The Role of Au in Catalysis by Pd-Au

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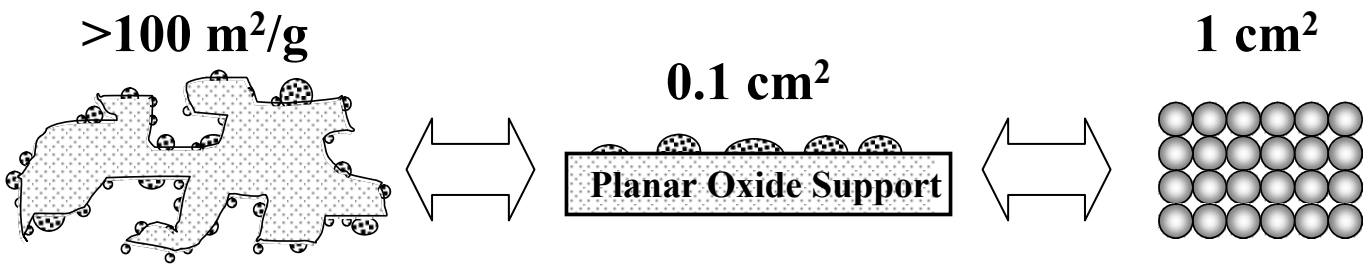
The Role of Au in Catalysis by Pd-Au

OUTLINE

- Introduction to issues and methodology
- Surface vs. bulk composition
- IRAS & TPD: CO as a local probe of surface sites
- Isolated Pd as a reactive site

Au-Pd Catalysis: Vinyl Acetate (VA) Monomer

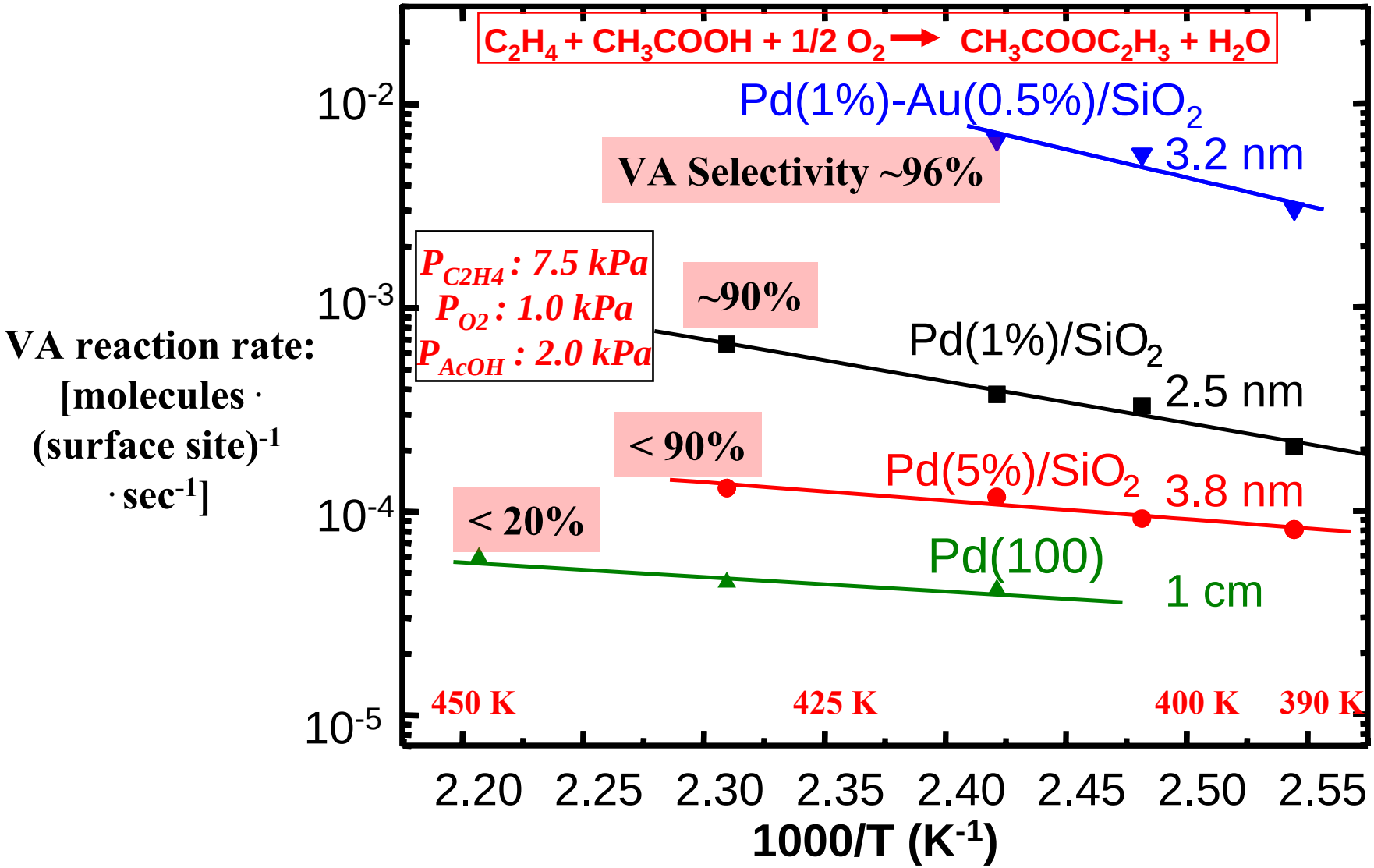
$$C_2H_4 + CH_3COOH + 1/2\ O_2 \xrightarrow[\text{130 – 200°C, 5-10 atm}]{\text{Pd/Au/K/silica}} CH_3COOC_2H_3 + H_2O$$



Key Targets of Study:

- Mechanism of Au promotion
- Active site description

Vinyl Acetate (VA) Synthesis over Various Pd Catalysts



Y.-F. Han, D. Kumar, C. Sivadinarayana and D. W. Goodman, J. Catal., 224, 60 (2004)
Y.-F. Han, D. Kumar, C. Sivadinarayana, A. Clearfield and D.W. Goodman, Catal. Lett., 94, 131 (2004)
Y.-F. Han, D. Kumar and D.W. Goodman, J. Catal., 230, 353 (2004)
Y.-F. Han, J.-H. Wang, D. Kumar, Z. Yan and D. W. Goodman, J.Catal., 232, 467 (2005)

Origin of Combustion Products

$$C_2H_4 + CH_3COOH + 1/2\ O_2 \longrightarrow CH_3COOC_2H_3 + H_2O$$

- $Ethylene + O_2 \rightarrow CO_2 + H_2O$
- $AcOH(2.0kPa) + O_2(1.0-10.0kPa) \not\rightarrow CO_2(CO) + H_2O$
- $VA + O_2 \not\rightarrow CO_2 + H_2O$

- No measurable rate of AcOH combustion at 413 K;
- Only 5.0% increase in combustion rates upon addition of 3.5 kPa VA to mixture of C_2H_4, AcOH, and O_2.

Conclusion: CO_2 produced primarily from ethylene

Y.-F. Han, D. Kumar, C. Sivadinarayana and D. W. Goodman, J. Catal, 224, 60 (2004)

TPD: Ethylene from Oxygen-covered Pd(100)

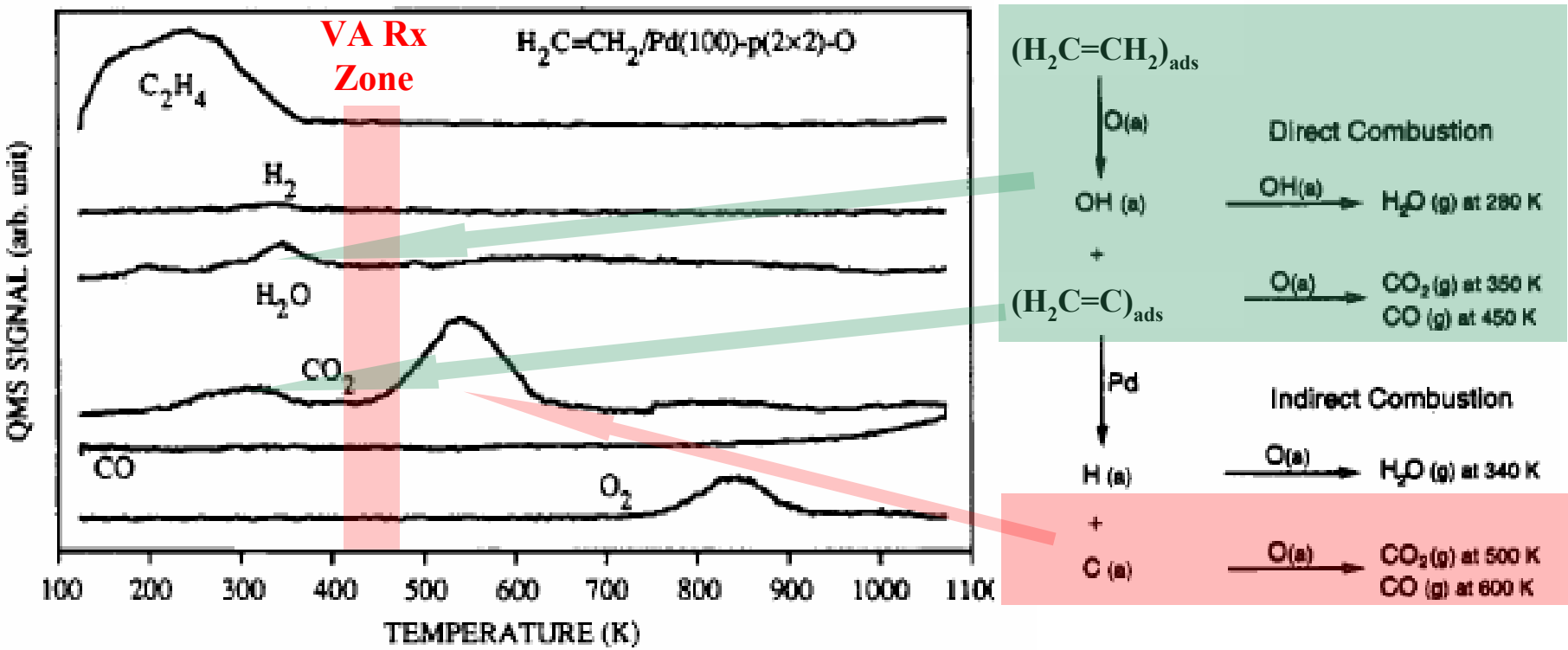
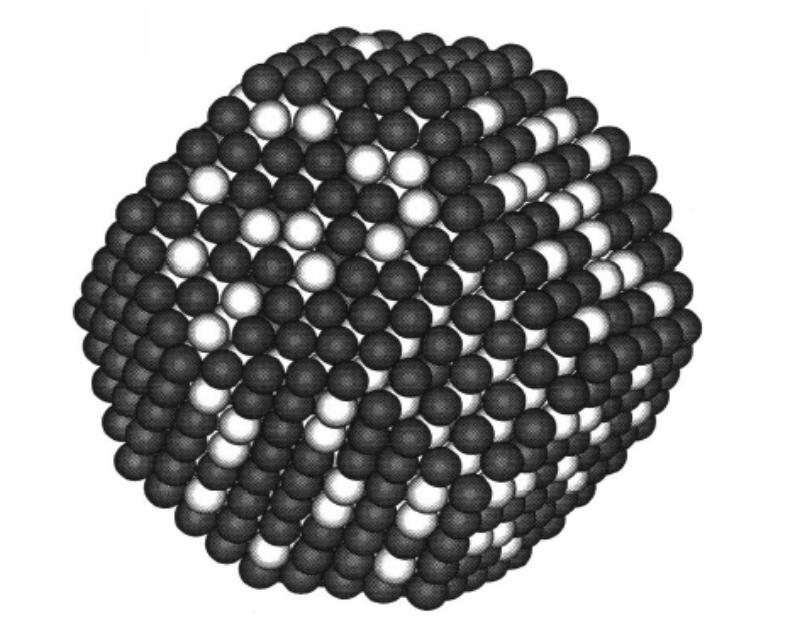
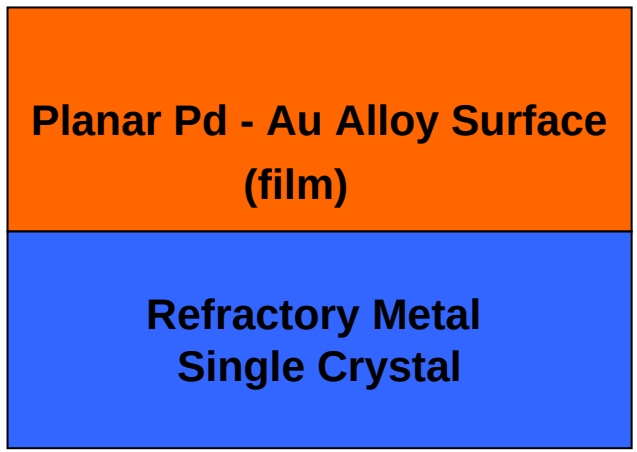


Figure 7. Temperature-programmed reaction spectra of ethylene adsorbed on Pd(100)-p(2 × 2)-O at saturation ethylene exposure. The product yields are listed in Table 2.

X.-C. Guo and R. J. Madix, *J. Am. Chem. Soc.*, 1995,117, 5523

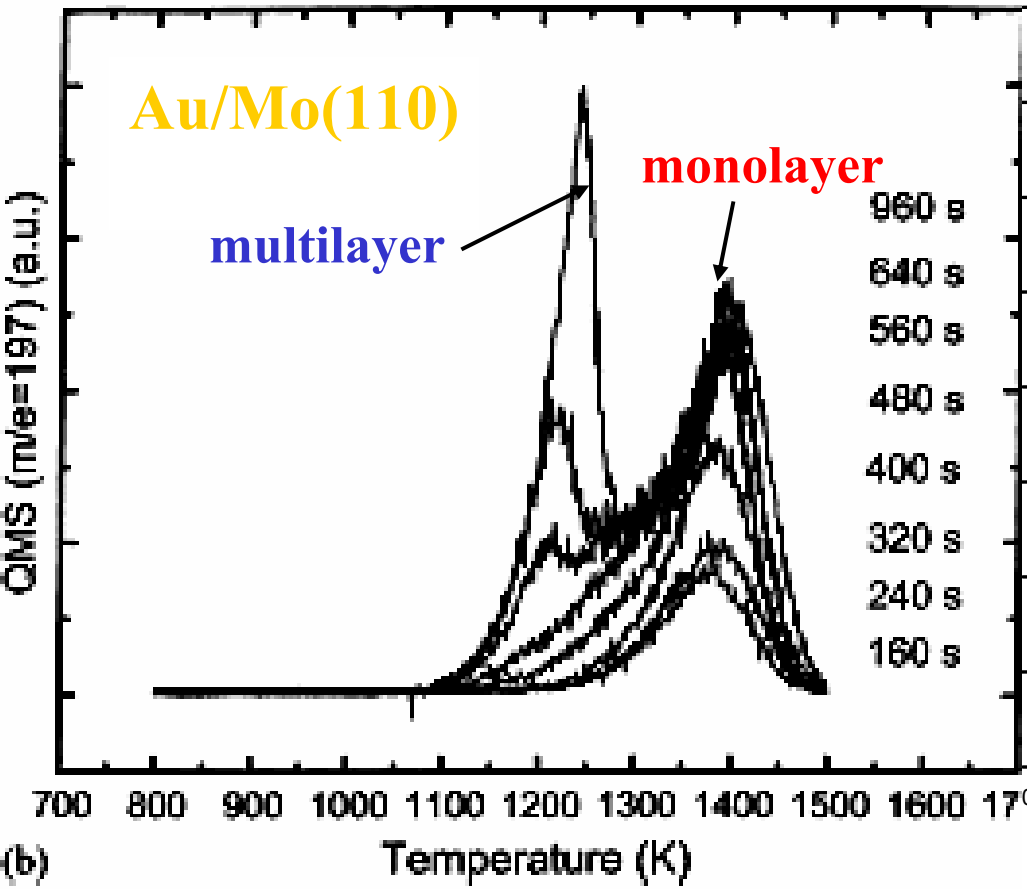
Pd-Au Bimetallic Surfaces

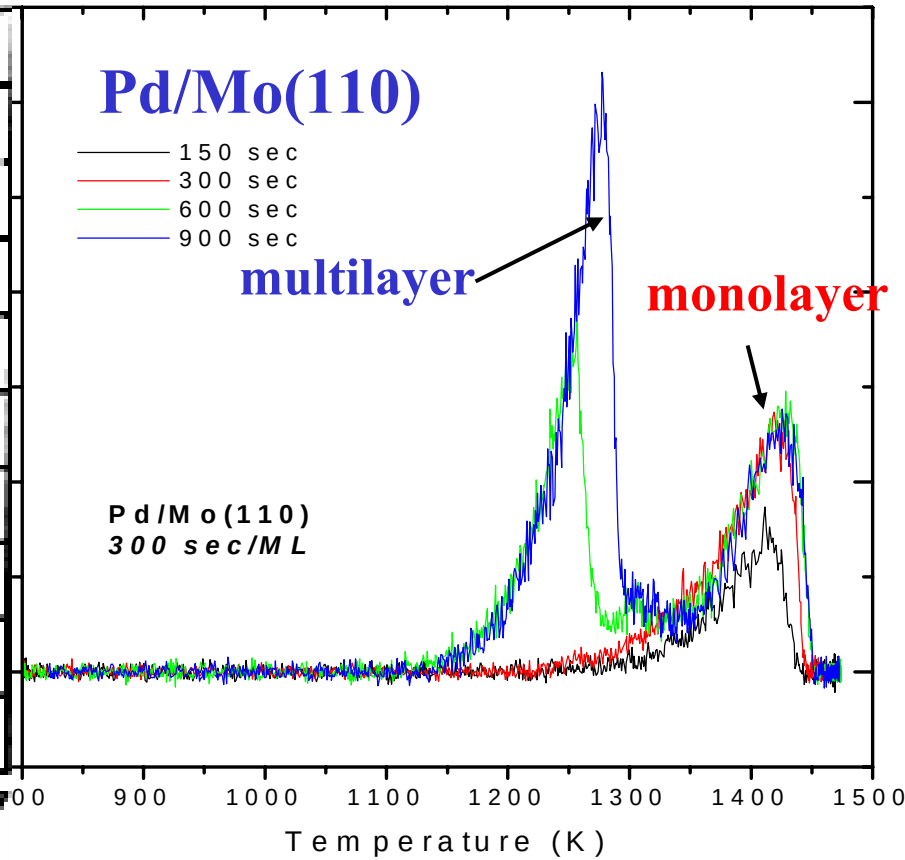




<u>Key Issues</u>: - Surface versus bulk composition?
- Distribution of surface atoms?

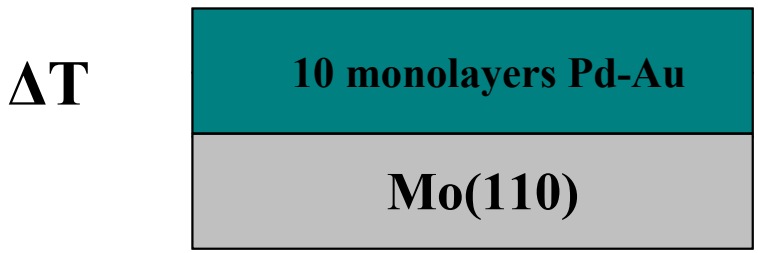
Temperature Programmed Desorption (TPD): Au and Pd from Mo(110)





Luo K, *et.al.* J. Mol. Catalysis A: Chemical 167 (2001) 191

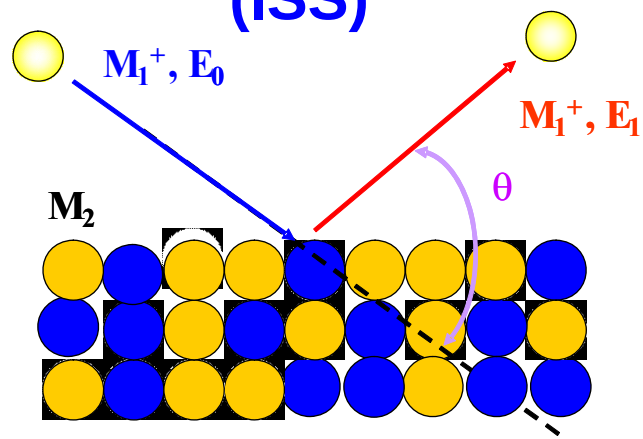
Pd-Au Alloys: Surface versus Bulk Composition

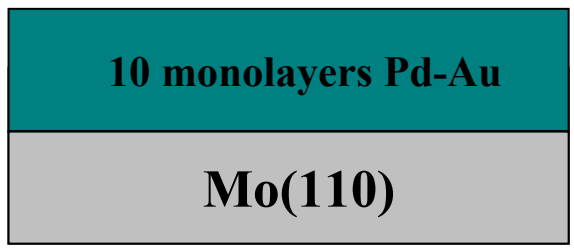


C.-W. Yi, K. Luo, T. Wei, and D. W. Goodman, J. Phys. Chem., 109, 18535 (2005).

Pd-Au Alloys: Surface versus Bulk Composition

Ion Scattering Spectroscopy (ISS)





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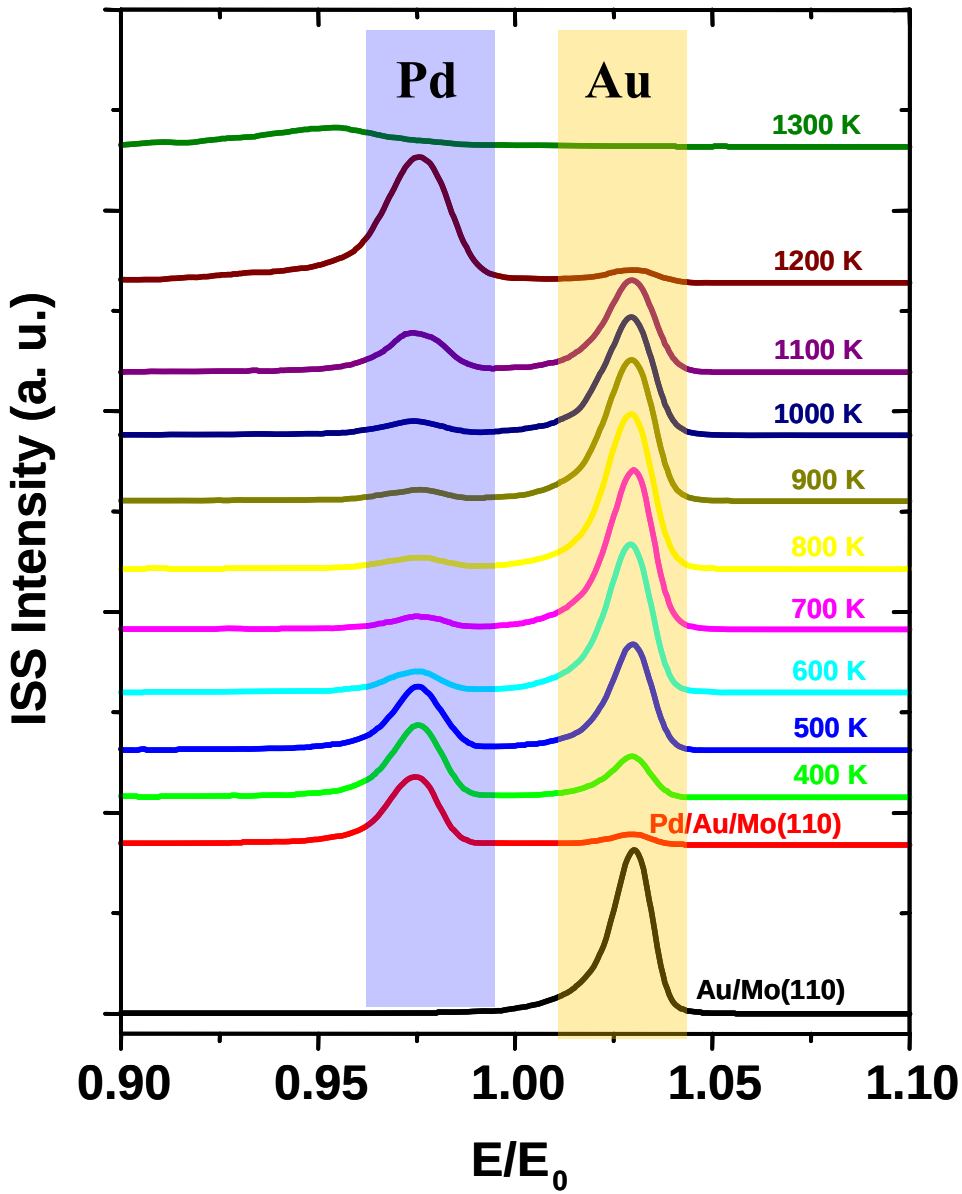

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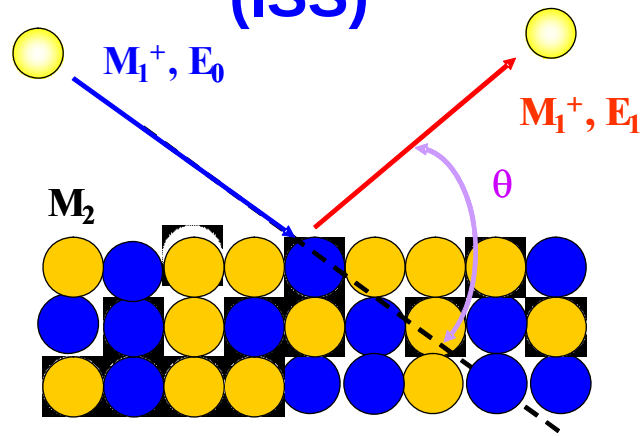
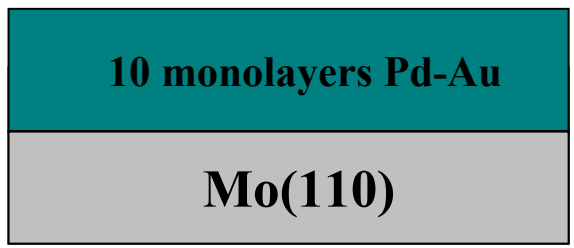
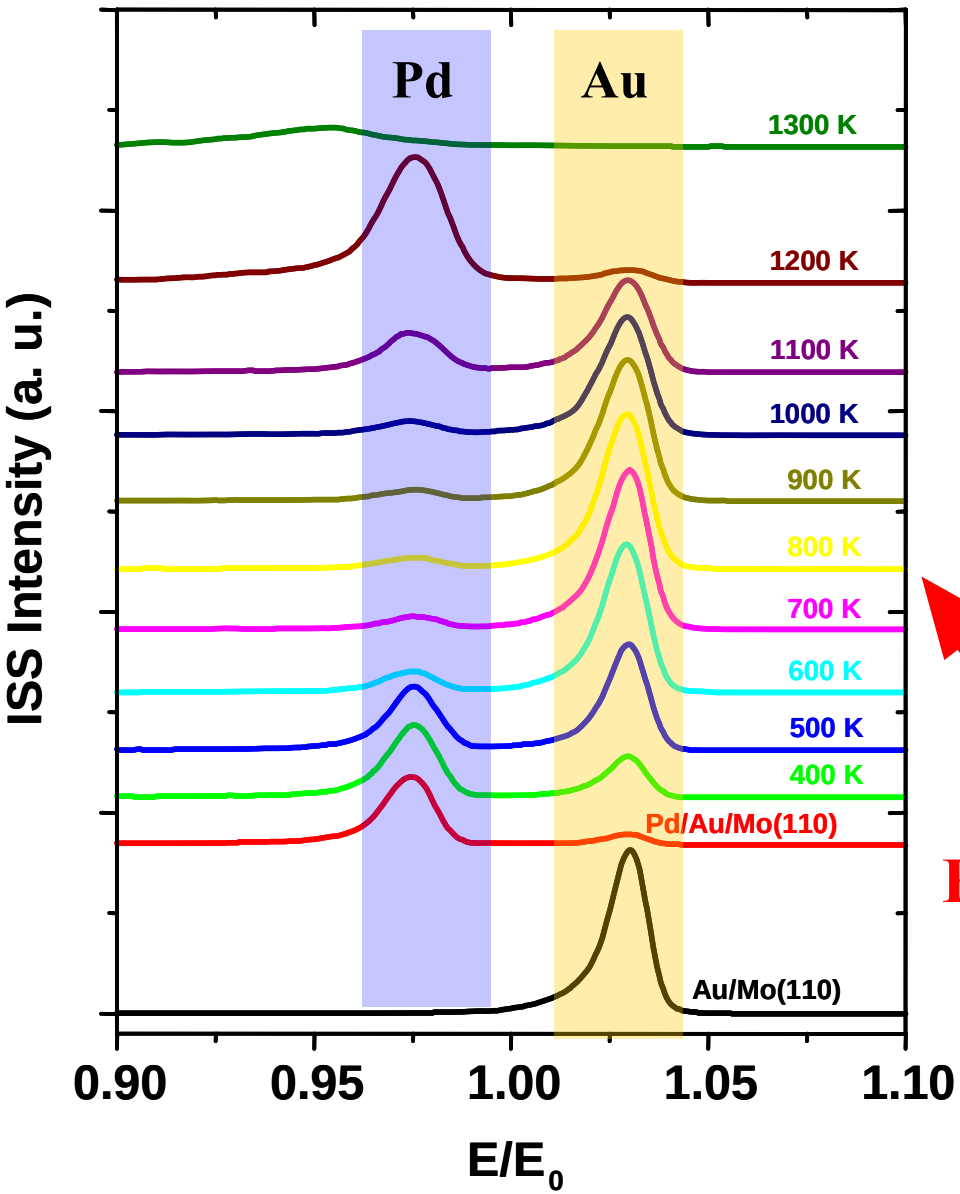


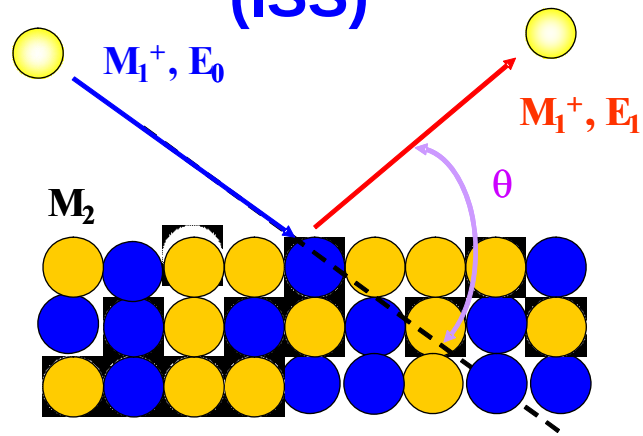


C.-W. Yi, K. Luo, T. Wei, and D. W. Goodman, J. Phys. Chem., 109, 18535 (2005).

Ion Scattering Spectroscopy (ISS): 5 ML Pd/5 ML Au/Mo(110)



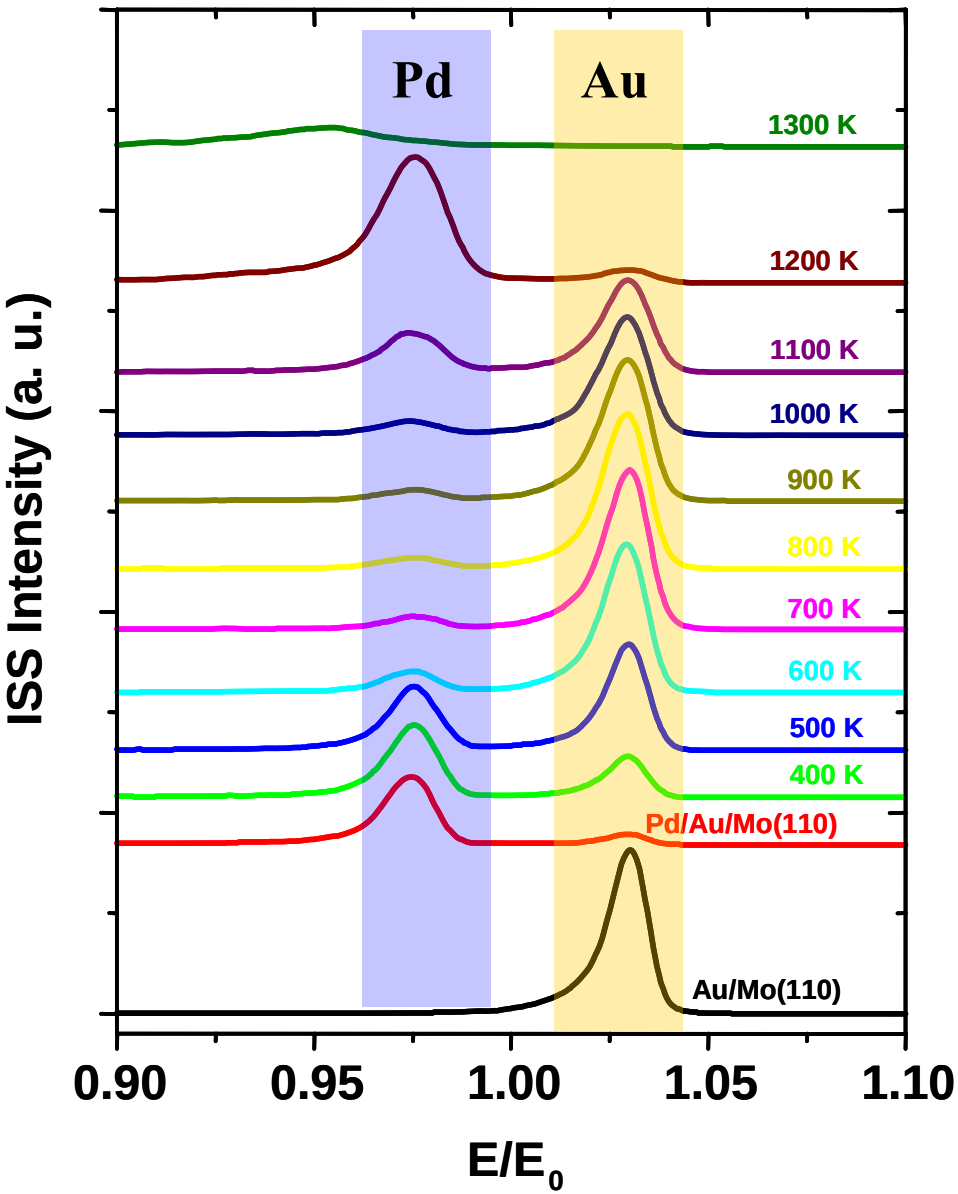
Ion Scattering Spectroscopy (ISS)

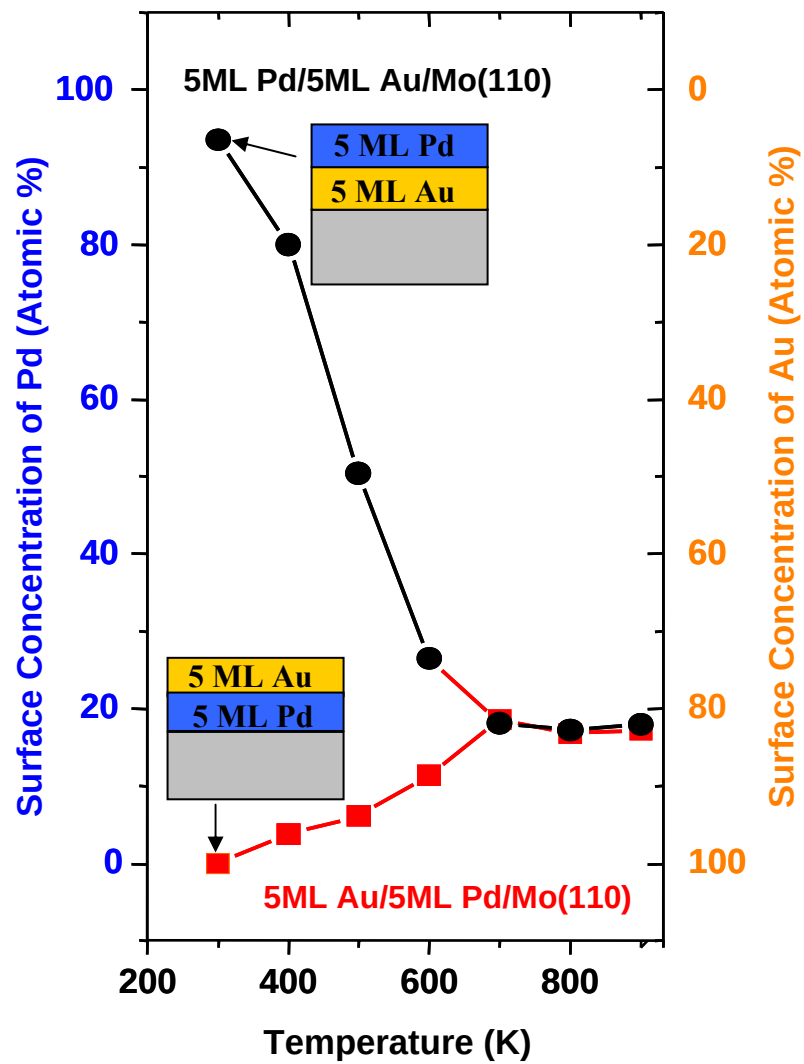


Equilibrium surface achieved with 800 K anneal!

C.-W. Yi, K. Luo, T. Wei, and D. W. Goodman, J. Phys. Chem., 109, 18535 (2005).

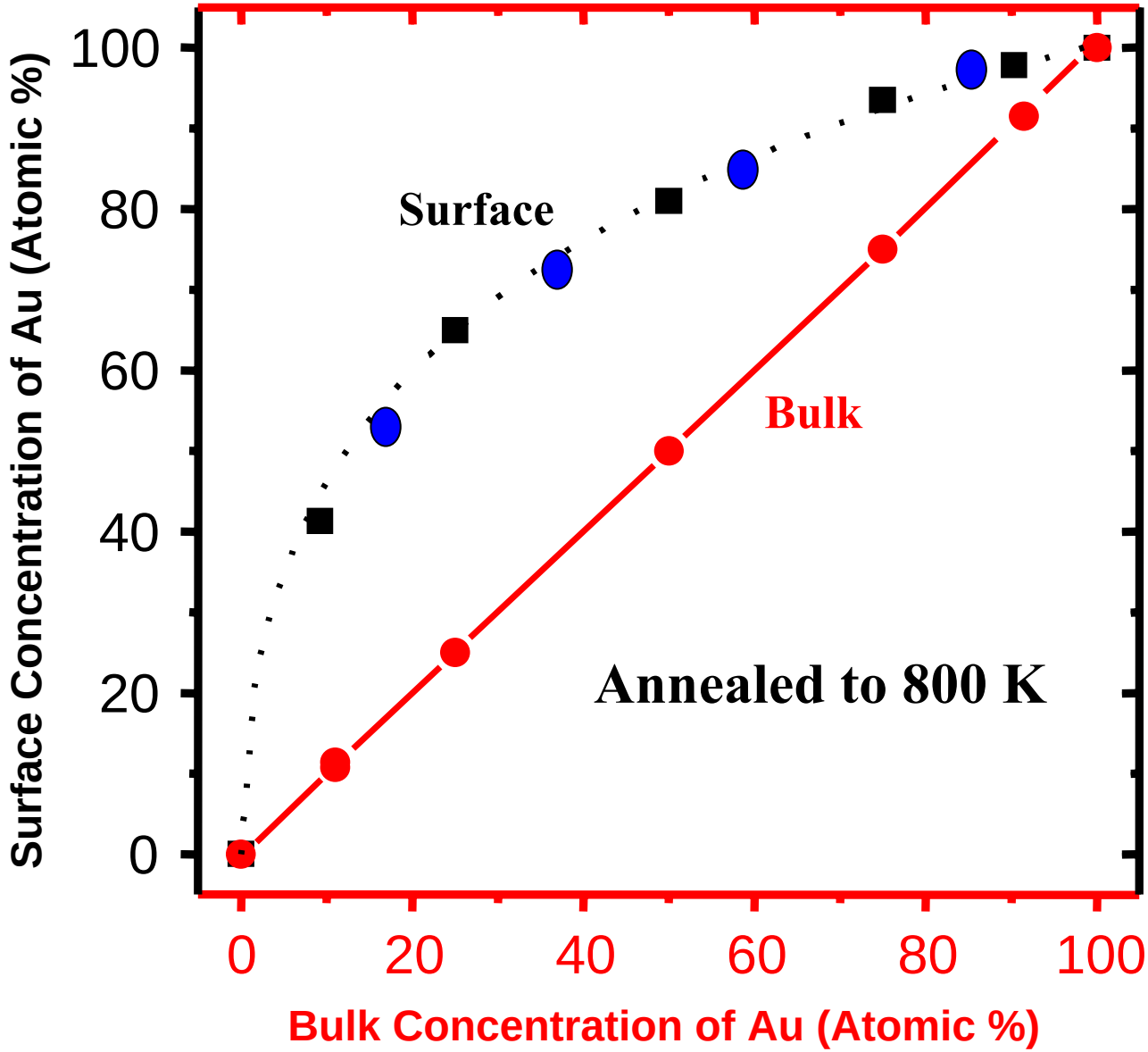
Ion Scattering Spectroscopy (ISS): 5 ML Pd/5 ML Au/Mo(110)





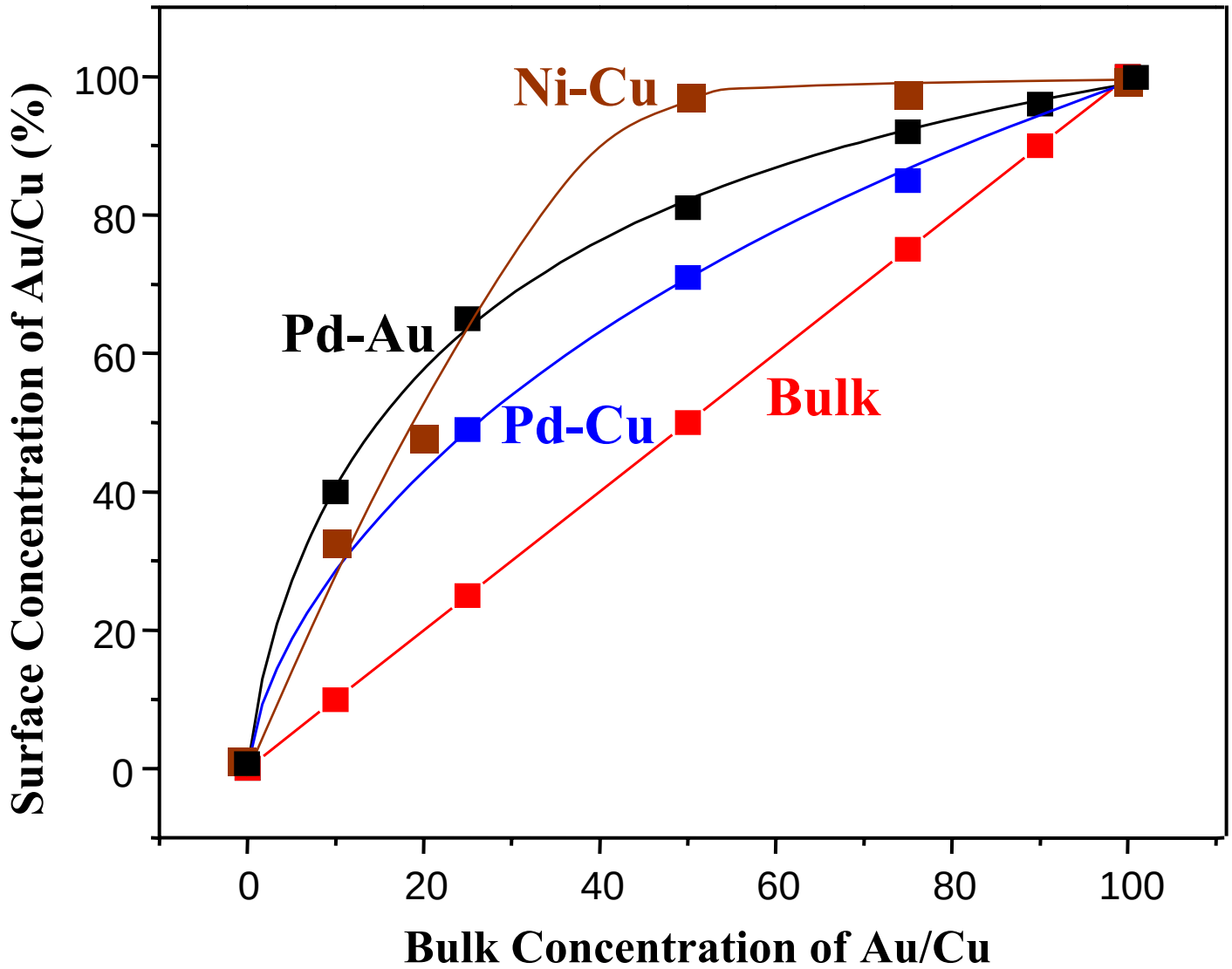
Pd-Au: Surface vs. Bulk Phase Diagram

C.-W. Yi, K. Luo, T. Wei, and D. W. Goodman, J. Phys. Chem., 109, 18535 (2005)

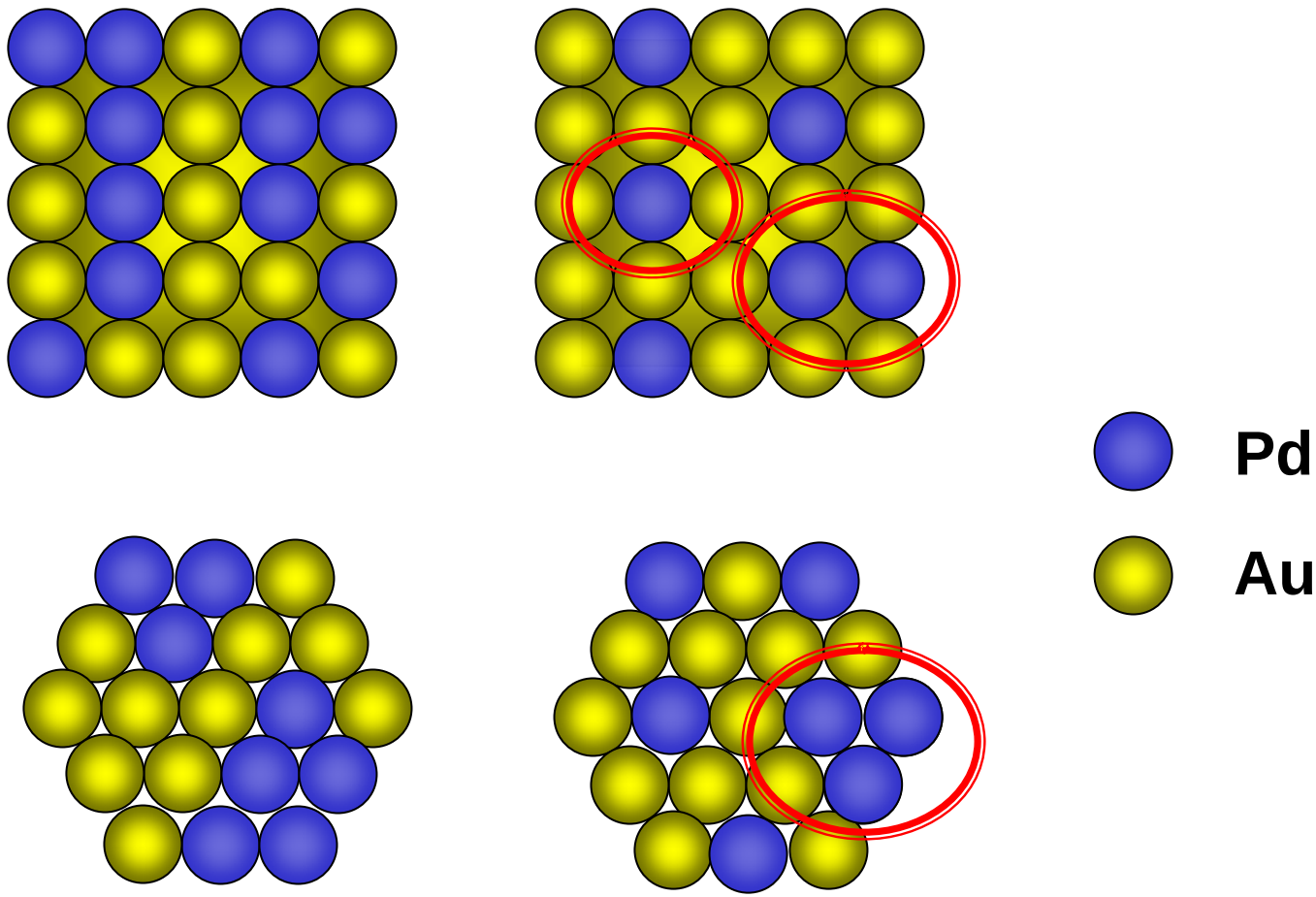


D. G. Swartzfager, S. B. Ziemecki, and M. J. Kelley, JVST 19(2), 185 (1982)

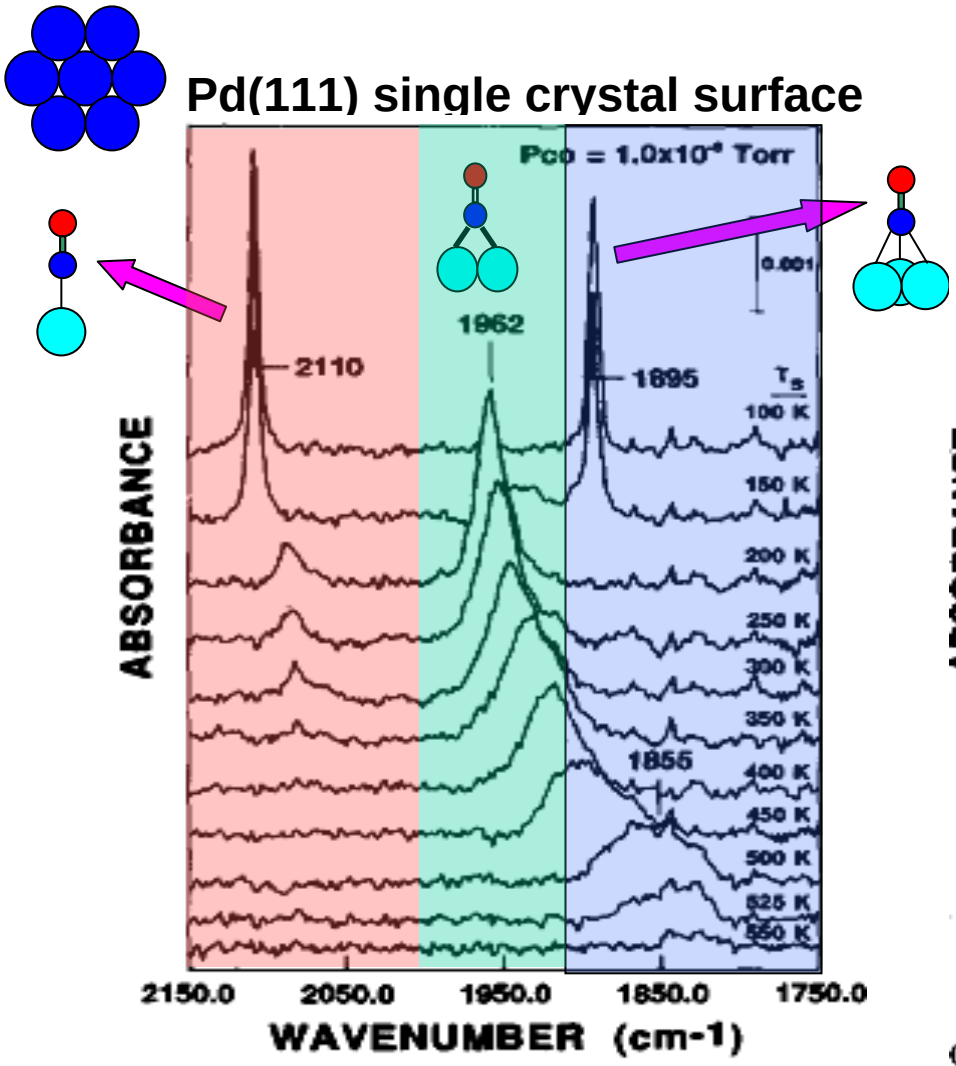
Surface vs. Bulk Phase Diagrams of Pd-Au, Pd-Cu, & Ni-Cu



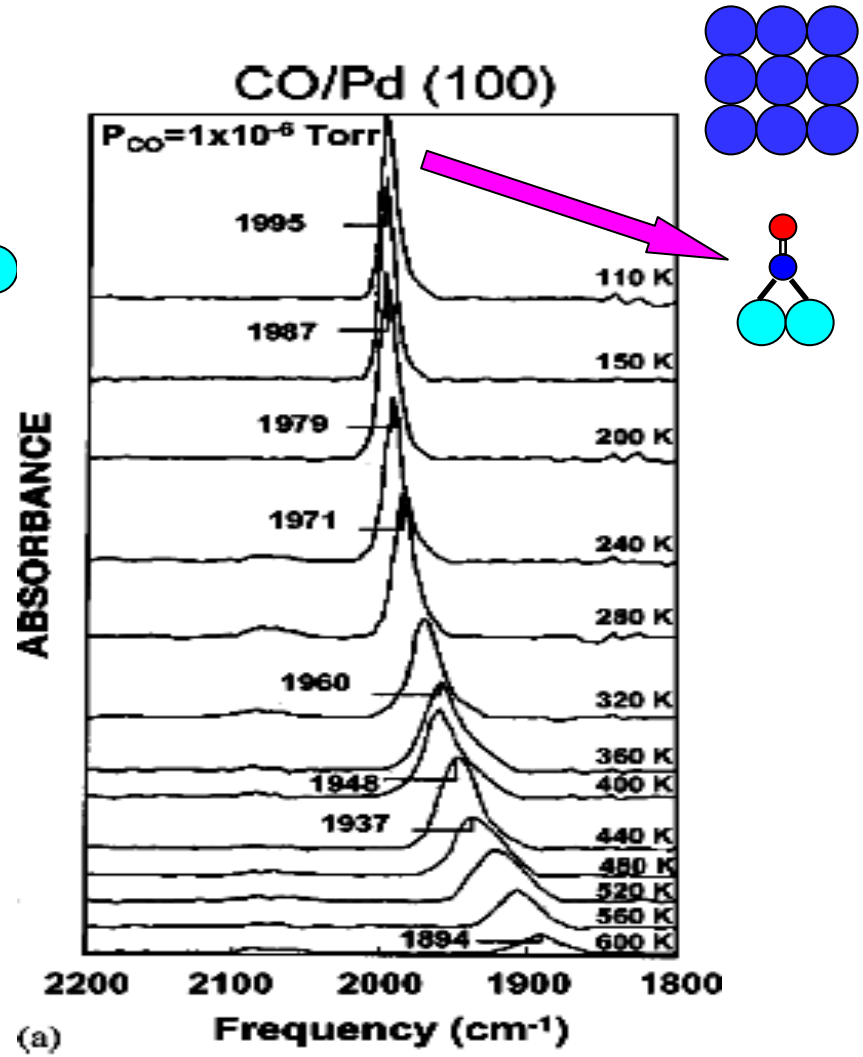
Differentiation of Site Geometries?



IRAS: CO on Pd(111) and Pd(100)



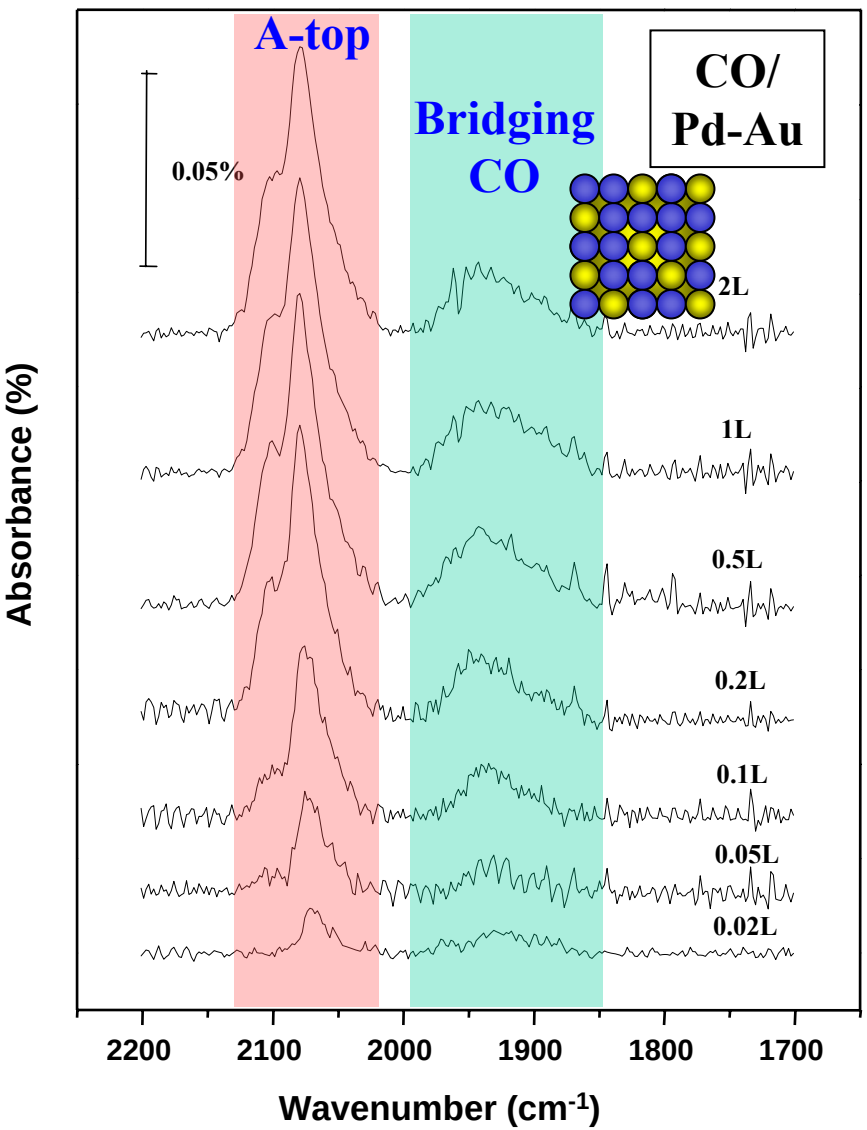
Kuhn, Szanyi and Goodman,
Surf. Sci. Lett. **1992**, 274, L611

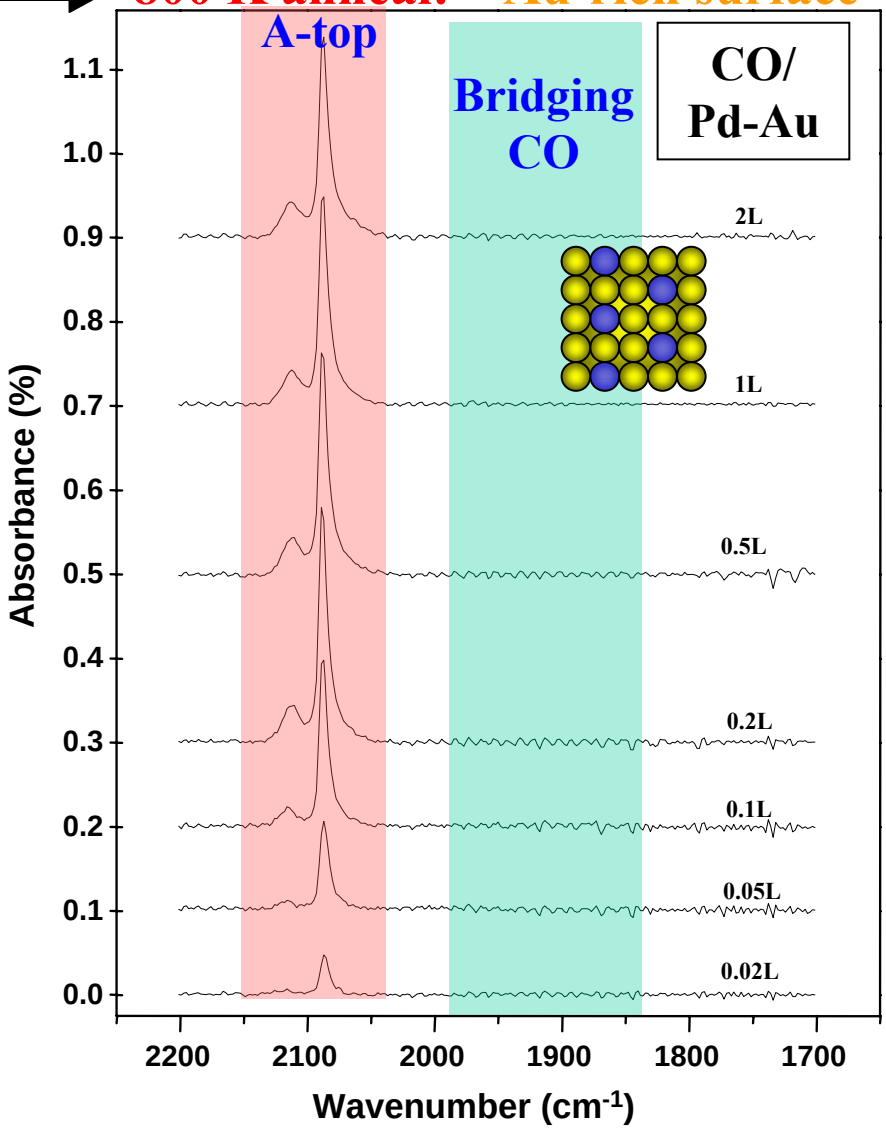


Szanyi, Kuhn and Goodman,
J. Vac. Sci. Technol. A. 1993, 11, 1969

IRAS: CO/5ML Pd/5ML Au/Mo(110)

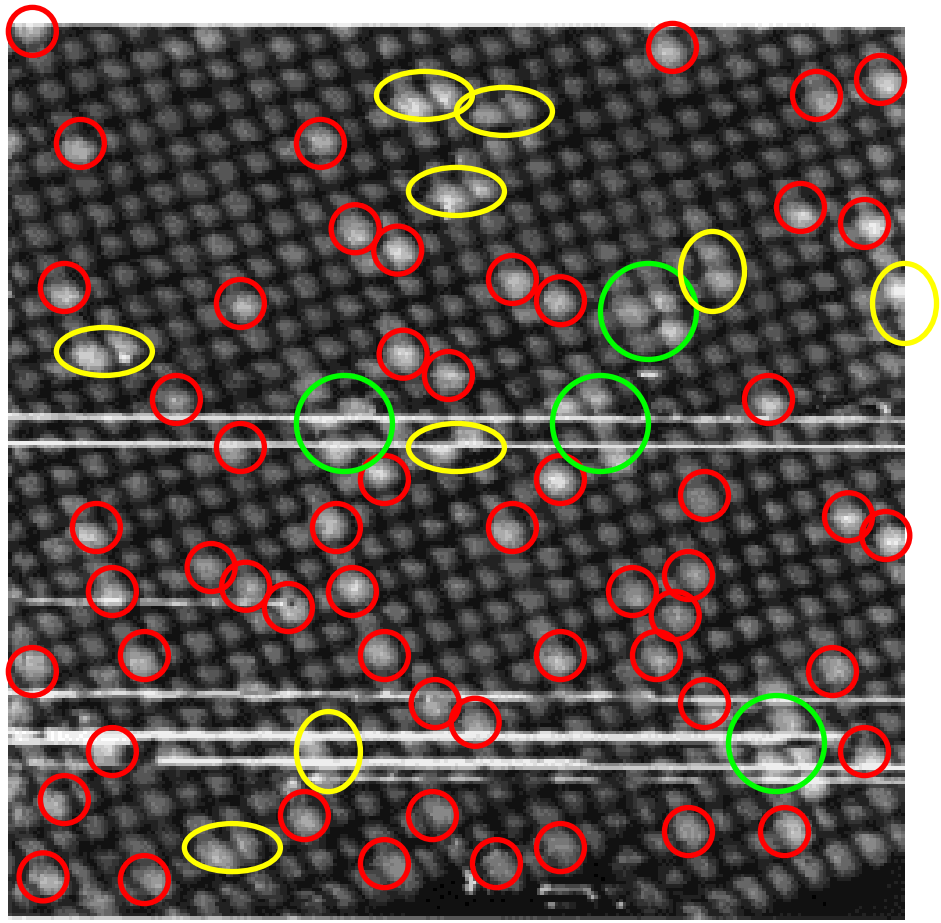
600 K anneal: "Pd-rich surface" → **800 K anneal: "Au-rich surface"**

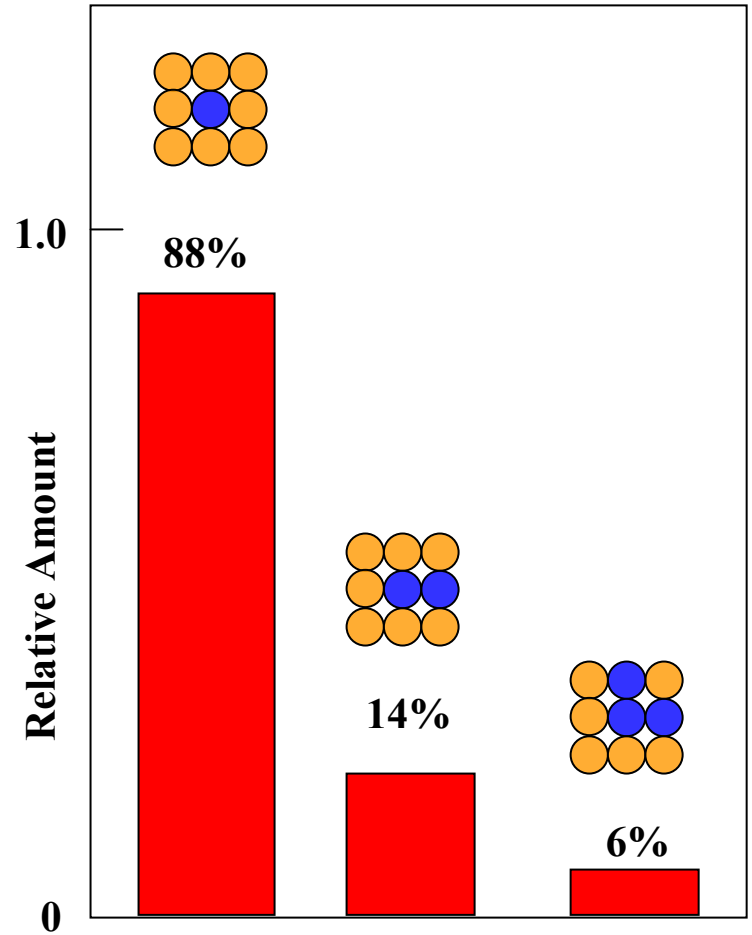




STM: $Au_3Pd(100)$ Alloy Surface

Aschoff, et al., *Surf. Sci.* 415 (1998) L1051





Pd monomers

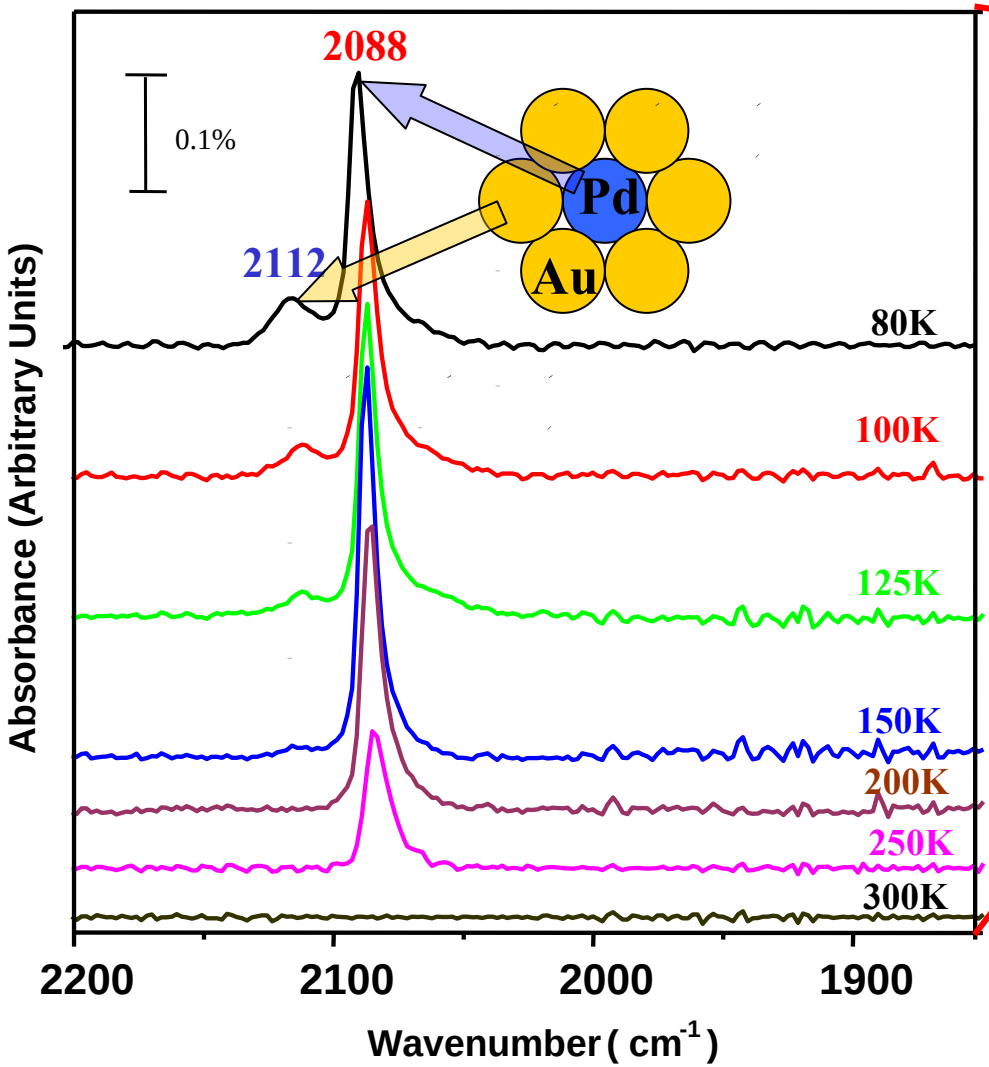
Pd dimers

Pd multimers

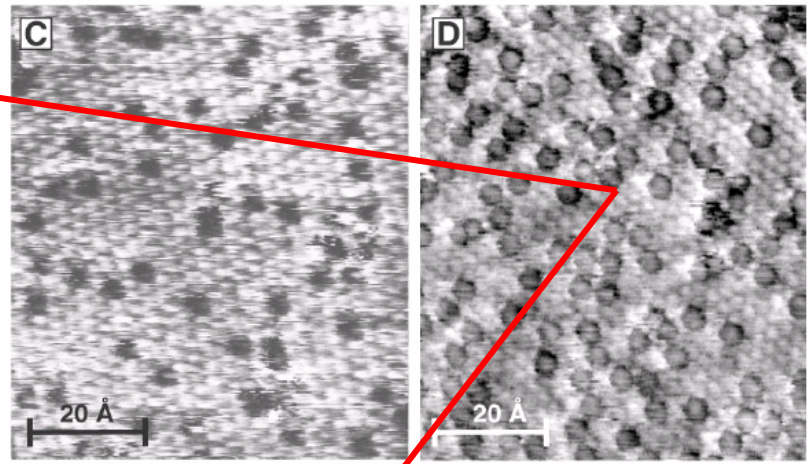
697 surface sites
86 Pd atoms
Surface Pd coverage = 12%

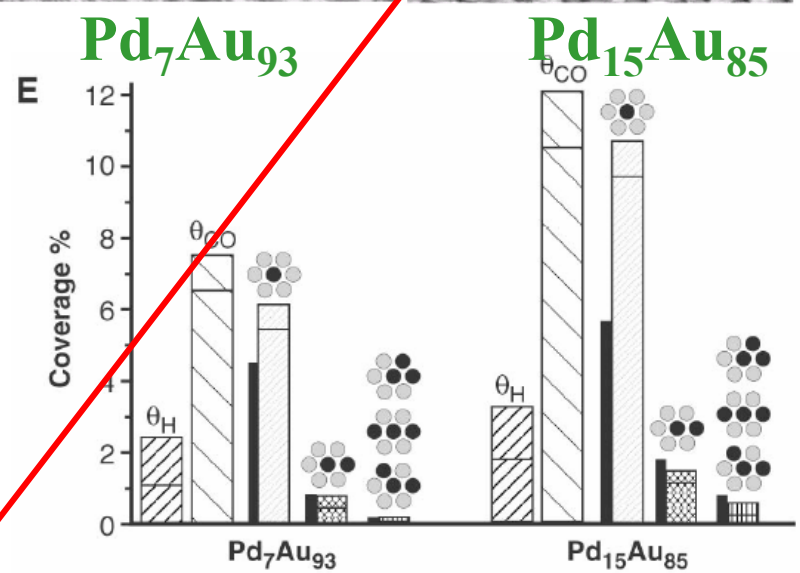
IRAS: CO on [(5ML Pd + 5MLAu)/Mo(110) + 800 K anneal]

Pd Atop site:U(CO atop) 2109 cm^{-1} ➔ 2088 cm^{-1}



STM: Pd (in dark) deposited onto Au(111)

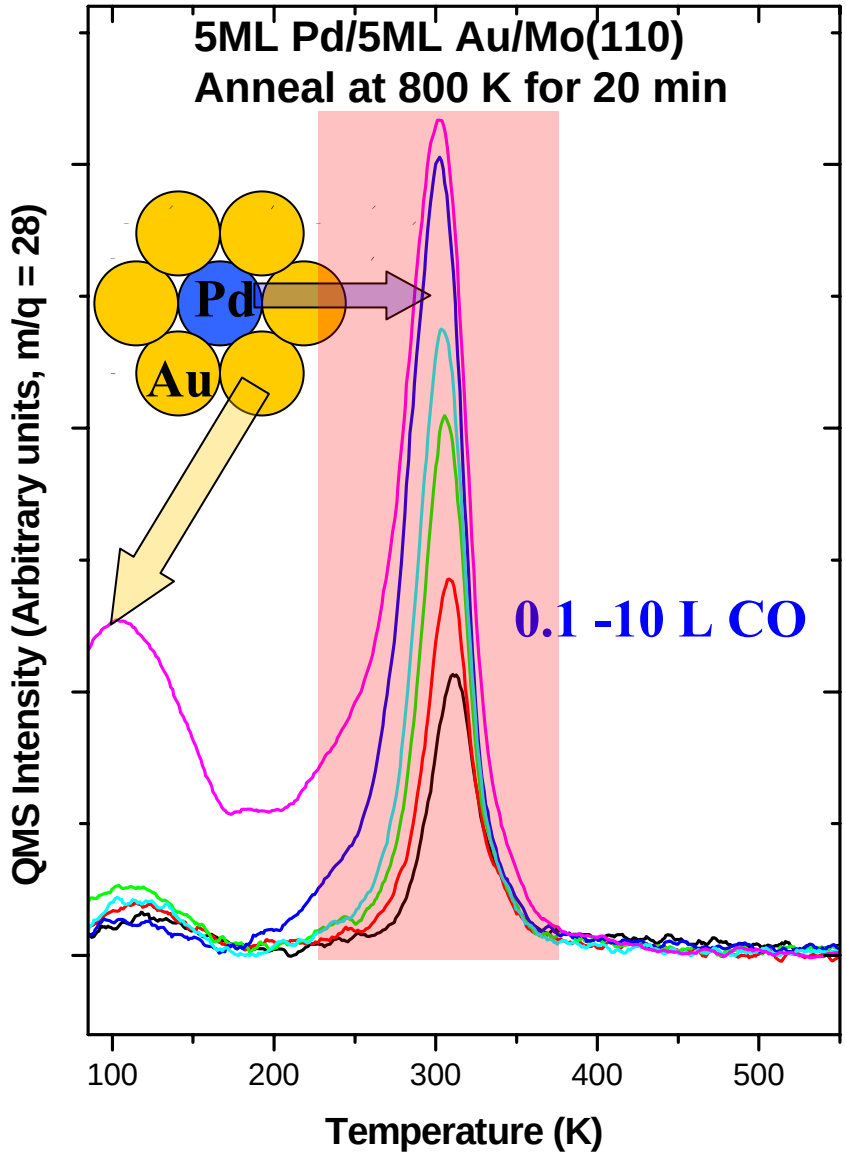


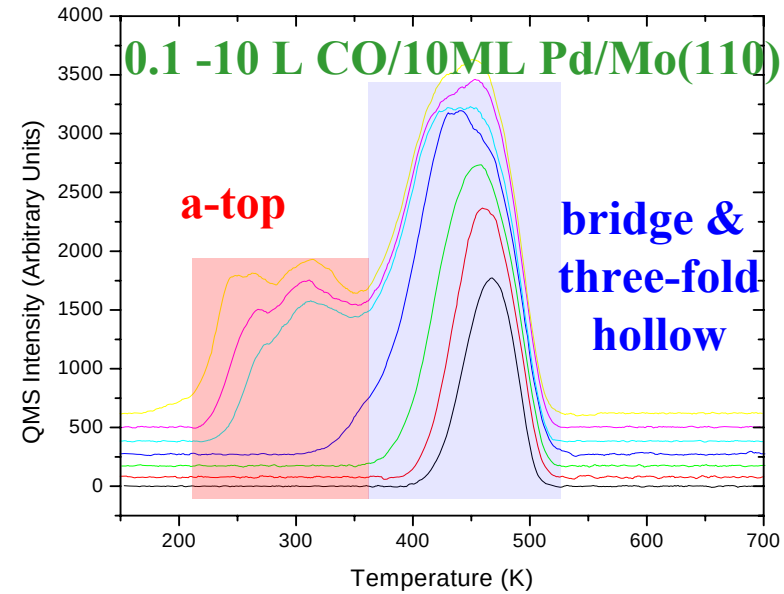


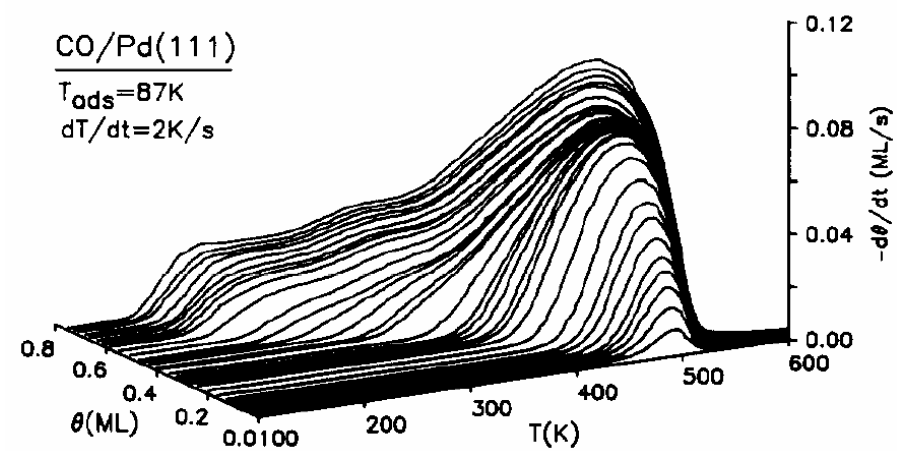
F. Maroun, F. Ozanam, O. M. Magnussen, R. J. Behm, Science, 293, 1811 (2001).

TPD: CO/(5ML Pd + 5 ML Au/Mo(110) + 800 K Anneal)

C.-W. Yi, K. Luo, T. Wei, D. W. Goodman, JPCB, 2005, 109, 18535

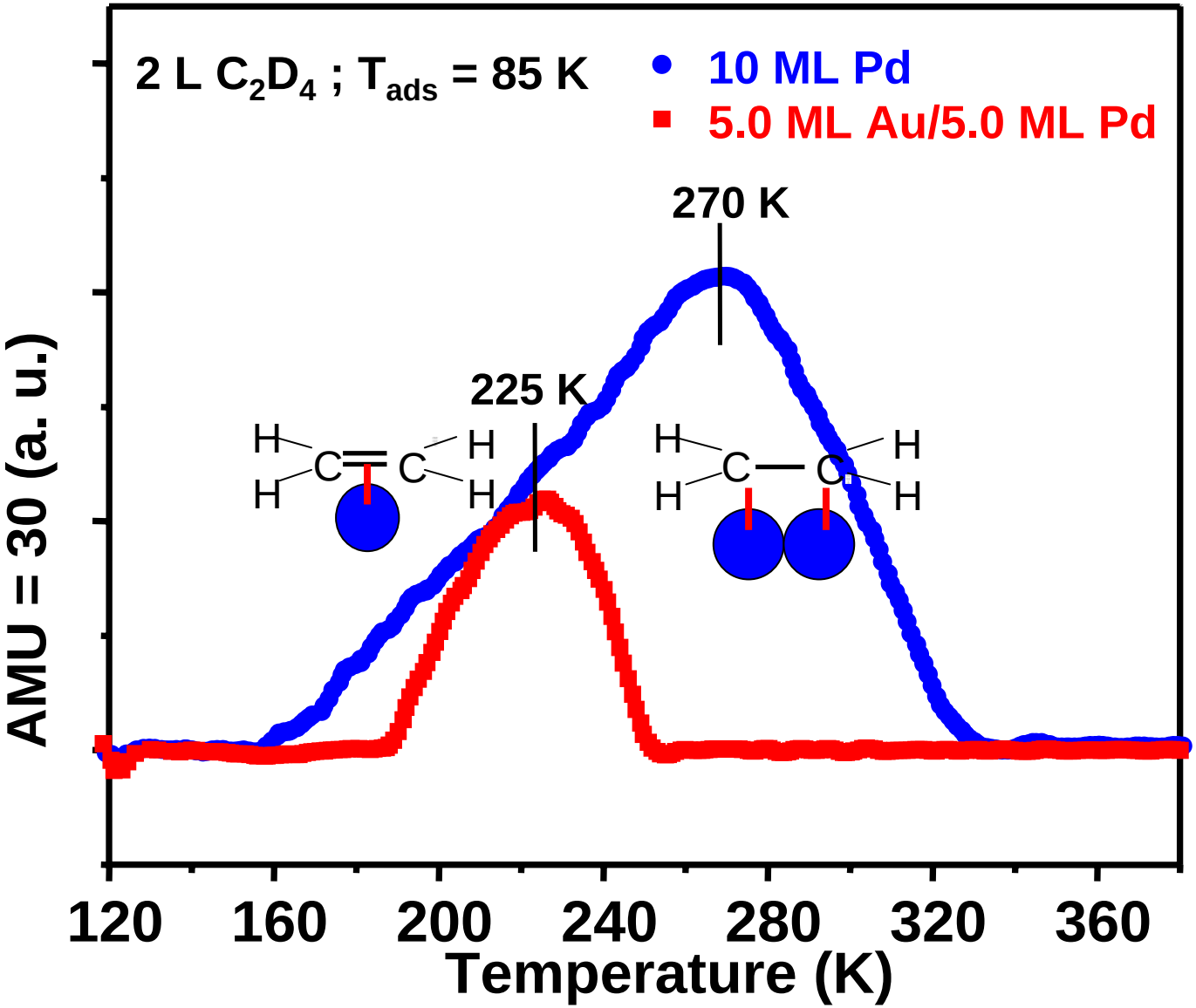






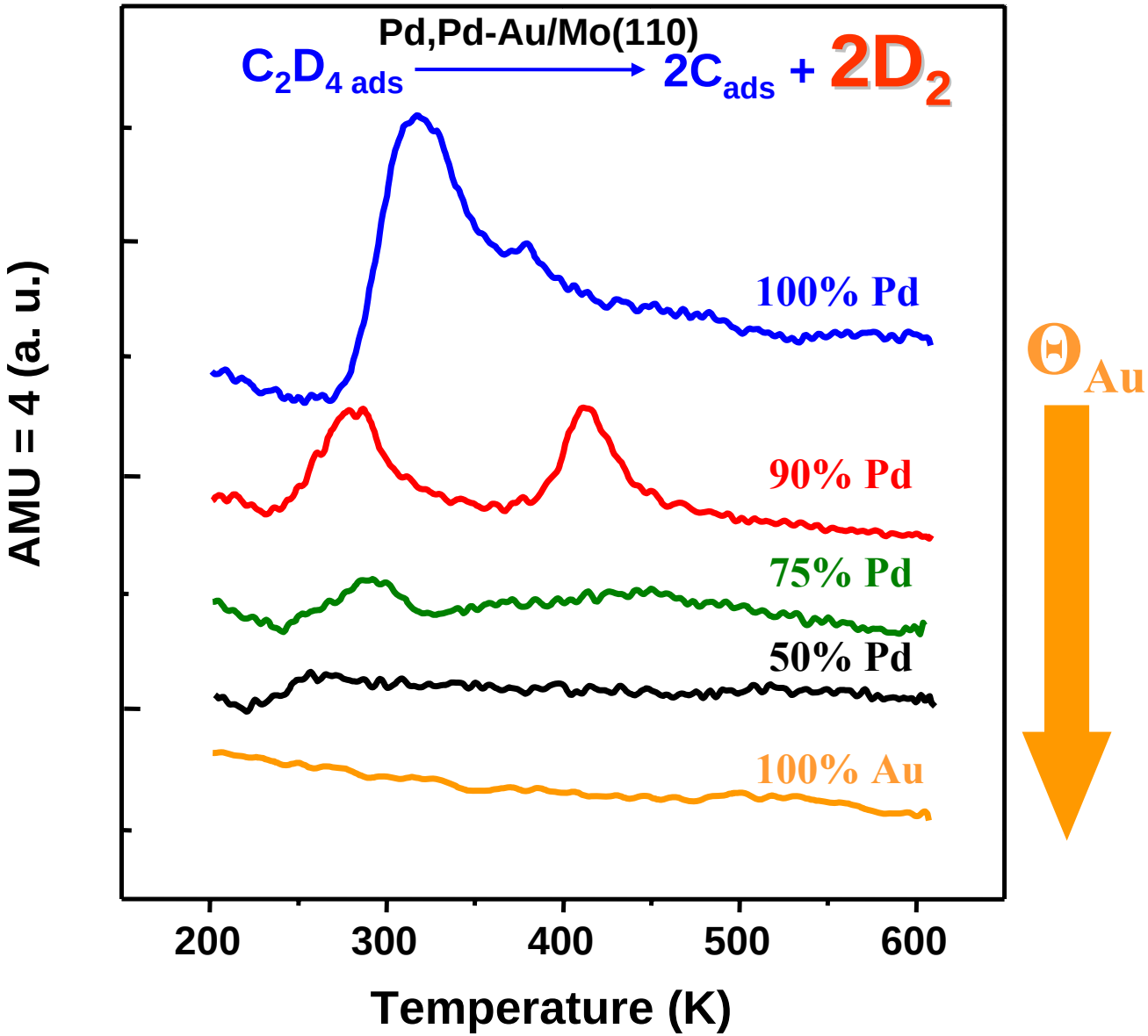
X. Guo and J. T. Yates, JCP 90(11), 6761 (1989)

TPD: C_2H_4 from Pd vs. Pd-Au



Significant destabilization of ethylene on Pd-Au compared with pure Pd

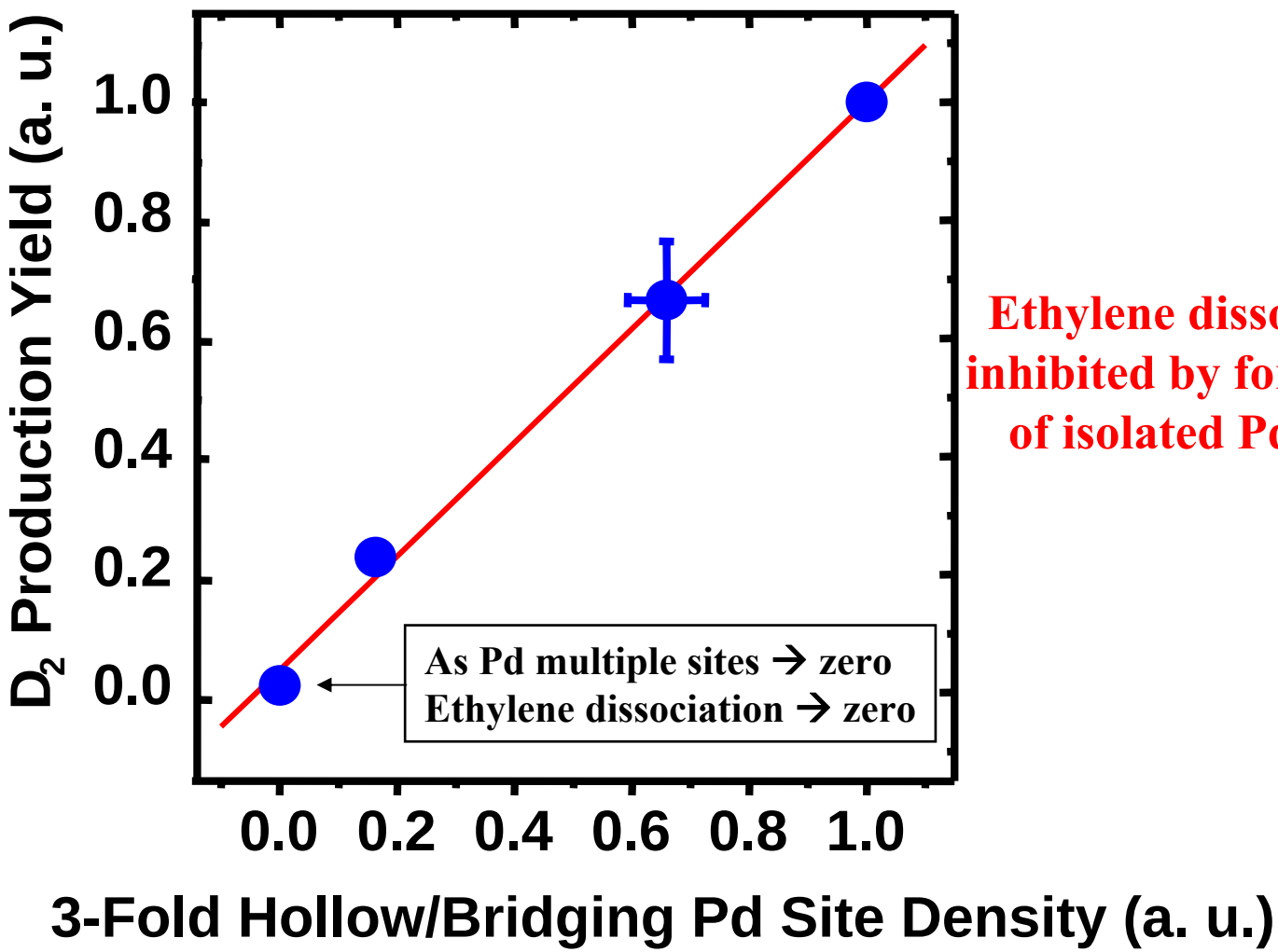
TPD: Ethylene decomposition on Pd-Au



Hydrogen from adsorbed ethylene vs. density of multiple Pd sites in Pd-Au

Pd, Pd-Au/Mo(110)

$$C_2D_{4\,ads} \longrightarrow 2C_{ads} + 2D_2$$

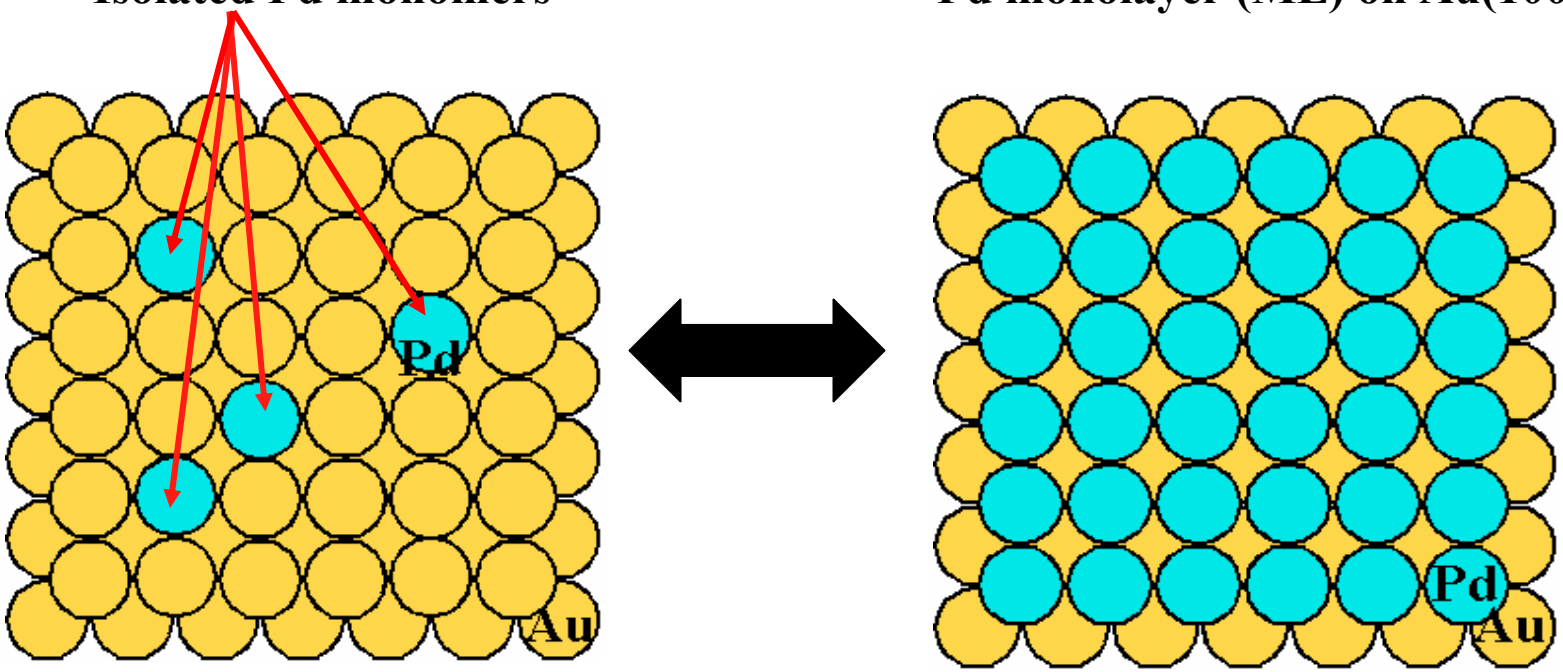


Ethylene dissociation inhibited by formation of isolated Pd sites!

Isolated Pd as active site for VA synthesis??

M. S. Chen, D. Kumar, C.-W. Yi and D. W. Goodman, Science, 310, 291(2005).

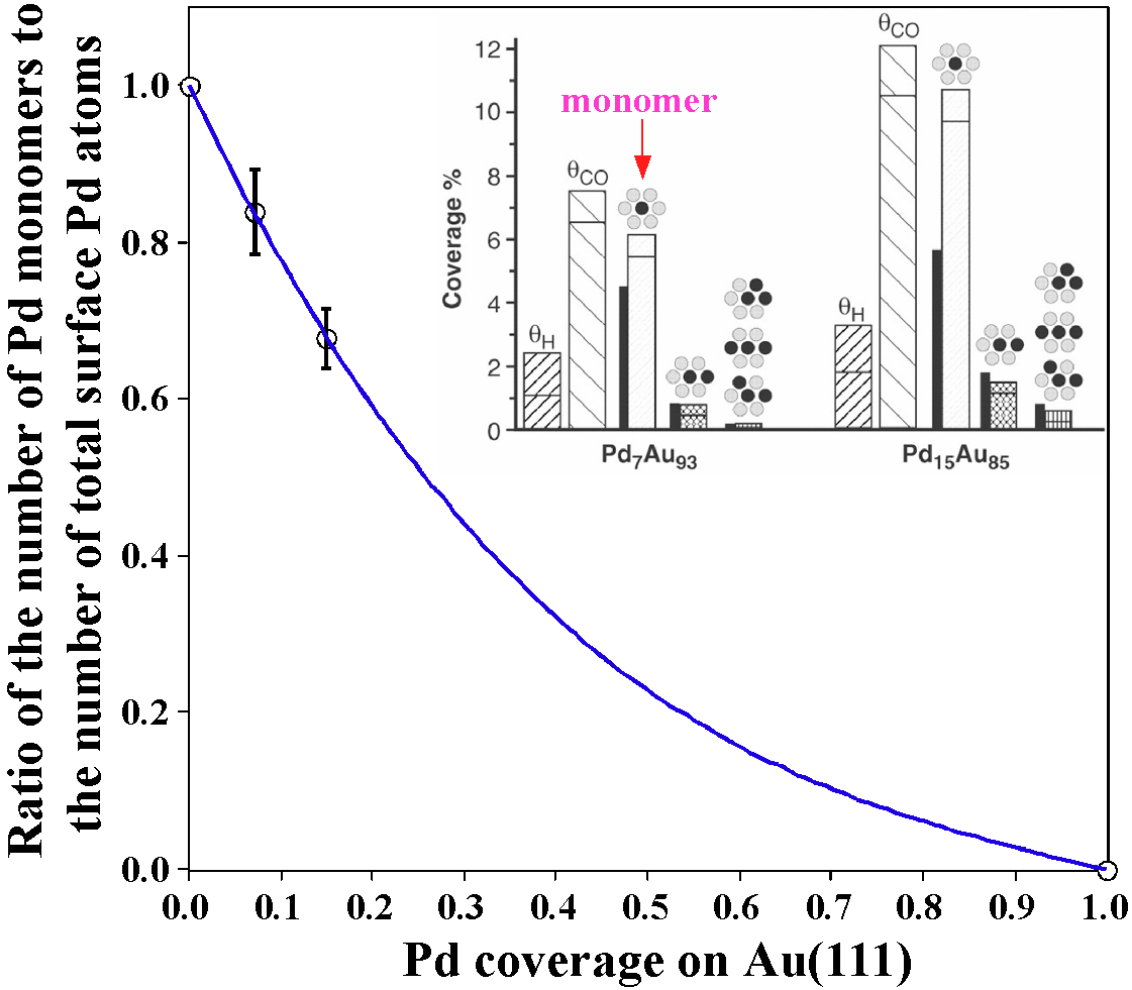
Isolated Pd monomers | **Pd monolayer (ML) on Au(100)**



Low Pd coverage ← **High Pd coverage**

Question: Does the VA activity of Pd change as a function of Pd coverage on a per atom basis?

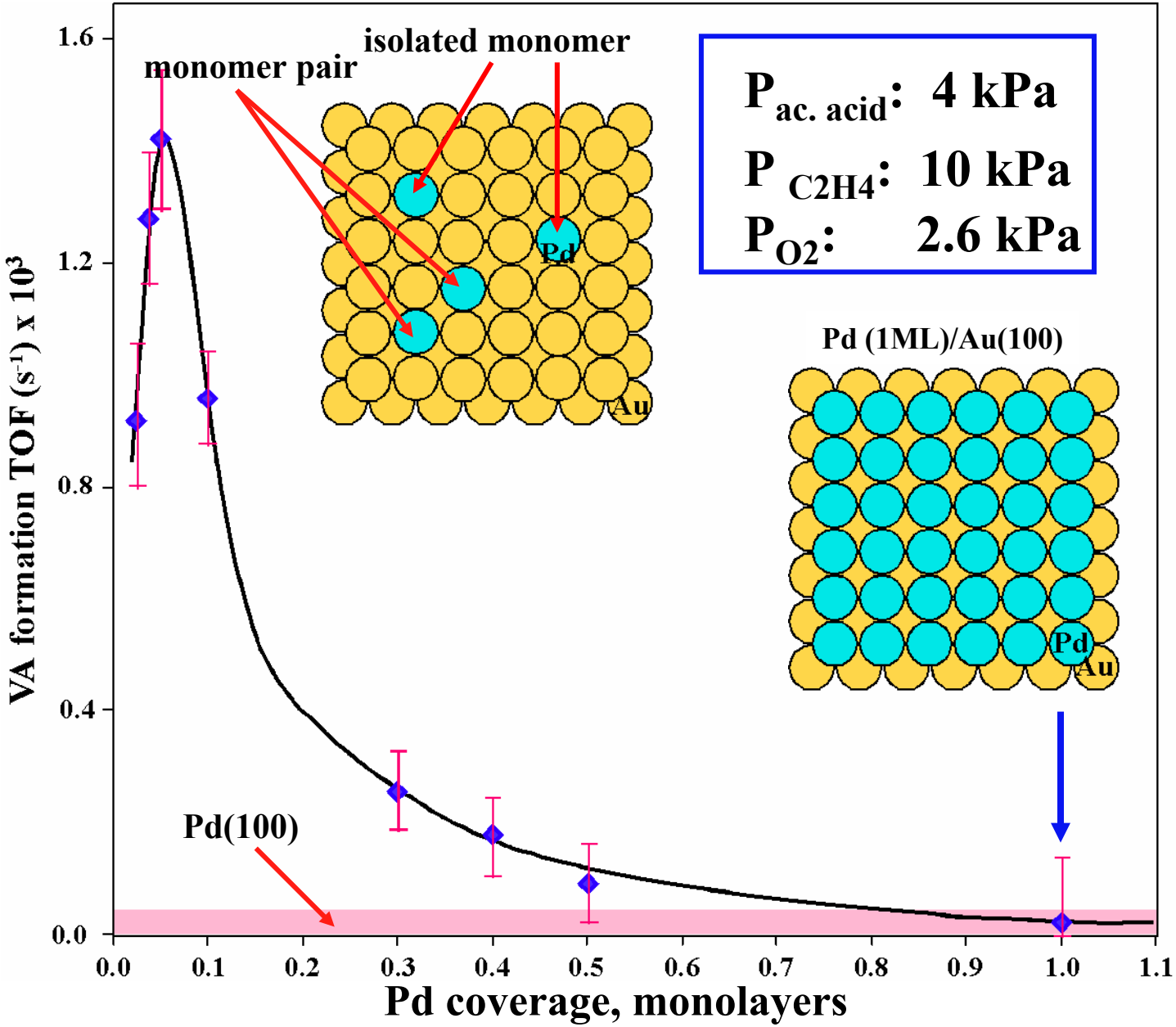
Pd monomers on Au(111)



F. Maroun,F. Ozanam, O. M. Magnussen, R. J. Behm, Science, 293, 1811 (2001).

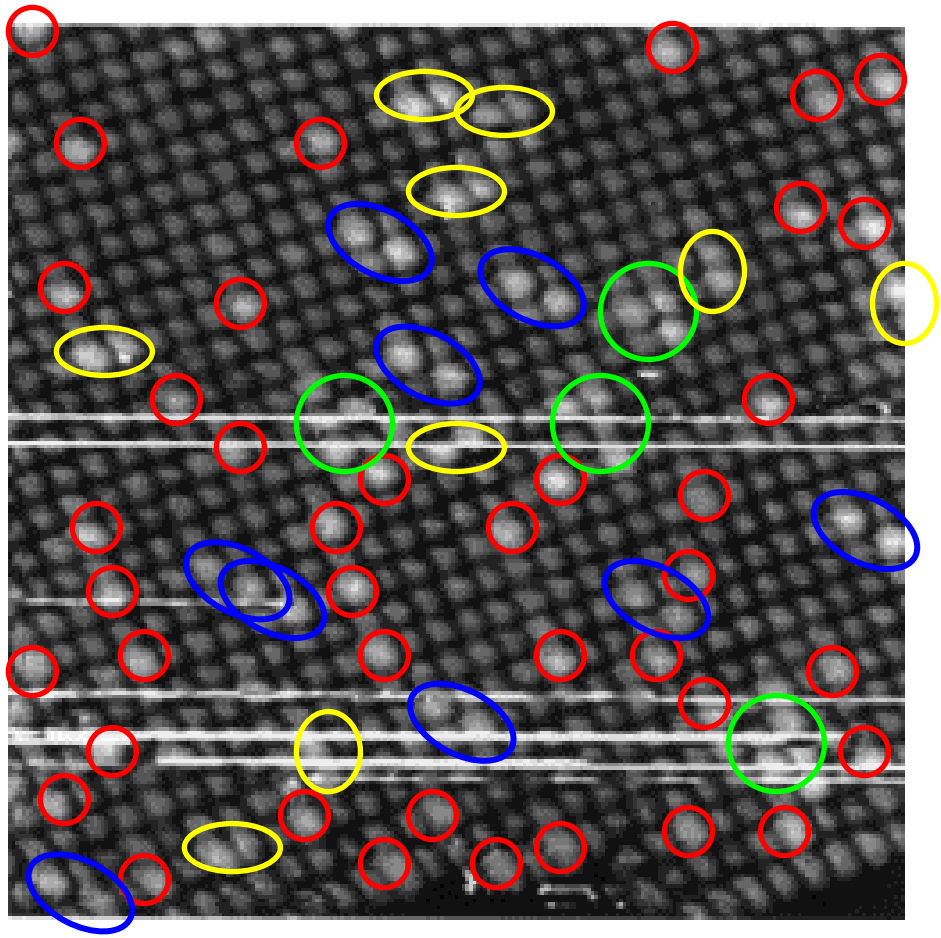
VA synthesis on Pd/Au(100) at 453 K

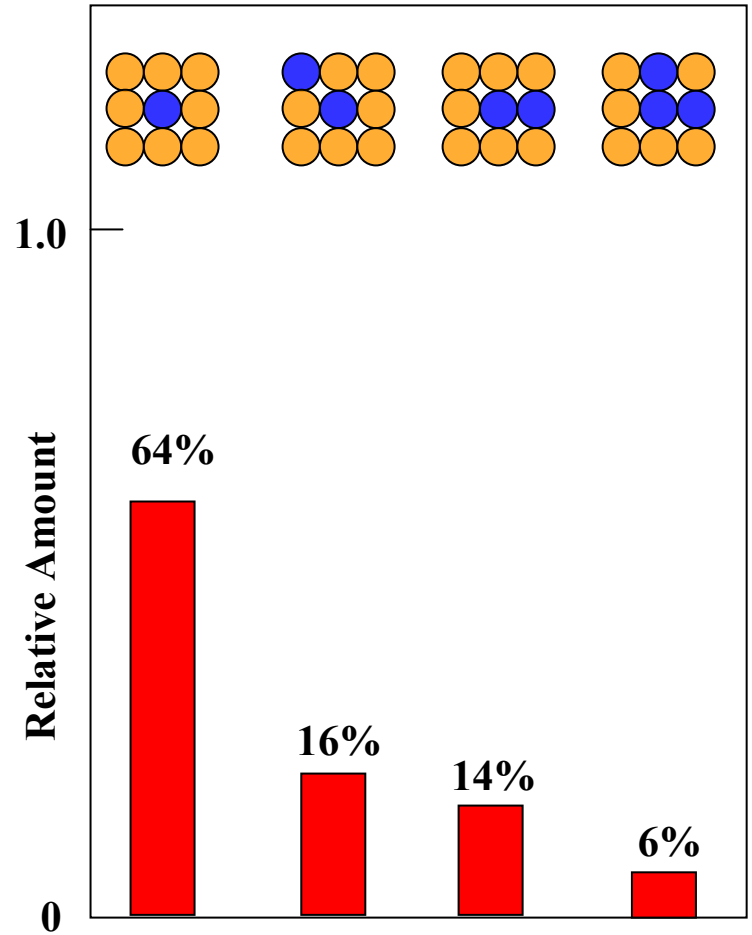
M. S. Chen, D. Kumar, C.-W. Yi and D. W. Goodman, Science, 310, 291(2005).



STM: $Au_3Pd(100)$ Alloy Surface

Aschoff, et al., *Surf. Sci.* 415 (1998) L1051





Pd monomers

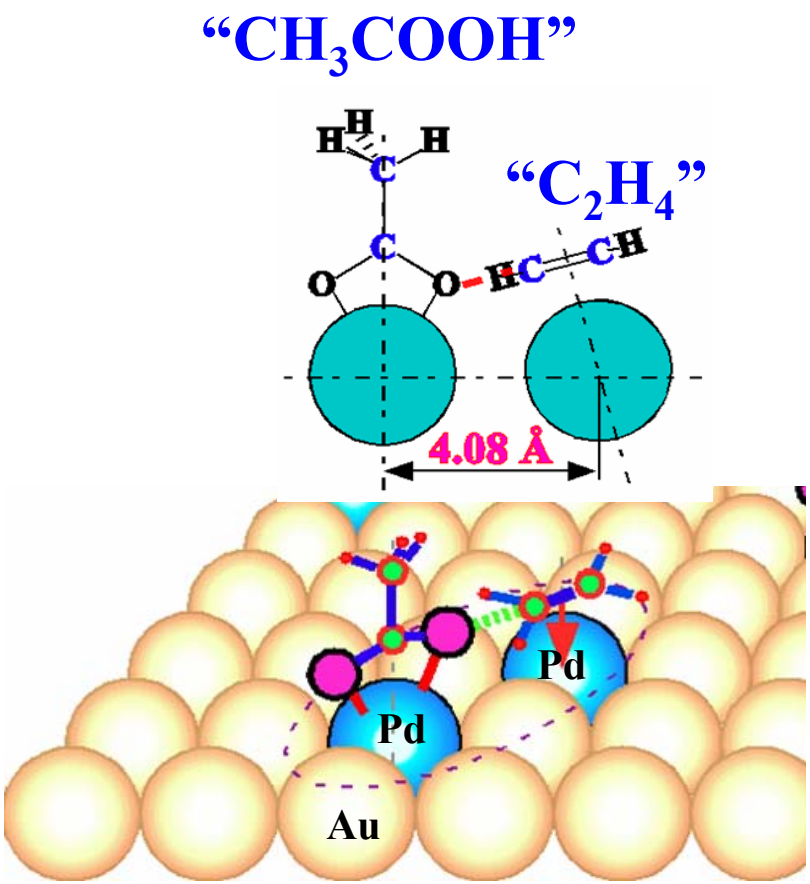
Pd monomer pairs

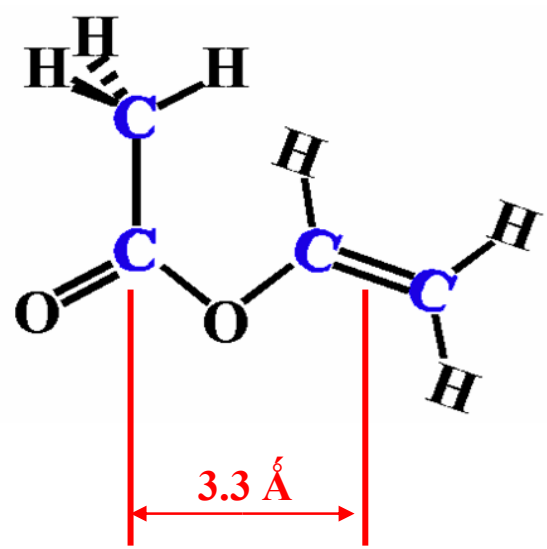
Pd dimers

Pd multimers

697 surface sites
95 Pd atoms
Surface Pd coverage = 14%

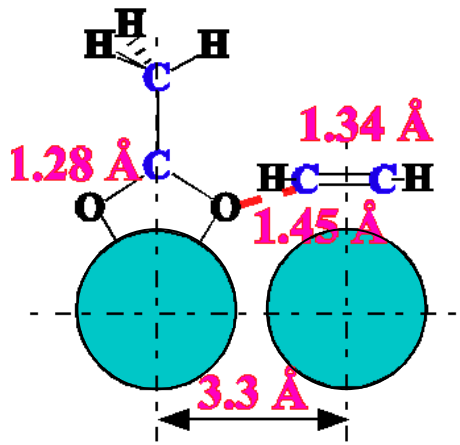
Coupling of vinyl & acetate species on Pd-Au alloy surface to form vinyl acetate



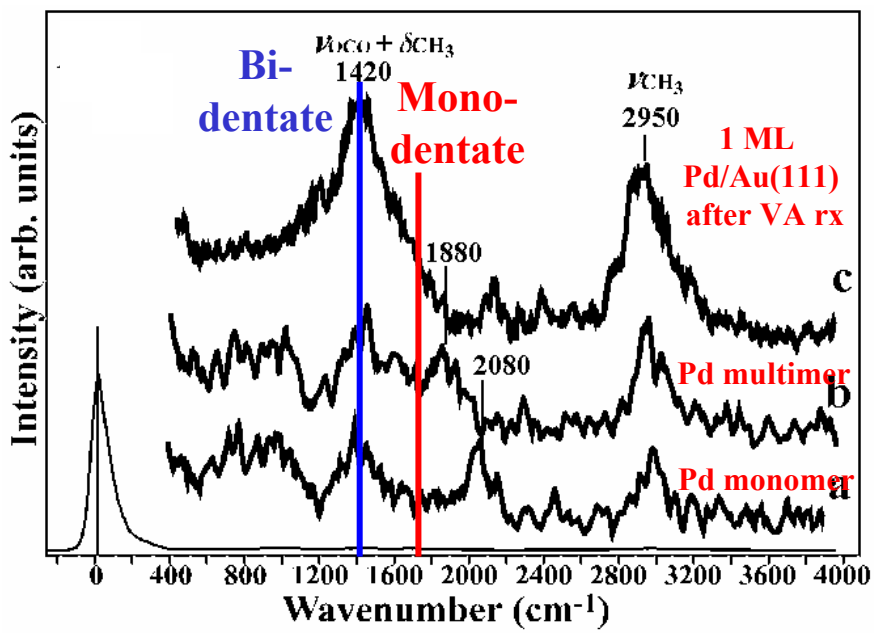


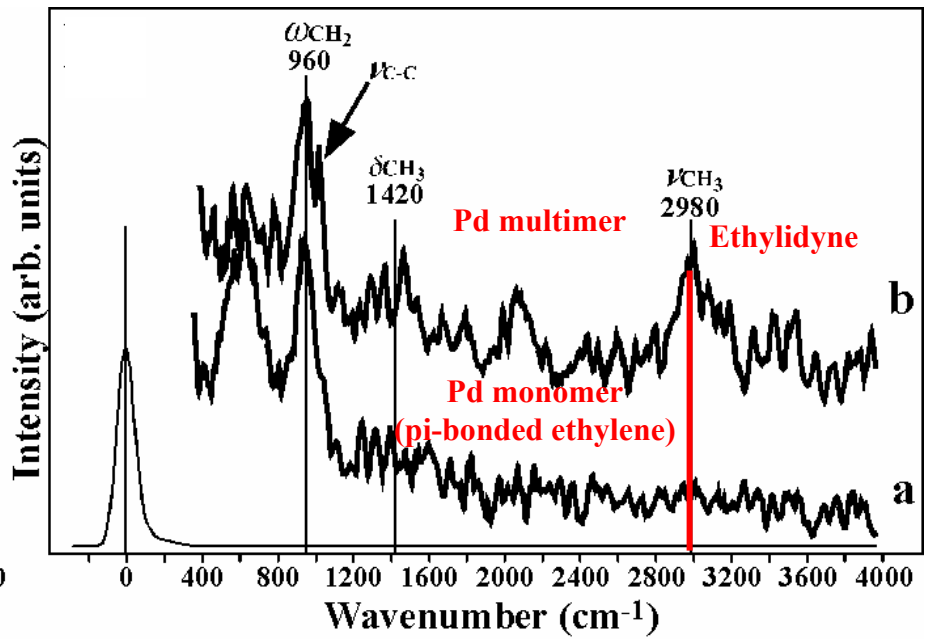
HREELS: Acetic Acid & Ethylene on Pd Monomer

Acetic Acid Adsorption Pd/Au(111)



Ethylene Adsorption Pd/Au(111)

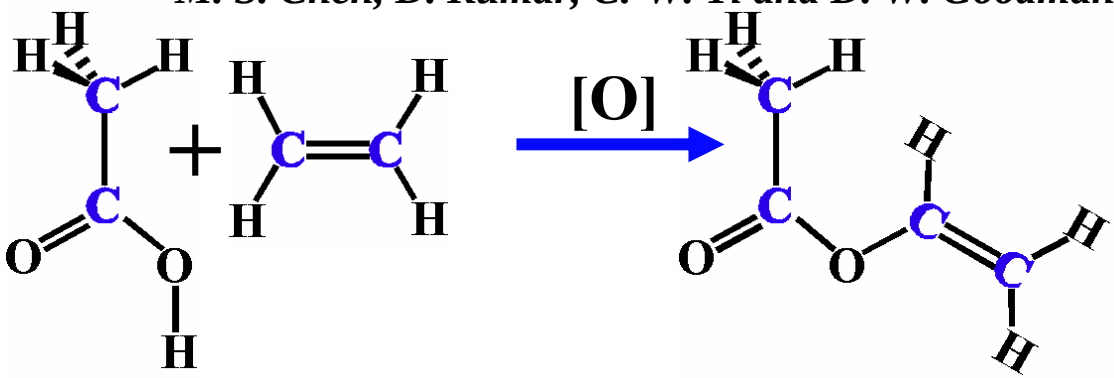


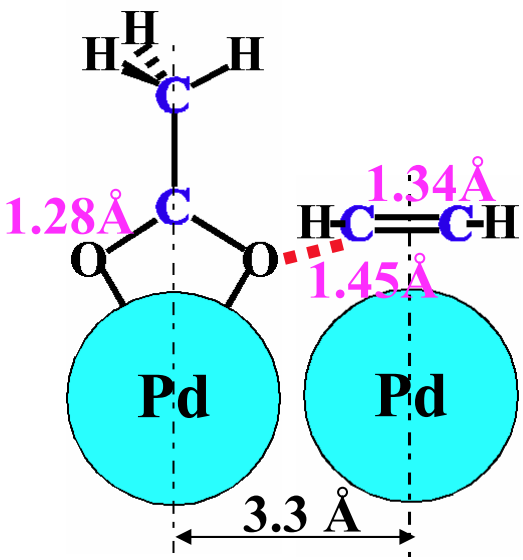


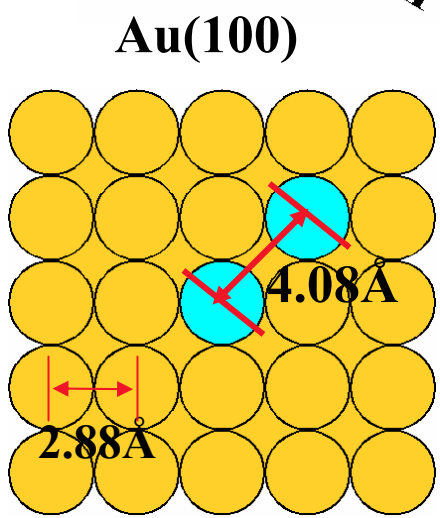
M.S. Chen, K. Luo, T. Wei, Z. Yan, D. Kumar, C.-W. Yi and D.W. Goodman, 2006

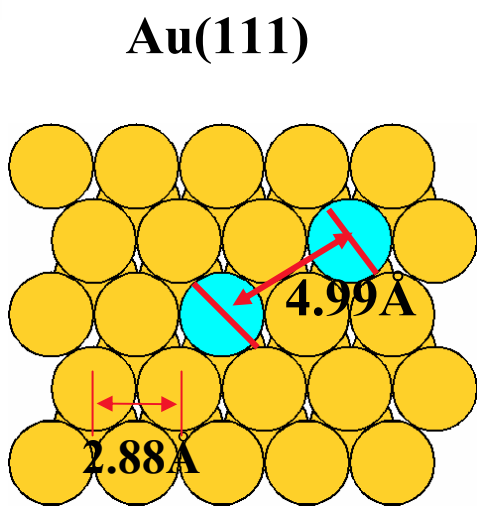
Model of VA synthesis reactive sites on Pd/Au

M. S. Chen, D. Kumar, C.-W. Yi and D. W. Goodman, Science, 310, 291(2005).





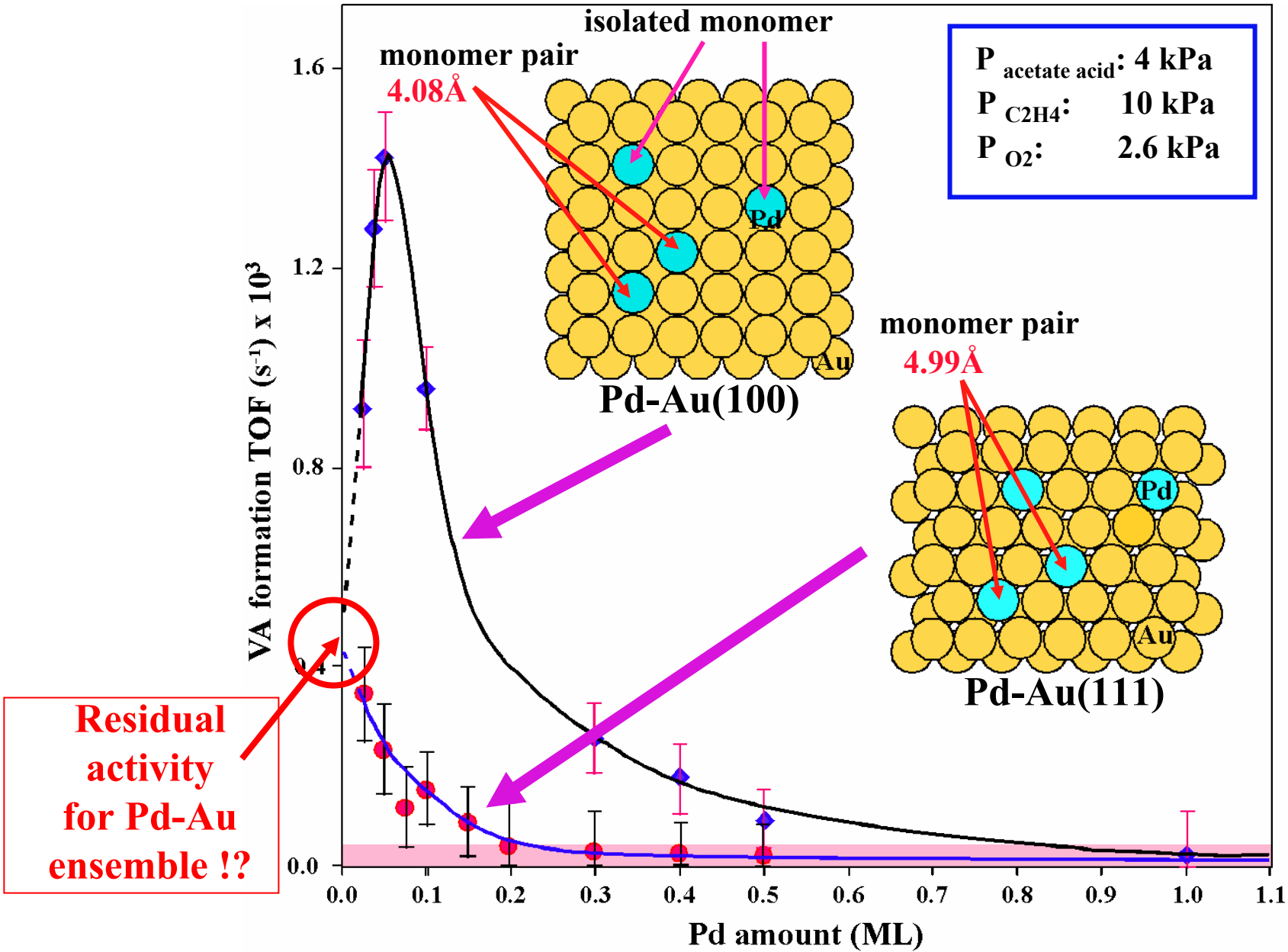




Optimized distance between two active sites

VA synthesis on Pd/Au(111) vs. Pd/Au(100) at 453 K

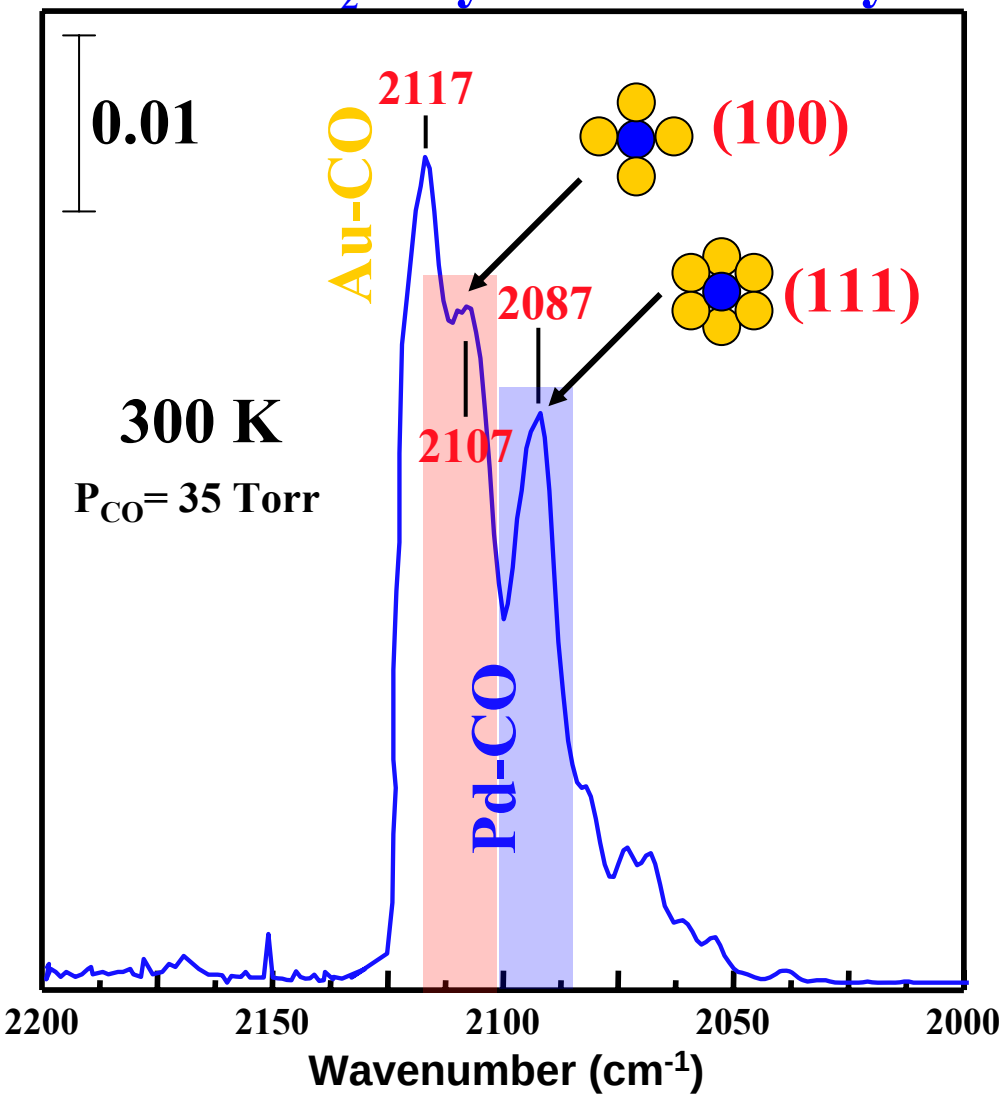
M. S. Chen, D. Kumar, C.-W. Yi and D. W. Goodman, Science, 310, 291(2005).

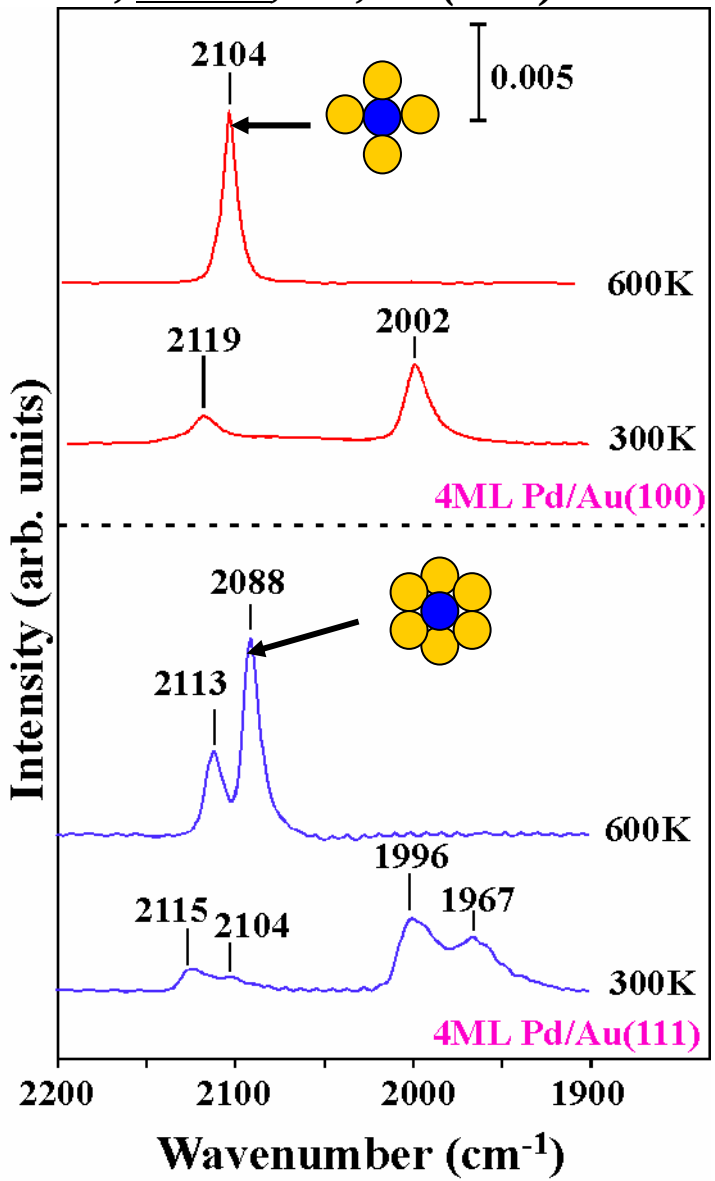


DRIFTS/IRAS of CO/Pd-Au

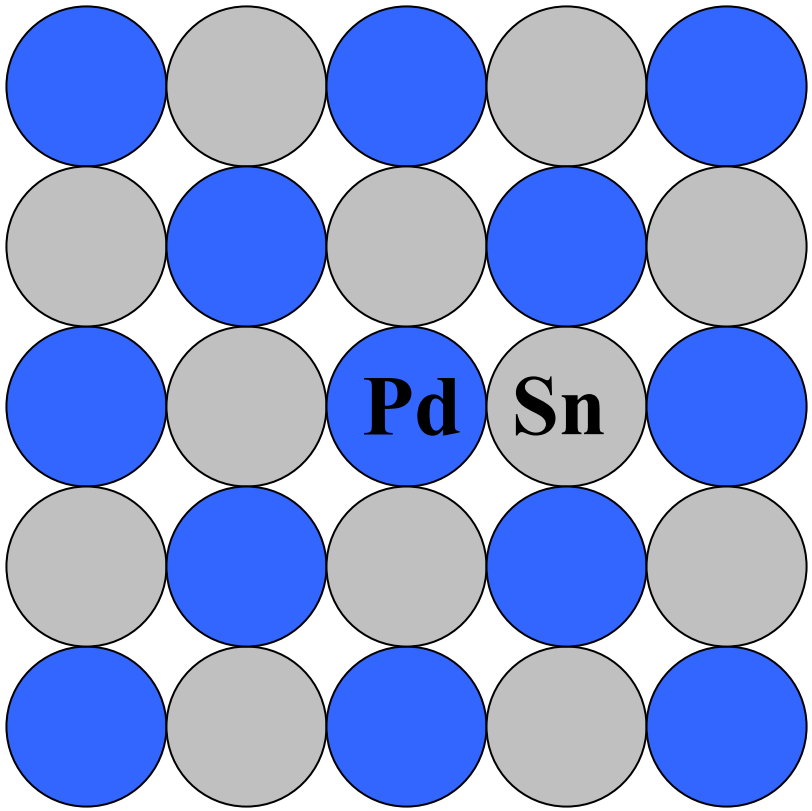
M. S. Chen, D. Kumar, C.-W. Yi and D. W. Goodman , Science, 310, 291(2005).

Pd-Au/SiO_2 vinyl acetate catalyst



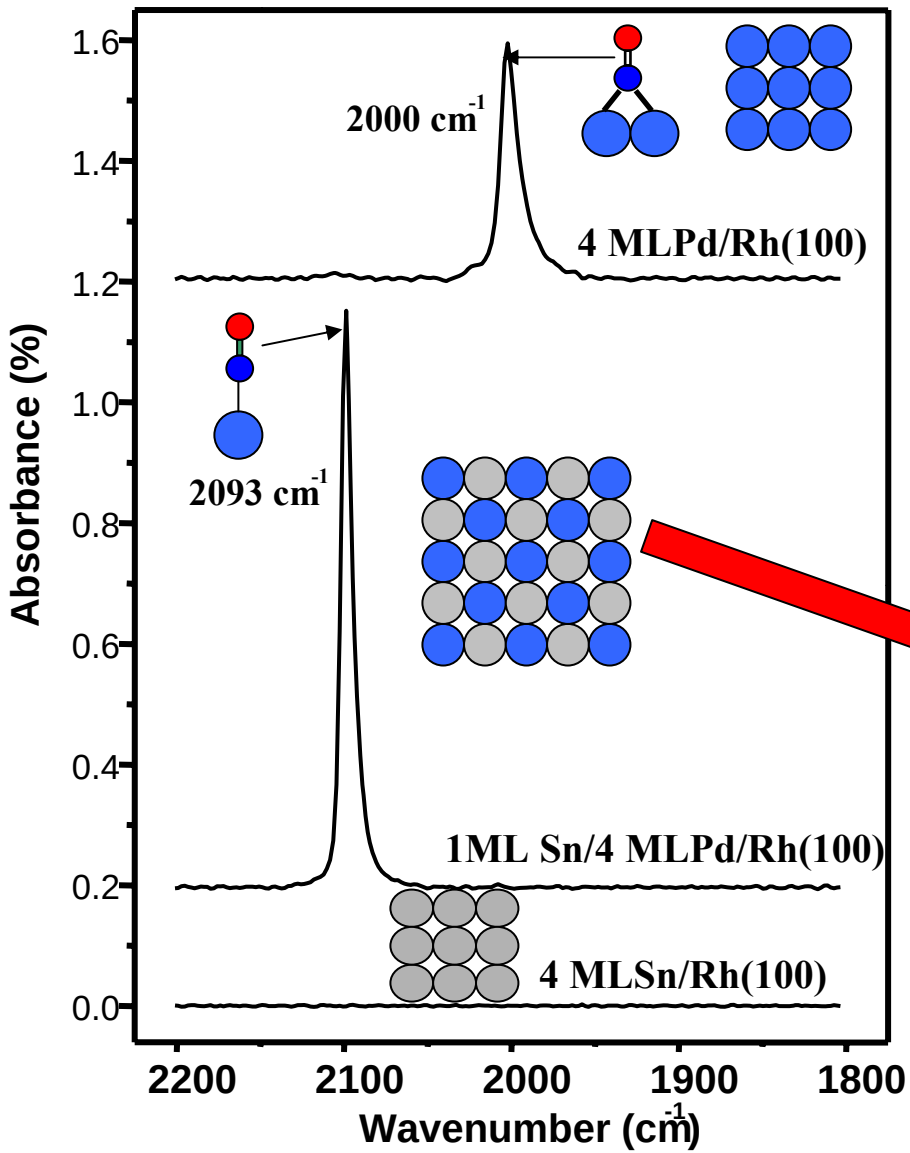


Optimum Pd-X Configuration



e.g. Pd(100)-c(2x2)-Sn

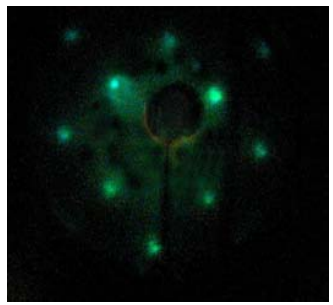
Pd-Sn Alloy Surfaces



4 ML Pd/Rh(100)

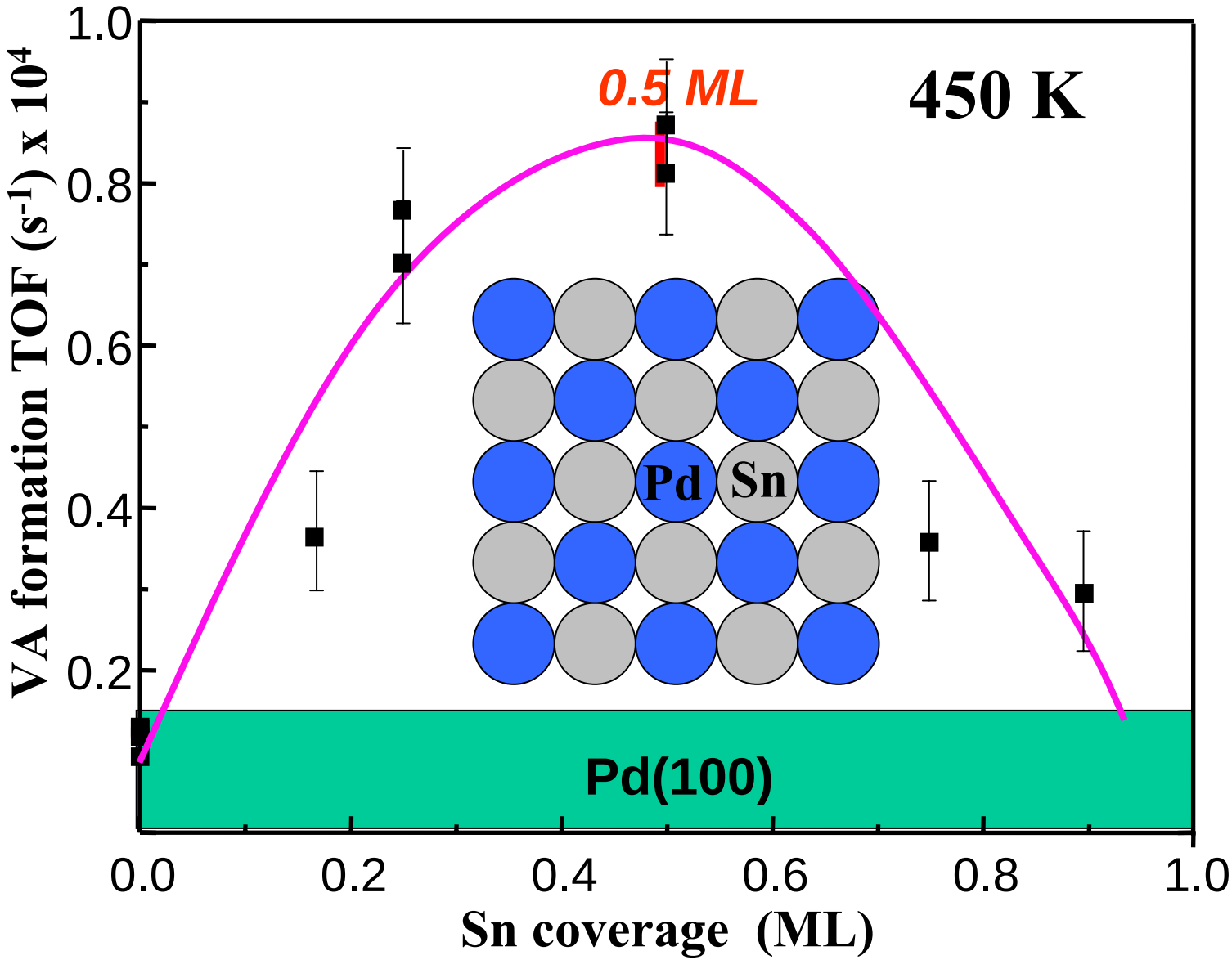
Clean Rh(100) surface

1 ML Sn/4 ML Pd/Rh(100) annealed at 700 K for 1 minute



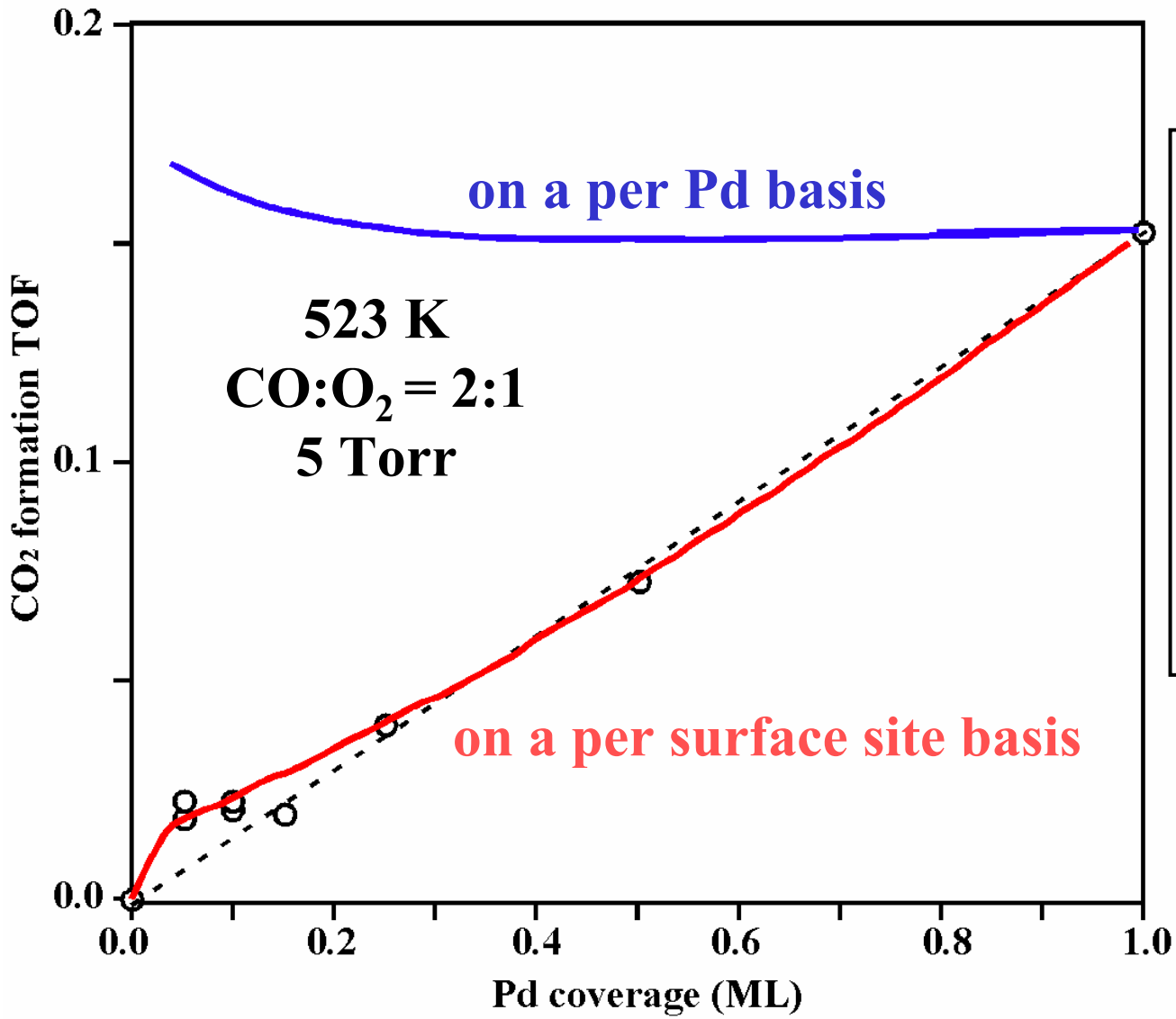
The film was annealed at 700 K for 1 minute; IRAS data were acquired at 80 K with saturation CO.

VA Synthesis on Sn-Pd(100)



D. Kumar, M. S. Chen, and D. W. Goodman , 2006.

CO oxidation on Pd/Au(111)



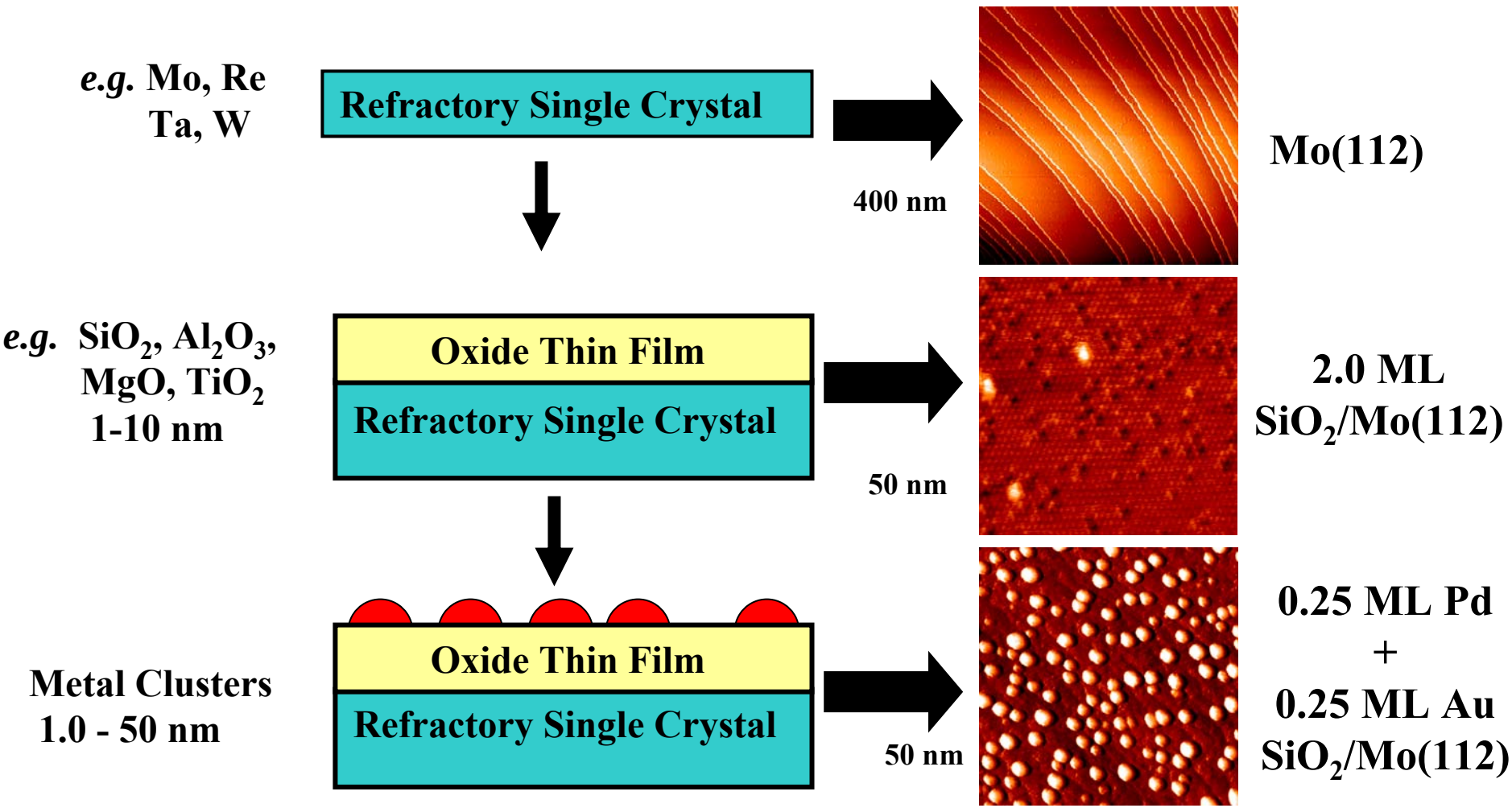
- Pd monomers & contiguous Pd sites have similar activities for CO oxidation
- Monomer can activate O_2

Pd-Au Catalysis:

Planar Surfaces → **Supported Catalysts**

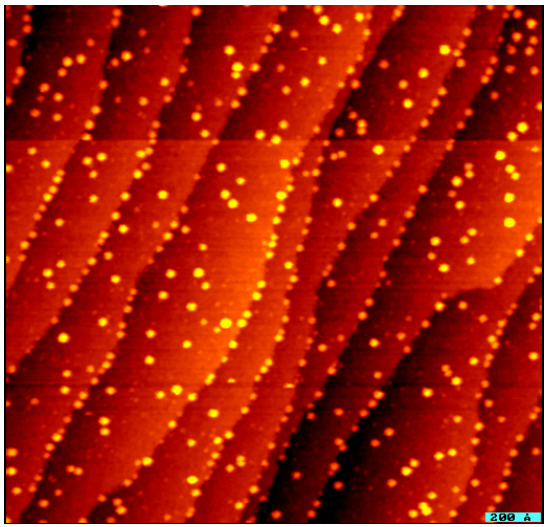
Model Oxide-Supported Pd-Au Catalysts

Luo, Wei, Yi, Axnanda, Goodman, JPC, 2005,109,23517



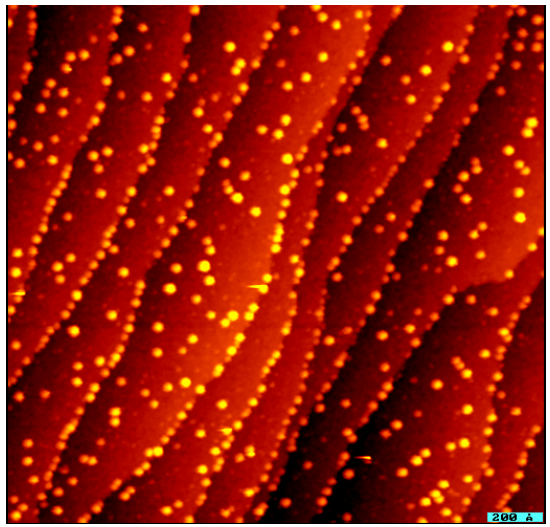
Synthesis of Mixed-Metal Particles

200 nm



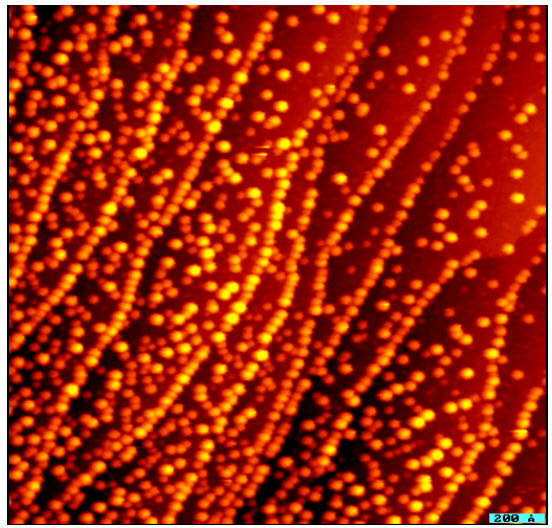
Ag/TiO_2

200 nm

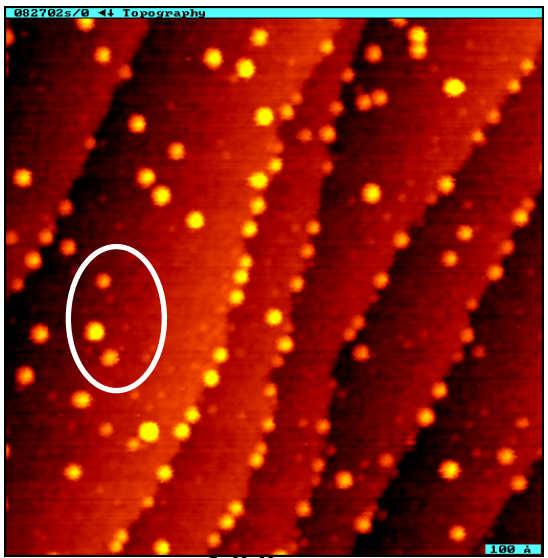


+1 min Au

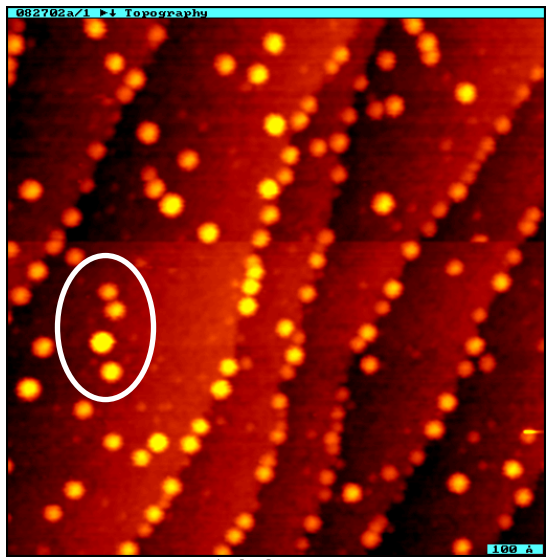
200 nm



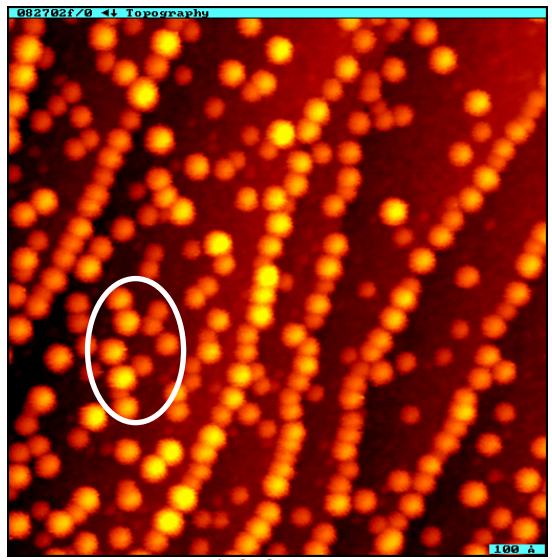
+9 min Au AgAu alloy



100 nm



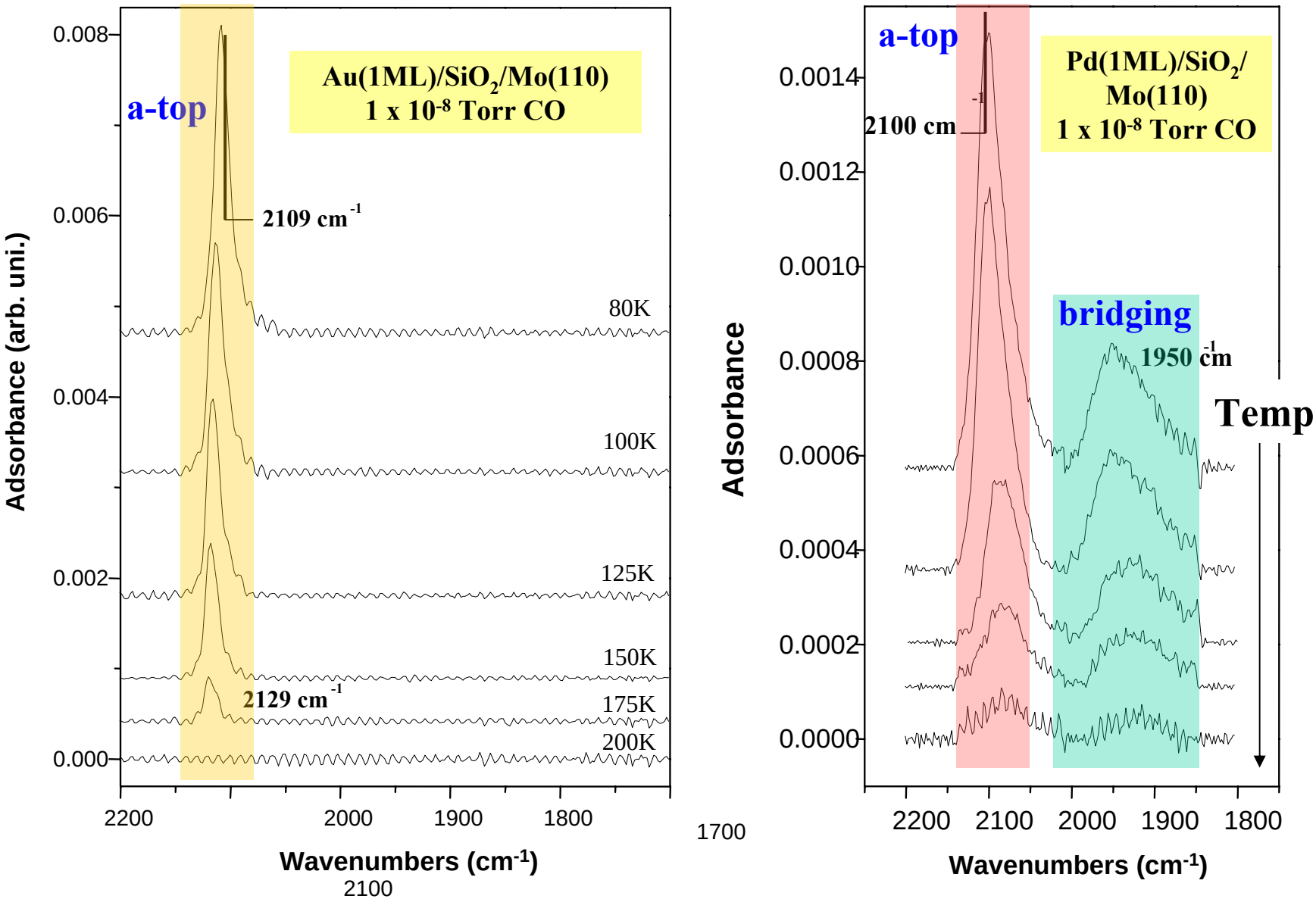
100 nm



100 nm

IRAS: CO/Pd & Au/SiO_2/Mo(110)

Luo, Wei, Yi, Axnanda, Goodman, JPC, 2005,109,23517

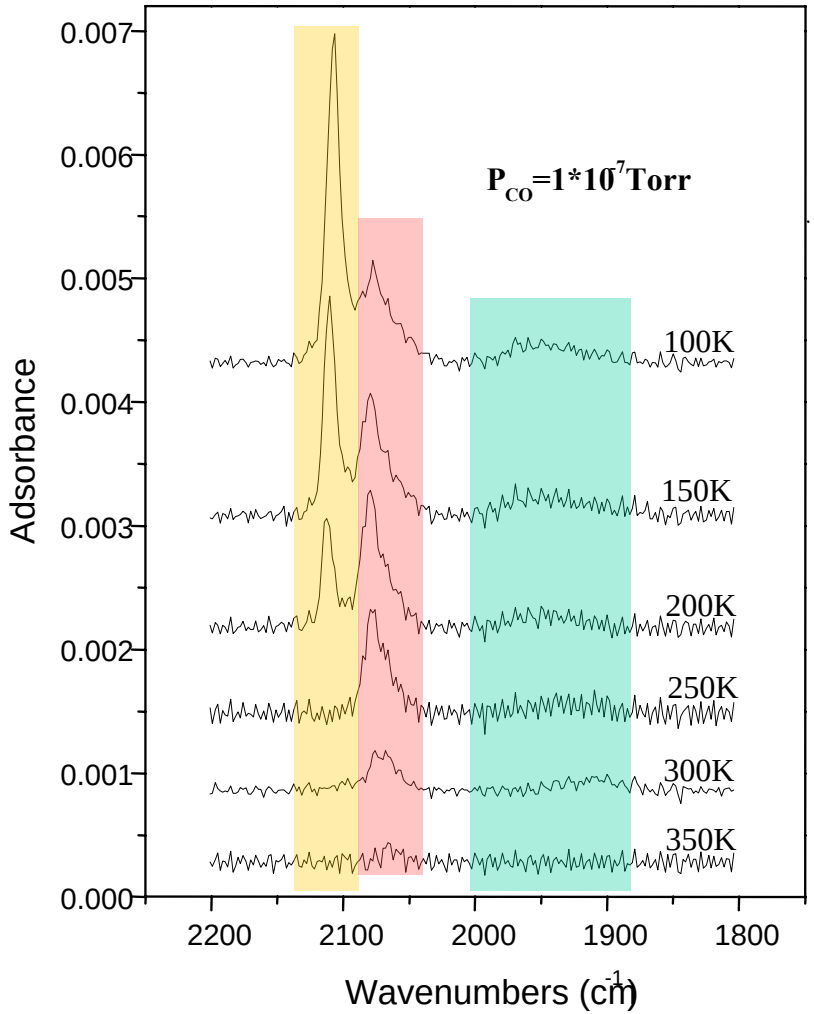


IRAS: CO/(Pd+Au)/SiO_2/Mo(110)

Luo, Wei, Yi, Axnanda, Goodman, JPC, 2005,109,23517

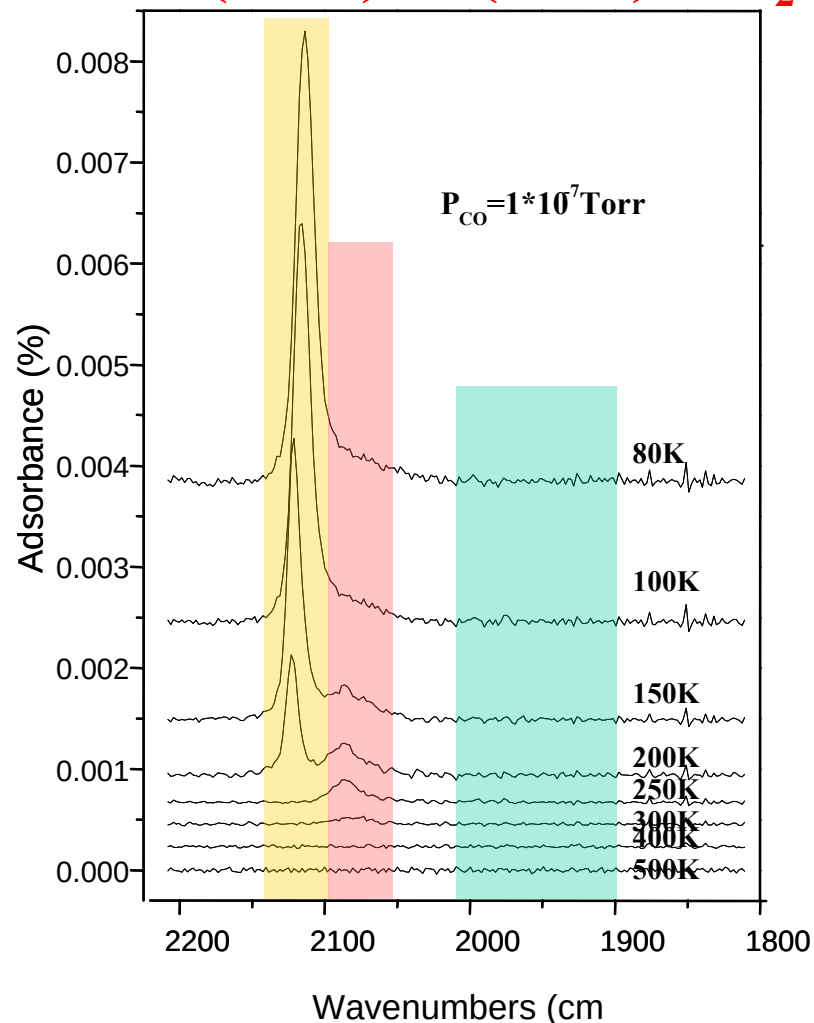
33%Au

Au(1ML)/ Pd(2ML)/SiO_2



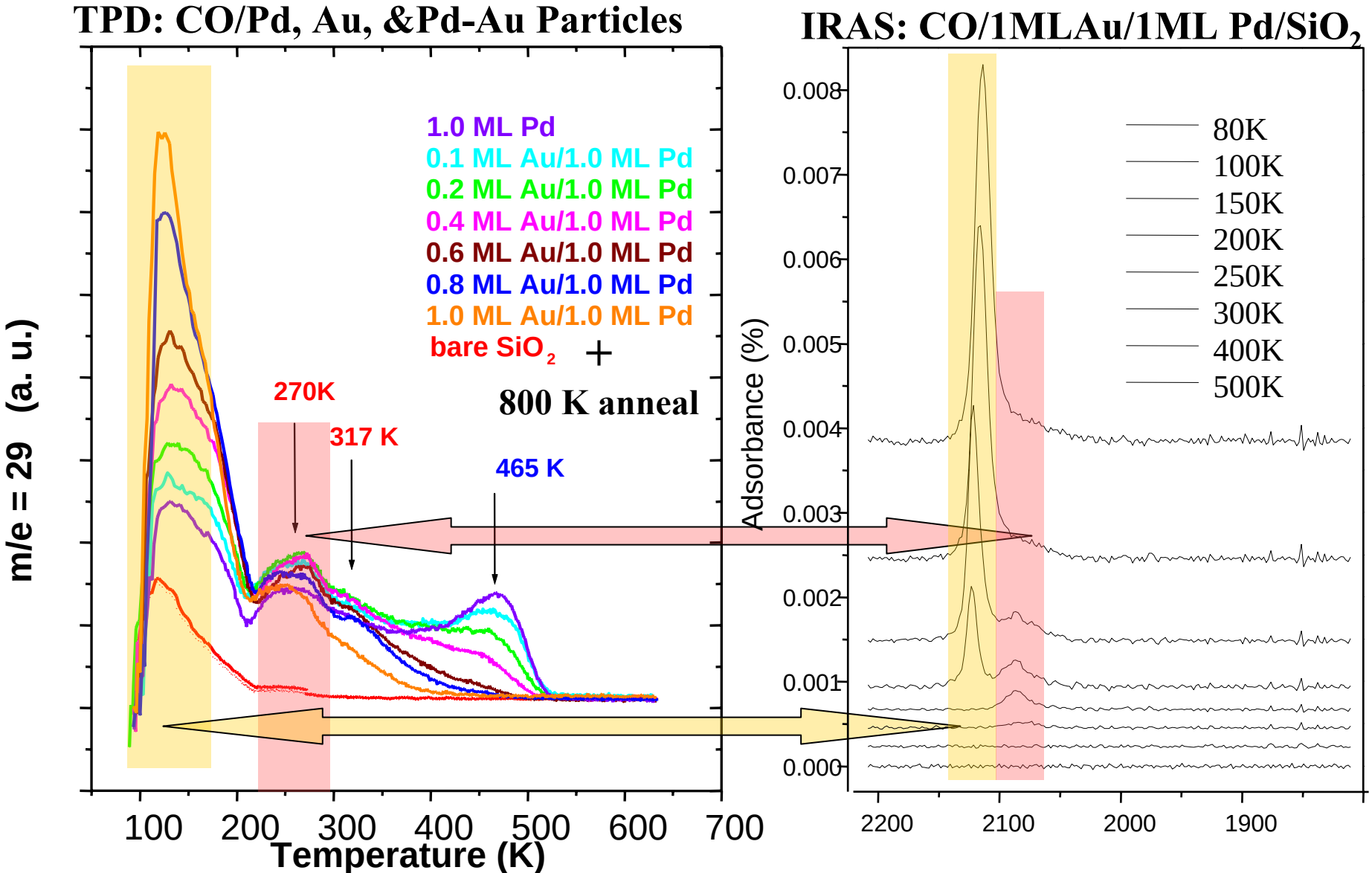
50% Au

Au(1ML)/Pd(1ML)/SiO_2

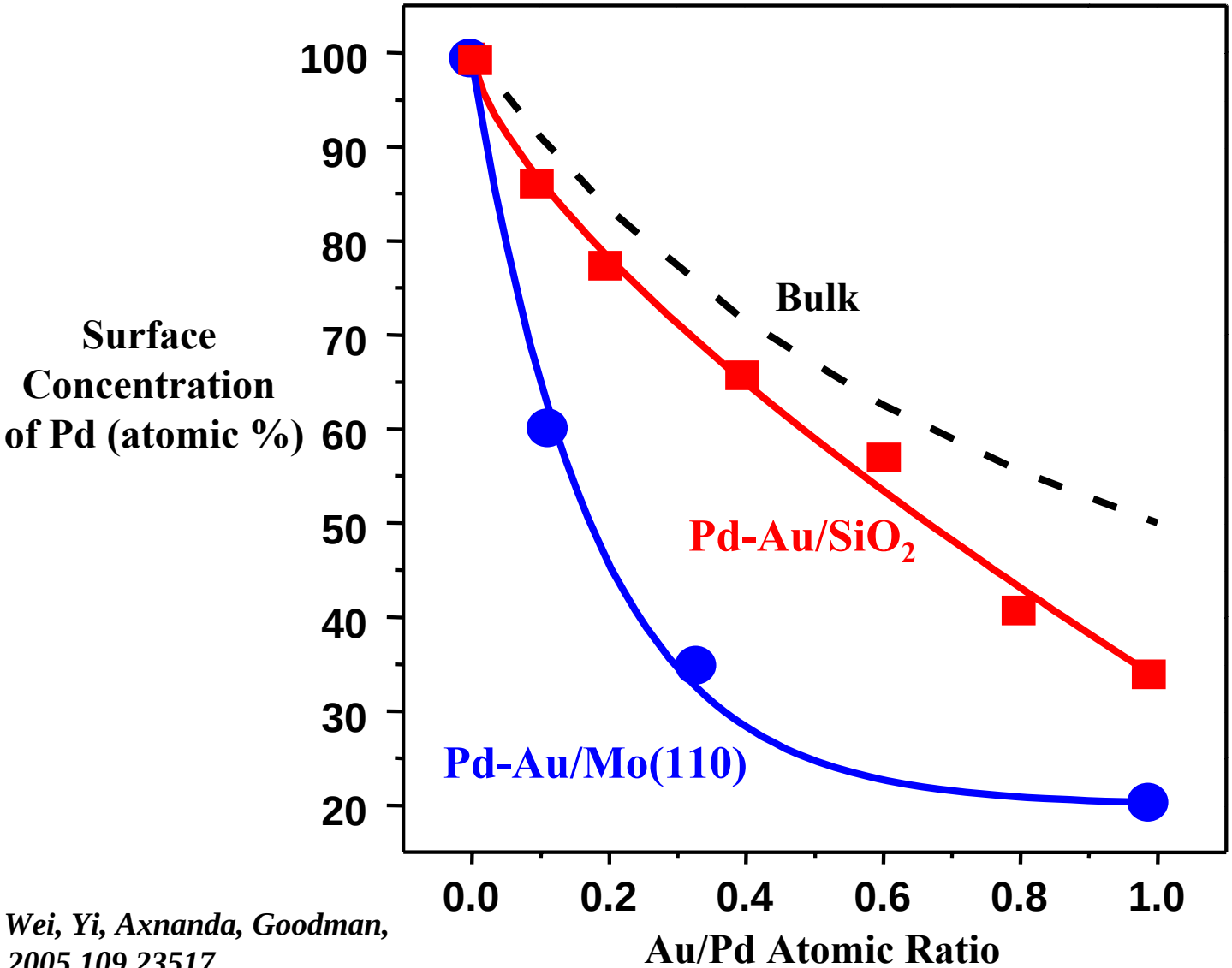


TPD & IRAS: CO on SiO_2-supported Pd, Au, and Pd/Au Particles

Luo, Wei, Yi, Axnanda, Goodman, JPC, 2005,109,23517



Pd-Au Alloy Surfaces: Planar vs. Supported Particle



Luo, Wei, Yi, Axnanda, Goodman, JPC, 2005,109,23517

Conclusions

- Au-Pd surfaces are significantly enriched in Au over a wide range of compositions.
- Isolated Pd sites can be identified by IRAS and TPD using CO as a probe.
- Isolated Pd sites are proposed to be the active site for vinyl acetate synthesis by Au-Pd alloy catalysts.

Coworkers

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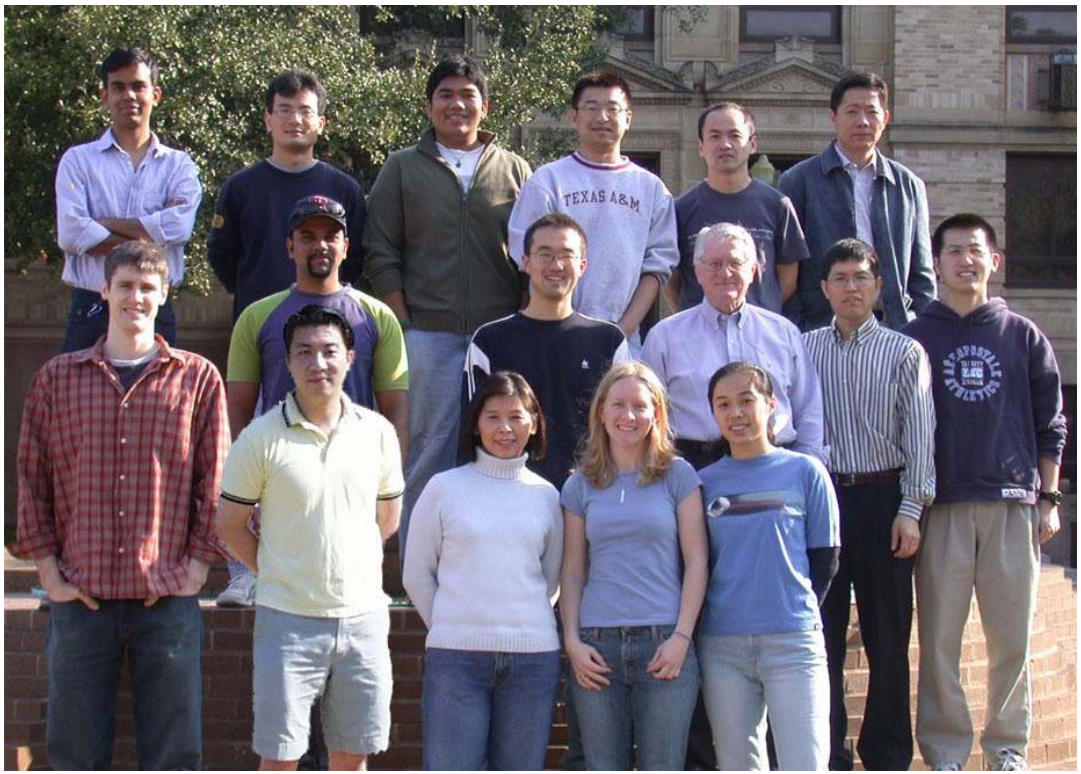

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