Emerging In-Situ Experimental Capabilities

in Surface Science at the CFN

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Center for Functional Nanomaterials

Brookhaven National Laboratory

Theory and Computation Workshop, 4th of November 2014. CFN/BNL.

Center for Functional Nanomaterials
Brookhaven National Laboratory

Definition of concepts

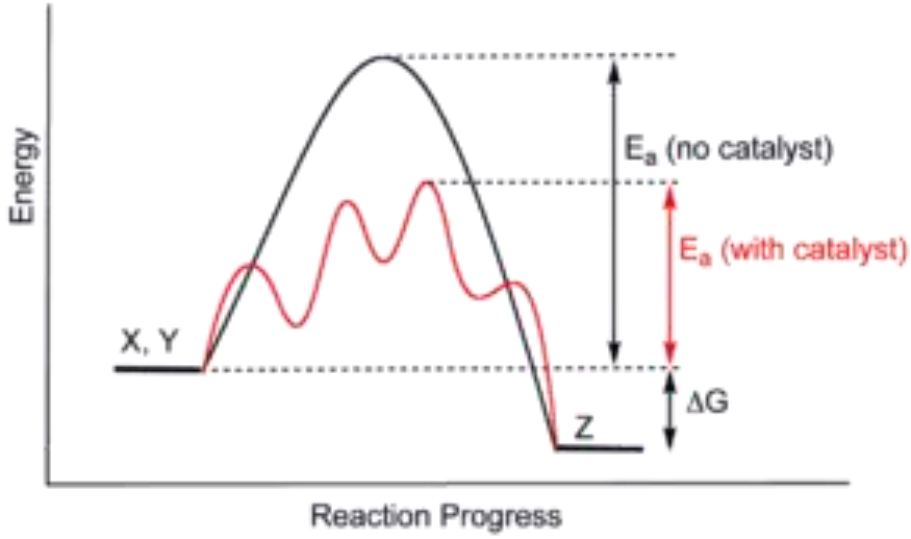
Catalysis

Model System

Catalysis

Acceleration of a chemical reaction by a **Catalyst**.

- A substance that changes the reaction mechanism resulting in a lower activation energy.



Model System

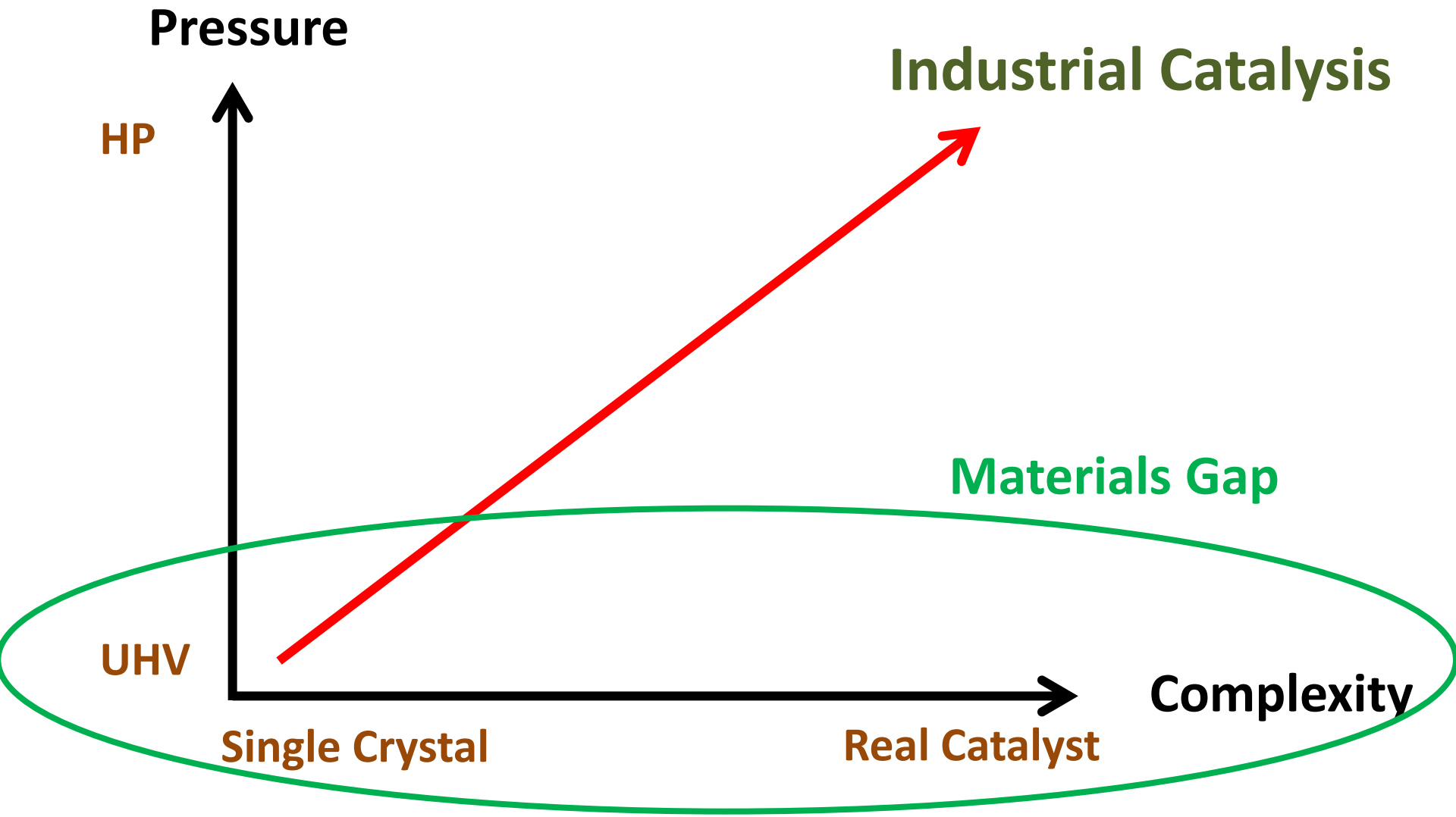
Simplified version of a commercial catalyst

- allows to disentangle different factors that can potentially affect the chemical reaction.
- used for surface science mechanistic studies

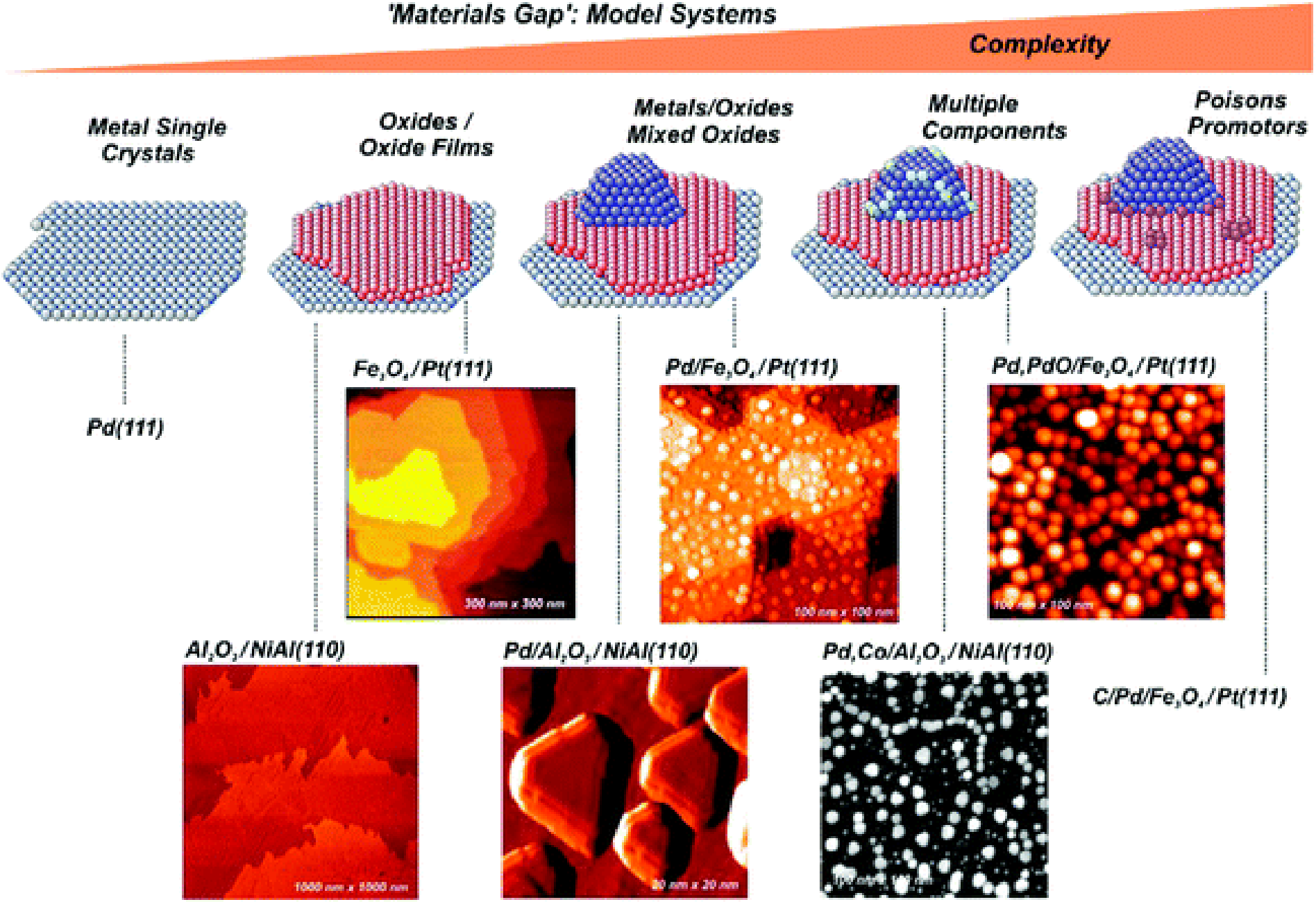
There is a vast set of surface science tools to study model systems:

- Scanning Tunneling Microscopy
- X-ray Photoelectron Spectroscopy
- Etc.

Quo Vadis Surface Science?

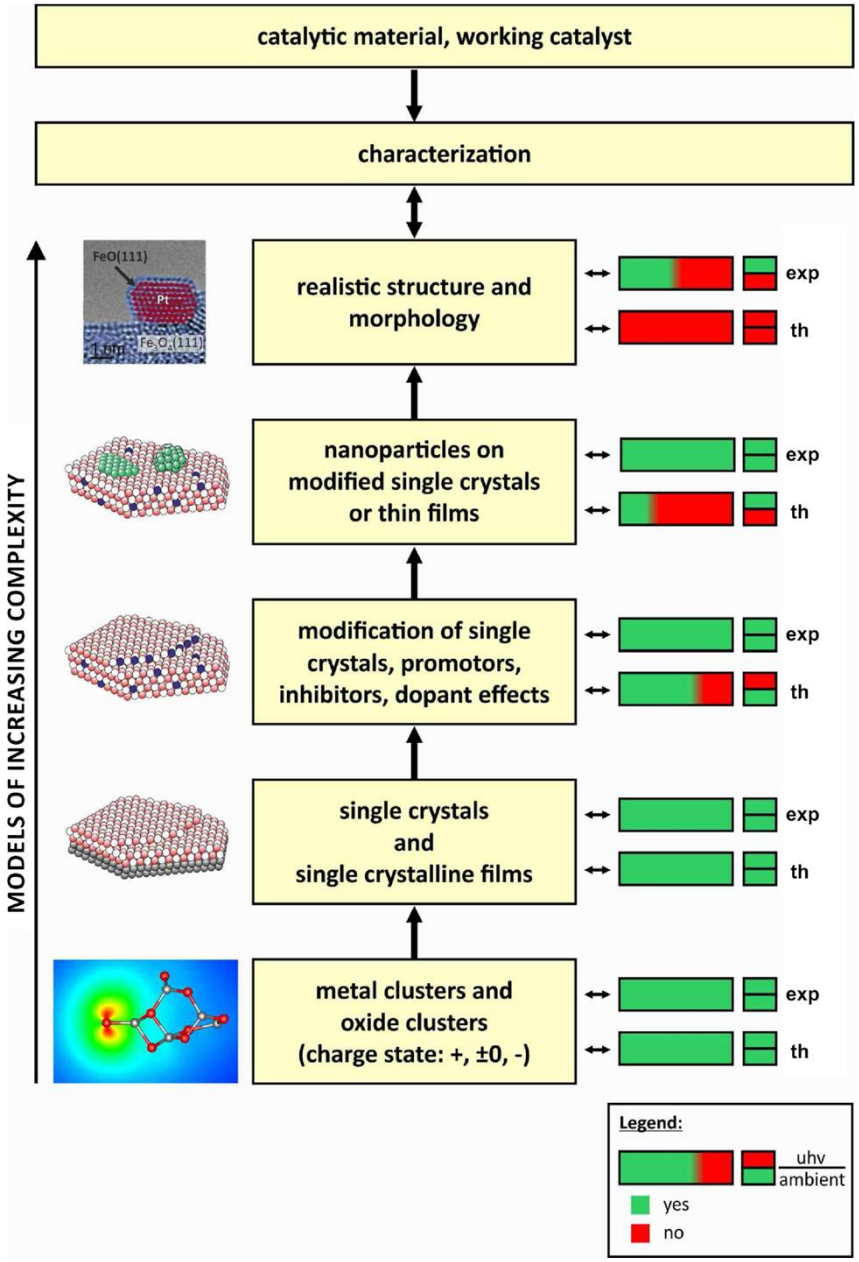


H.-J. Freund et al.:Models in Heterogeneous Catalysis: Surface Science Quo Vadis? Phys. Stat. Sol. (a) 187, No. 1, 257–274 **(2001)**



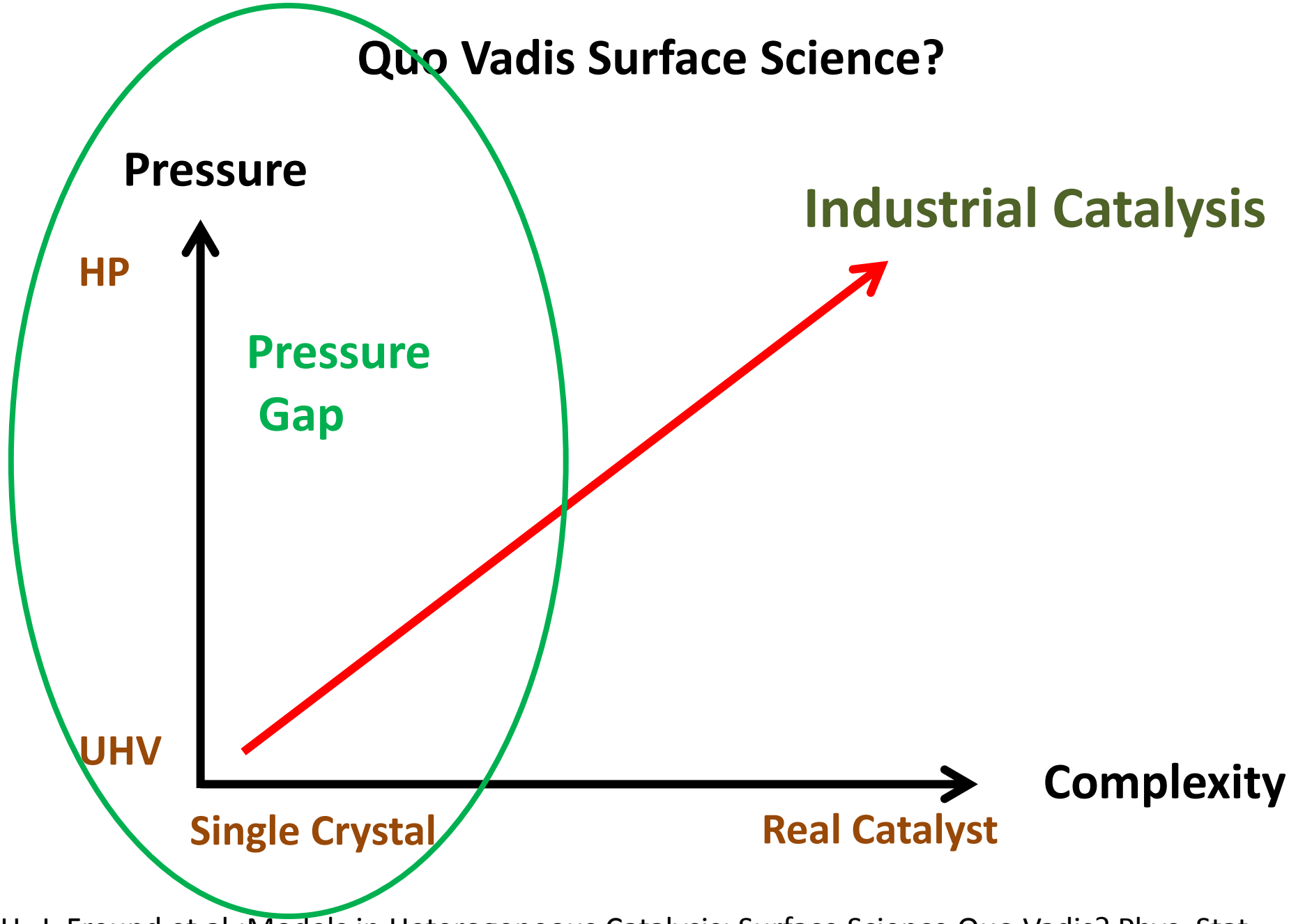
Bäumer et al. *Phys. Chem. Chem. Phys.* **2007,** 9, 3541-58

Experiment and Theory



Joachim Sauer, Hajo Freund. Models in Catalysis. *Catal. Lett.* DOI 10.1007/s10562-014-1387-1

Quo Vadis Surface Science?



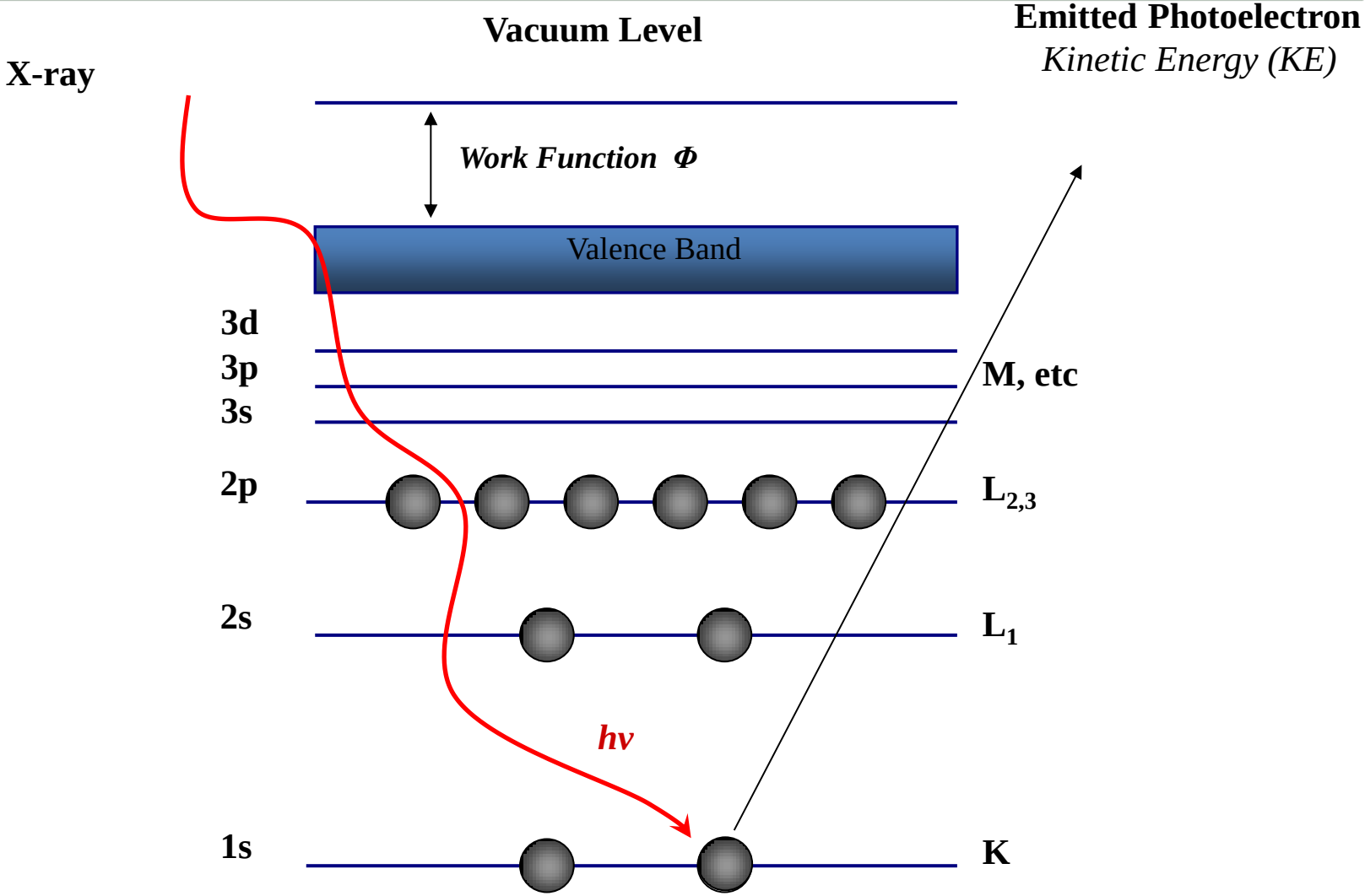
H.-J. Freund et al.:Models in Heterogeneous Catalysis: Surface Science Quo Vadis? Phys. Stat. Sol. (a) 187, No. 1, 257–274 **(2001)**

Quo Vadis CFN/BNL?

Catalytically Relevant Pressures

- Ambient Pressure Photoelectron Spectroscopy (AP-PES)
- Reactor Scanning Tunneling Microscopy (r-STM)
- Polarization Modulation Infrared Reflection Absorption Spectroscopy (PM-IRAS)
- Environmental Transmission Electron Microscopy (E-TEM) – Eric Stach (11/6)

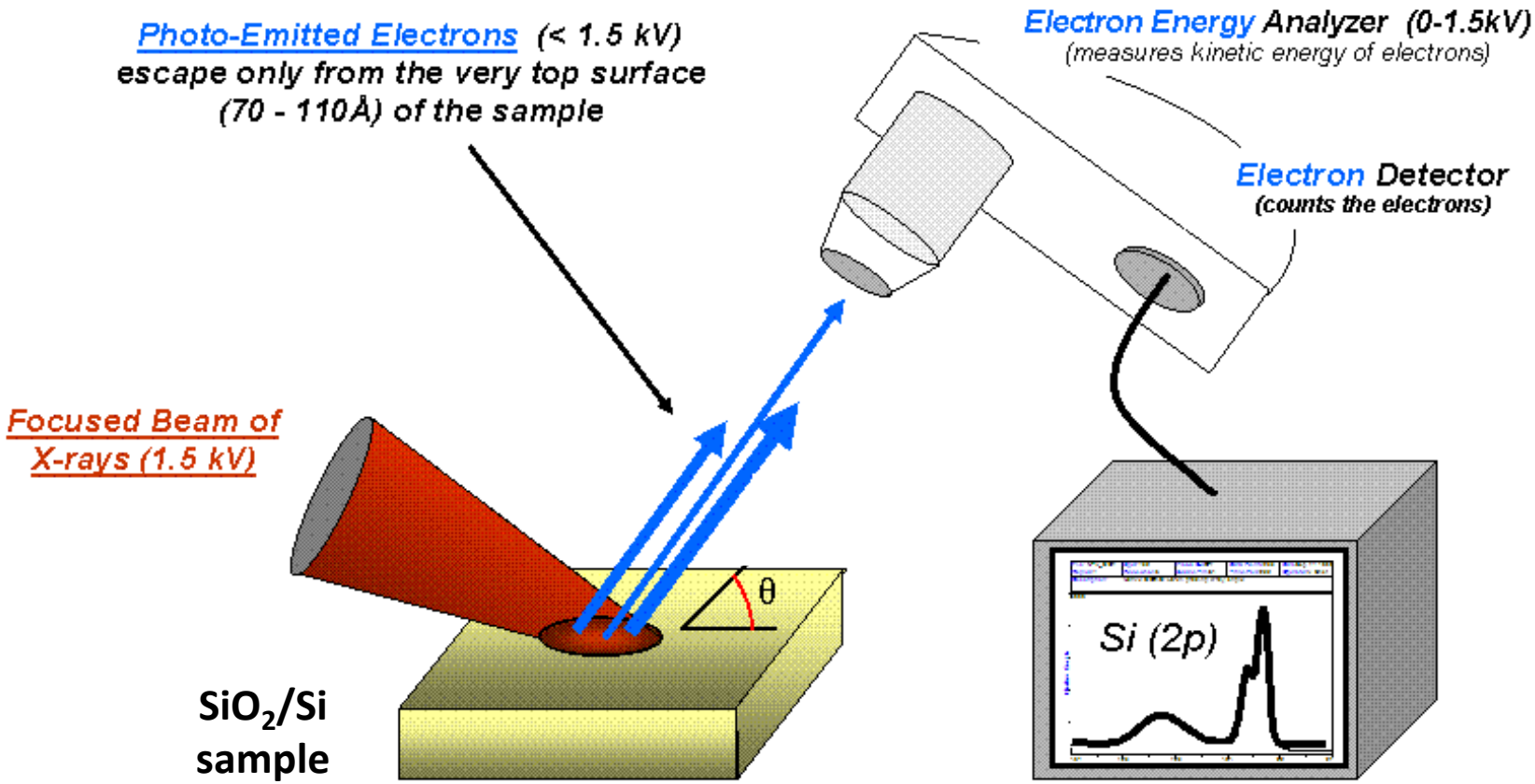
X-ray Photoelectron Spectroscopy (XPS)



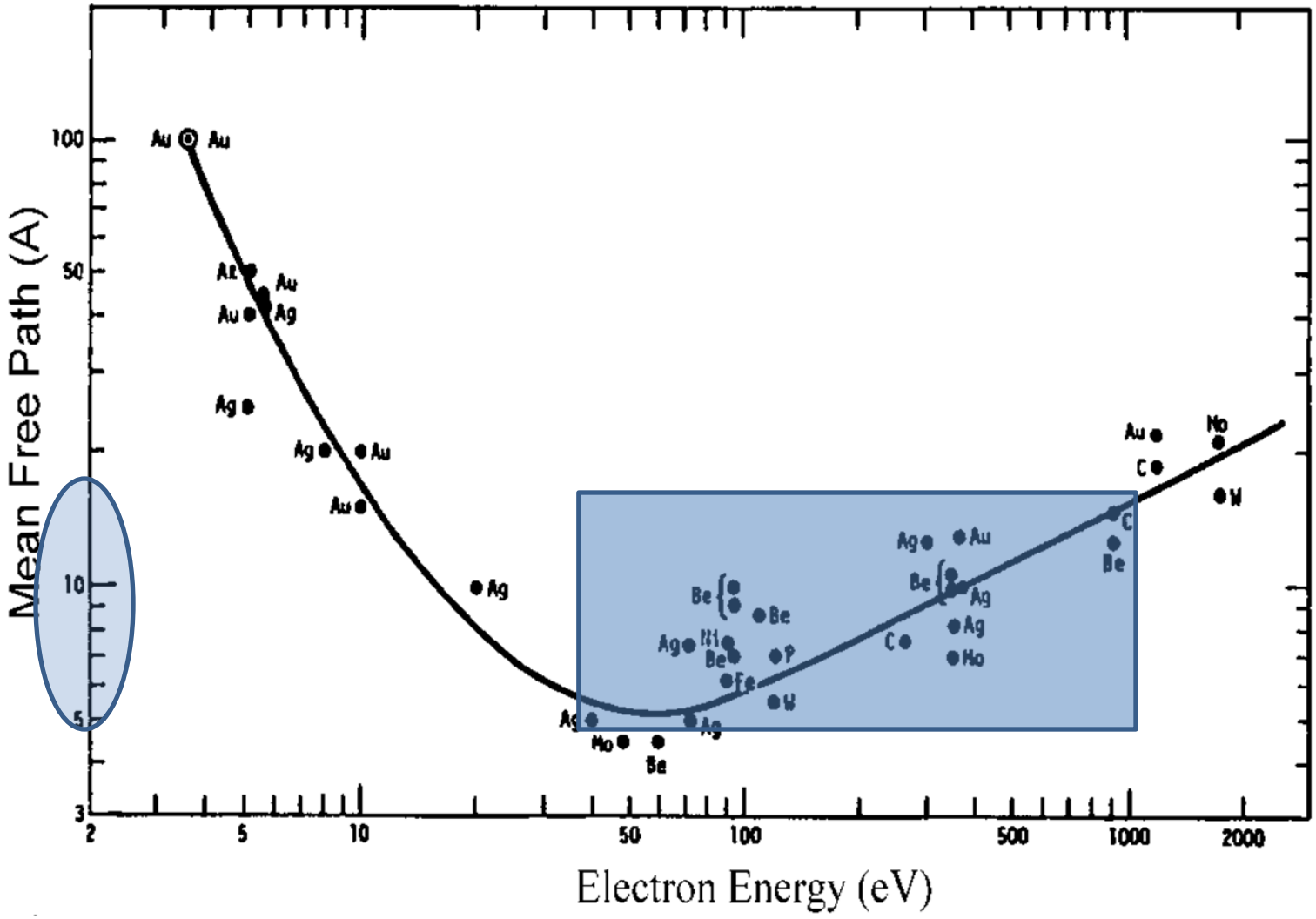
Courtesy of O. Furlong (UNSL)

XPS system

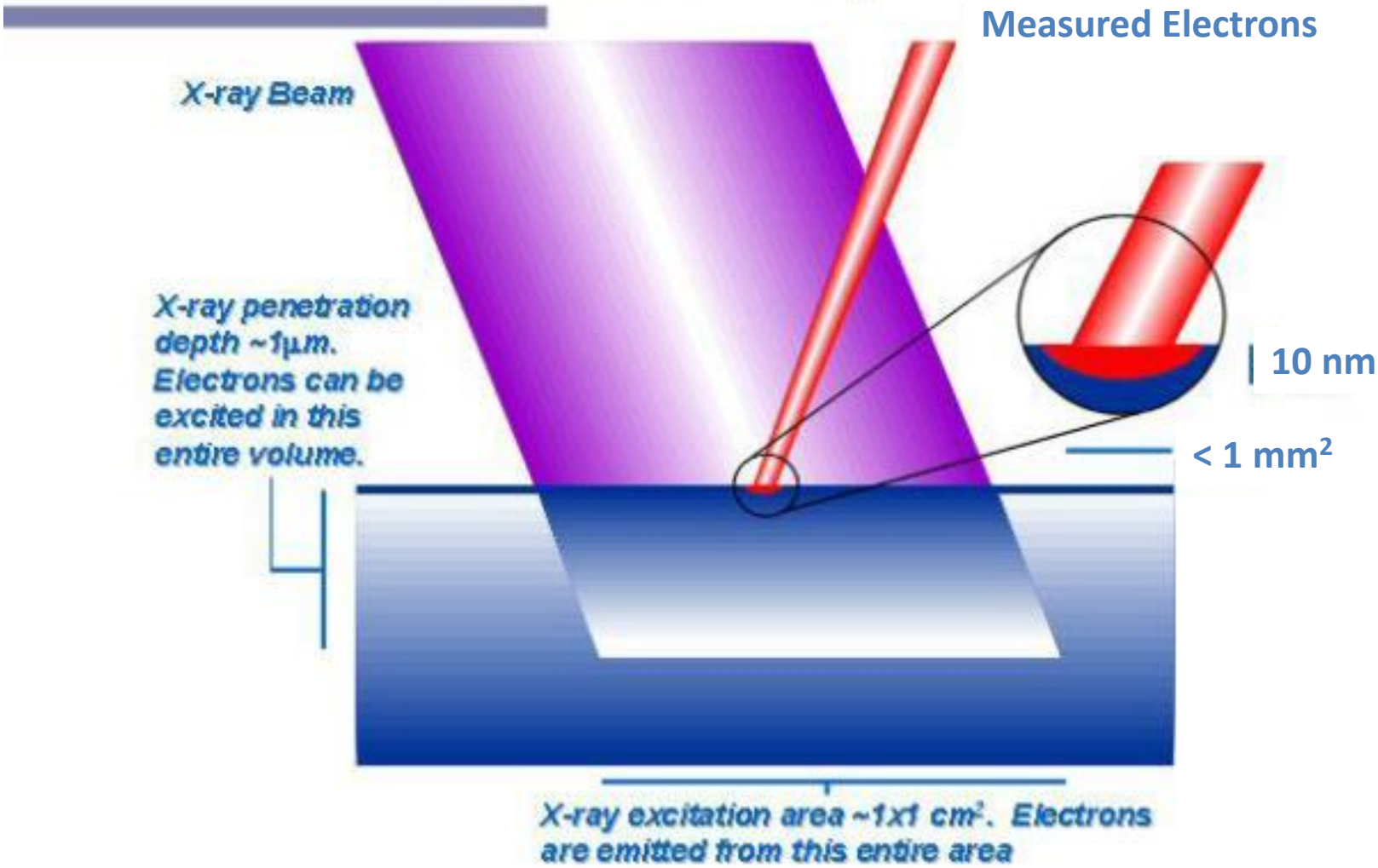
Ultra-high vacuum



Universal Curve



X-ray Photoelectron Spectroscopy (XPS)



X-ray photoelectron spectroscopy (XPS)

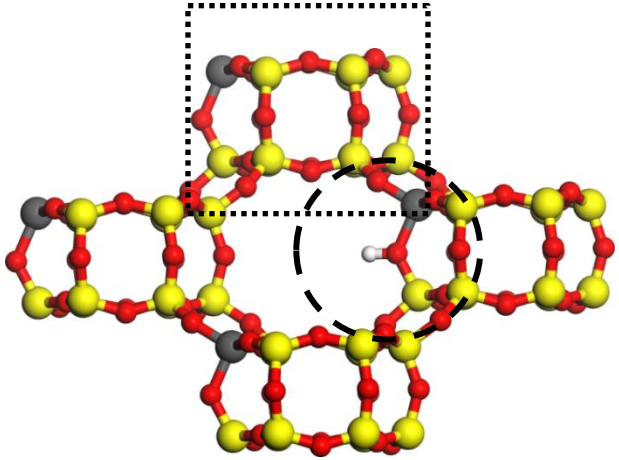
- Surface sensitive
- Chemical state of the elements at the surface
- Traditionally carried out in UHV
- Many relevant systems require higher pressures.
  - **Catalysis**
  - Environmental and Atmospheric Chemistry

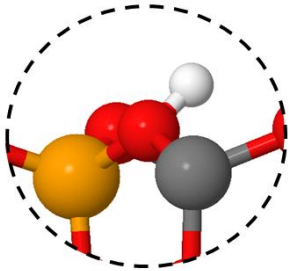
Zeolite

Three dimensional porous crystalline aluminosilicate.

- Pores and channels of the size of small molecules
- More than 200 different frameworks
- Catalytically active

Zeolite Chabasite





ν_{OH}= 3594 cm^{-1}

ν_{OD}= 2654 cm^{-1}

Si Al O H

Catalytic
Cracking of Crude Oil

Luján de Cuyo Refinery (Argentina)

http://www.repsol.com

Breaks down heavy fractions of crude oil

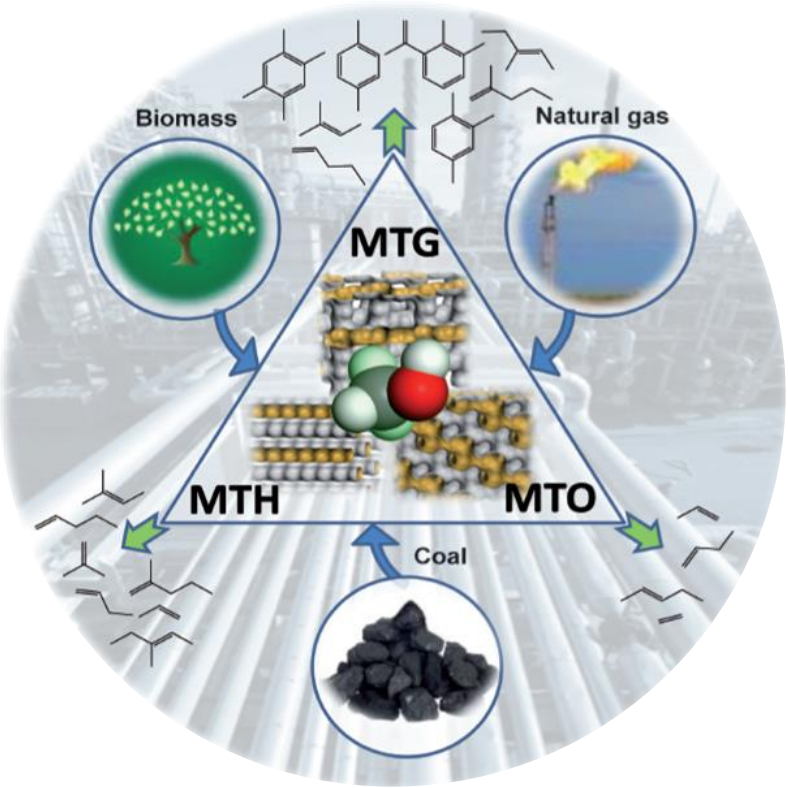
Every drop of gasoline that we consume has gone through a zeolite

Methanol to Gasoline

Motunui synthetic petrol plant (New Zealand)

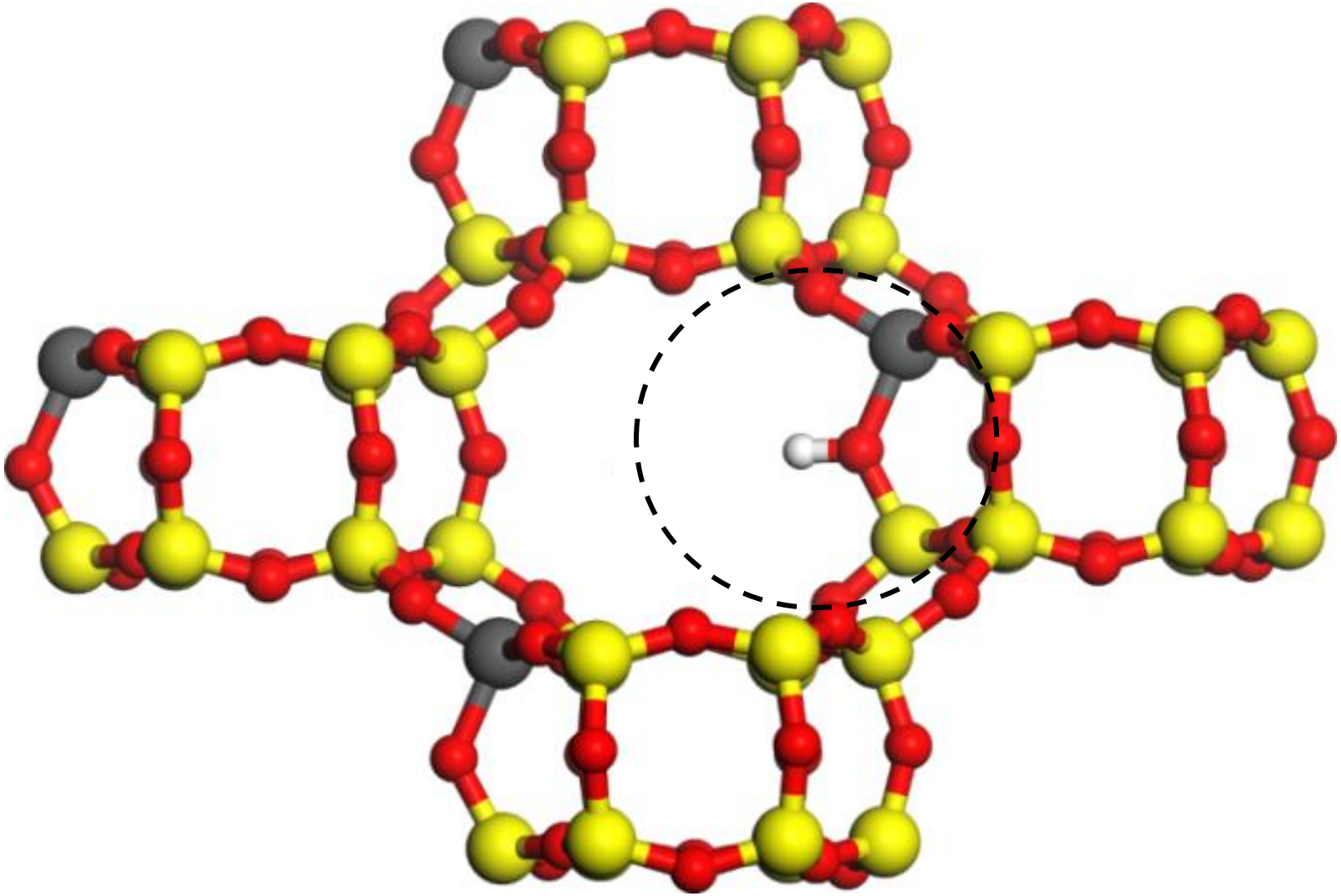
http://www.teara.govt.nz

CH_3OH → Hydrocarbons

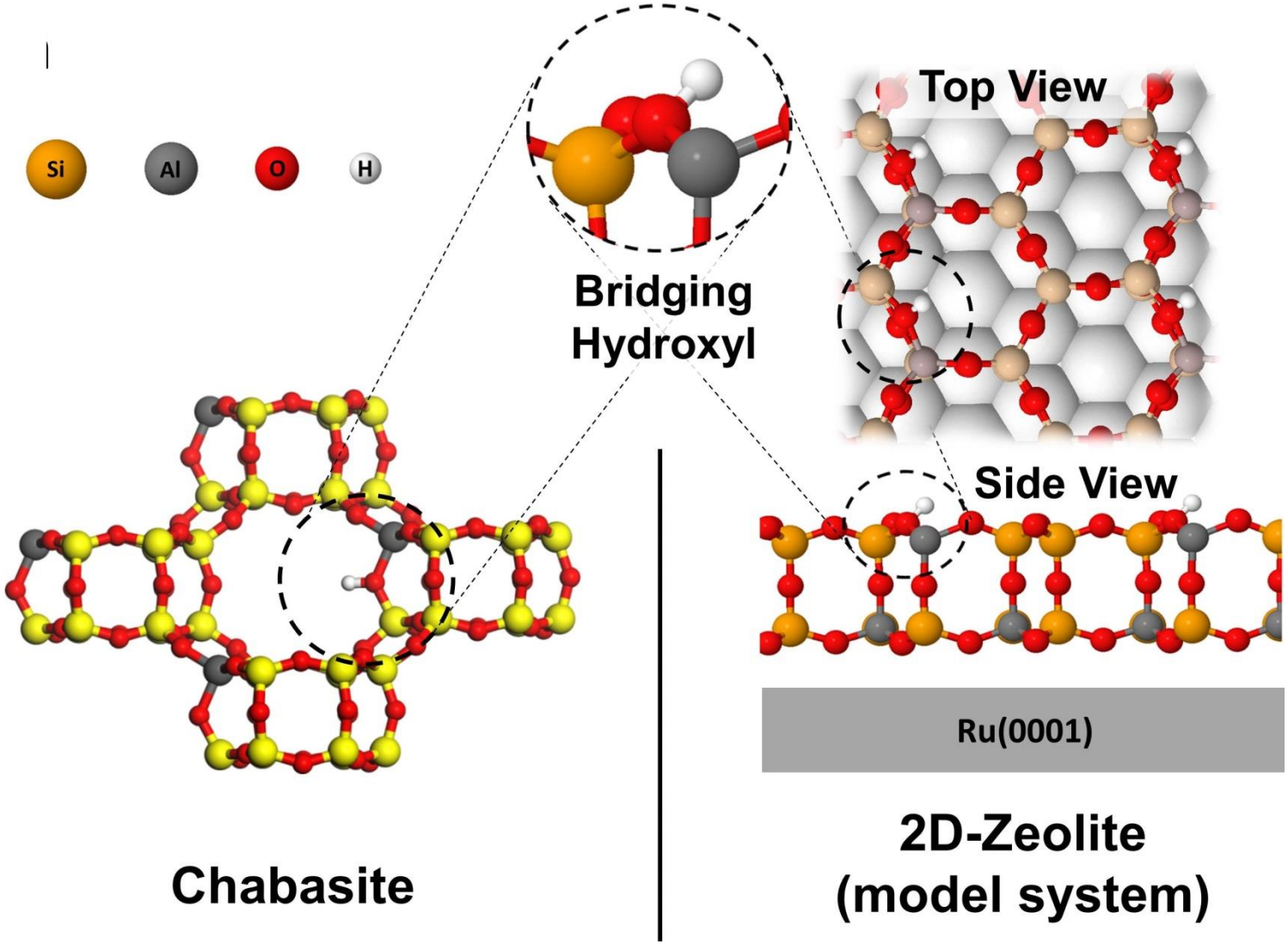


Olsbye et al. Angew. Chem. Int. Ed. 2012, 51, 5810 – 5831

The Problem

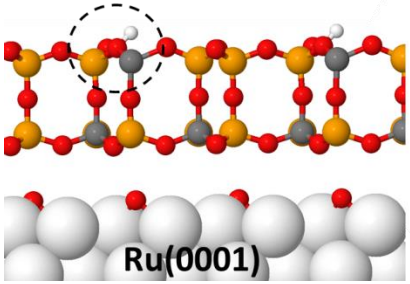


A model System for Zeolites



J.A. Boscoboinik, S.K. Shaikhutdinov. *Catal. Lett.* **2014** DOI: 10.1007/s10562-014-1369-3.

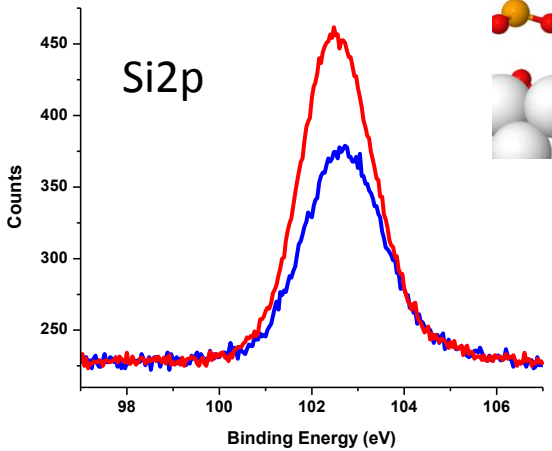
The model System: Composition

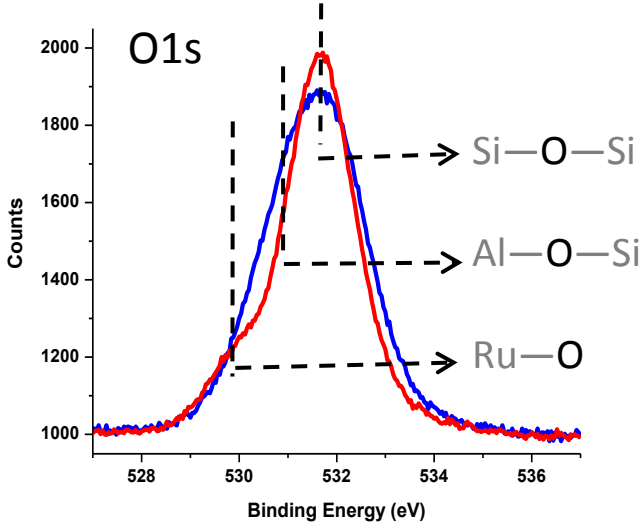


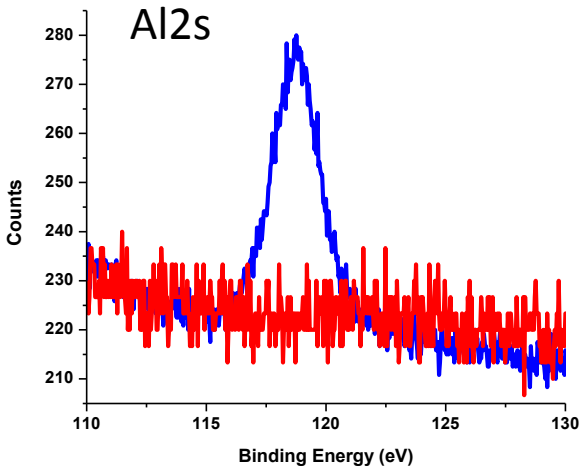
X-ray photoelectron spectroscopy (XPS)

SiO_2

$Al_{0.34}Si_{0.66}O_2$

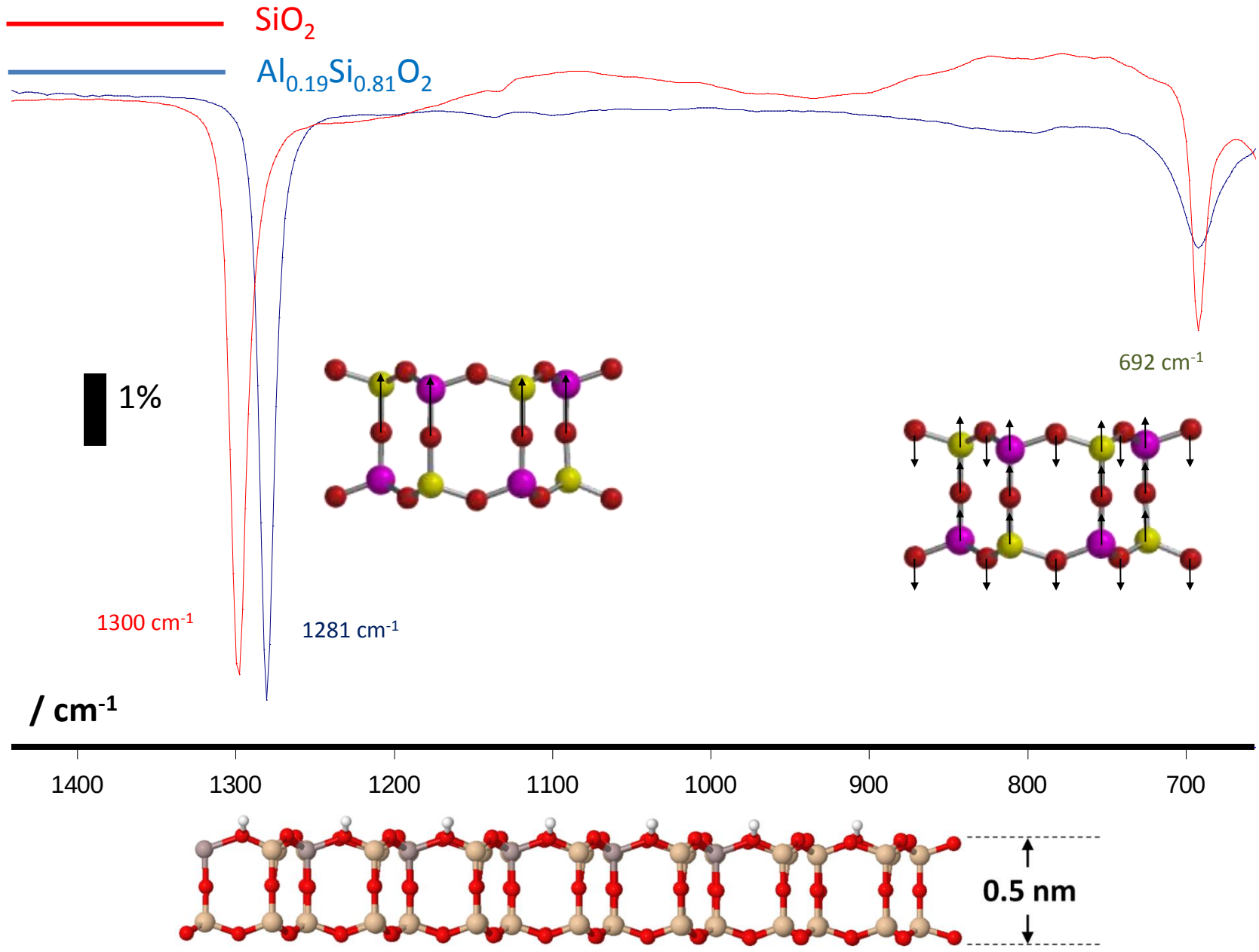




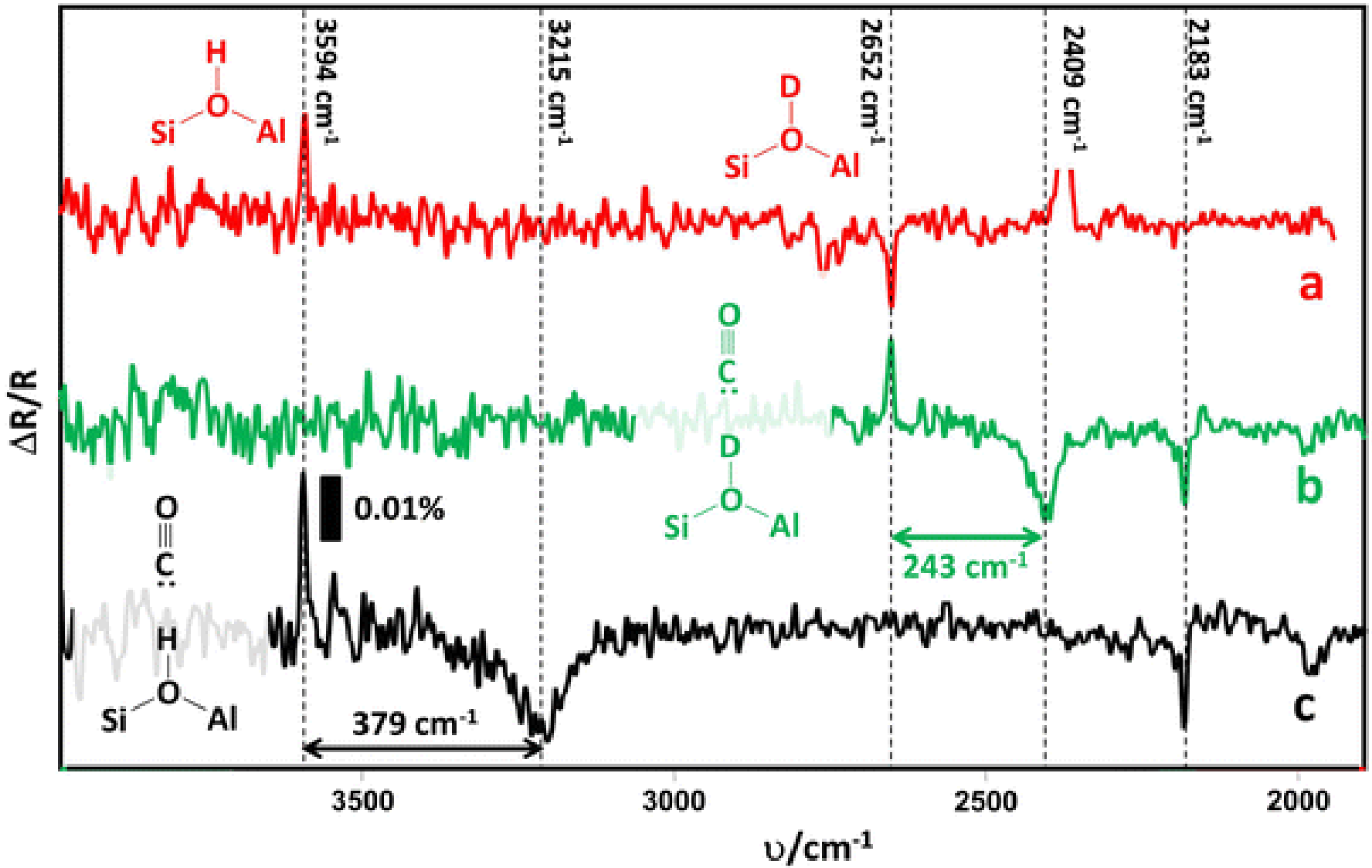


Boscoboinik et al. *Angew. Chem. Int. Ed.* **2012**, 51, 6005.

Infrared reflection-absorption spectroscopy



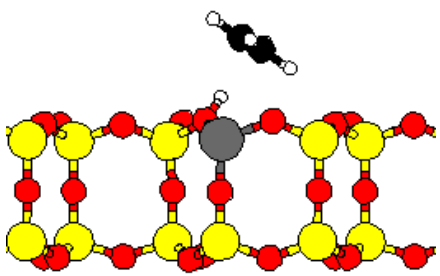
Probing the active site

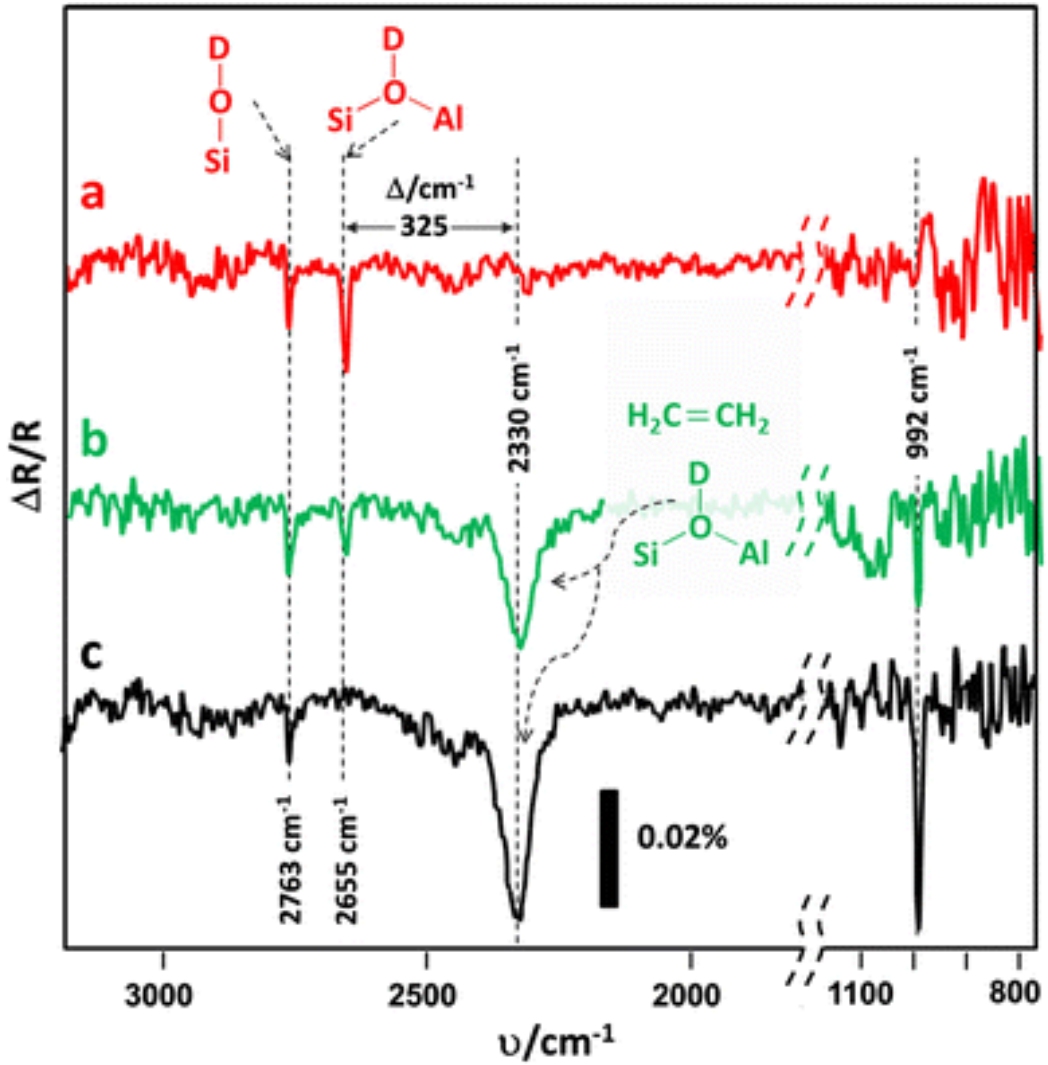


Boscoboinik et al. *J. Phys. Chem. C* **2013**, 117, 13547–13556.

Probing the active site

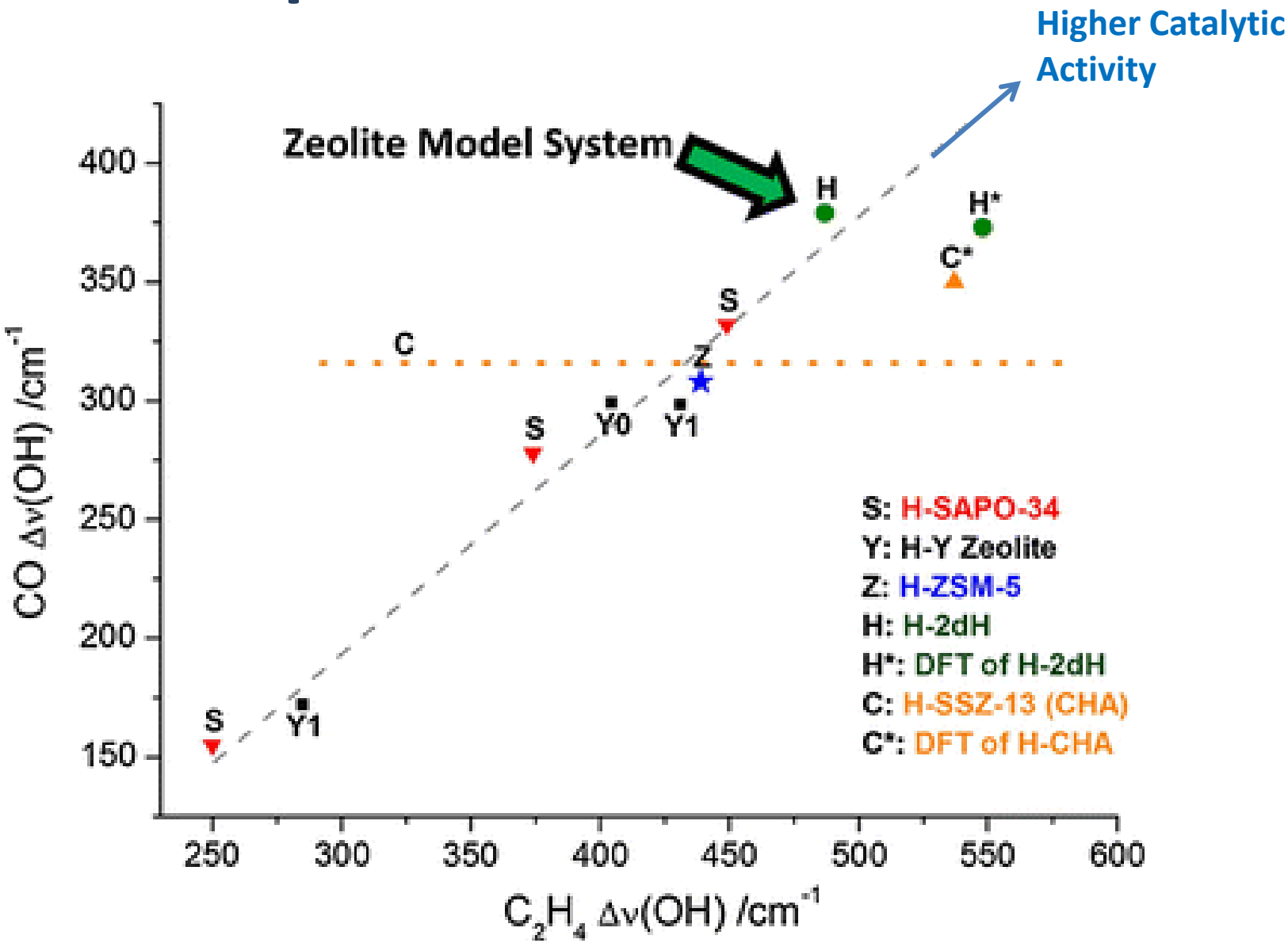
C_2H_4 Adsorption





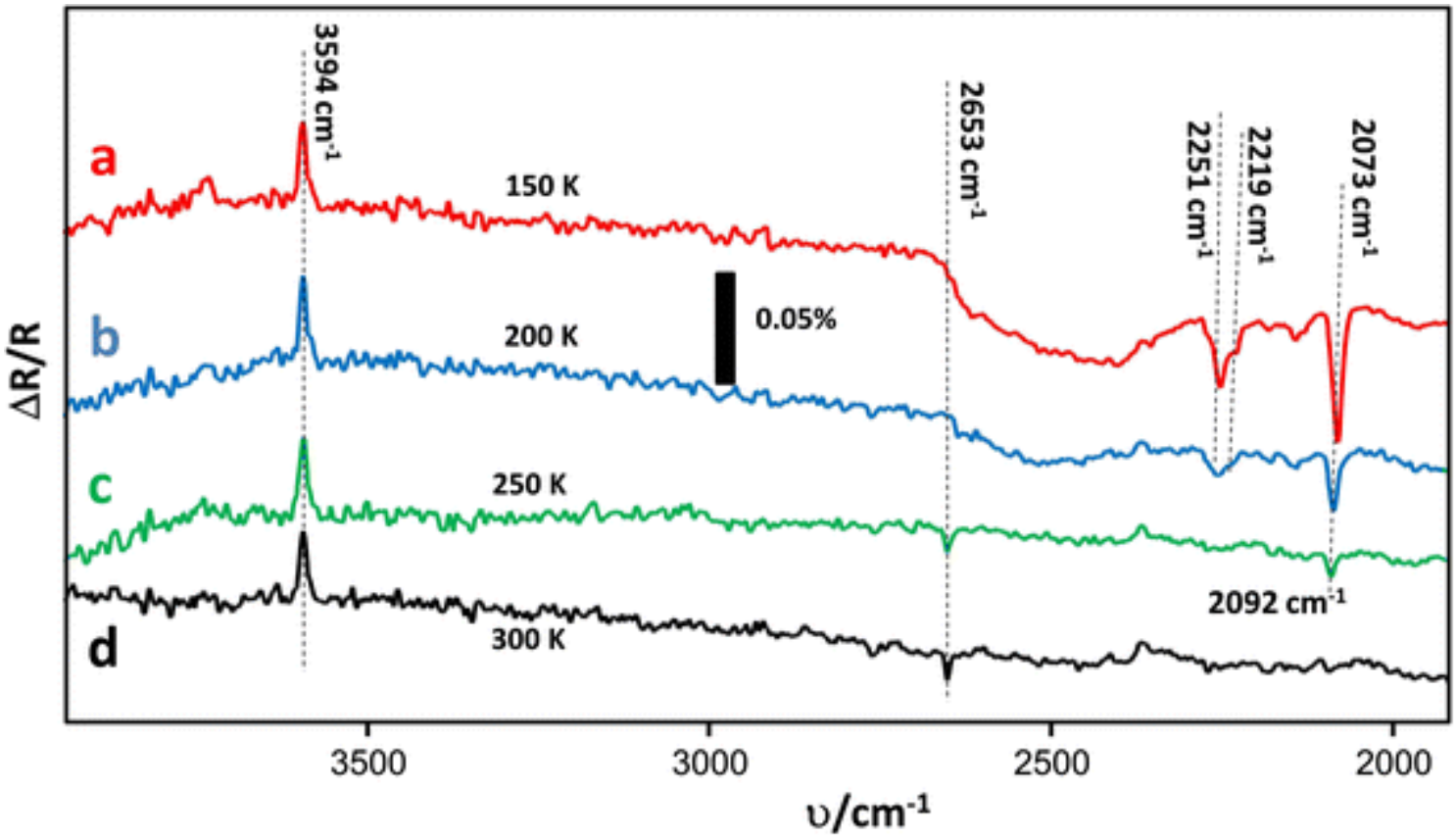
Boscoboinik et al. *J. Phys. Chem. C* **2013**, 117, 13547–13556.

Comparison with 3D Zeolites



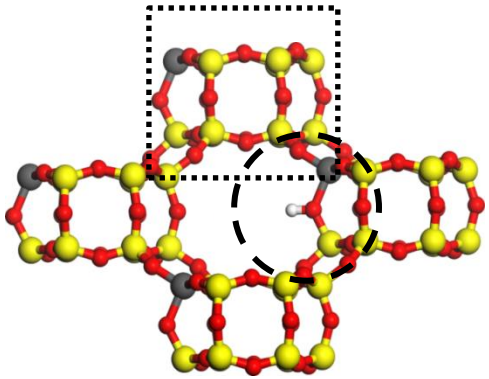
Boscoboinik et al. *J. Phys. Chem. C* **2013**, 117, 13547–13556.

Methanol on Bridging Hydroxyls

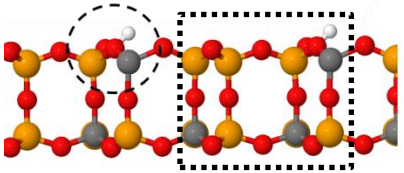


J.A. Boscoboinik, S.K. Shaikhutdinov. *Catal. Lett.* **2014** DOI: 10.1007/s10562-014-1369-3.

Summary



3D Zeolite

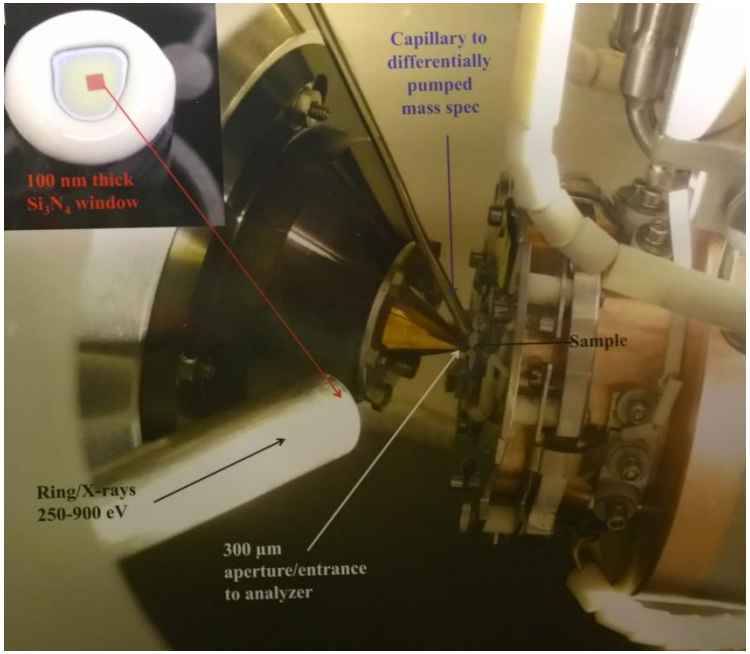


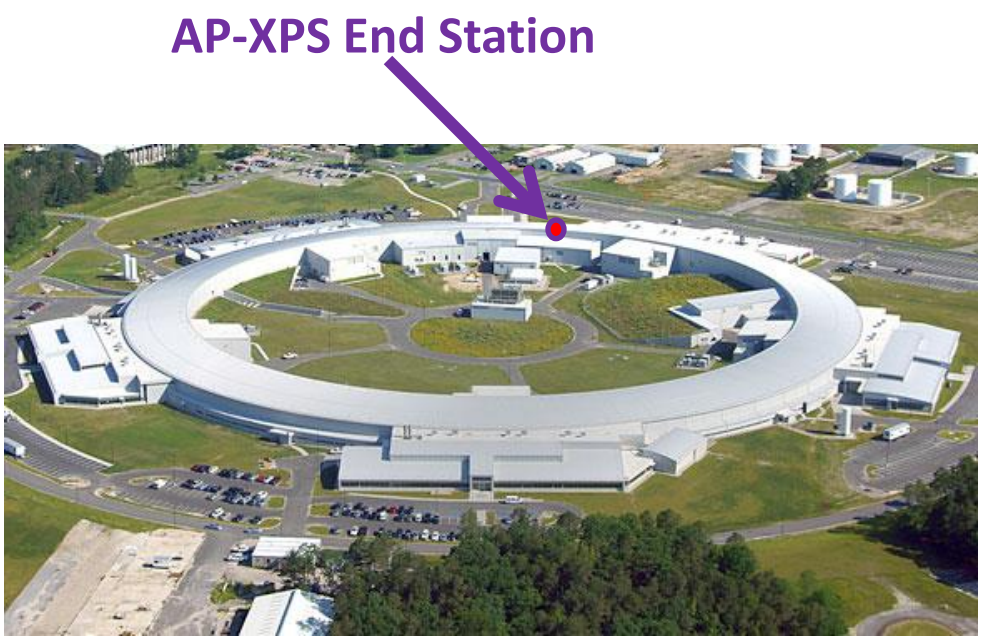
"Zeolite Model System"

- **Well-defined** aluminosilicate film
- Same **active site** as zeolites: **Bridging Hydroxyl**
- Similar interaction with **probe molecules**
- Tools of **Surface Science**

Ambient Pressure X-ray Photoelectron Spectroscopy (AP-XPS) endstation at NSLS-II

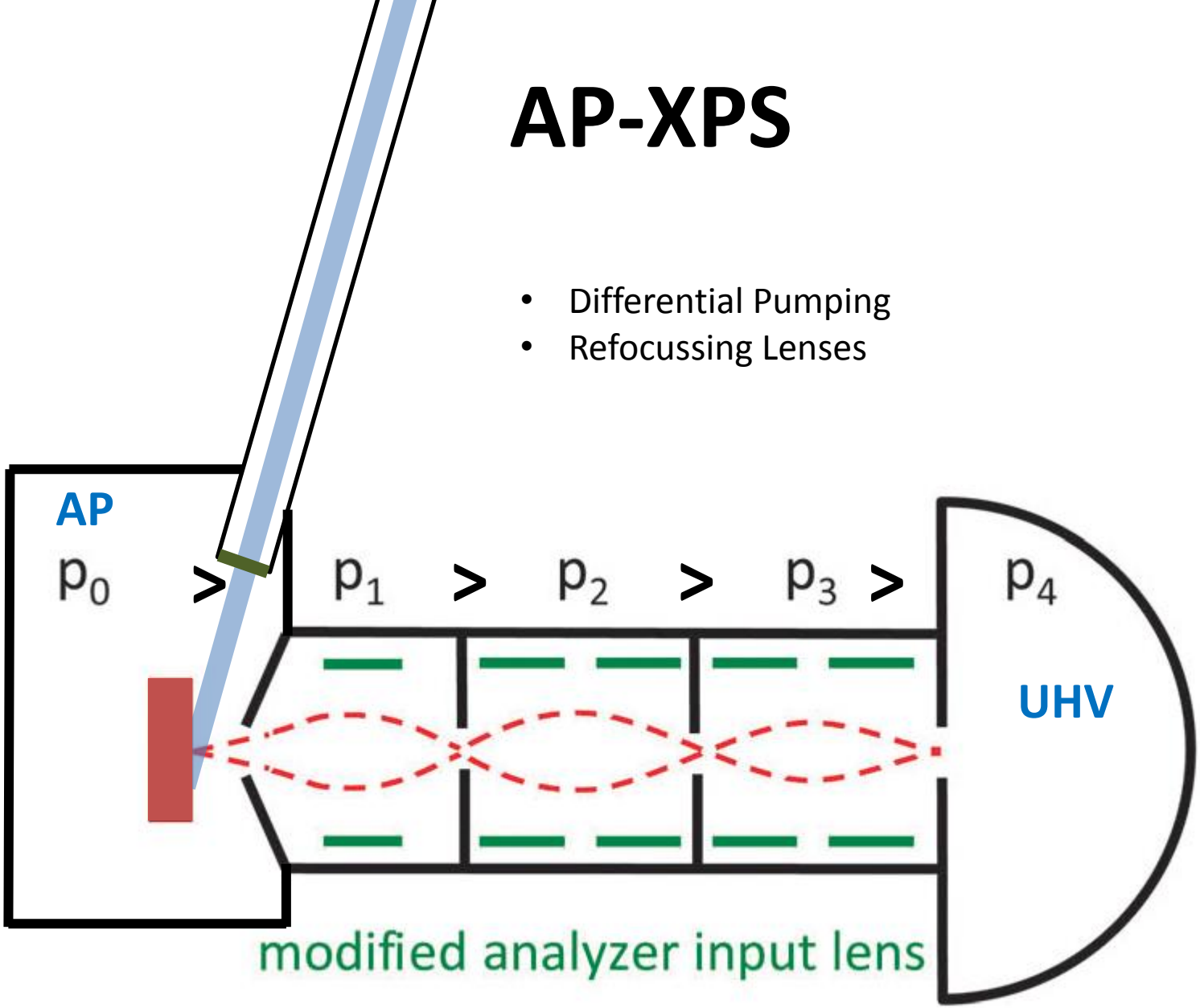
This endstation allows the collection of XPS spectra while the sample is at elevated pressures (currently 5 Torr). A capillary tube collects gas phase molecules in vicinity of the surface, as shown in figure below, to feed into a differentially pumped mass spectrometer.





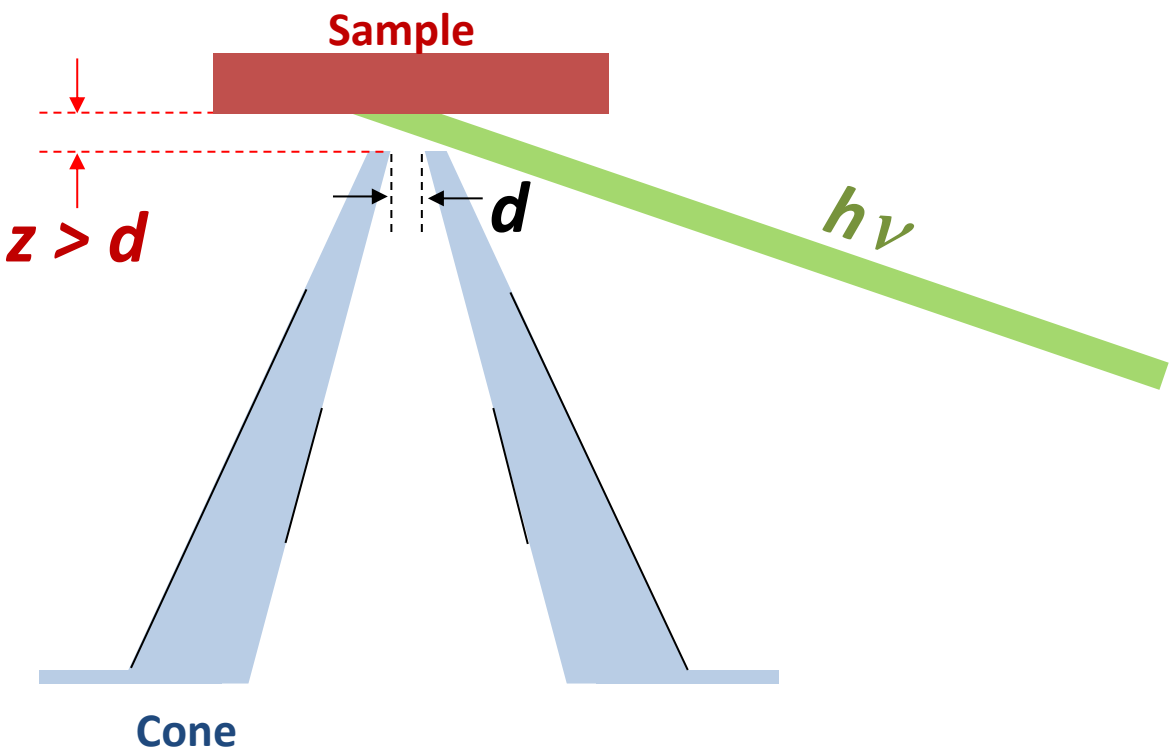
AP-XPS

- Differential Pumping
- Refocussing Lenses



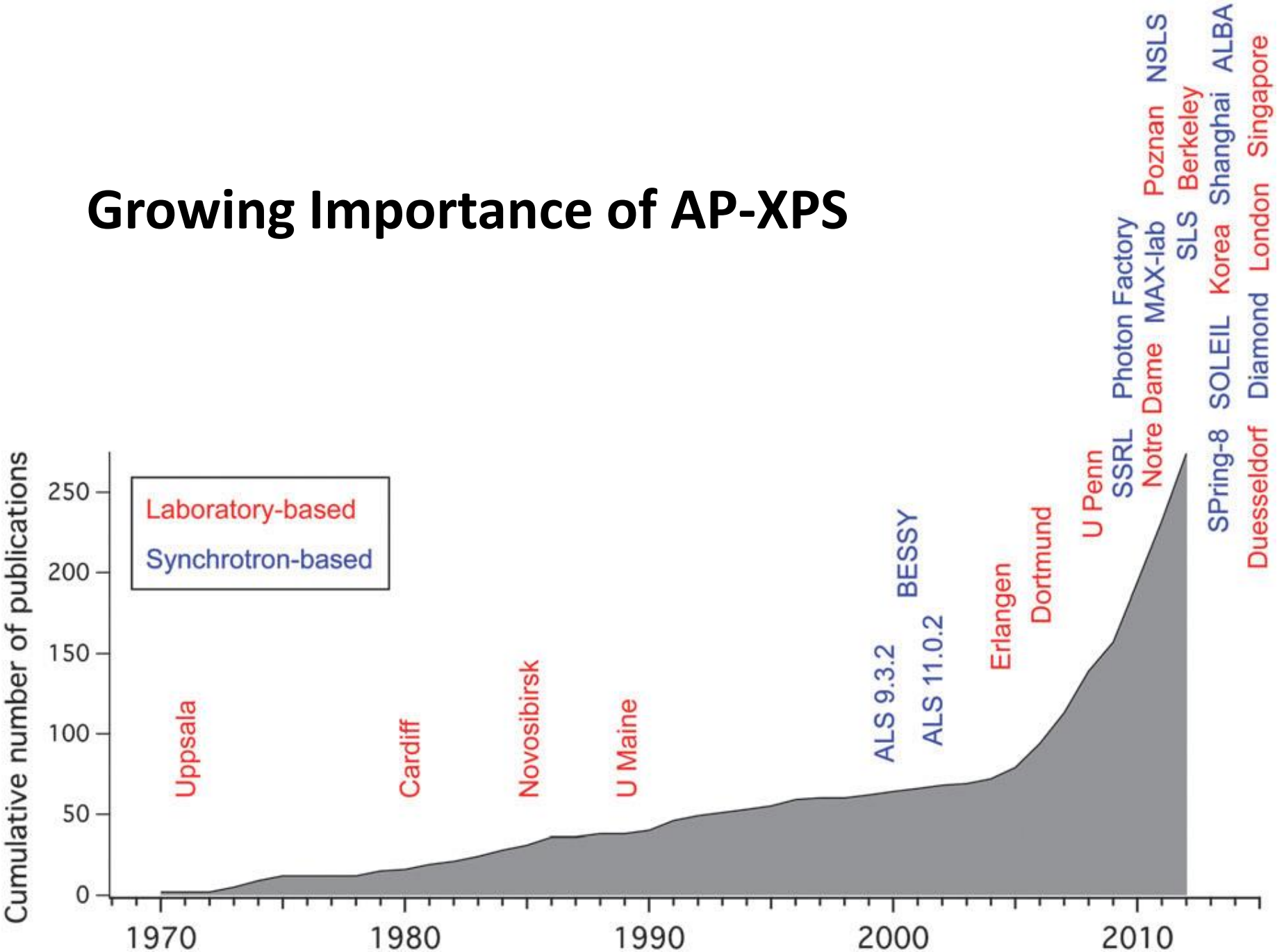
D. E. Starr, Z. Liu, M. Hävecker, A. Knop-Gericke, H. Bluhm. ***Chem. Soc. Rev.***, 2013,**42**, 5833-5857

Importance of a tightly focused beam



The smaller **z**, the higher $\mathbf{P_0}$

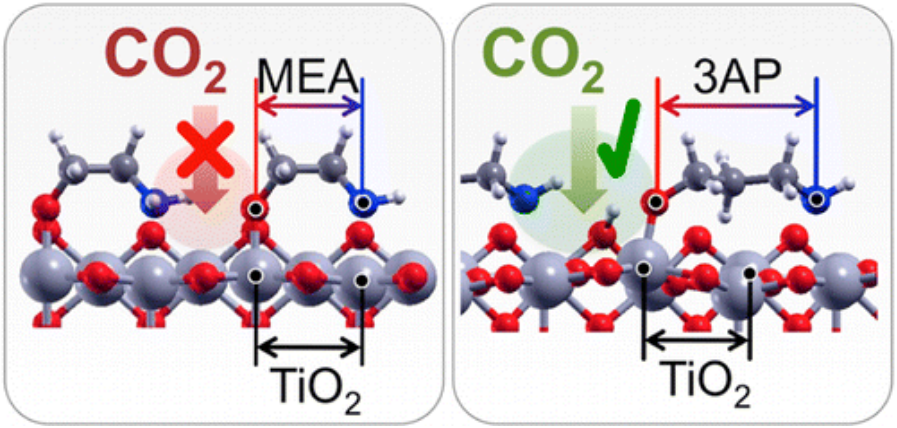
Growing Importance of AP-XPS



D. E. Starr, Z. Liu, M. Hävecker, A. Knop-Gericke, H. Bluhm. ***Chem. Soc. Rev.***, 2013,**42**, 5833-5857

Solid-state CO_2 capture

Tenney, Starr, Sutter, CFN, NSLS X1A



Conventional liquid-phase CO_2 capture

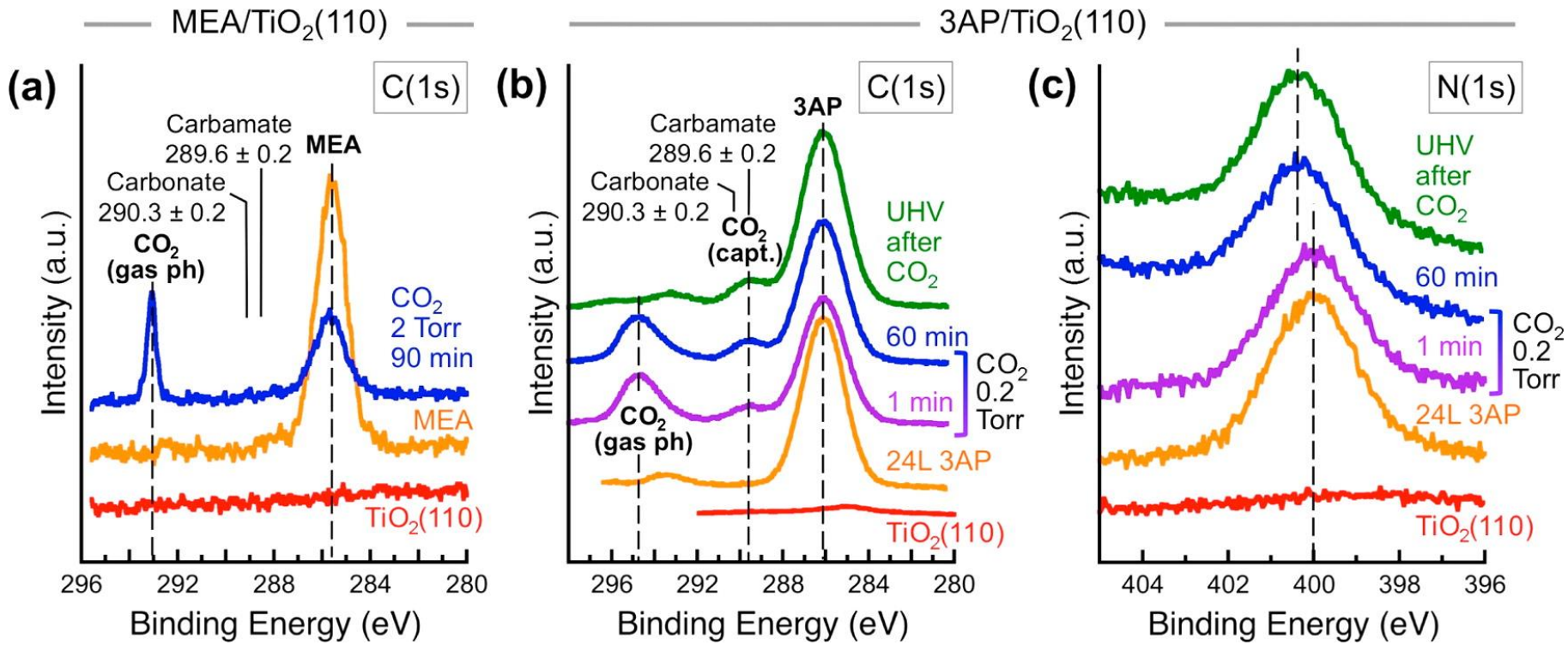
$CO_2(aq) \xrightarrow{H_2O} H_2CO_3 \xrightarrow{MEA} HCO_3^- + AH^+$

$CO_2(aq) + MEA \rightarrow {}^-OOCHNC_2H_4OH + AH^+$

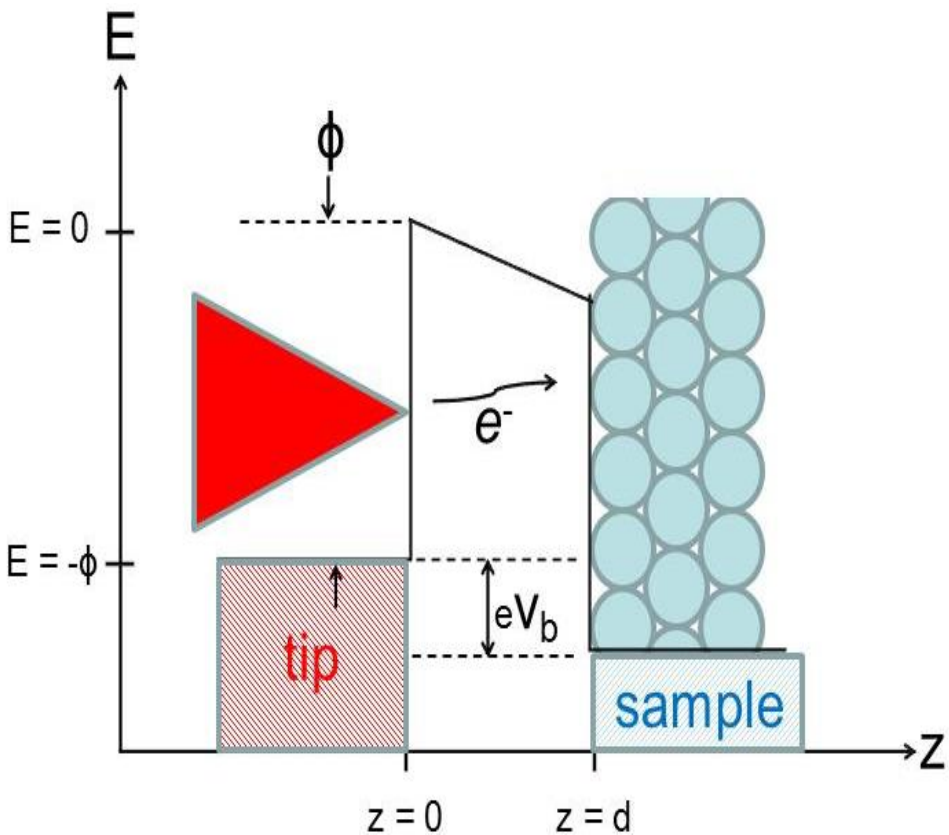
A = monoetanolamine [MEA] = $H_2NC_2H_4OH$

Issues:
- Energy intensive CO_2 removal.
- MEA solution corrosive.
- NO_x/SO_x poison solution.

Tenney et al. *J. Phys. Chem. C*, **2014**, *118* (33), pp 19252–19258



Scanning Tunneling Microscopy



$$\mathcal{H}\Psi(z) = E_t\Psi(z)$$

$$-\frac{\hbar^2}{2m}\frac{d^2}{dz^2}\Psi(z) + U(z)\Psi(z) = E_t\Psi(z)$$

$$\Psi(z) = \Psi(0)e^{-Kz} \qquad K = \frac{\sqrt{2m(U - E_t)}}{\hbar}$$

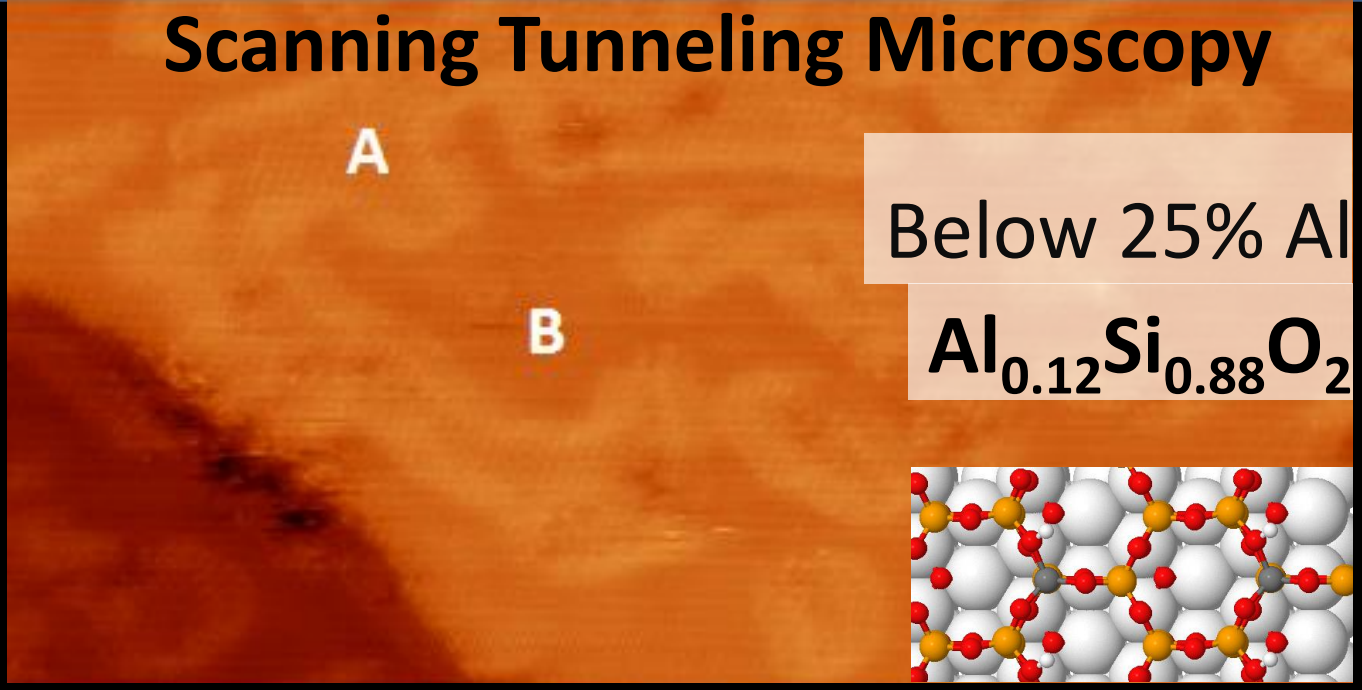
$$P = |\Psi(z)|^2 = |\Psi(0)|^2 e^{-2Kd}$$

STM animation

By Jubobroff (Own work) [CC-BY-SA-3.0 (http://creativecommons.org/licenses/by-sa/3.0)], via Wikimedia Commons

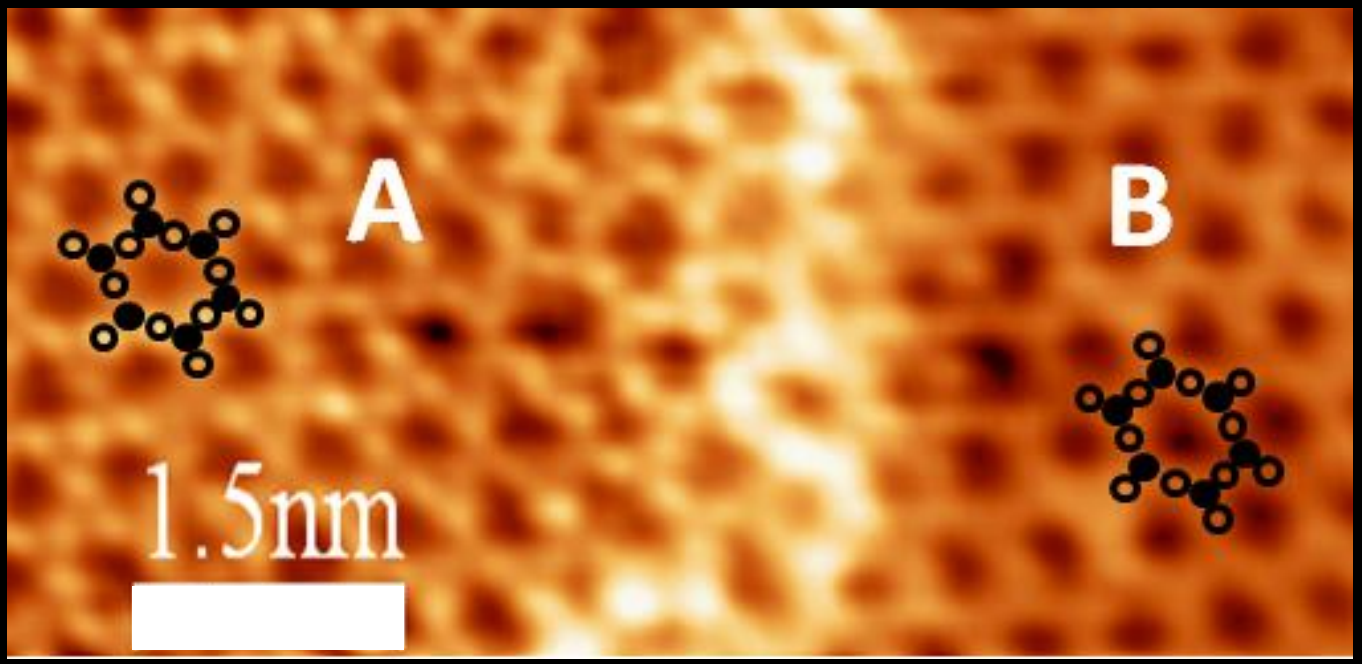
http://commons.wikimedia.org/wiki/File%3AQuantum_tunnel_effect_and_its_application_to_the_scanning_tunneling_microscope.ogv

Scanning Tunneling Microscopy

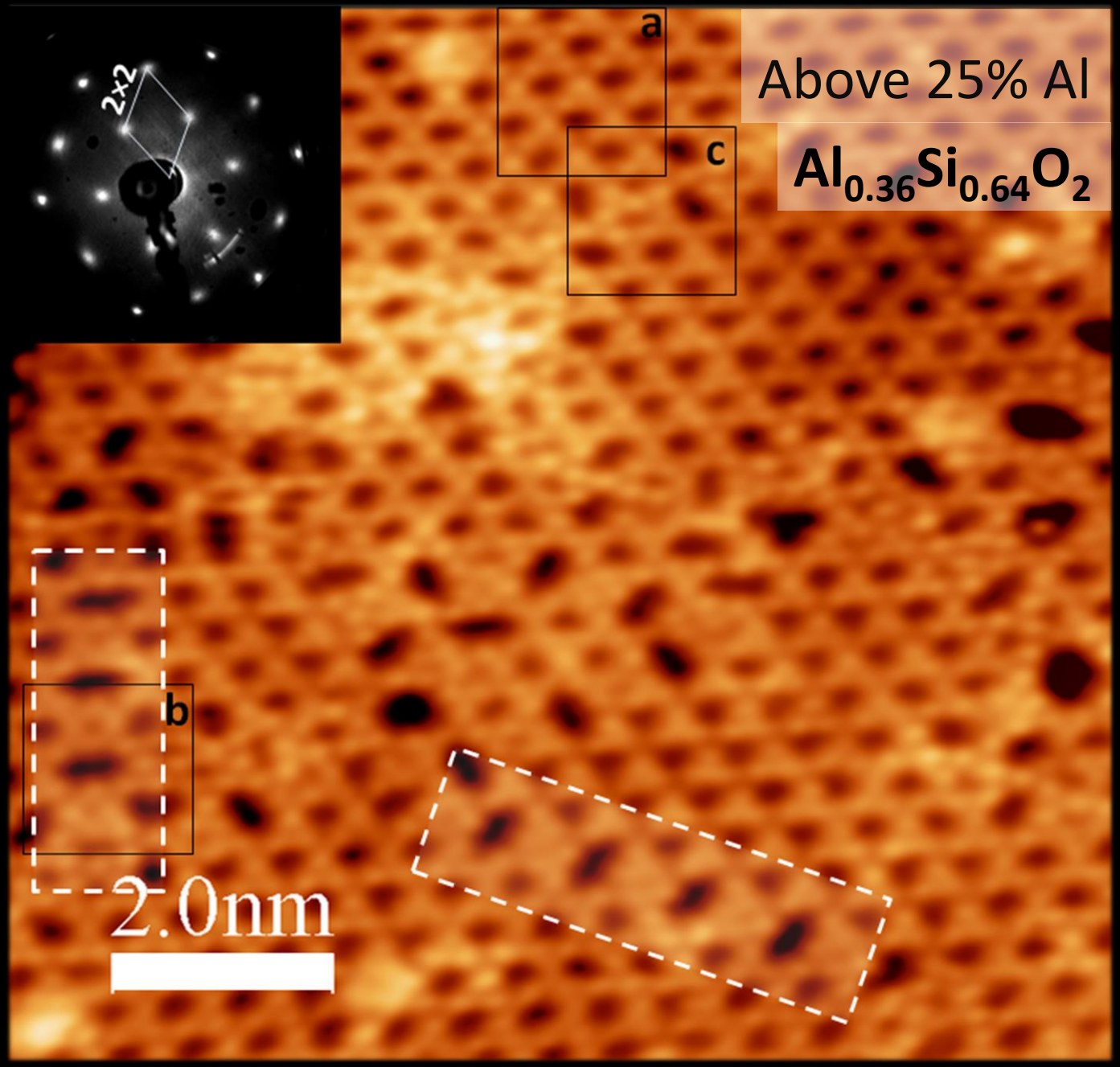


Below 25% Al

$Al_{0.12}Si_{0.88}O_2$



Boscoboinik et al. *Angew. Chem. Int. Ed.* 2012, 51, 6005.



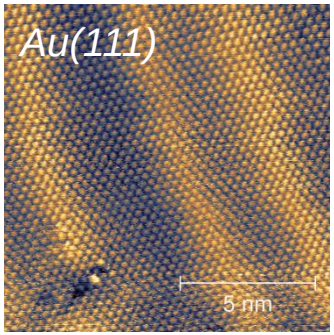
Above 25% Al

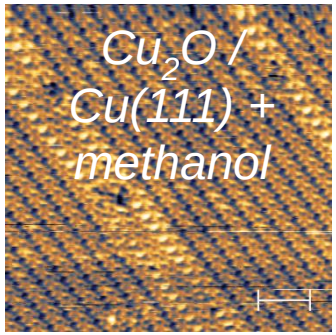
$Al_{0.36}Si_{0.64}O_2$

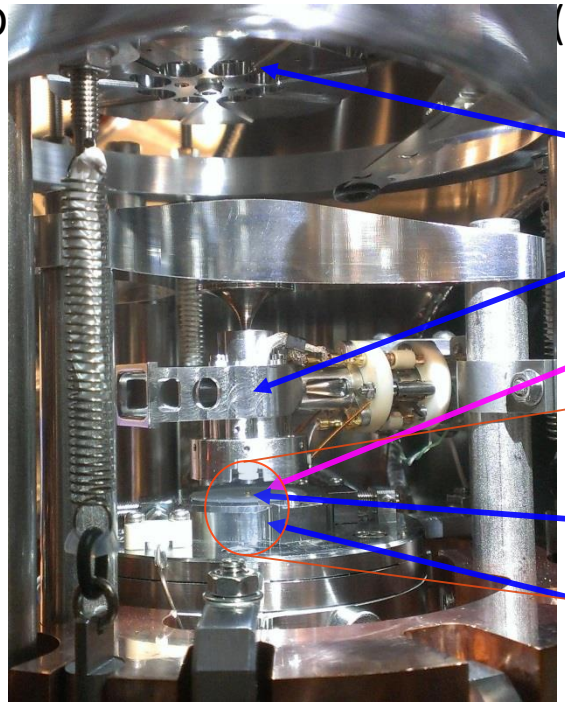
Boscoboinik et al. *Micropor. Mesopor. Mater.* 2013, **165**, 158-162

Reactor STM at CFN

- STM integrated into a 0.5 cm^3 flow reactor
- 50mbar < P < 5 bar
- RT < T < 570K
- Time resolved gas analysis
- Controlled gas mixture
- D (Leiden)







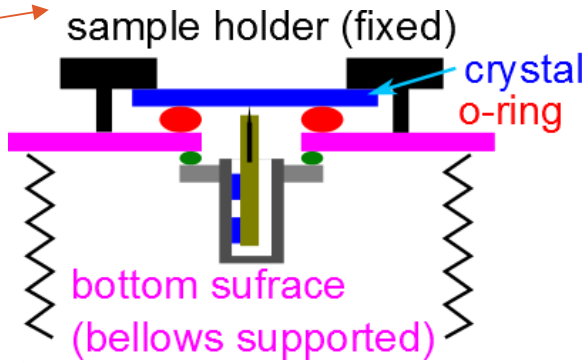
Seal storage carousel

Sample holder with integrated heater

Seal position

Tip

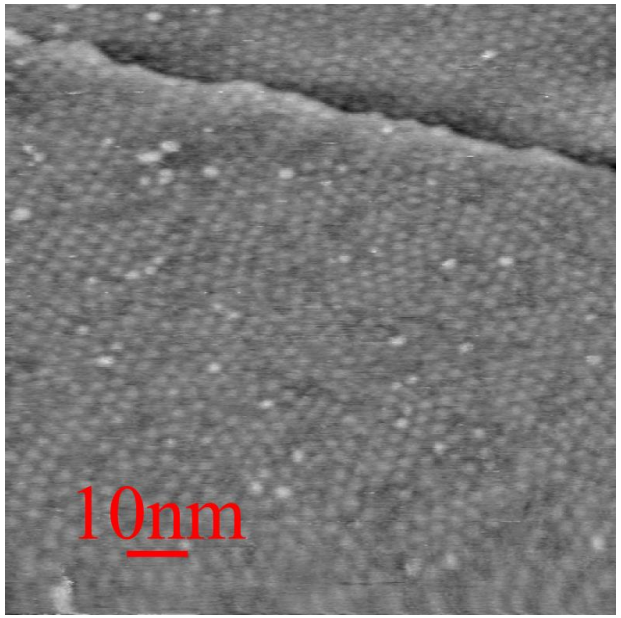
Reactor base



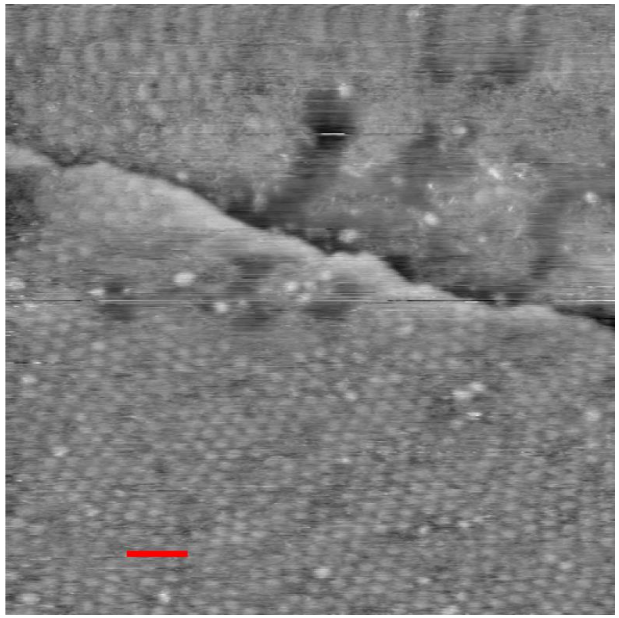
Courtesy of Niv Levy, CFN

Co-Pd on Graphene / Ru(0001)

Co-deposition of Co:Pd at a 20:8 ratio



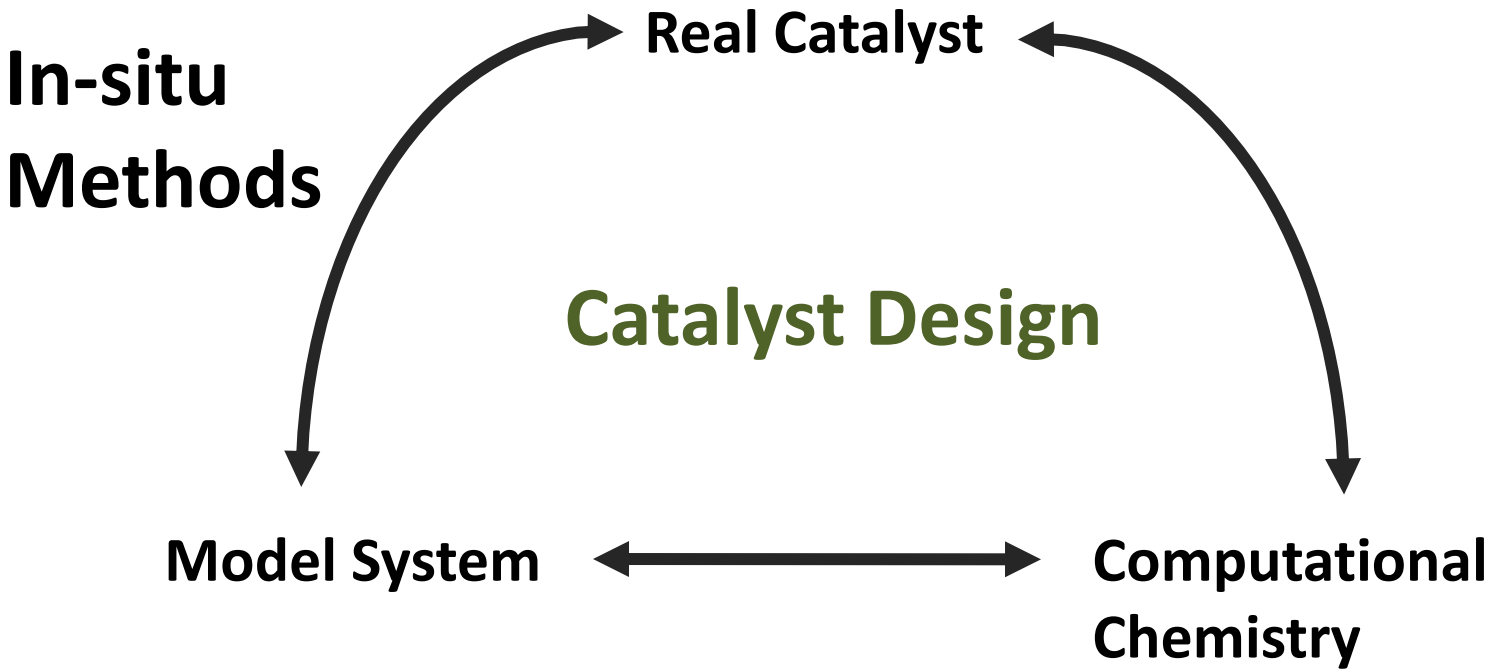
- 18 min
- RT
- 1 bar
- 1:1 H_2 : C_2H_4



Surface changes correlated with clusters near step edge

Often times the active phase is a metastable phase

Courtesy of Niv Levy, CFN

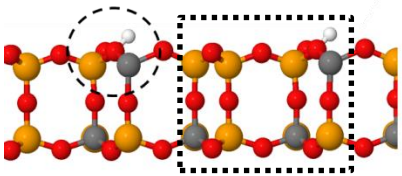

In-situ
Methods
Real Catalyst
Catalyst Design
Model System
Computational
Chemistry

Emerging Capabilities at CFN/BNL

- **AP-XPS, using catalysts model systems, is one of the most important tools to achieve a better understanding of how catalysts work under reaction conditions.**
- **The combination with other techniques, such as IRRAS and comparison with powder studies using *IO*-XAS will be of fundamental importance.**
- **STM during the reaction will aid the understanding of structural aspects of the active phase.**

It’s an exciting time in Surface Science!

- We have a Model System for Zeolites and



- We have new tools for Model System studies at more realistic pressures.

Acknowledgements

BROOKHAVEN NATIONAL LABORATORY

U.S. DEPARTMENT OF ENERGY

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Center for Functional Nanomaterials
Brookhaven National Laboratory

Alexander von Humboldt Stiftung/Foundation

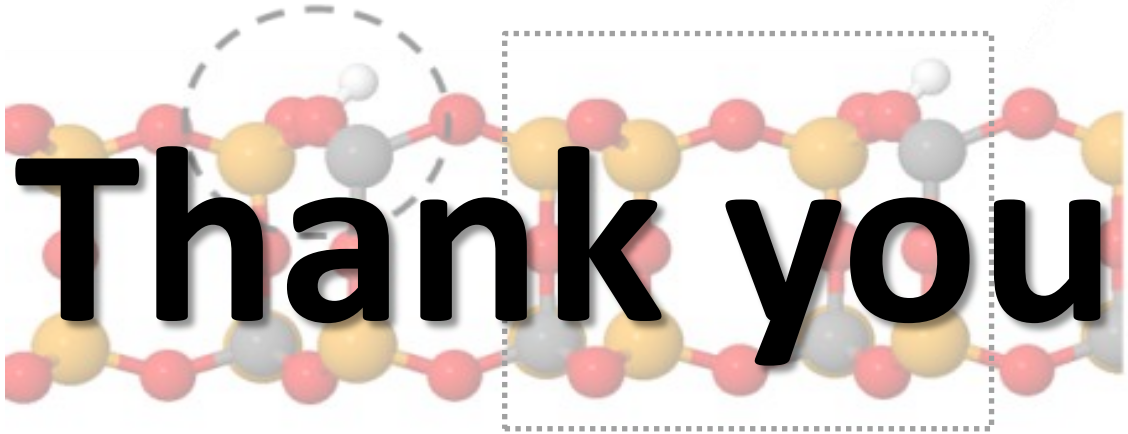
At CFN: current work in progress:

Peter Sutter, Sam Tenney, Niv Levy, Deyu Lu

Previous Zeolite Model System Work

Experiment: *Yu, Yang, Emmez, Shaikhutdinov,* ***Freund.*** (FHI Berlin)

Theory: *Fischer, Wlodarczyk, Sierka,* ***Sauer*** (Humboldt-Universität zu Berlin).



Thank you