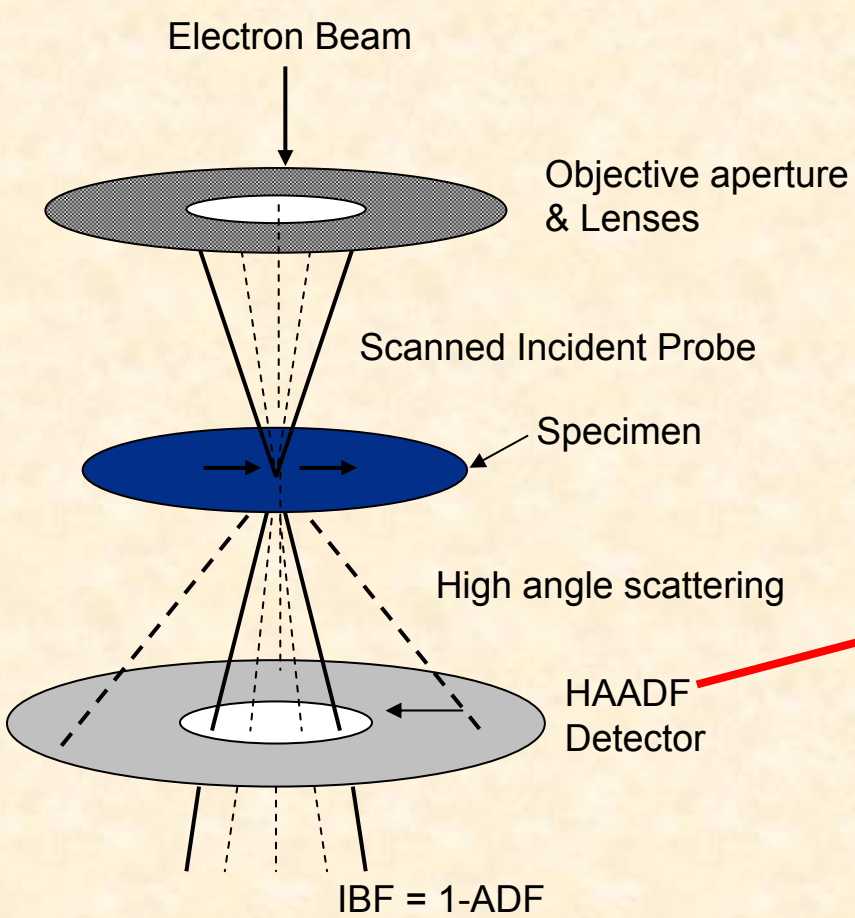

STM of $Au/TiO_2$

M. Valden et al., *Science* **281** 1649 (1998)

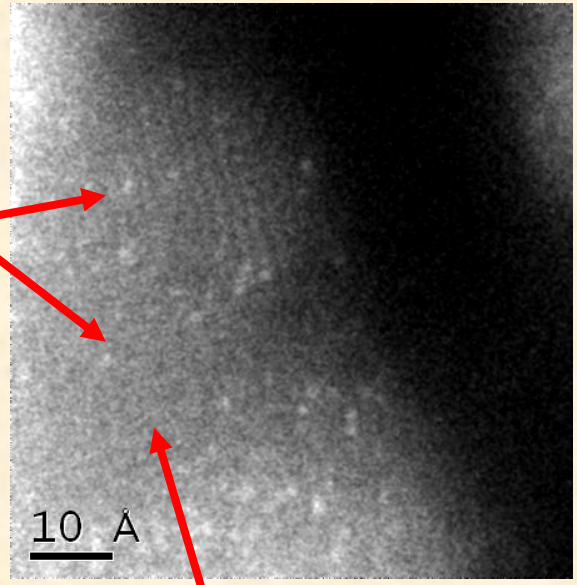


**Need atomic-scale information to understand and control catalyst properties**

# HAADF STEM – Imaging of Real Catalysts

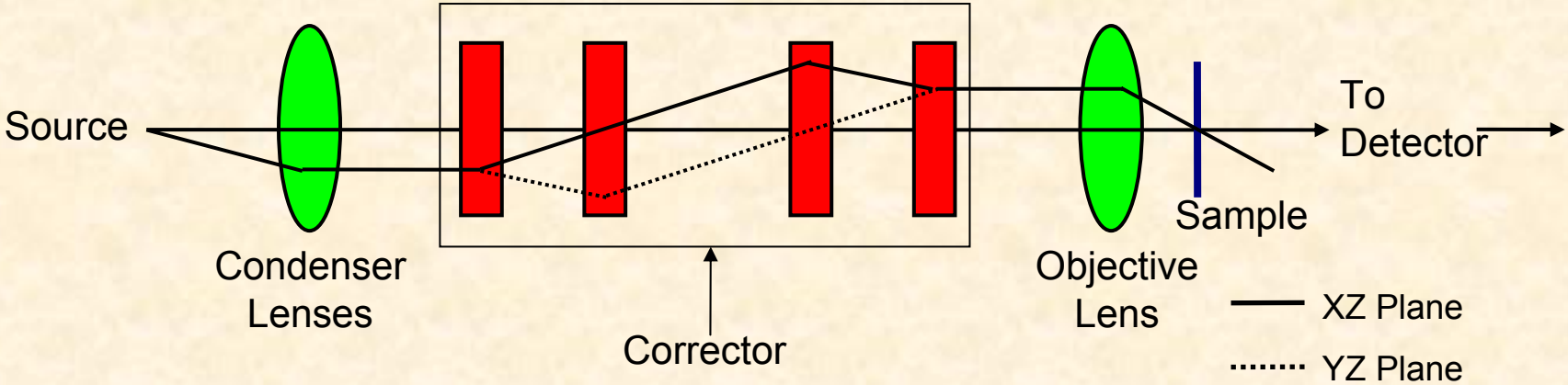



$I \propto Z^2$

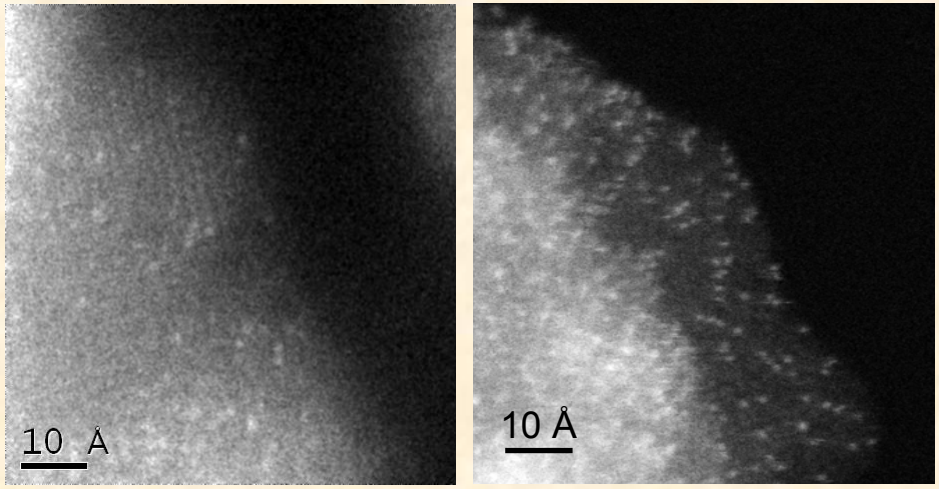



**Z-contrast STEM can detect heavy dopants on light supports**

# Aberration Correction in STEM

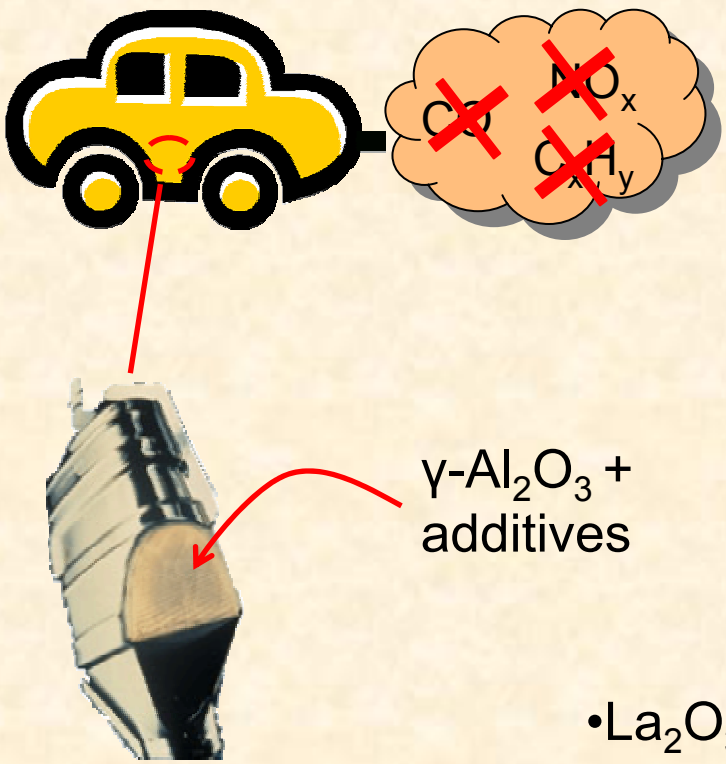



- Non-round lenses
- Resolution and signal-to-noise ratio are improved
- Routine detection of single atoms




Before After

# Stabilization of γ-$Al_2O_3$ by La Doping




**γ-$Al_2O_3$** is widely used as catalyst and catalytic support

higher operating temperature ⟷ higher efficiency

**Problem:**

$$\gamma\text{-}Al_2O_3 \xrightarrow{\sim 1000^{o}C} \alpha\text{-}Al_2O_3$$

**Solution:**

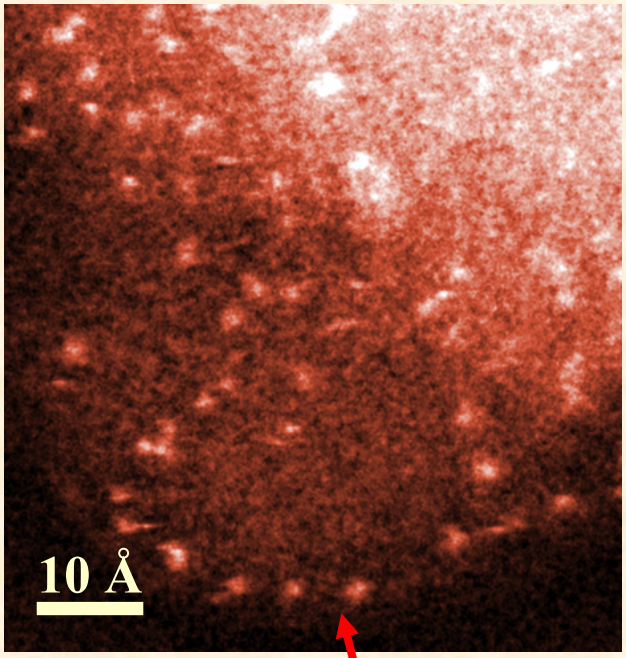
$$\gamma\text{-}Al_2O_3 + La \xrightarrow{\sim 1250^{o}C} \alpha\text{-}Al_2O_3$$

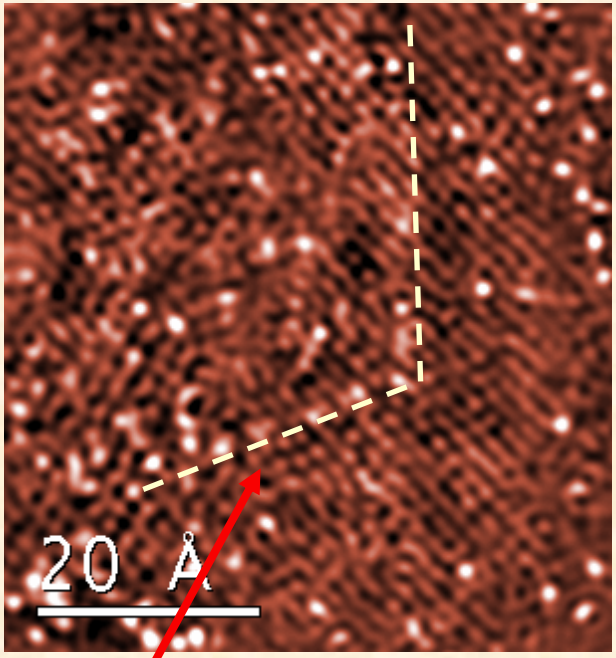
**How?**

- $La_2O_3$ or $LaAlO_3$ monolayers ?
- Bulk substitution of Al by La ?
- Single atoms or clusters on the surface?

**Need to determine La distribution**

# La Atoms on the Surface?



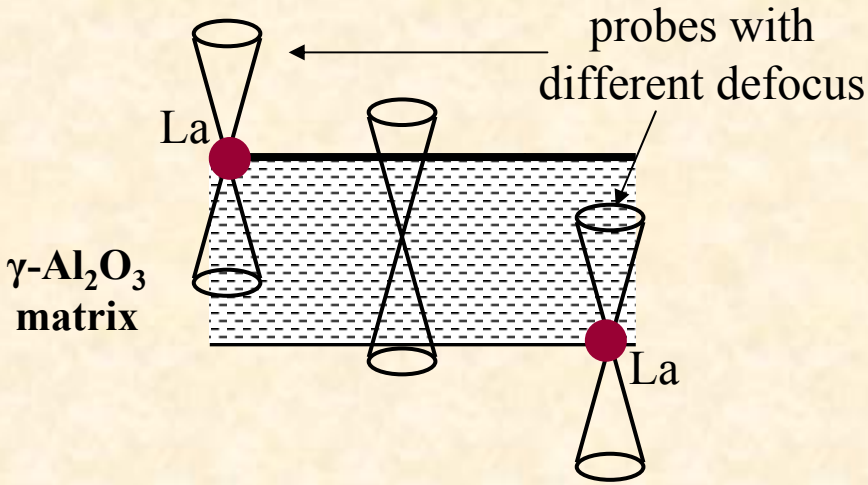



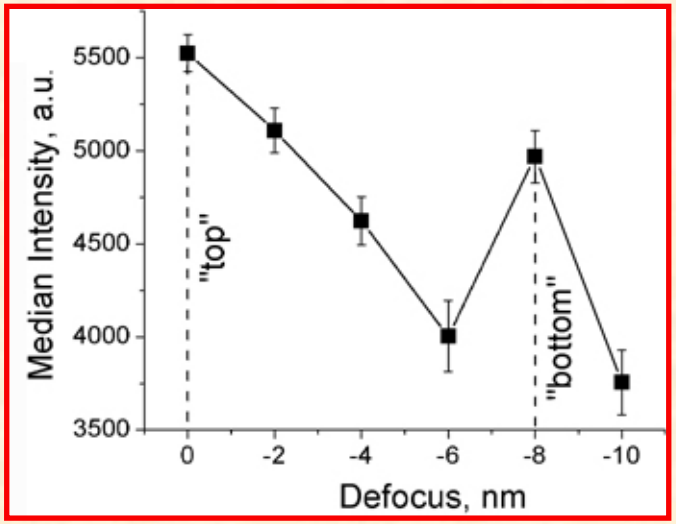

particle edges

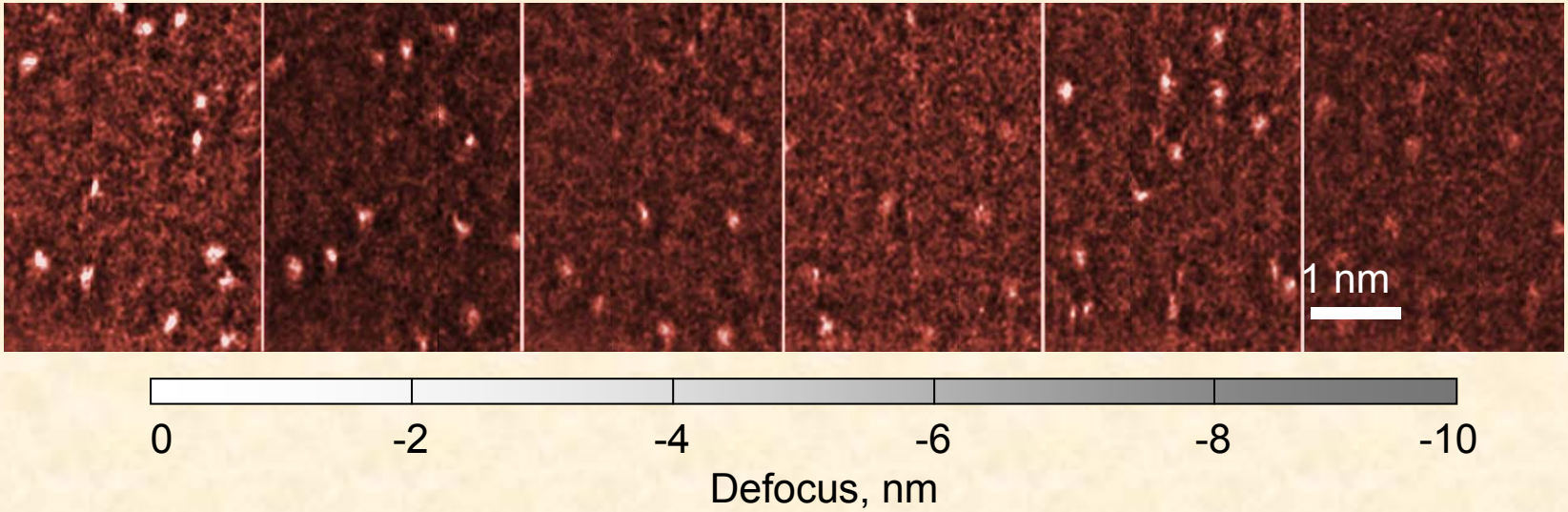
surface steps

Samples courtesy of M. Glazoff, Alcoa Technical Center

# Results: Through-Focal Series

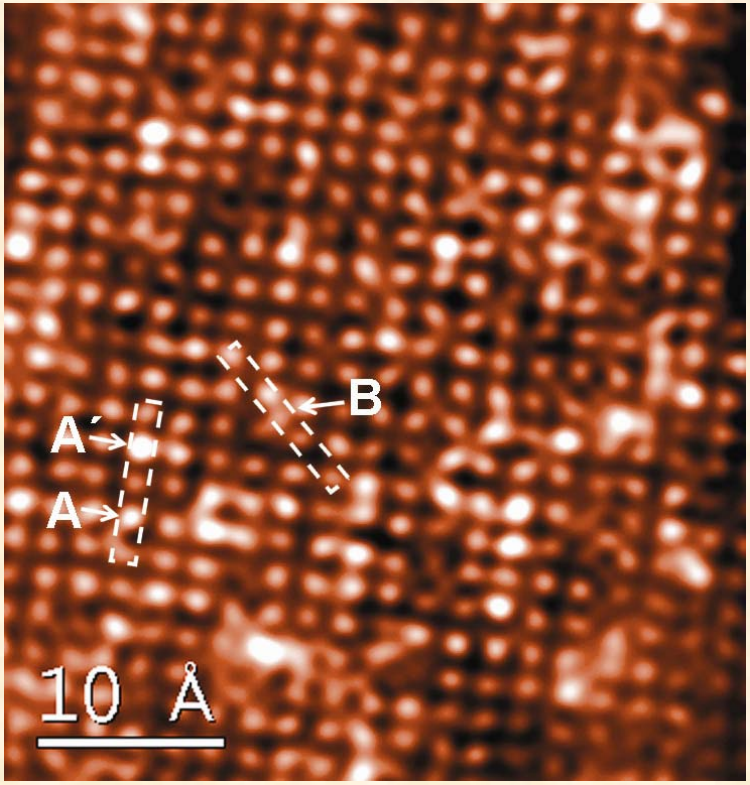


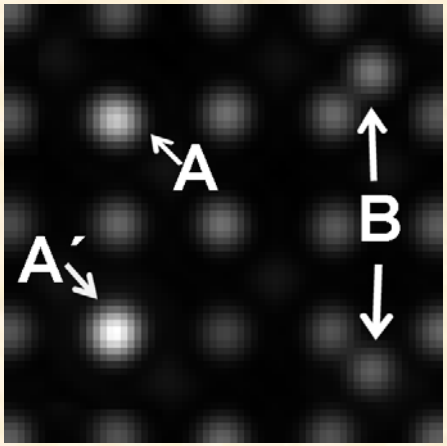



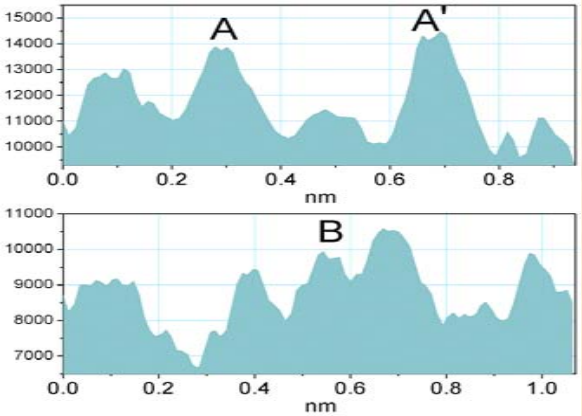




S. Wang, A. Borisevich et al., *Nature Materials*, March 2004

# La on (100) surface of γ-$Al_2O_3$

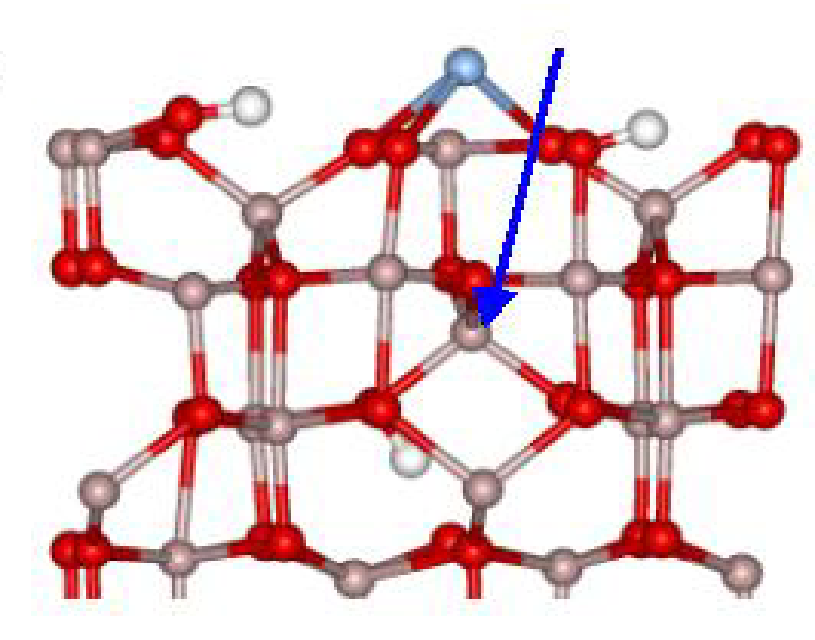



- Uncorrelated distribution
- La atoms above and below oxide flake can be distinguished
- Two distinct sites, more common one - above Al-O column

# First-Principles Calculations



- lowest-energy position - **above Al-O column**, CN=**4**
- prefers to stay on surface

***E*(La:bulk) – *E*(La:surface) = 3-5 eV**

- does not cluster

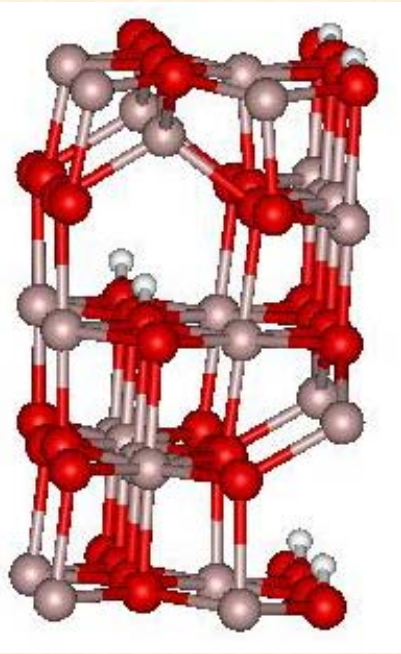
Results confirmed by independent EXAFS study:

T. Yamamoto et al., *Chem. Mater.* **15** 4830 (2003):

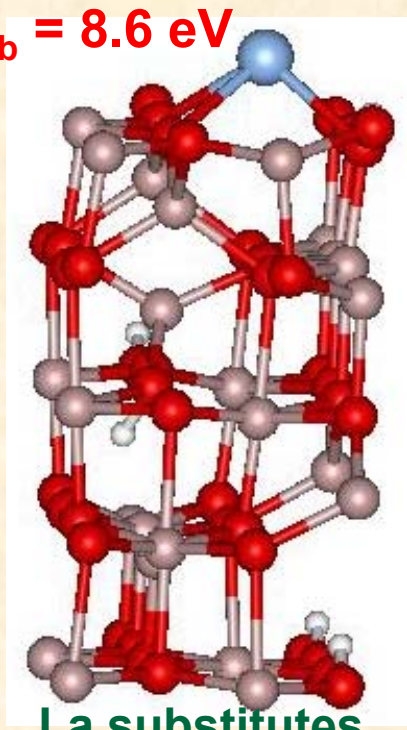
La is isolated at low concentrations; in $O_2$- and $CO_2$-free atmosphere CN **~4**

# First-Principles Calculations (cont.)

$E_b$ = 8.6 eV



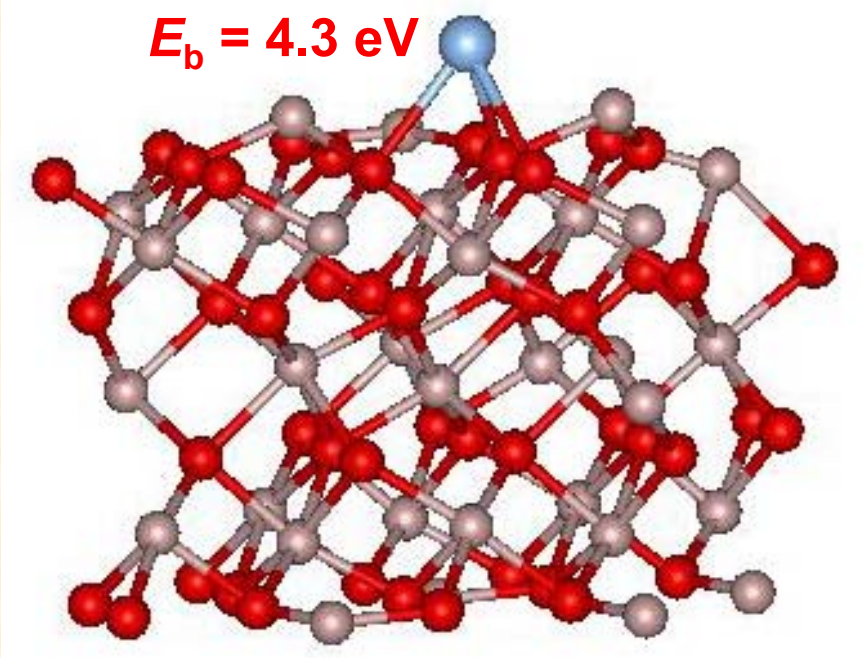
Clean relaxed



La substitutes for surface Al

$\gamma$-$Al_2O_3$(100)

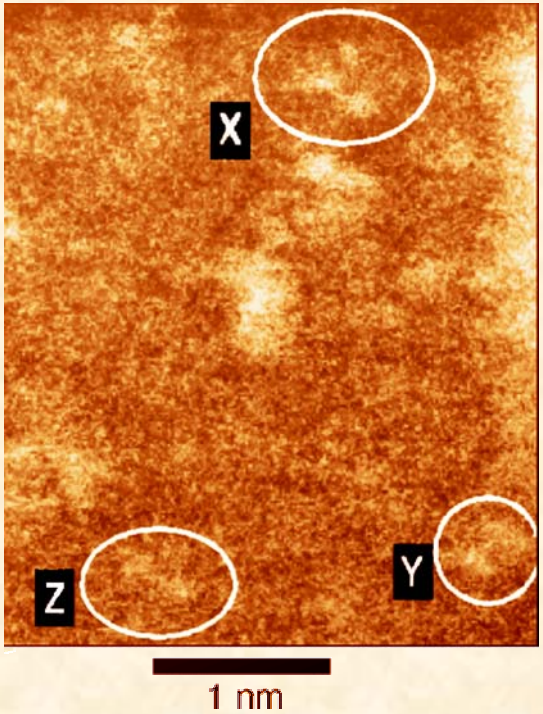
$E_b$ = 4.3 eV



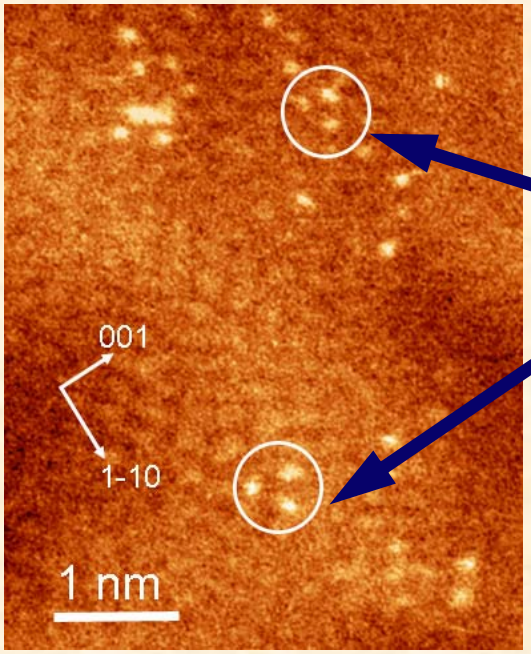
La/$\alpha$-$Al_2O_3$(0001)

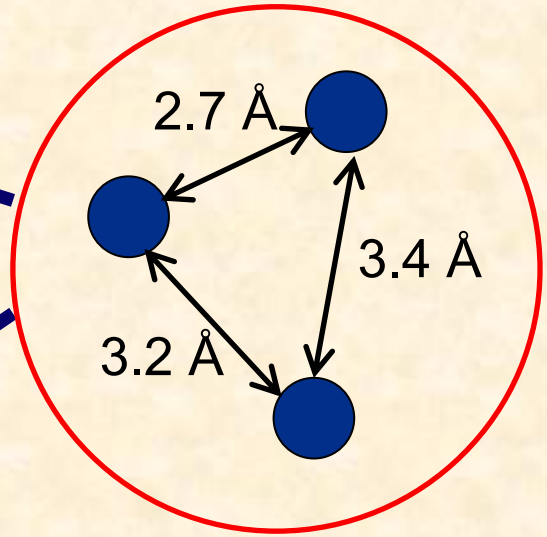
La on the $\gamma$-$Al_2O_3$ surface decreases driving force for transition

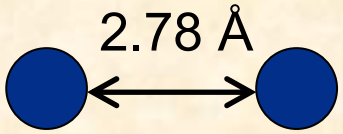
# Pt Trimers on the γ-$Al_2O_3$ (110C) Surface




P.D. Nellist, S.J. Pennycook, *Science* **274** 413 (1996)



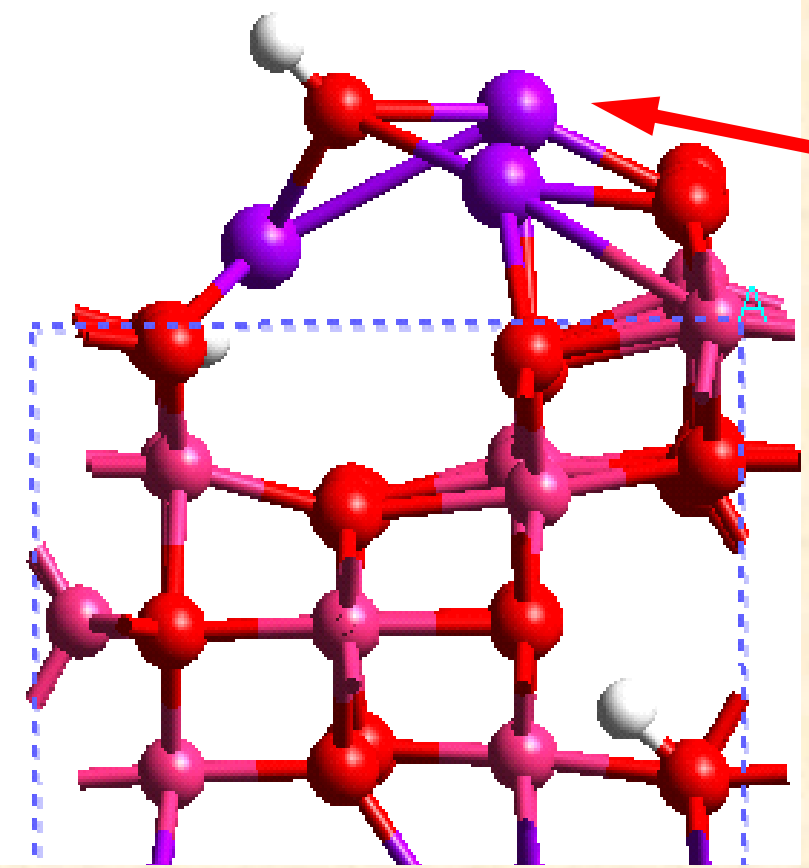



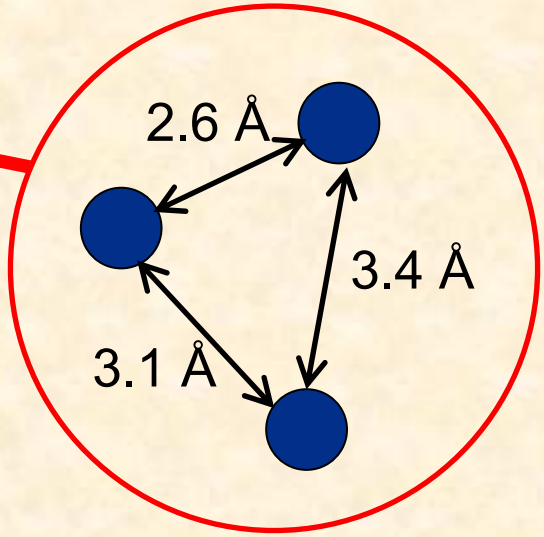

Pt metal

K. Sohlberg *et al.*, *ChemPhysChem*, accepted (2004)

Can we use STEM/theory to determine properties of the trimer?

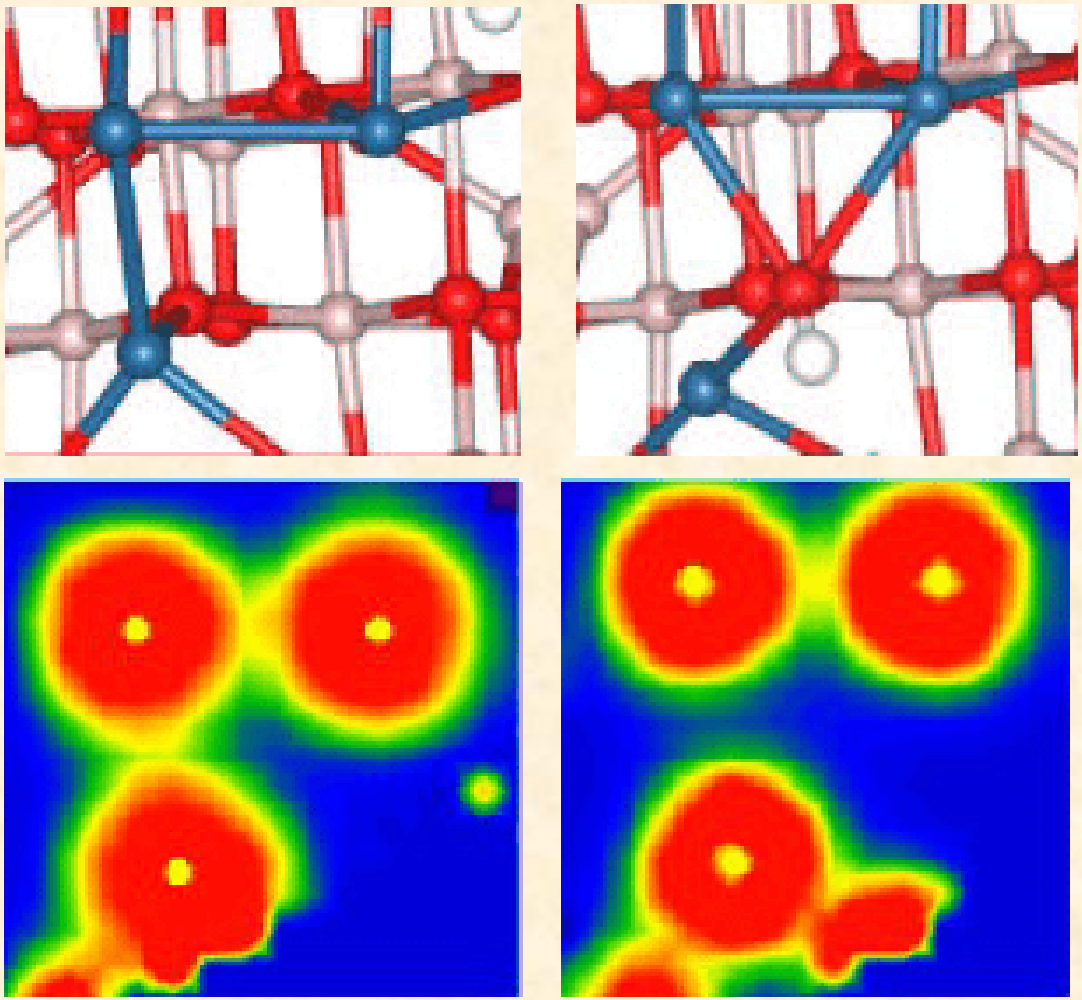
# First-Principles Calculations






Pt-Pt distances in the trimer are distorted because of OH-capping

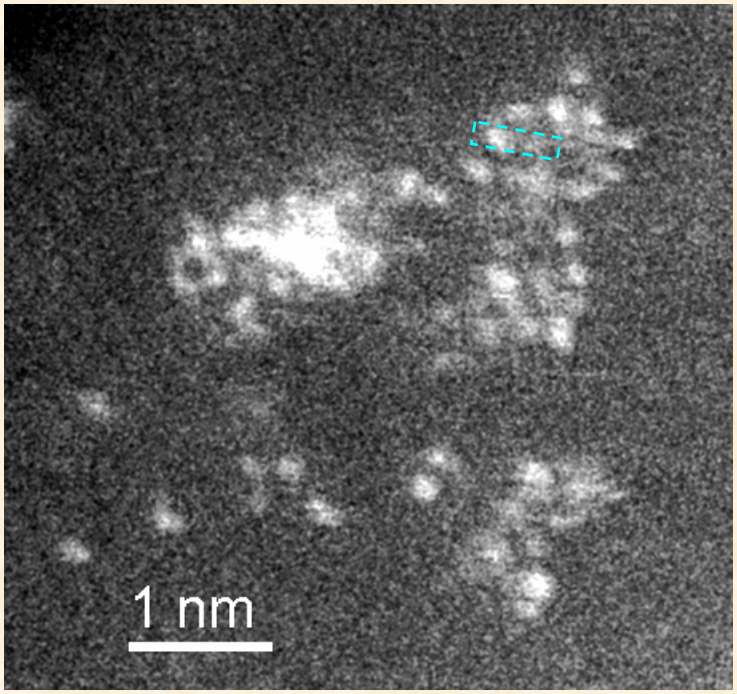
# First-Principles Calculations (cont.)

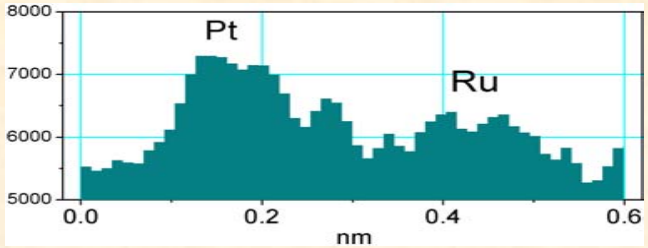


$Pt_3$ $Pt_3OH$

- $Pt_3$ trimer is metastable with respect to 3 isolated adatoms
- $Pt_3OH$ structure is more stable than 3 isolated adatoms
- OH-capping makes Pt atoms good Lewis acid sites

# Distinguishing Atoms in Bimetallic Catalysts




Z-contrast STEM can be used to distinguish different types of atoms in bimetallic catalysts

γ-$Al_2O_3$ supported Pt/Ru catalyst derived from $Pt_2Ru_4(CO)_{18}$; $Z^2(Pt)/Z^2(Ru) \approx 4:1$

Sample courtesy of R.Adams, USC

# 3D Imaging in STEM

- Aberration correction in STEM allows the use of larger probe-forming apertures
- The resulting probes are smaller, brighter, and have high convergence angles
- Focal depth decreases as aperture angle increases, enabling 3D sensitivity:

$$\Delta z \approx \frac{\lambda}{\vartheta^2}$$

"Ultra STEM" 200kV with 3rd generation corrector :

$c_s$ = 1.3 mm, $c_c$ = 1.3 mm, aperture – 50 mrad

$\Delta z \approx 1.2$ nm

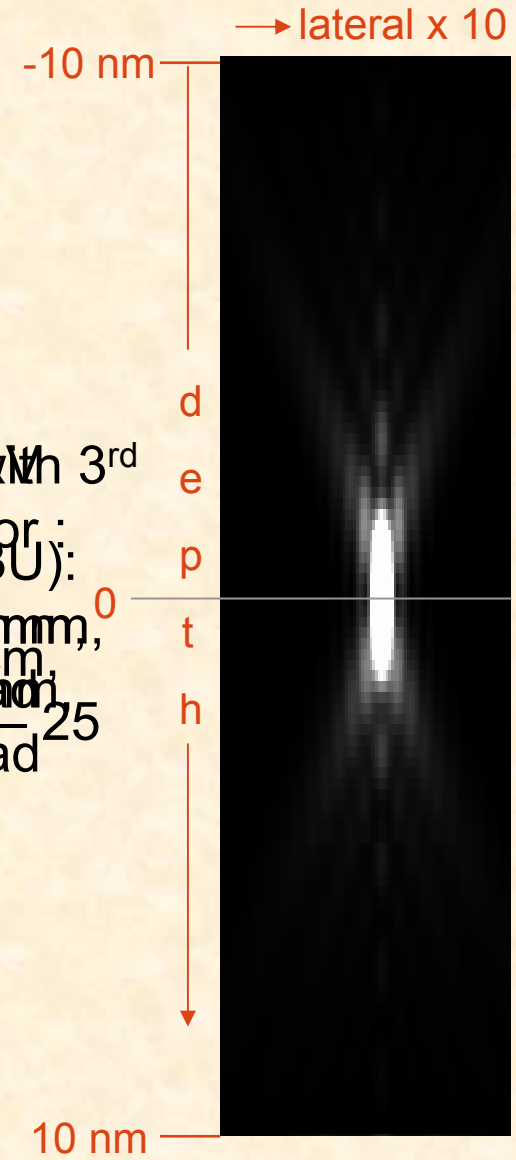
Corrected 300kV microscope:

$c_s$ = -40μm, $c_c$=10 cm, aperture – 10 mrad

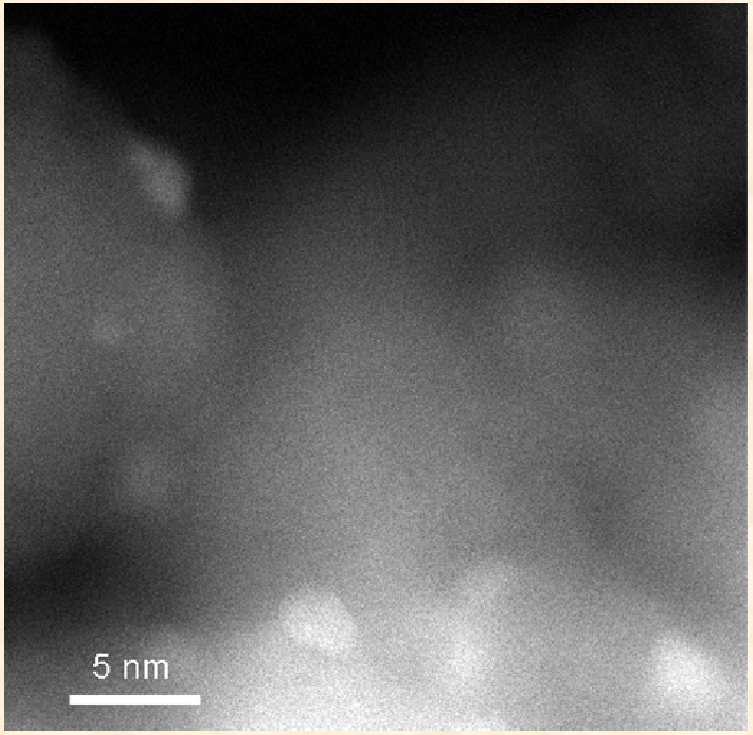
$\Delta z \approx 45$ nm

Uncorrected 200kV microscope:

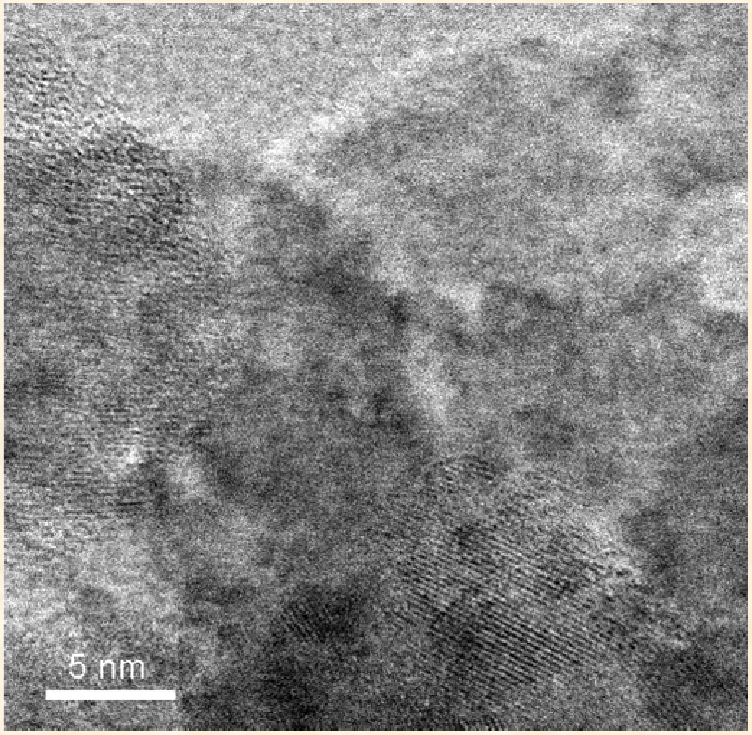
$c_s$ = 1.3 mm, $c_c$ = 1.3 mm, aperture – 25 mrad



# 3D Structure of Catalysts from STEM Focal Series



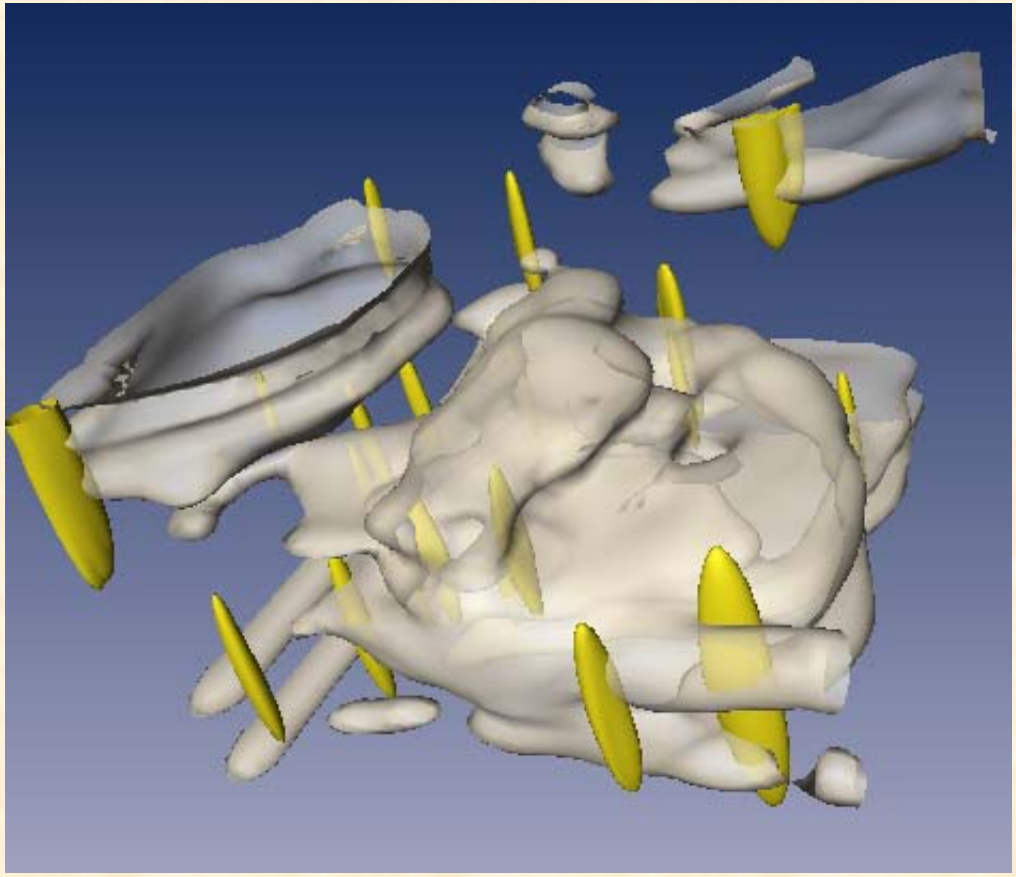

HAADF: sensitive to metal particles




BF: sensitive to substrate structure

Samples ($Pt_2Au_4/TiO_2$) courtesy of M. Amiridis, USC

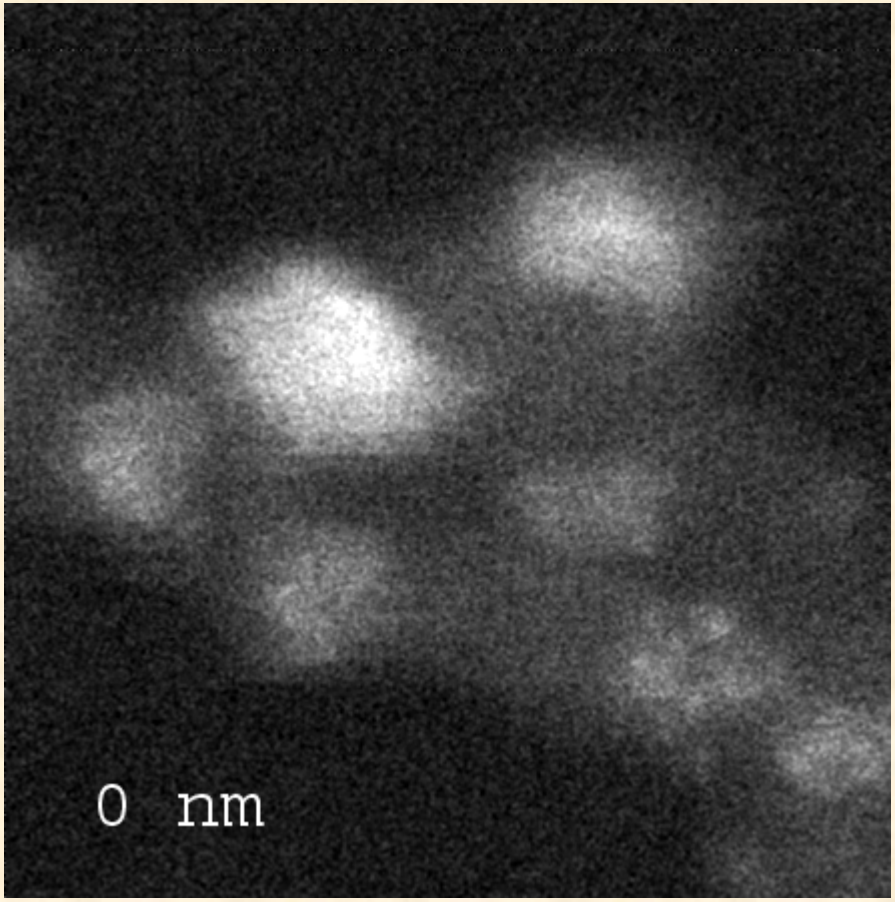
# 3D Reconstruction



Reconstruction by A. Lupini

- Both metal and substrate shapes can be characterized using the focal series
- Metal particles appear elongated because of defocus spread
- Development of new deconvolution algorithms is needed for building real 3D models of the data

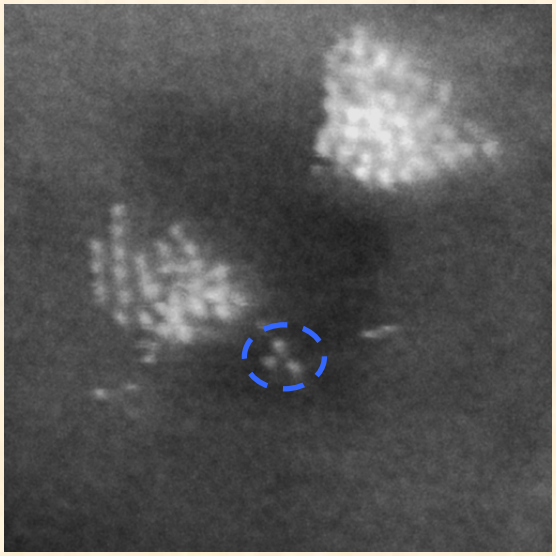
# Atomic Resolution in 3D

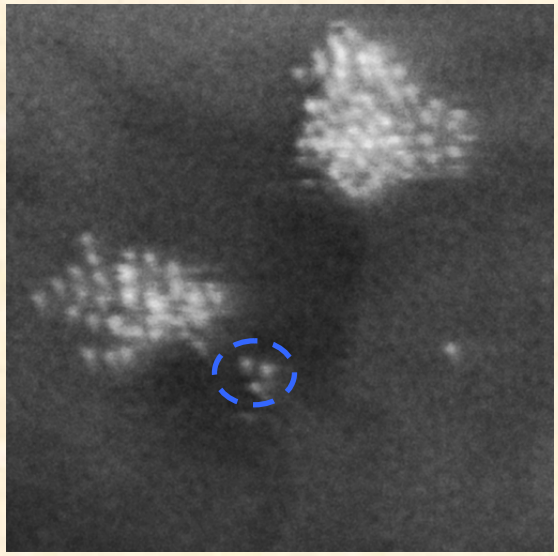


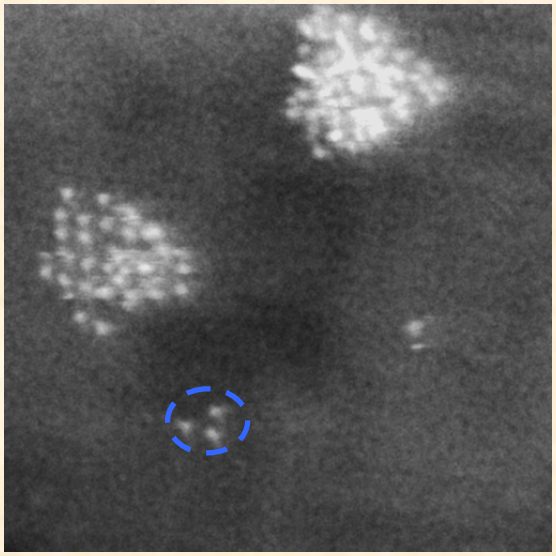

- STEM focal series can be used for collecting 3D datasets with resolution down to atomic
- TEM tomography using tilt series relies on projection approximation, which is less valid for high resolution because of decreasing focal depth

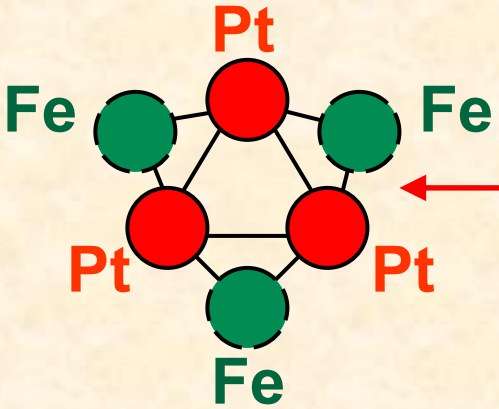
$Pt_2Ru_4$ on $\gamma$-$Al_2O_3$; sample courtesy of R.Adams, USC

# Towards the 4th Dimension: Prospects for *In Situ* Imaging



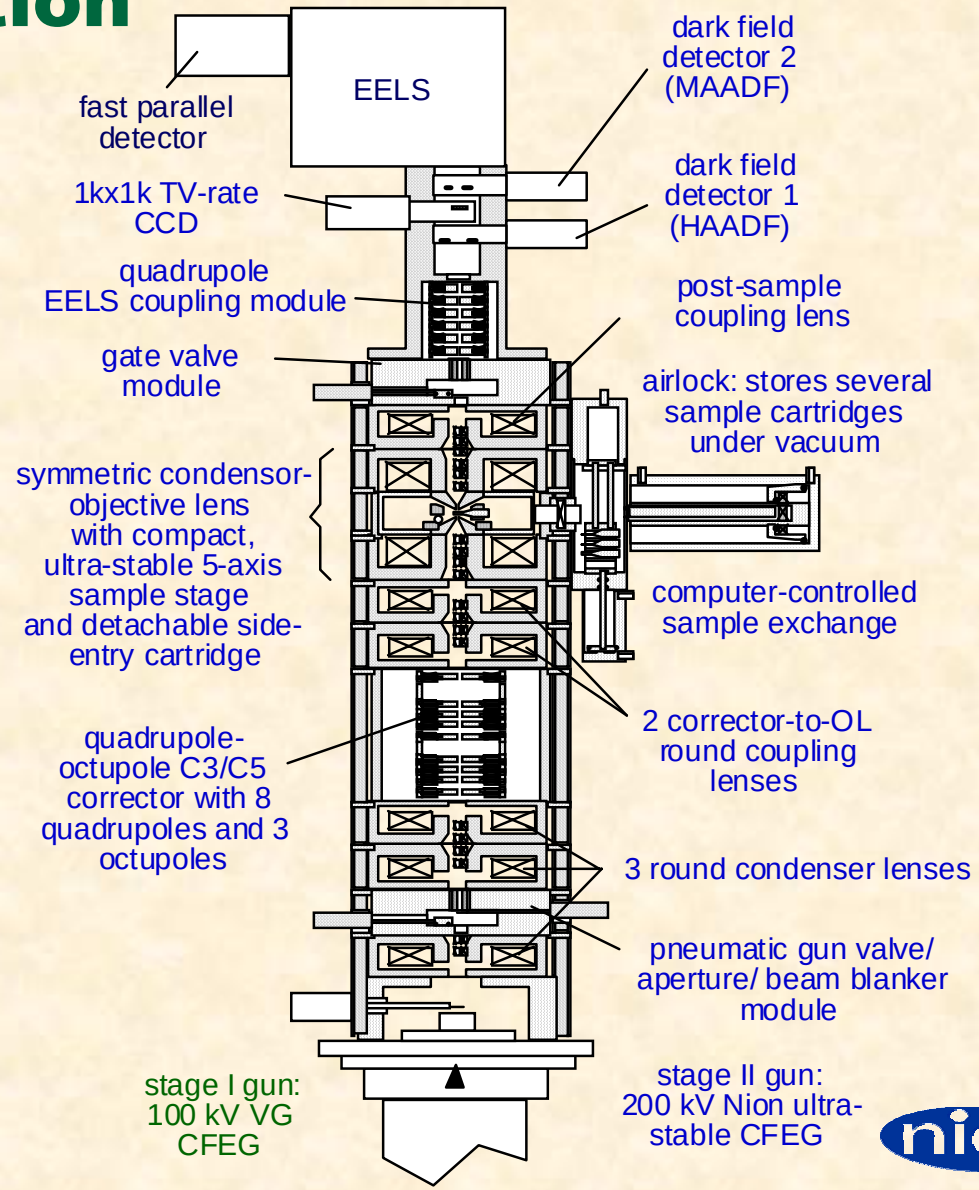







Metal core of the $Pt_3Fe_3(CO)_{15}$ cluster

Sample courtesy of R. Adams, USC

# Future: 3rd generation STEM

- **0.5 Å resolution**
  - ***light atom sensitivity***
  - ***atomic dynamics***
- **Aberration corrected EELS**
  - ***single atom senstivity***
  - ***local electronic structure***
- **Monochromated gun**
  - ***0.1 eV resolution***
  - ***test of theories***
- **In-situ imaging of catalysts**
  - ***pressures ~ mtorr***
  - ***temperatures <800°C***
- **3D Imaging through depth sectioning**