M. Armbrüster, K. Kovnir, R. Giedigkeit, J. Grin, MPI CPFS

Robert Schlögl
Fritz-Haber-Institut der MPG

Pd and its Intermetallics in Heterogeneous Catalysis

FUNDAMENTALS

The function of a catalyst: The single crystal approach

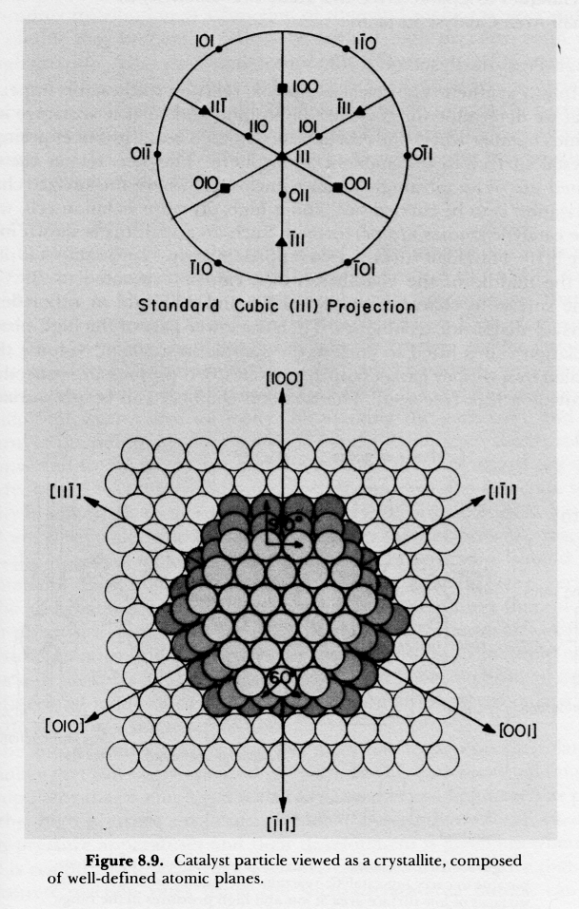
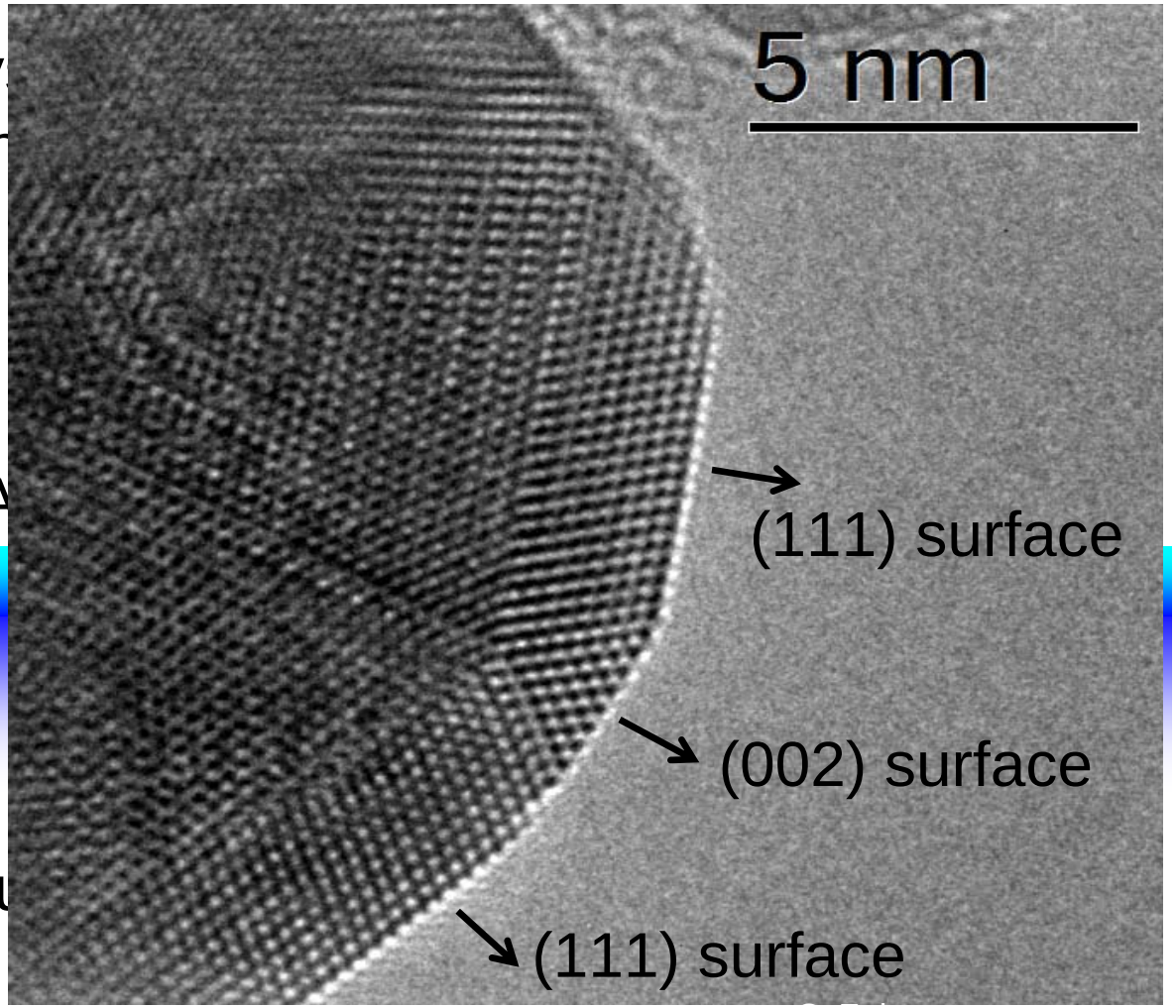


Figure 8.9. Catalyst particle viewed as a crystallite, composed of well-defined atomic planes.

Somorjai 1981



Bulk is "irrelevant",

Reactivity?

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Hydrogenation Catalysis

- The most active catalyst for hydrogenation reactions is Pd metal as nano-particles on supports.
- Selectivity controlled by additives (poorely reproducible).
- Concept: Size of active site controls selectivity.
- Concept: sub-surface “hydride” is relevant or detrimental.

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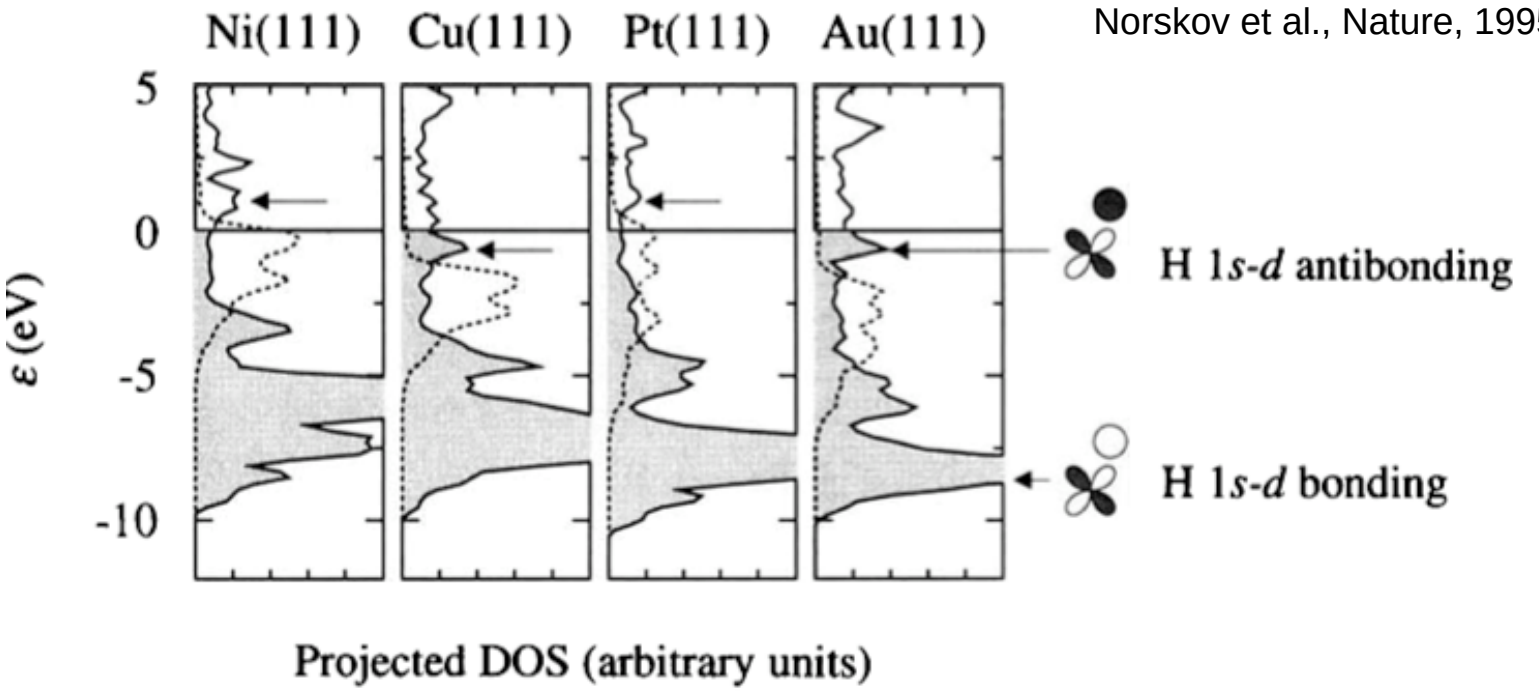
AC FHI

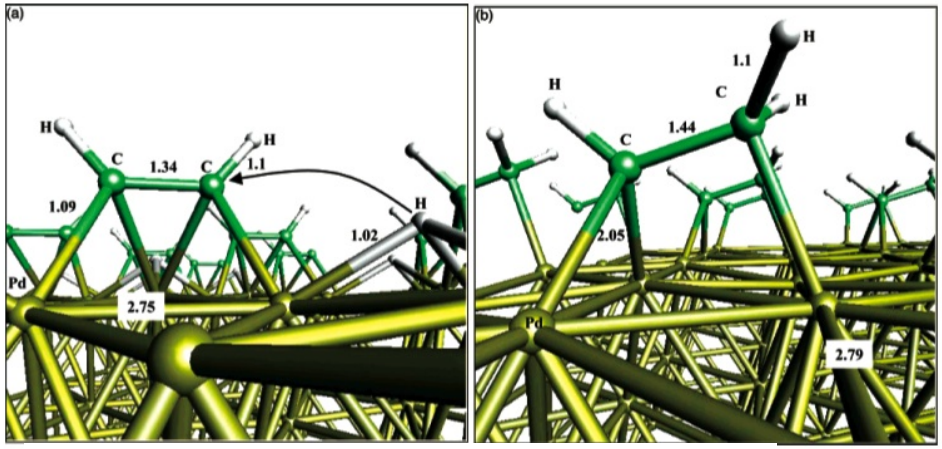
Abundance of “active hydrogen”

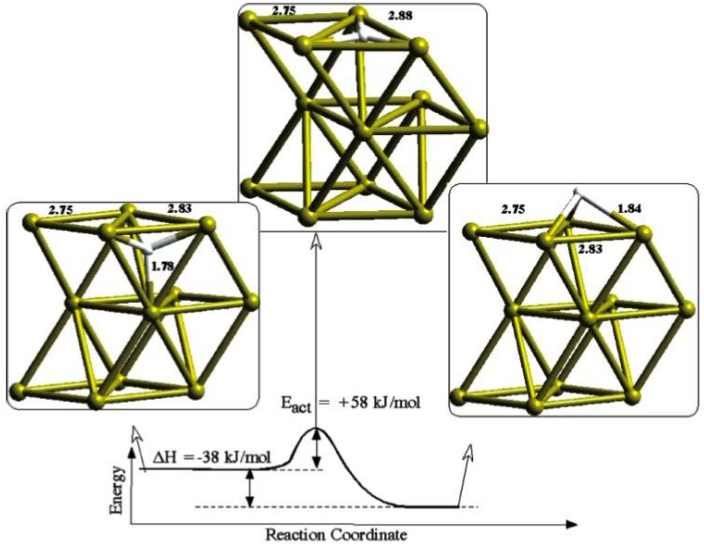


Norskov et al., Nature, 1995

Competition between hybridisation and Pauli repulsion determines bond strength; any effect that shift metal surface d-band has great effects

Reaction pathway: role of H_{sub}





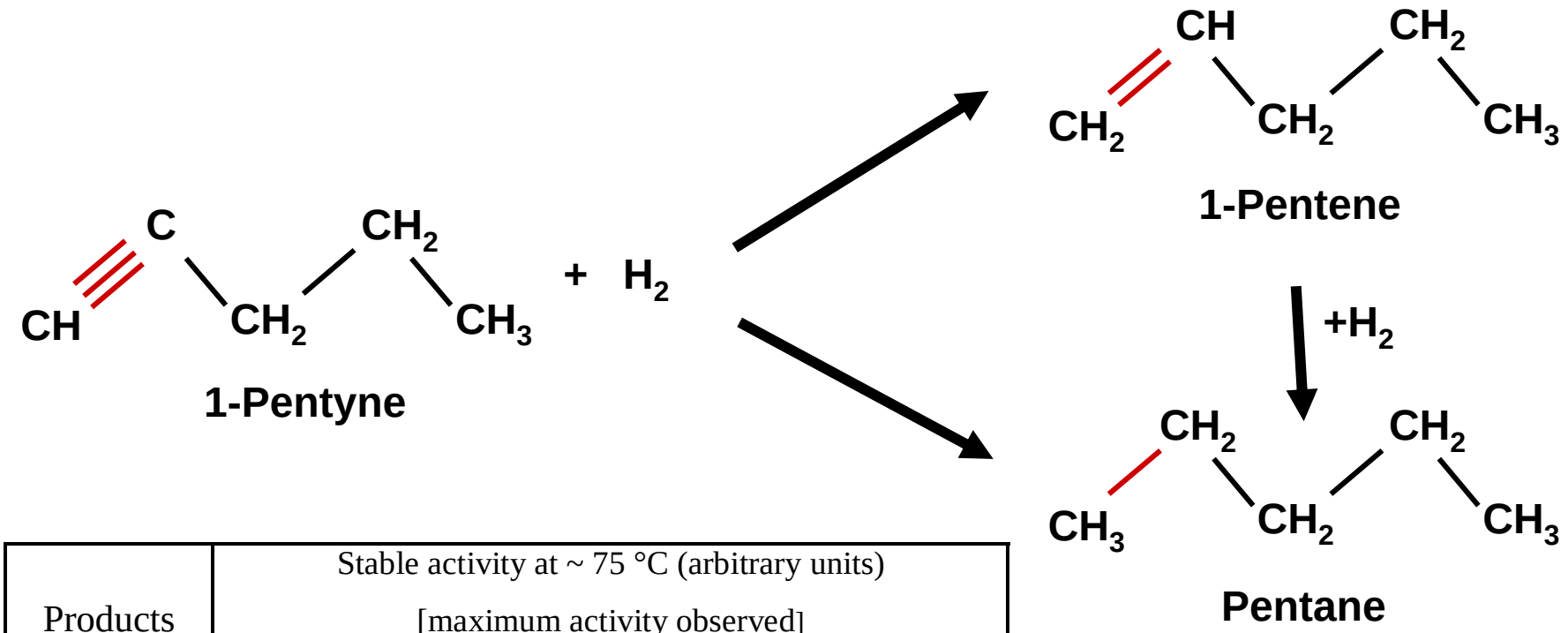
Active site: 6 Pd atoms: Rate controlled by equal chemical potentials of [H] and [substrate].

Sub-surface hydrogen strongly increases [H] above surface sticking:
+ activity
- selectivity.

M. Neurock, 2003, 2005

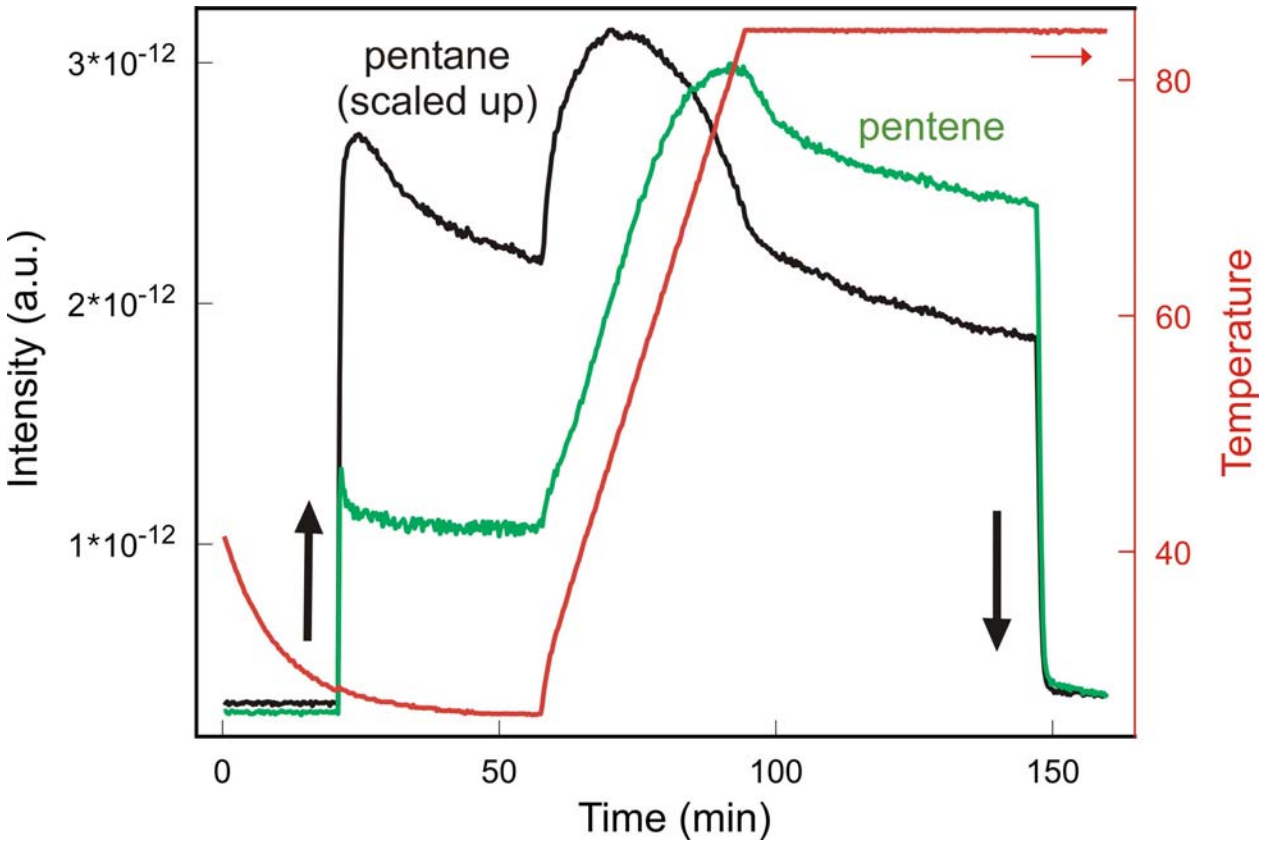
Metal (?)
Hydrogenation Catalysts

Pd in *selective* hydrogenation



Products	Stable activity at ~ 75 °C (arbitrary units) [maximum activity observed]			
	5% Pd/CNT	3% Pd/Al_2O_3	Pd foil	Pd(111)
Pentene	210 [240]	150 [170]	58 [75]	18 [22]
Pentane	20 [42]	15 [28]	~ 0.5 [1]	0

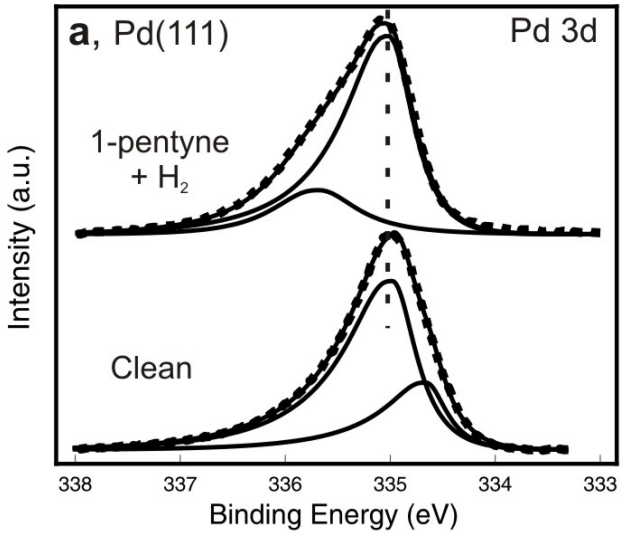
A consecutive reaction



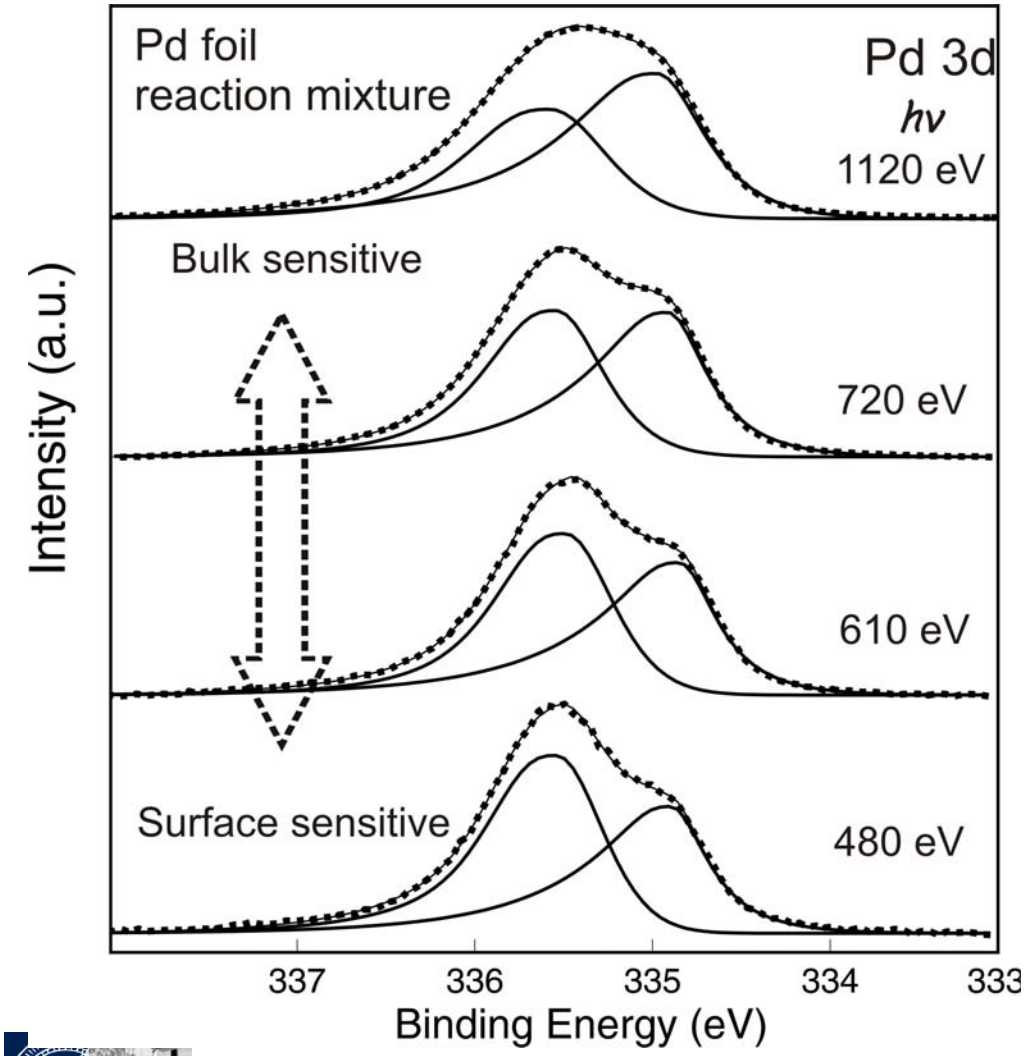
Deep hydrogenation
before
selective hydrogenation

0.03 mbar pentyne
0.85 mbar H2

In-situ XPS: Pd 3d (720 eV): sub-surface C



In-situ XPS: Pd 3d depth profiling



unambiguous localisation of carbon-induced component in the surface-near region

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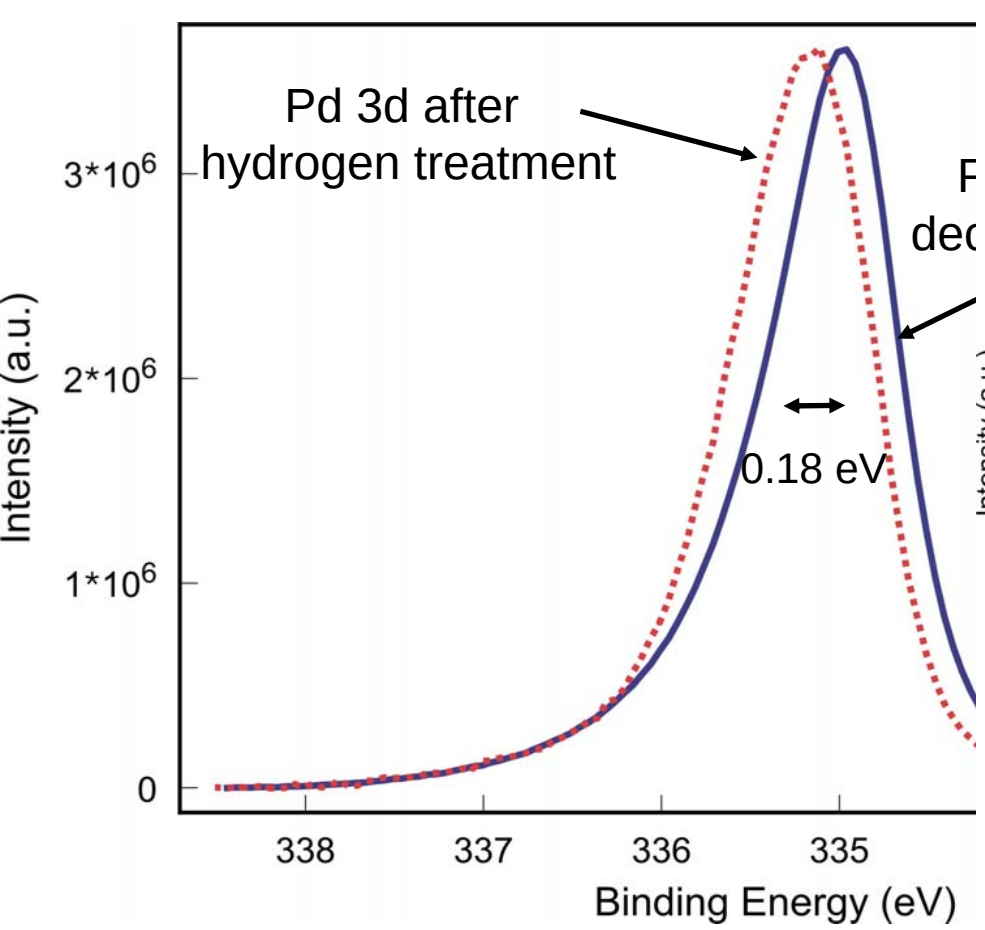
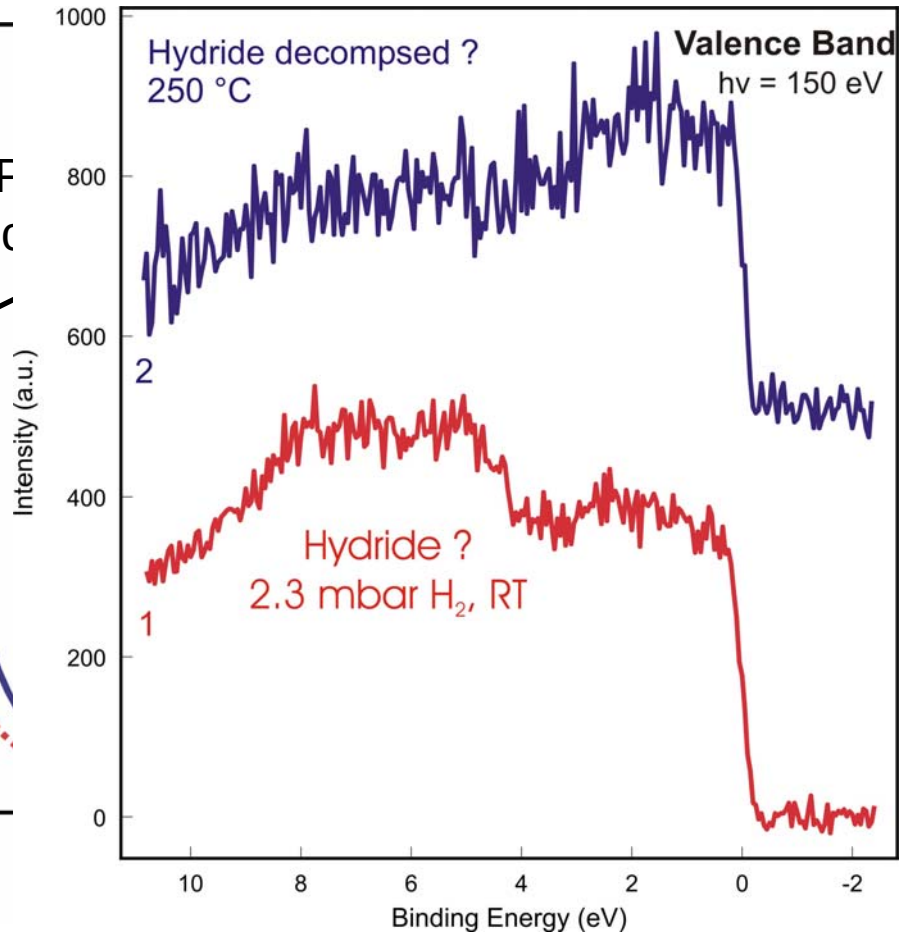
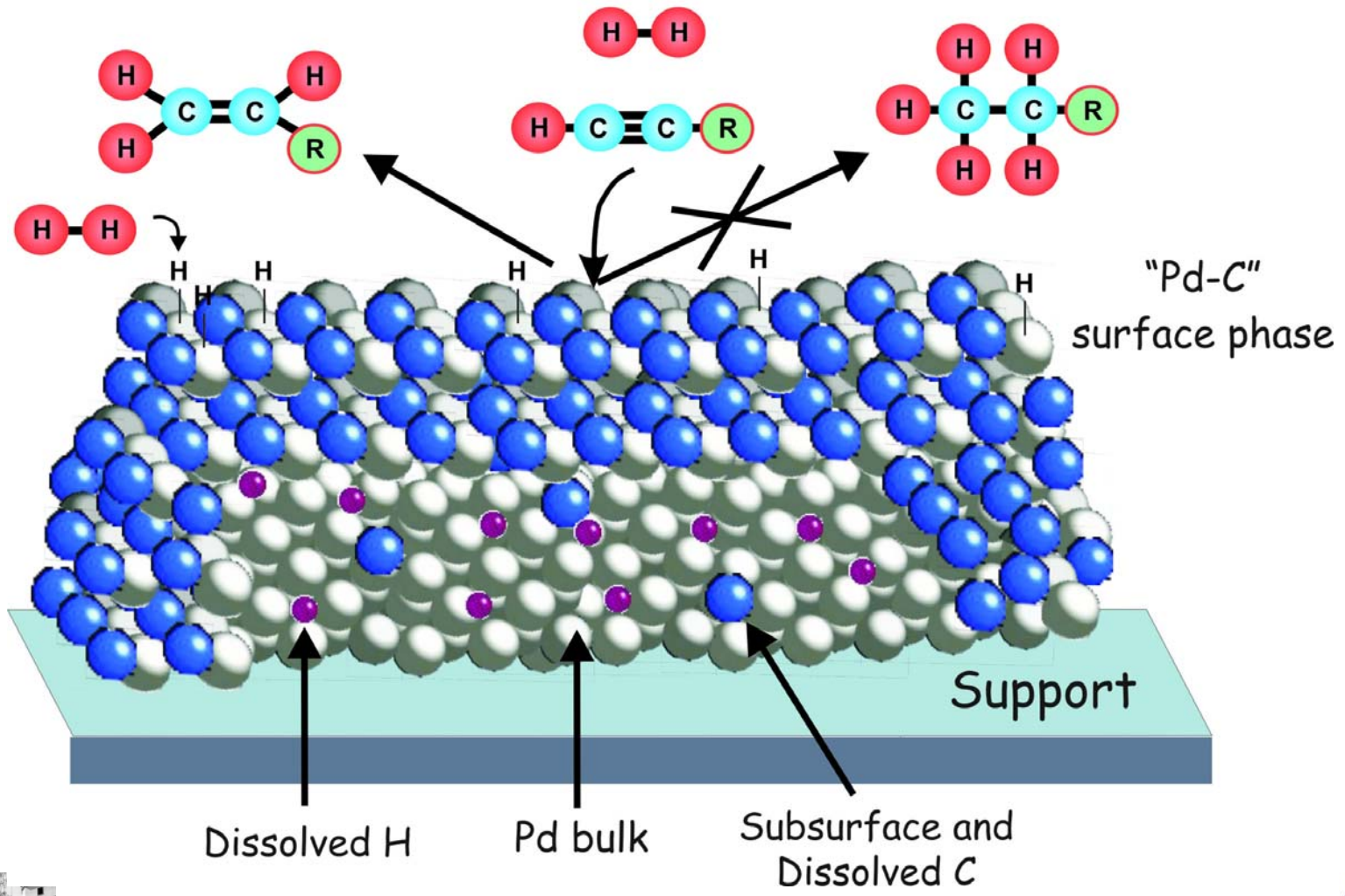
Sub-surface H vs. sub-surface C

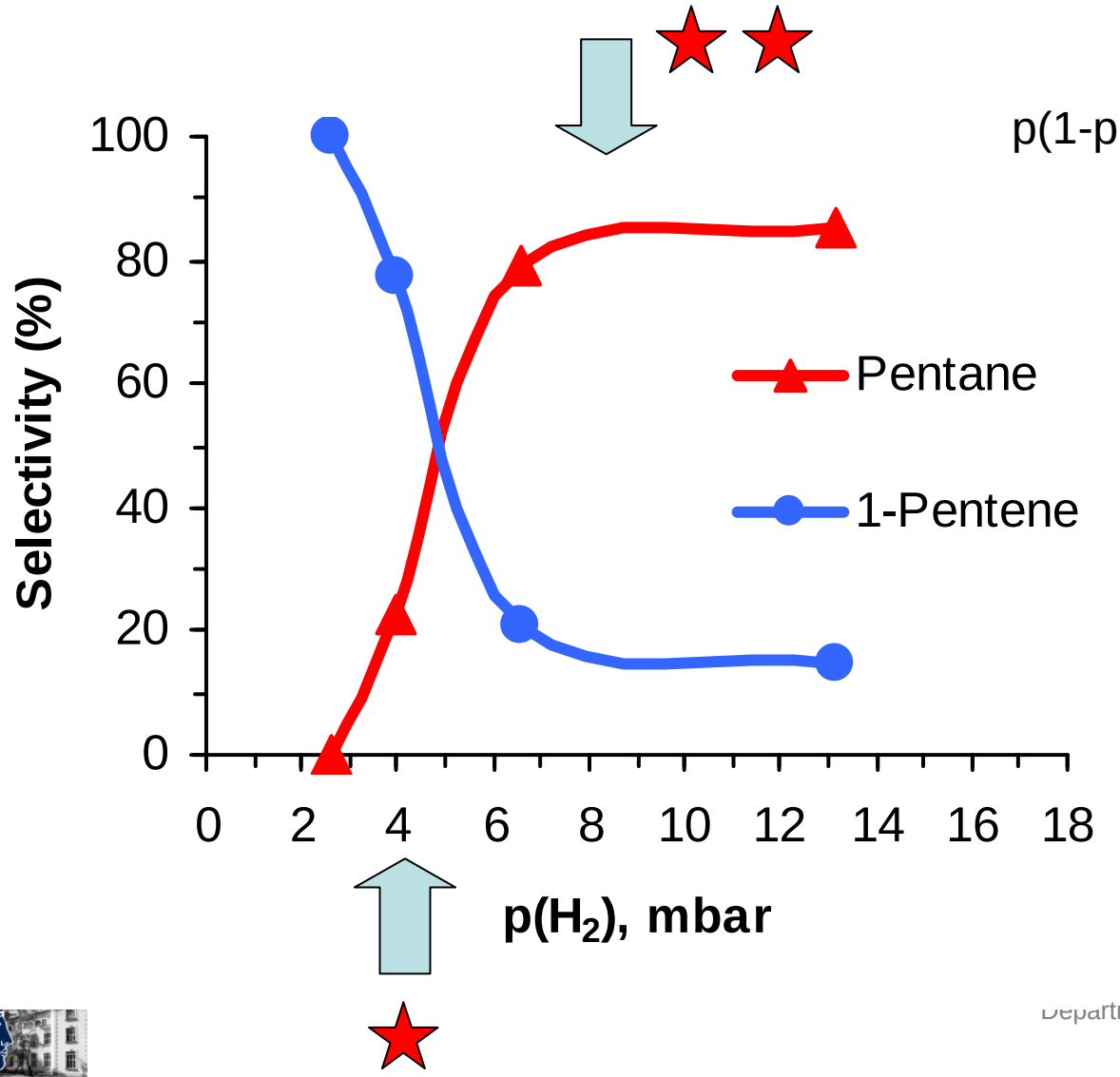




The Model


H
H
C
C
R
"Pd-C"
surface phase
Support
Dissolved H
Pd bulk
Subsurface and
Dissolved C

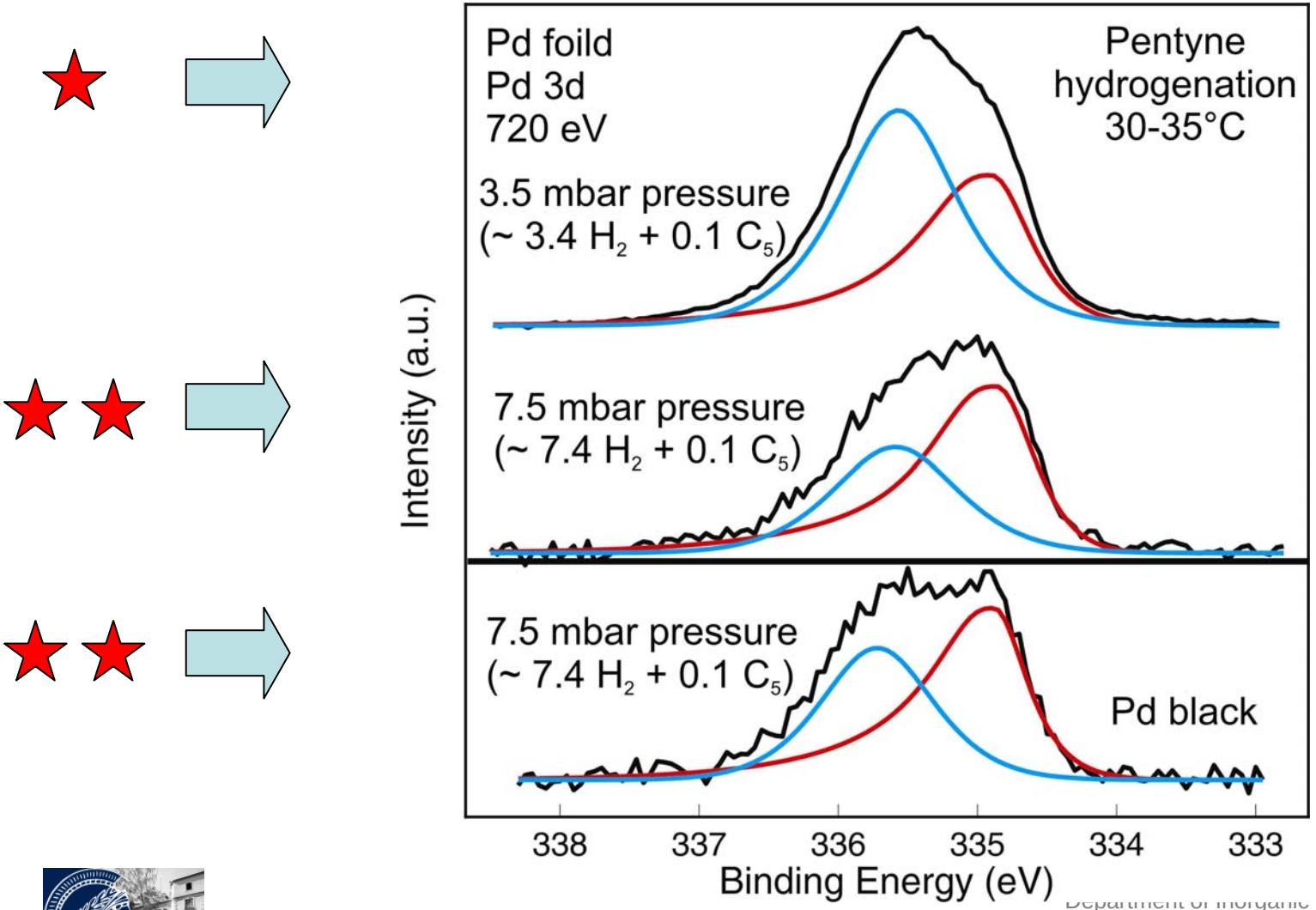
Pressure gap: reaction



p(1-pentyne) = 0.66 mbar
T = 35°C

Unsupported Pd black

Pressure gap: origin



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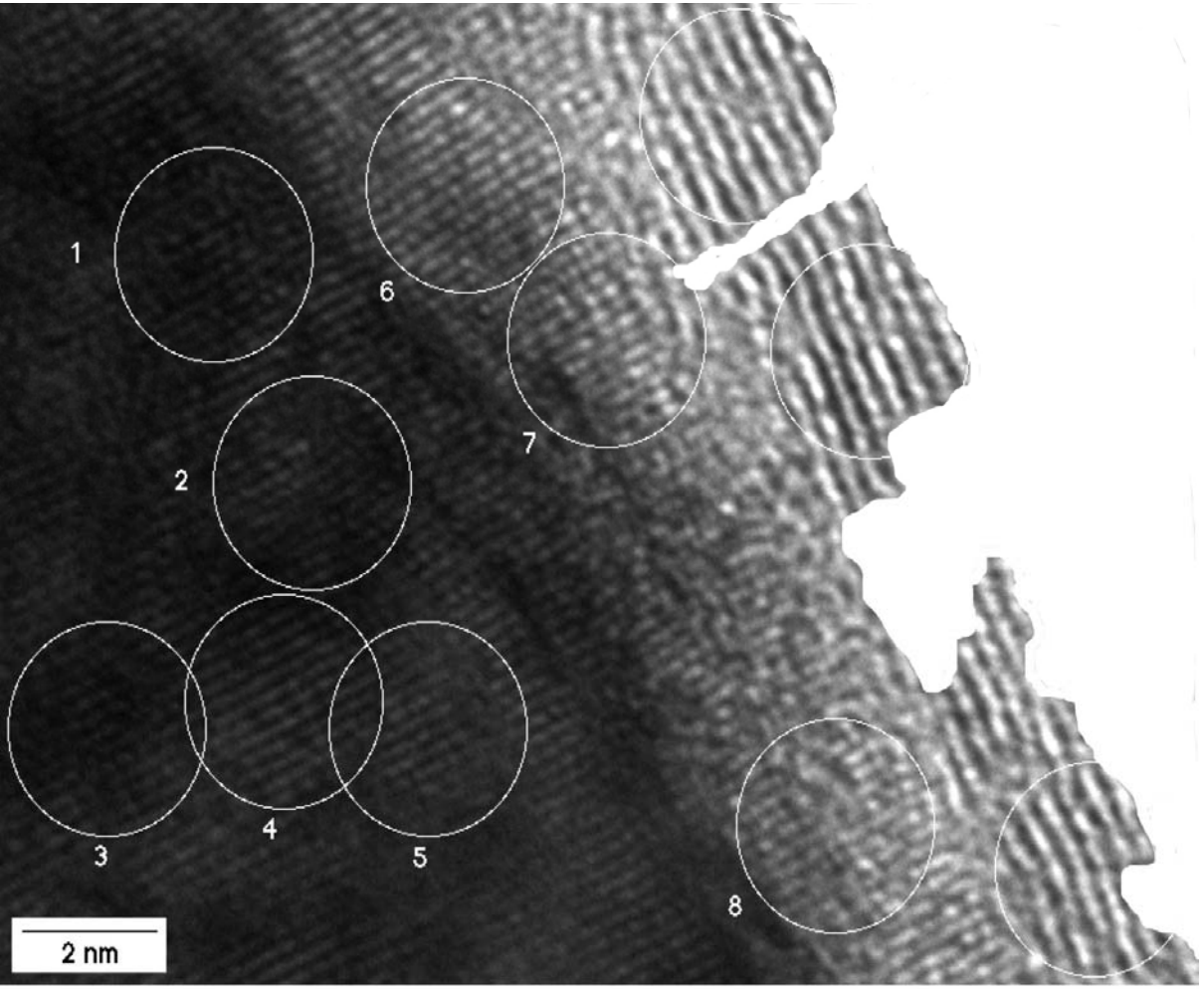
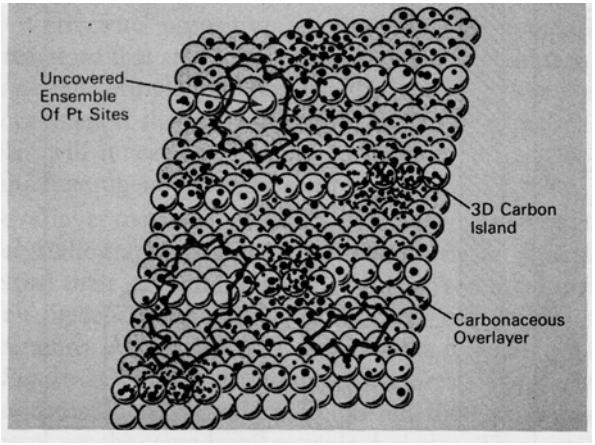
Real structue: the role of nanostructuring

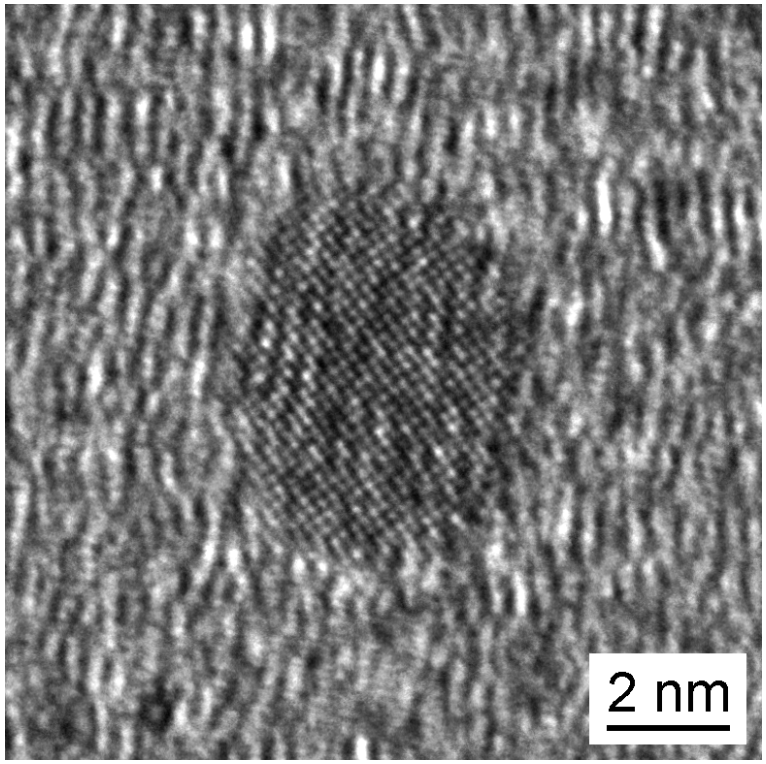


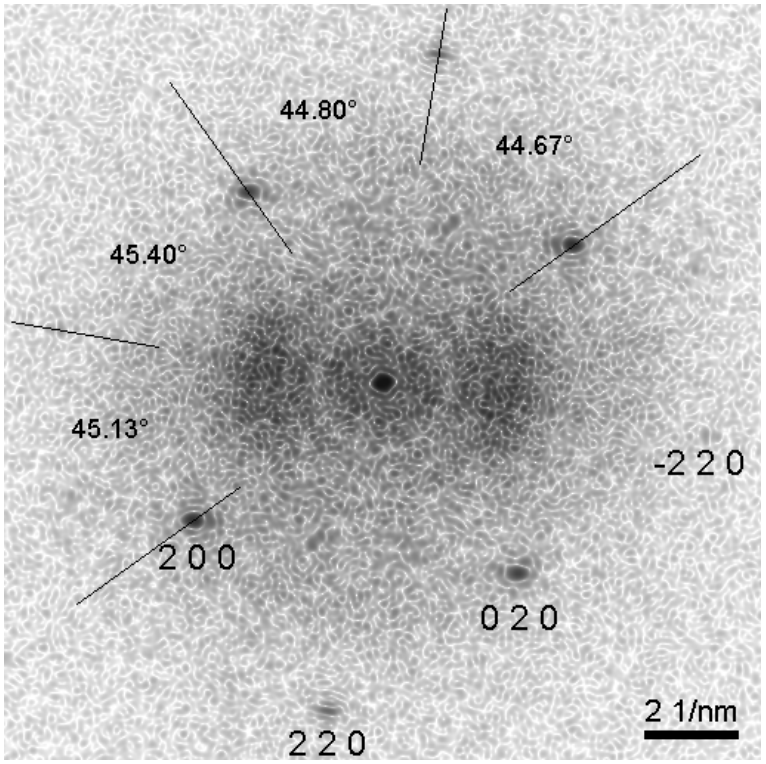


Somorjai 1994

Hydrogen dissolution under carbon!

“Structure sensitivity”





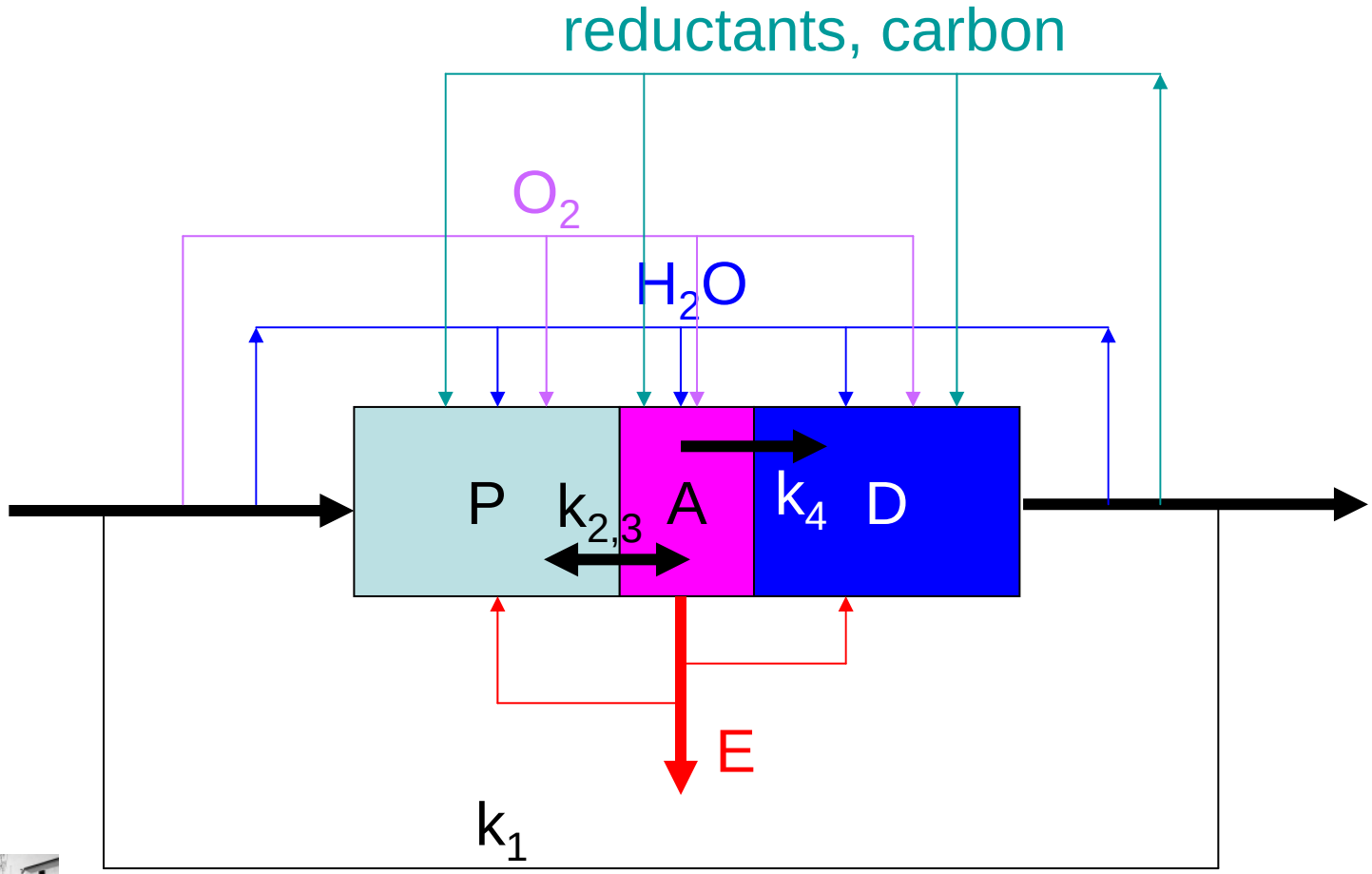
5% Pd/CNT after reaction

0.2025 nm	+4.2%	0.1944 nm	2 0 0
0.2027 nm	+4.3%	0.1944 nm	0 2 0
0.1421 nm	+3.4%	0.1374 nm	2 2 0
0.1434 nm	+4.4%	0.1374 nm	-2 2 0

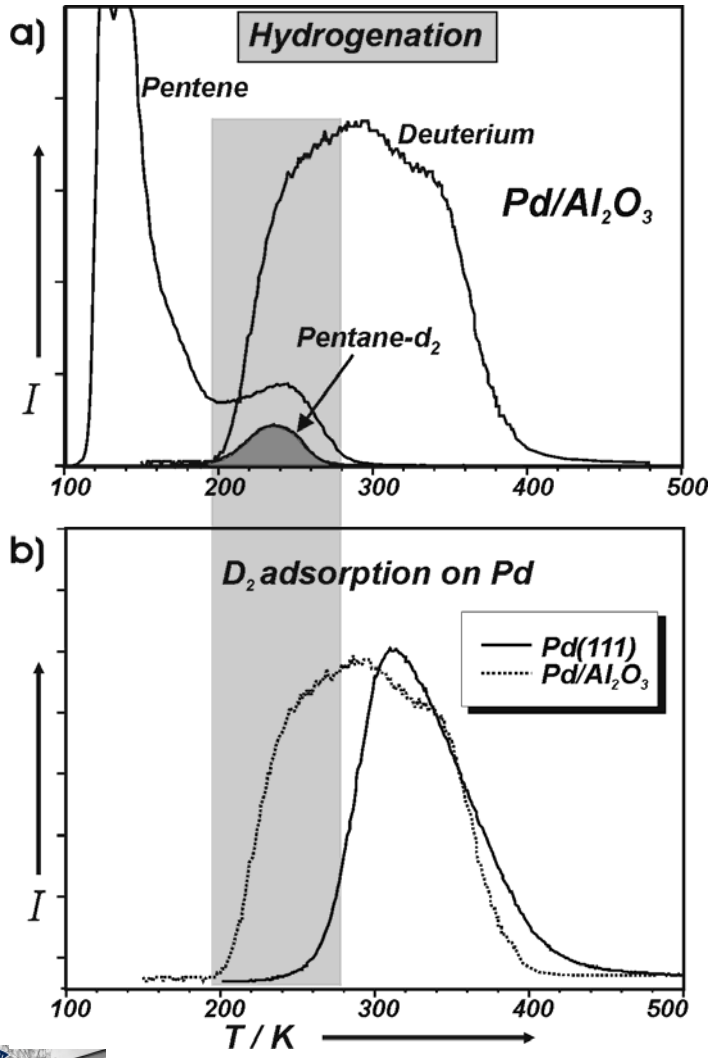
FIRST SUMMARY

Catalyst dynamics

Finite values of $k_{2,3}$ and k_4 under selective reaction conditions only when nanostructured



Comparison to model studies: role of sub-surface hydrogen



Pentenes to pentane

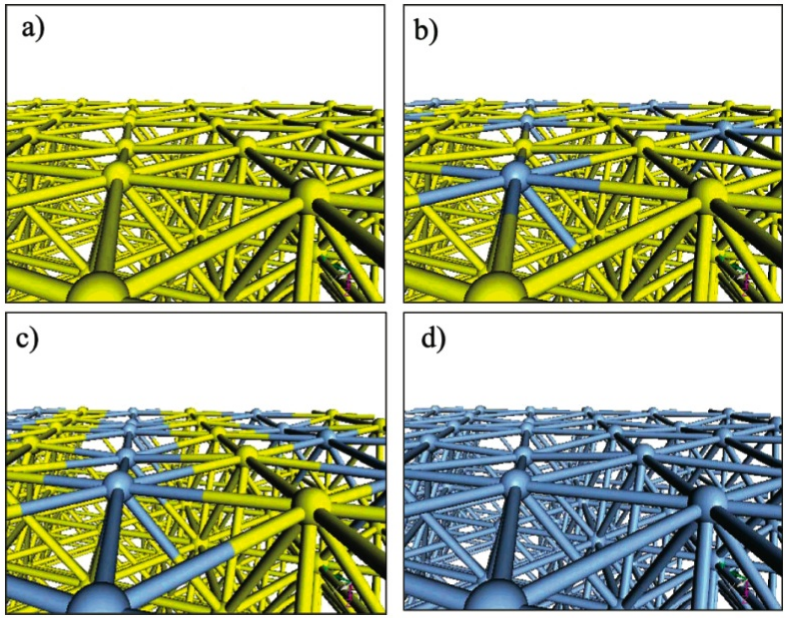
Hydrogenation in the presence of subsurface H [Pd particles]

No hydrogenation without subsurface H [Pd(111)]

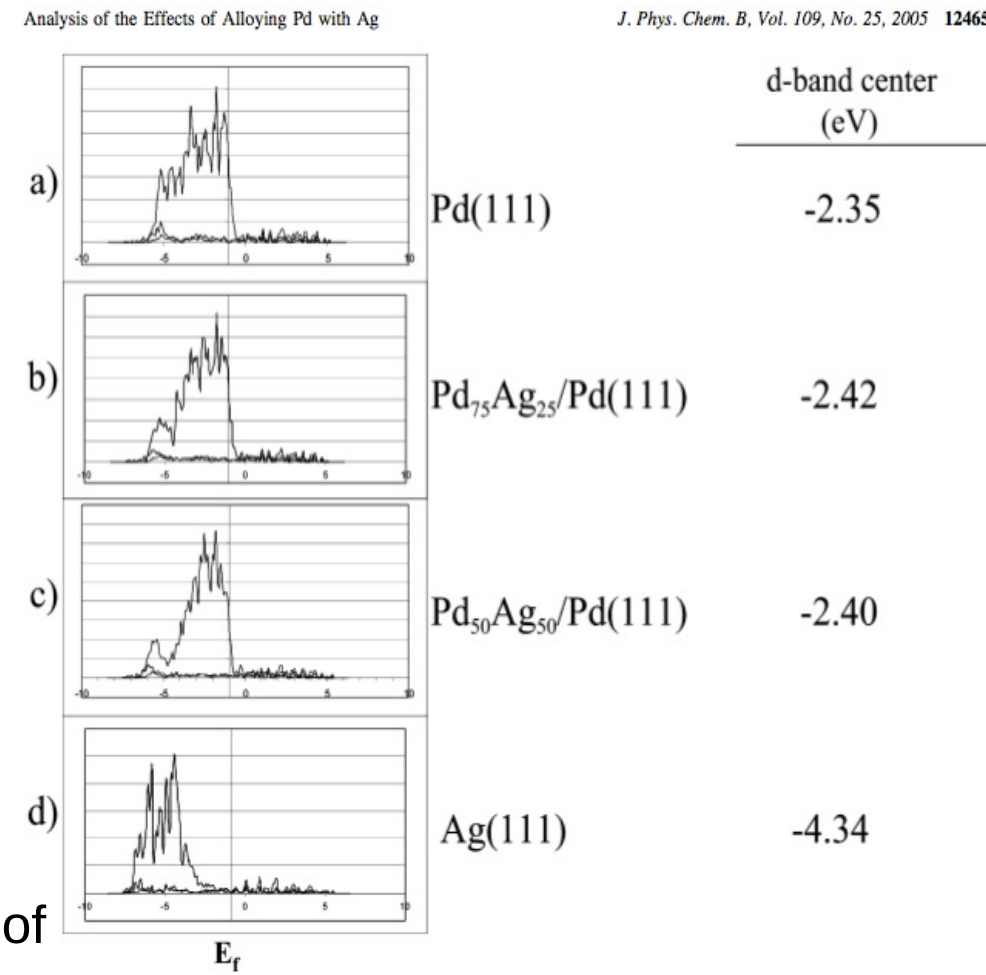
Doyle AM, Shaikhutdinov SK, Jackson SD, Freund HJ
ANGEWANDTE CHEMIE-INTERNATIONAL EDITION
42 (42): 5240-5243 2003

Alloys and Intermetallics As Catalysts

Alloy Catalysis



M. Neurock, 2003, 2005

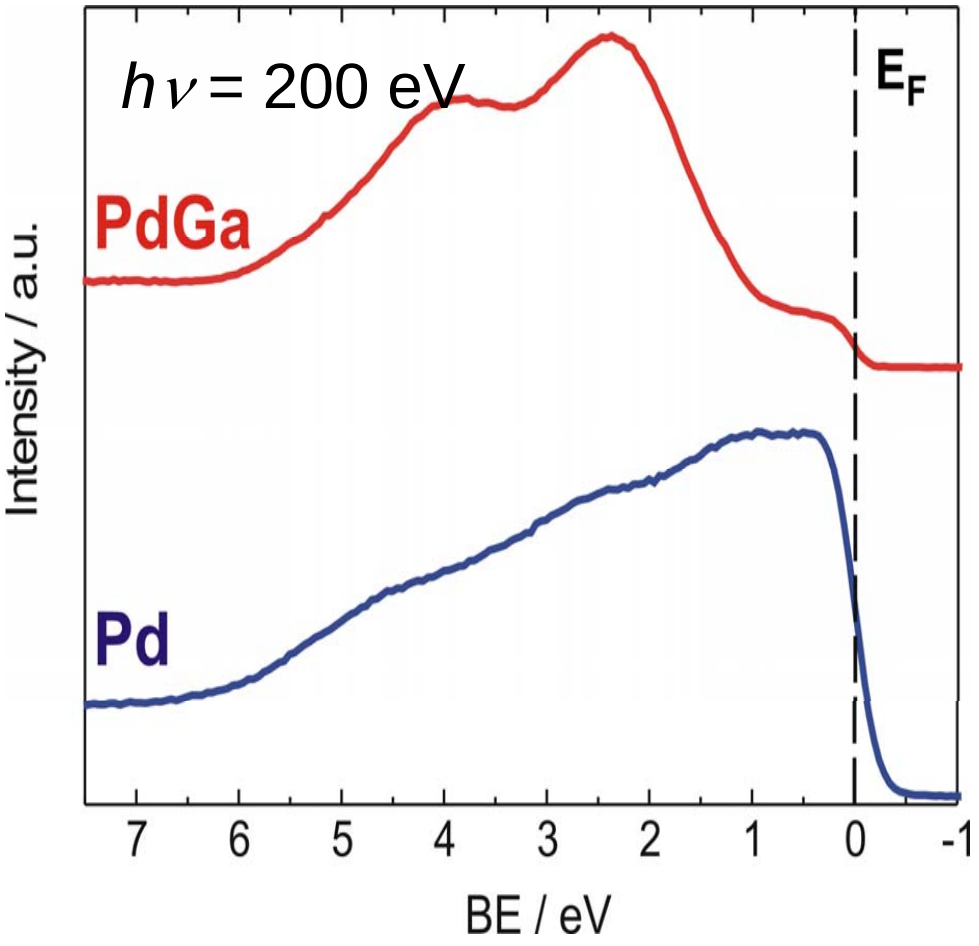


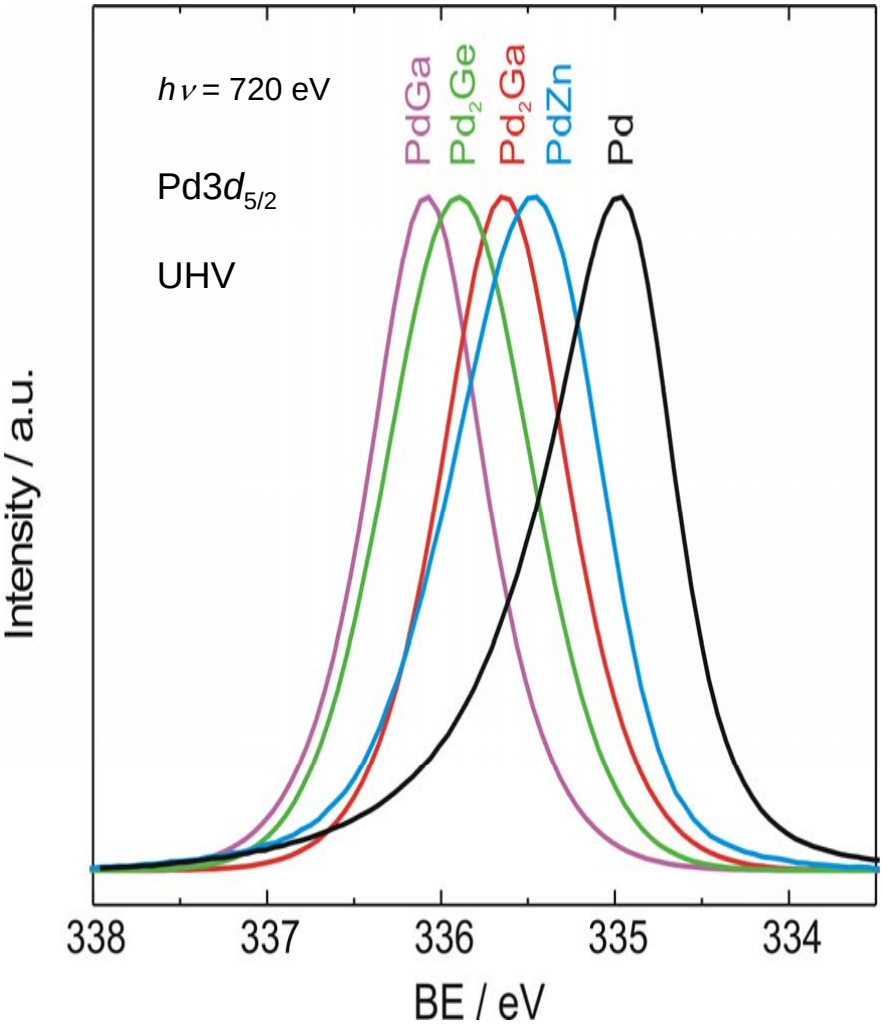
Combined benefits of site isolation and of electronic structure modification

Opportunities

- Alloys are chemically unstable and segregate: rapid loss of site-isolating effect.
- Alloys exhibit only weak modifications of electronic structure: strong influence of local geometry, (ensemble effect).
- Concept: use intermetallics:
  - Covalent metal-metal interaction: High structural stability
  - No sub-surface chemistry: Design of active site.

Meet the challenge: Intermetallics of Pd





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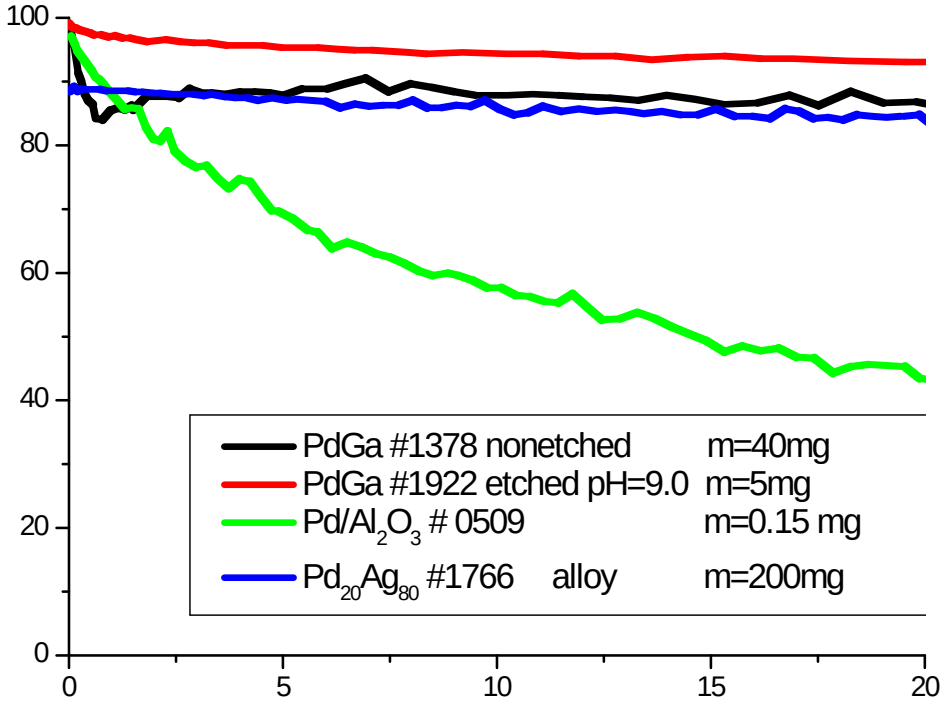
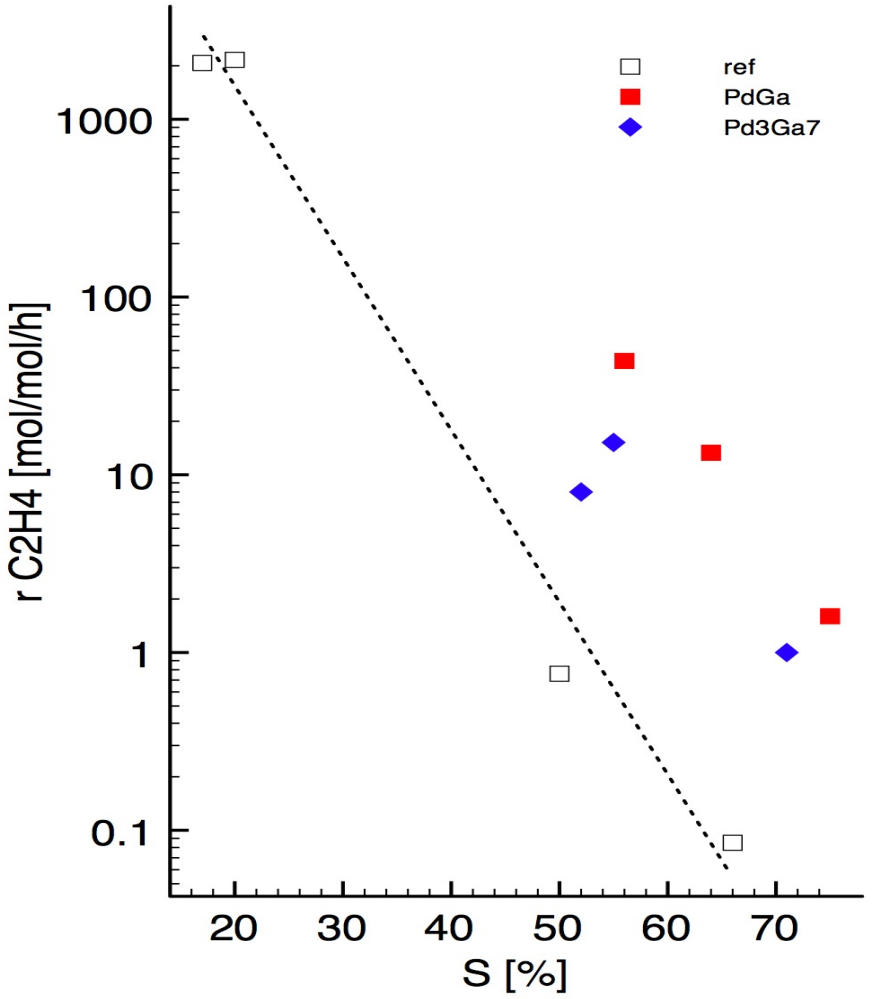
PdGa: a designer system





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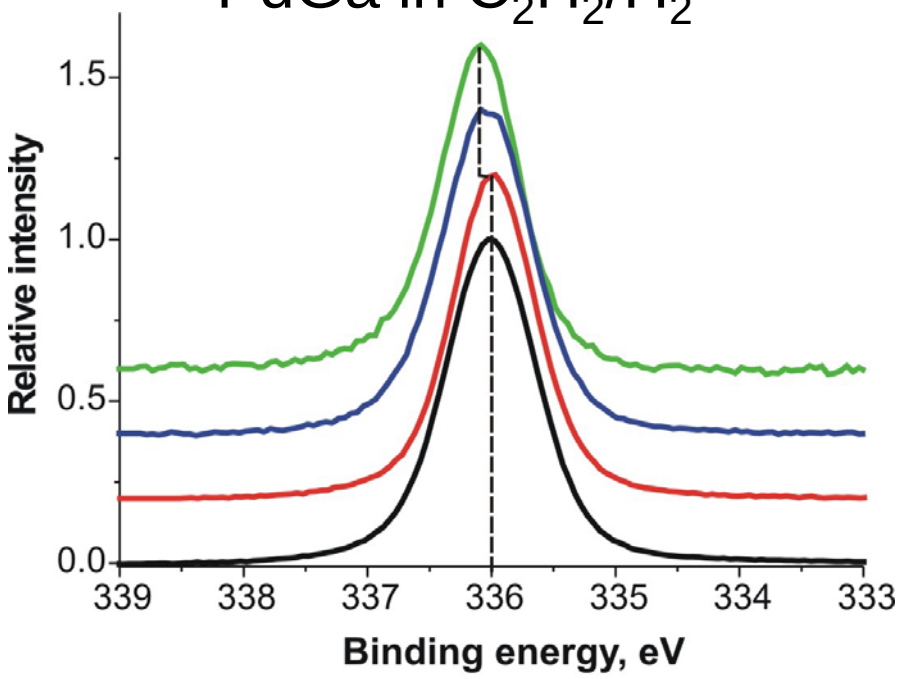
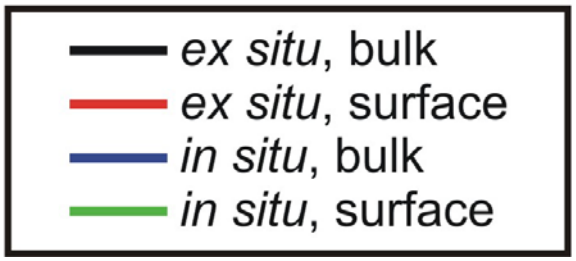
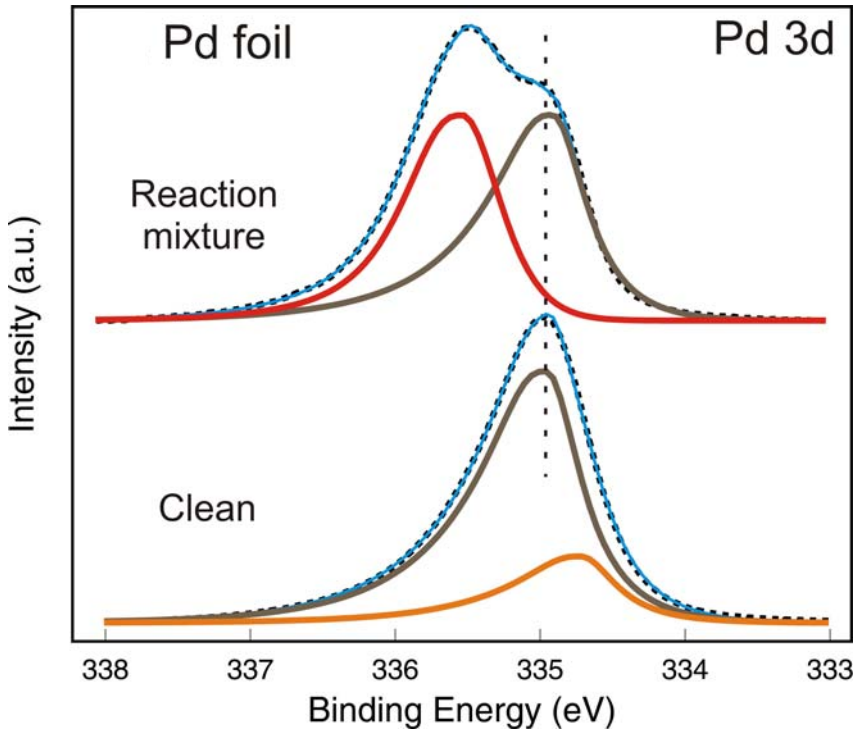
A stable sub-surface regime

PdGa in C_2H_2/H_2







D. Teschner et al., J. Catal. ***2006****, 242 26.*

Pd in alkyne/H_2

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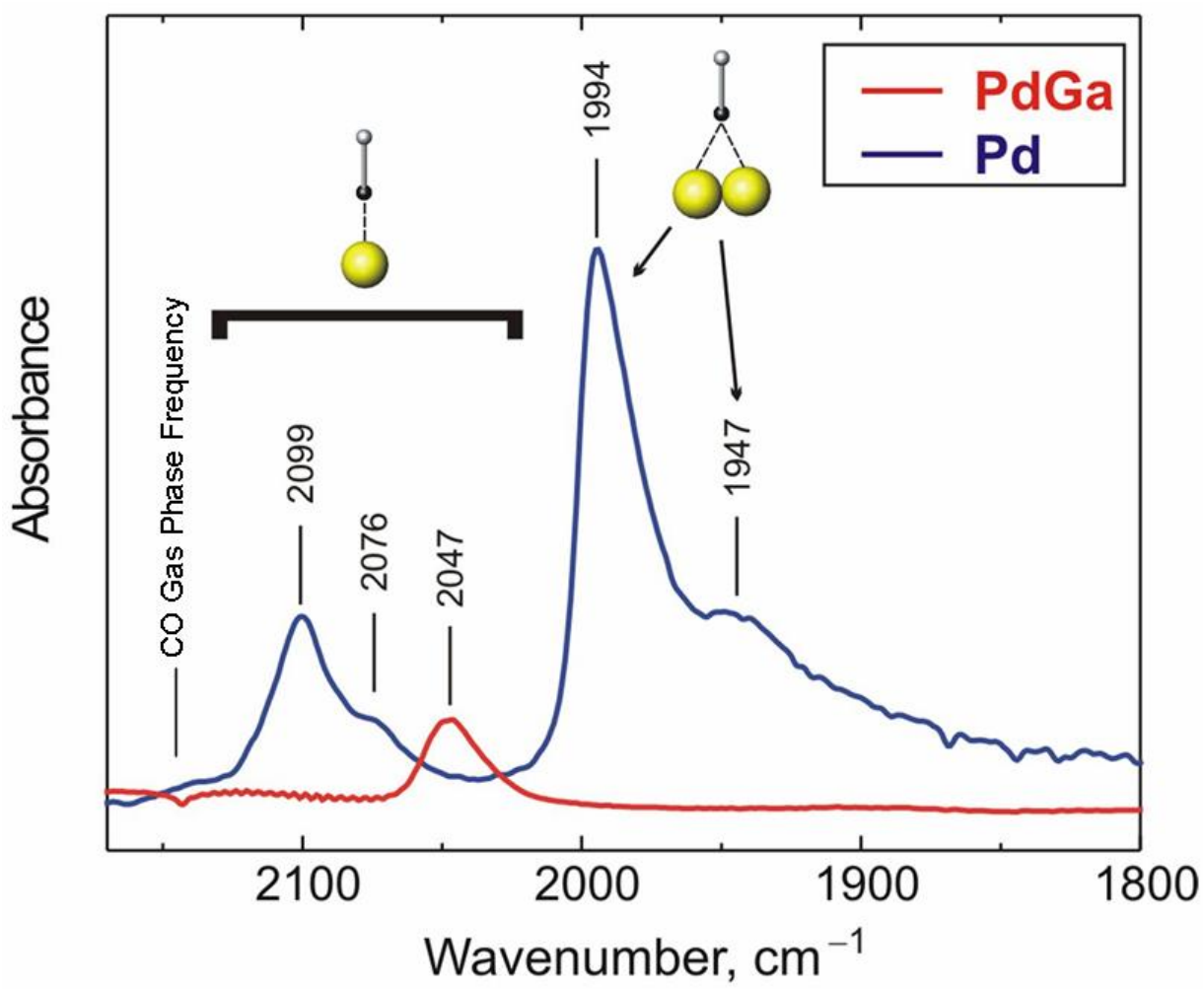
Site isolation: experimental



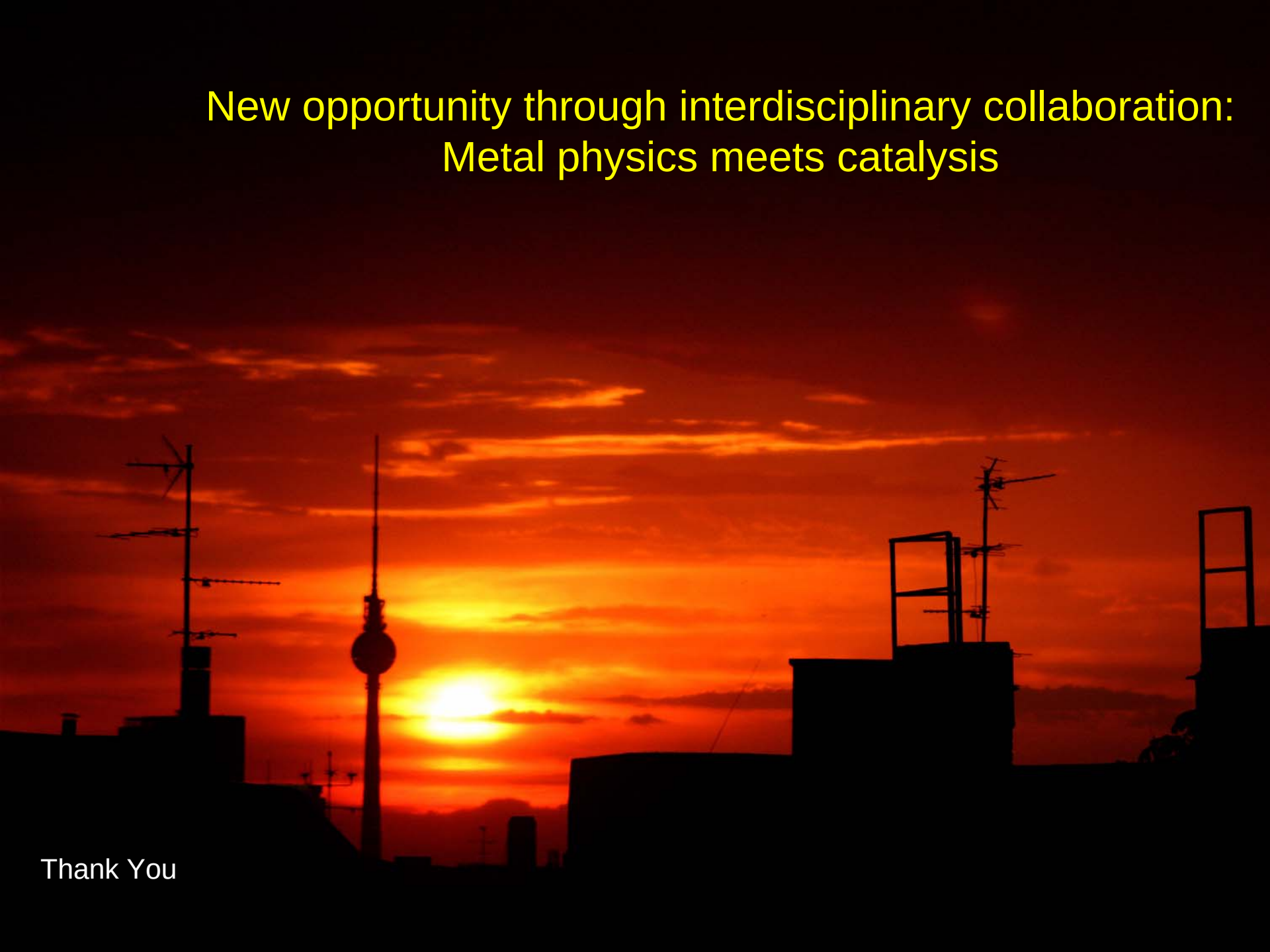
SECOND SUMMARY

Materials

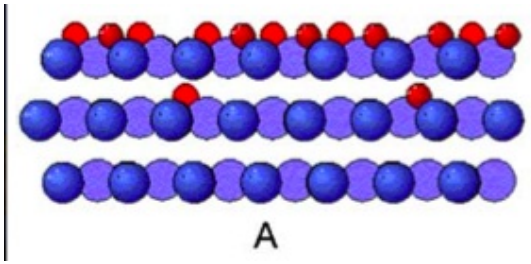
- Intermetallics provide a novel and robust opportunity for selective catalysis:
- Decoupling of surface catalysis and sub-surface reactant storage.
- Strong modification of electronic structure: “design”.
- Chemically robust surface termination: site isolation.

Outlook

- Combination of intermetallics and nano-structuring should allow control over catalytic material properties: no more material dynamics.
- Enhanced chance to apply theory as predictive tool.
- Synthesis of system with yet unknown catalytic properties (“pseudo Pt”) for largest challenges in catalysis: energy conversion.

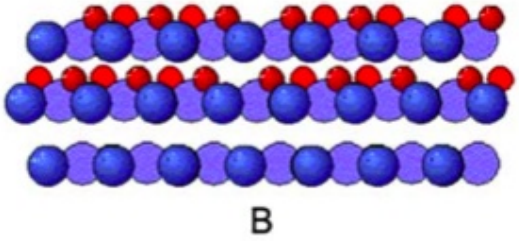

New opportunity through interdisciplinary collaboration:
Metal physics meets catalysis
Thank You

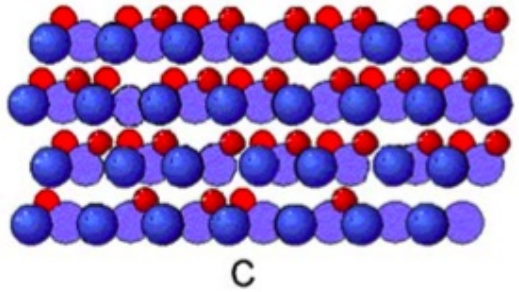
Metastable sub-surface species



At low potential: metal plus dissolved species (“dirt”)

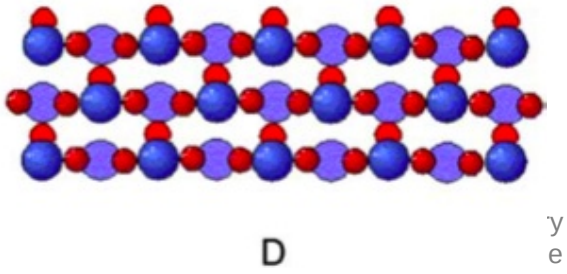
At slightly elevated potential: “trilayer” (theory)



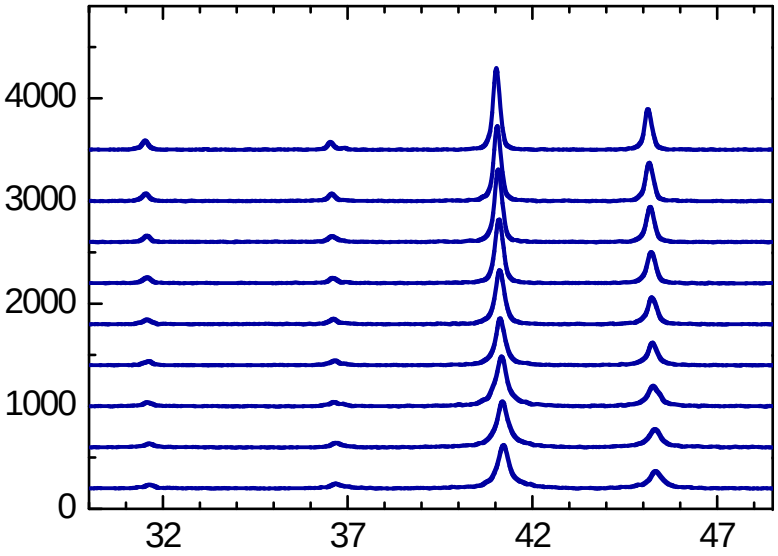


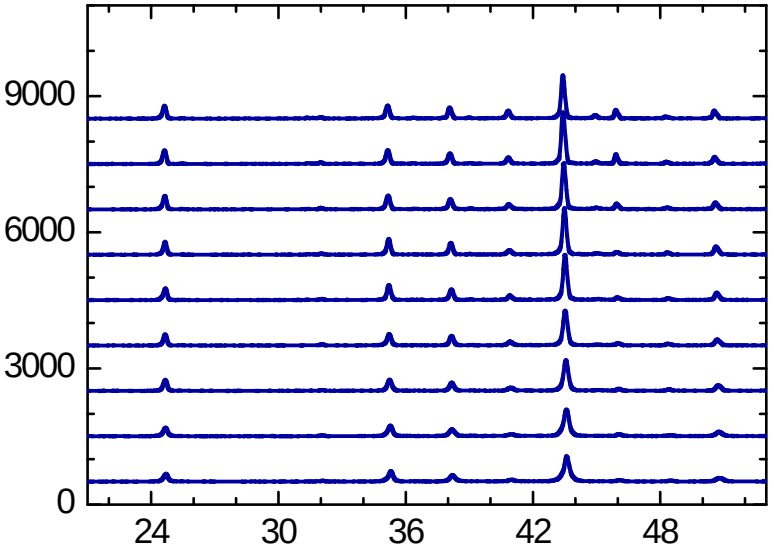
At potentials bejond the “pressure gap”: sub-oxide, sub-surface oxide, TSO (HP-XPS)

At high potential: oxide; when defective: nucleo and electrophilic



Structural stability: No bulk reaction





PdGa und Pd_3Ga_7 in 50% H_2 + 50% He

No hydrides, no segregation, no phase transformations.

The catalysts

Pd metal

supported on oxides

✓ activity

✘ selectivity

✘ long-time stability

Pd-Ga intermetallics:

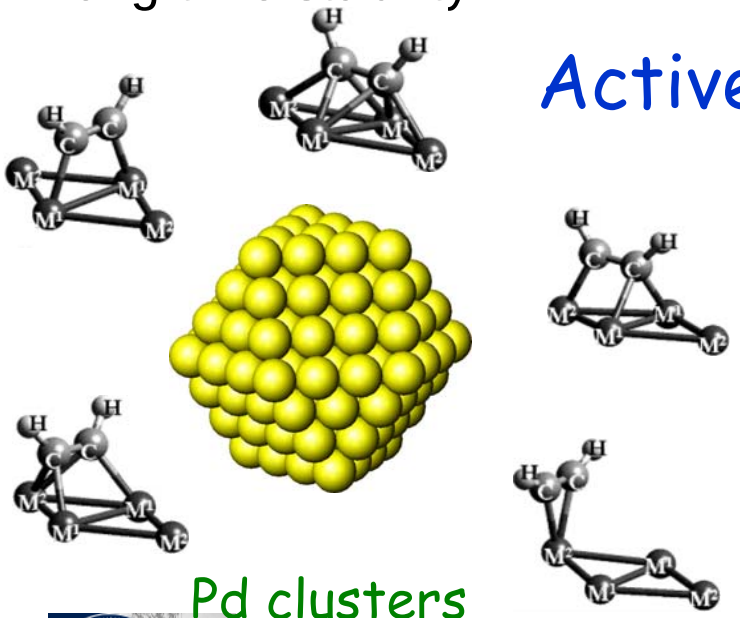
PdGa and Pd_3Ga_7

✓ activity

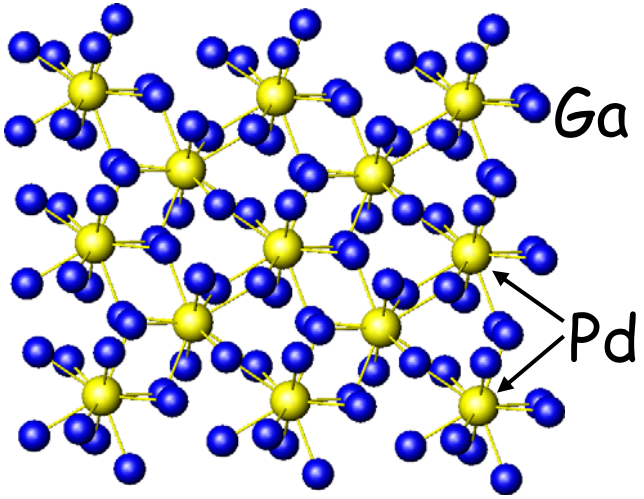
✓ selectivity

✓ long-time stability

Active sites



Pd clusters



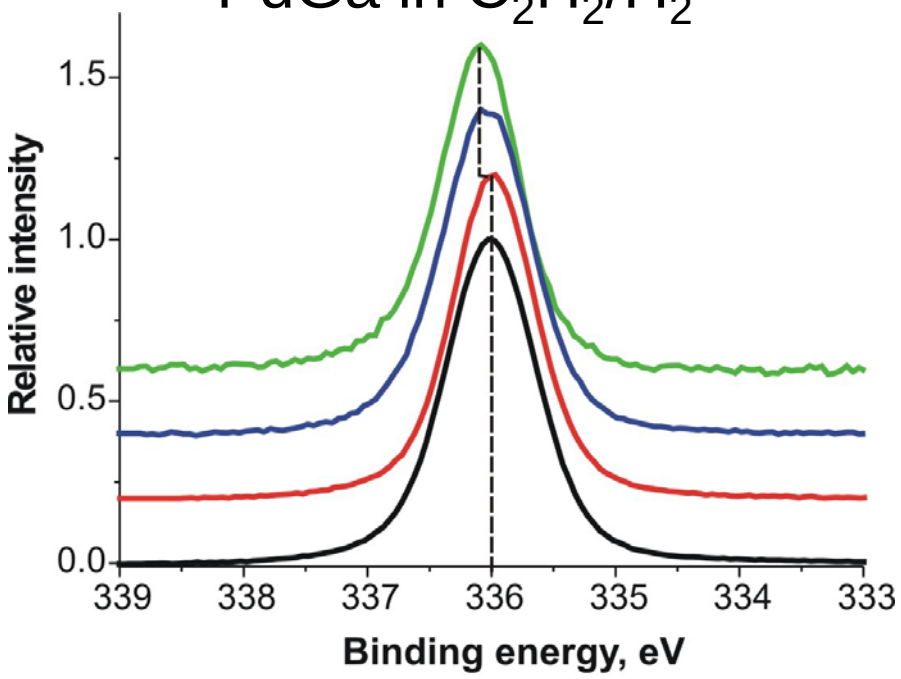
Isolated Pd atoms

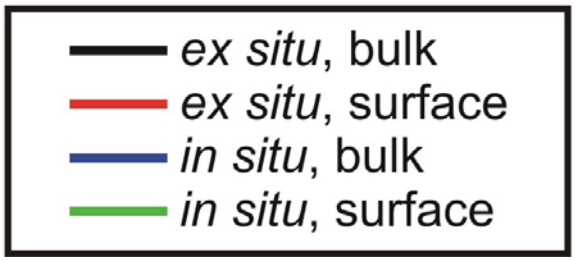
Consequences

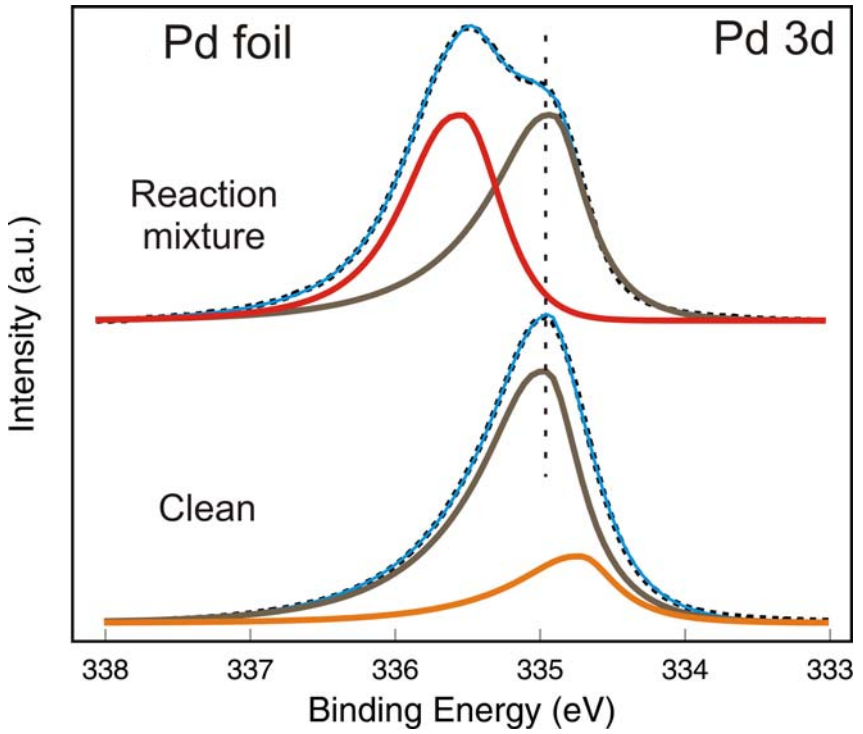
- Well-ordered extended (model) materials slow down activation and stay often non-reactive (gaps);
- Except for kinetically non-demanding reactions (single step processes);
- Where they also reach only moderate performance.
- High performance catalysis needs addition of complexity:
  - Nanostructuring (for synthesis)
  - In-situ methods (for functional analysis and optimization)

A stable sub-surface regime

PdGa in C_2H_2/H_2







D. Teschner et al., J. Catal. ***2006****, 242 26.*

Pd in alkyne/H_2

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The reactions

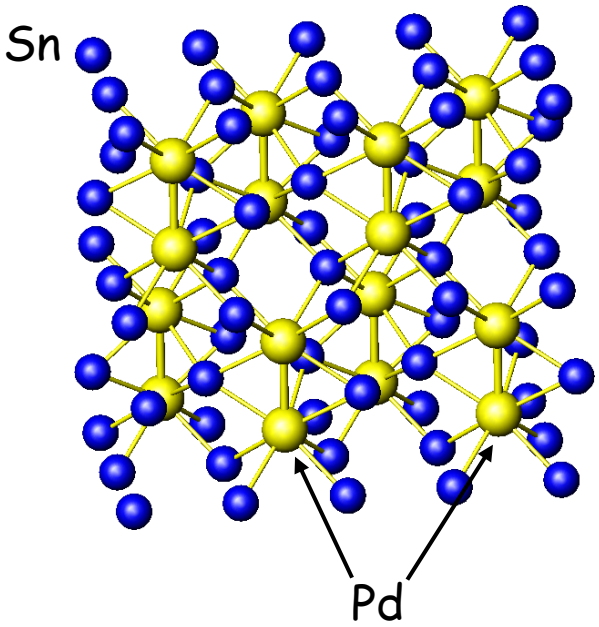
Selective hydrogenation of C-C triple bonds in medium-sized molecules to olefins:
Key step in vitamin and pharmaceutical synthesis

Extremely critical reaction conditions
Severe stability problems

Selective hydrogenation of acetylene in ethylene as pre-requisite for effective poly-ethylene synthesis

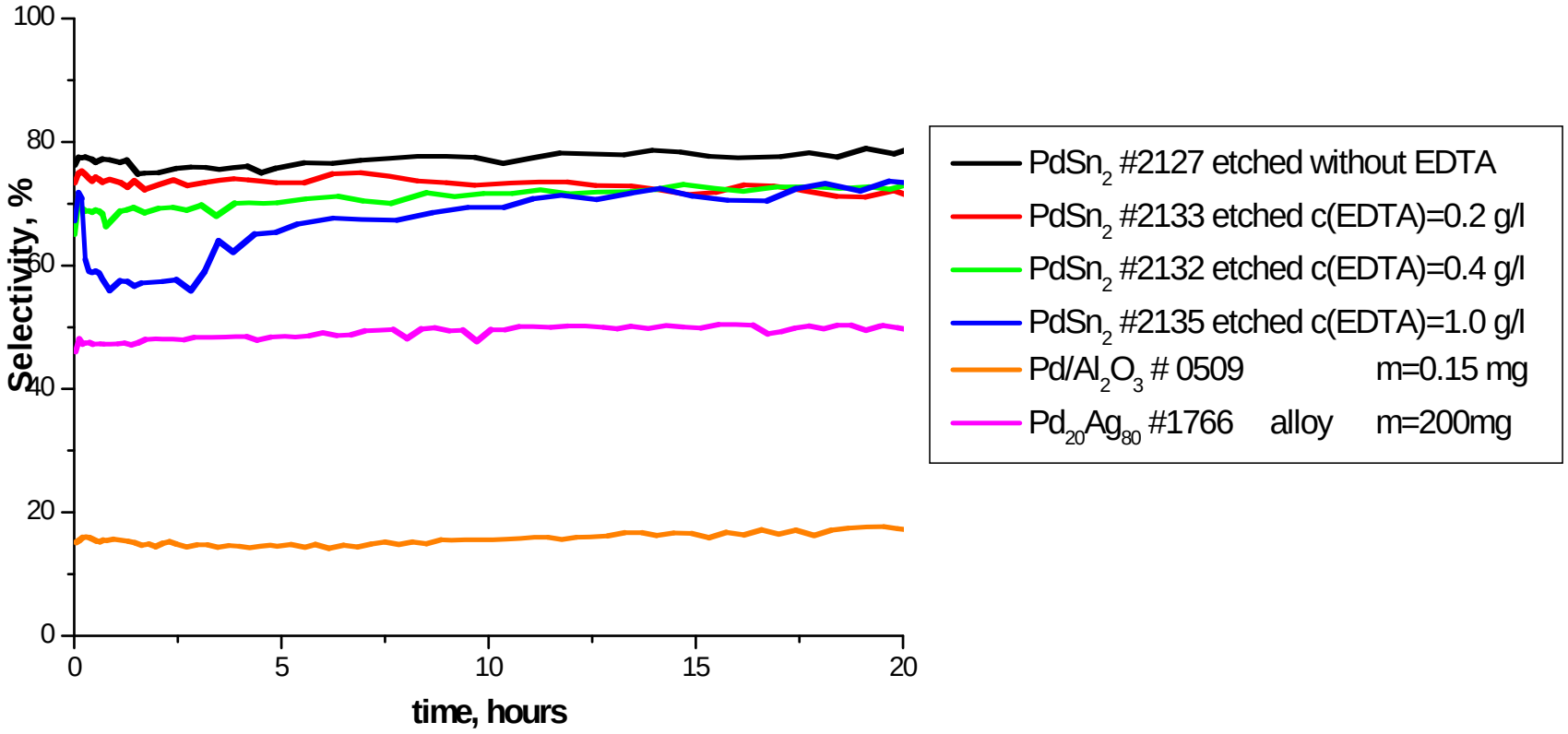
Flexibility of concept?

$PdSn_2$



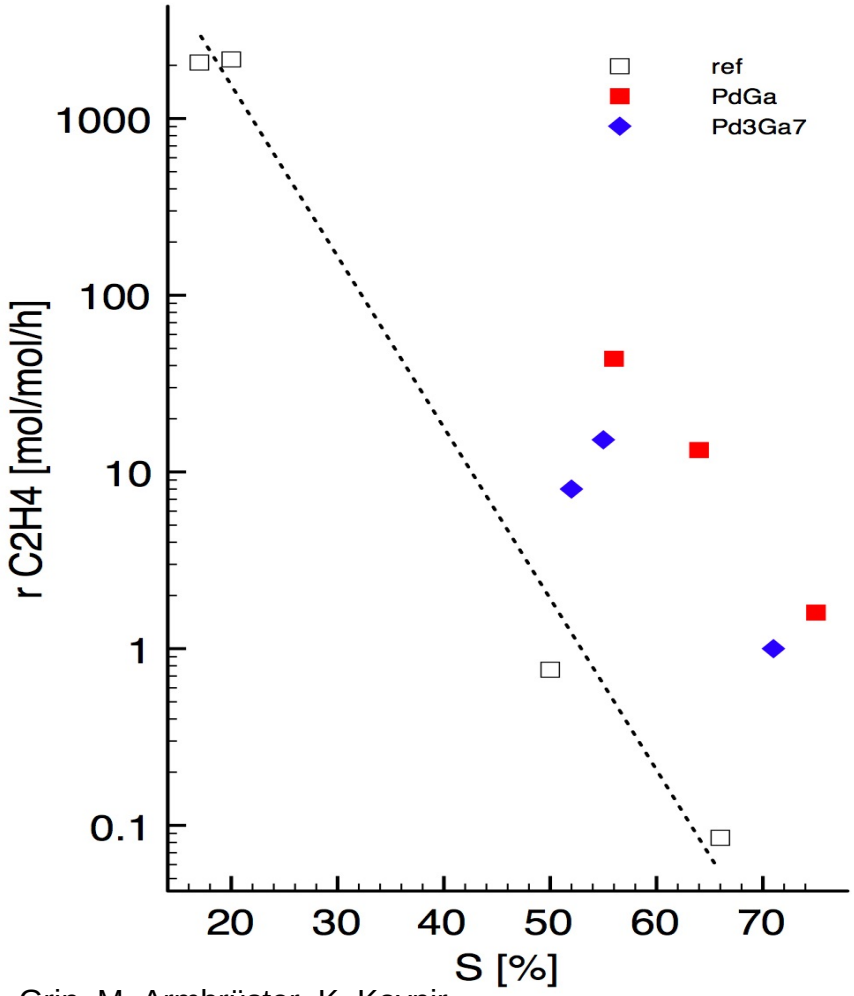
Sample	*Etching solution*	*Conversion after 1 hour*	*Conversion after 3 hour*
# 2039	100mg of sample, no etching	4 %	–
# 2040	saturated EDTA	15%	10%
# 2041	EDTA/NH_3, pH=10.3	21%	15%
# 2042	EDTA/NH_3/H_2O_2, pH=10.5	> 10%	–
# 2049	EDTA/NaOH, pH=12.8	25%	12%
# 2051	EDTA/NaOH, pH=13.3	43%	20%
# 2015	EDTA/NaOH, pH=13.8	37%	5%

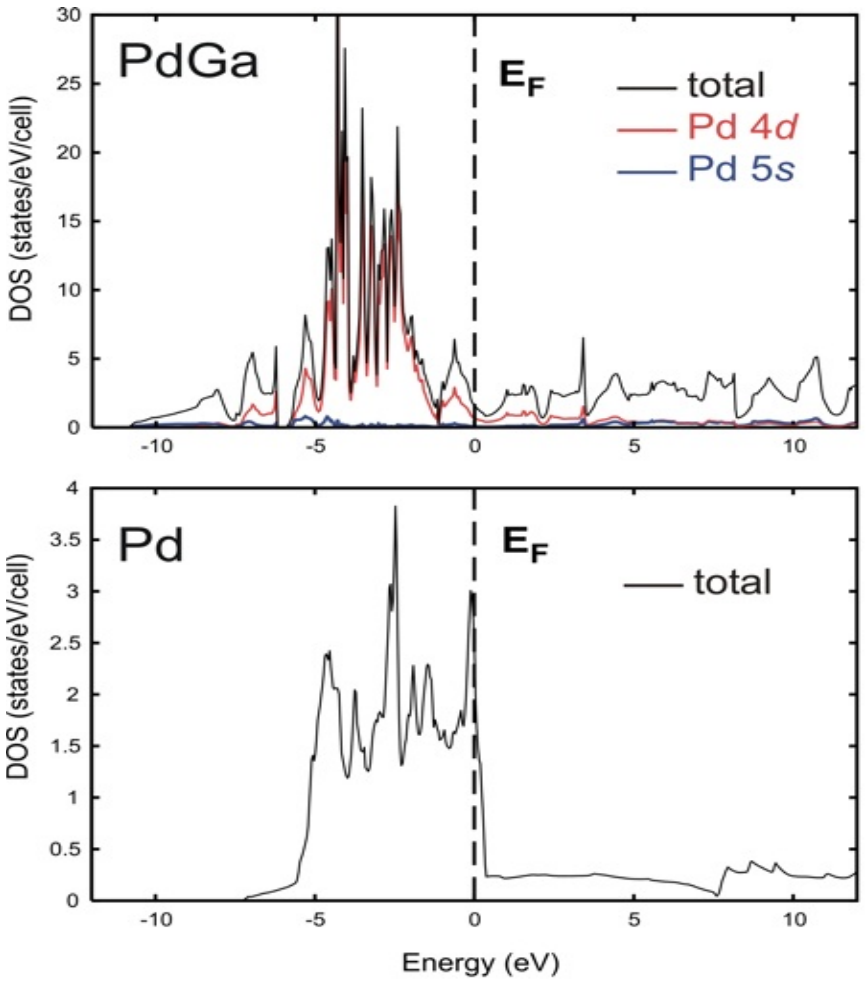
Good active sites but solid state dynamics?



85 mg after washing with EDTA at pH 13

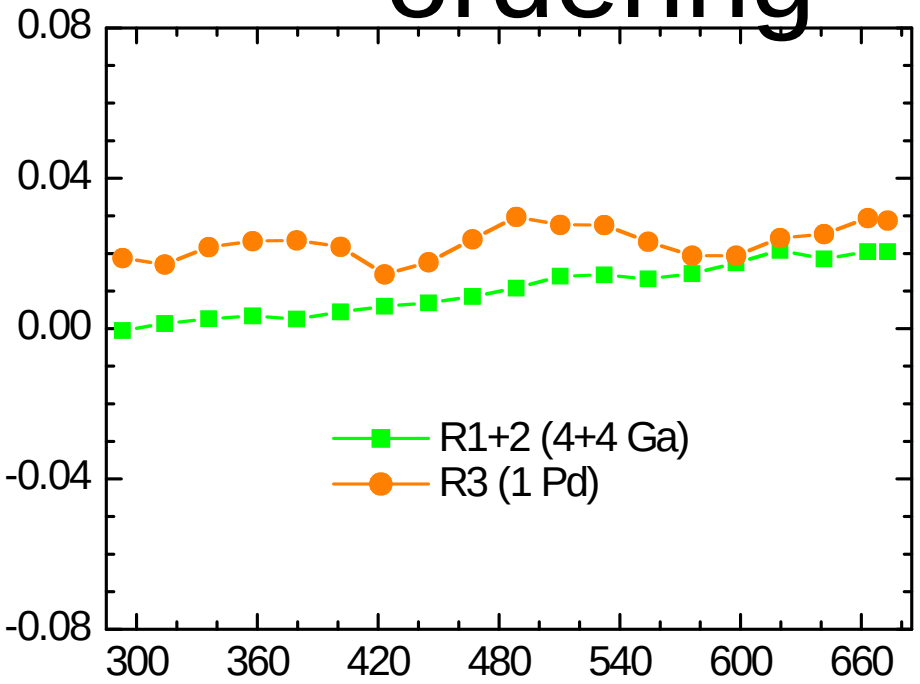
Proof of concept: new hydrogenation systems

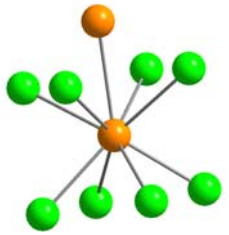




J. Grin, M. Armbrüster, K. Kovnir

Structural stability: no modification of local ordering





Pd_3Ga_7

EXAFS analysis

Pd_3Ga_7 in 10% C_2H_2 + 20% H_2

Active sites in a high performance catalyst

- An active heterogeneous catalyst contains adaptive sites for reaction.
- They adapt their structure according to the local chemical potential and guarantee selective operation on progressively more reactive adsorbates.
- The complex structure of the precursors is required to fix the chemical potential of the active phase in the reaction environment.

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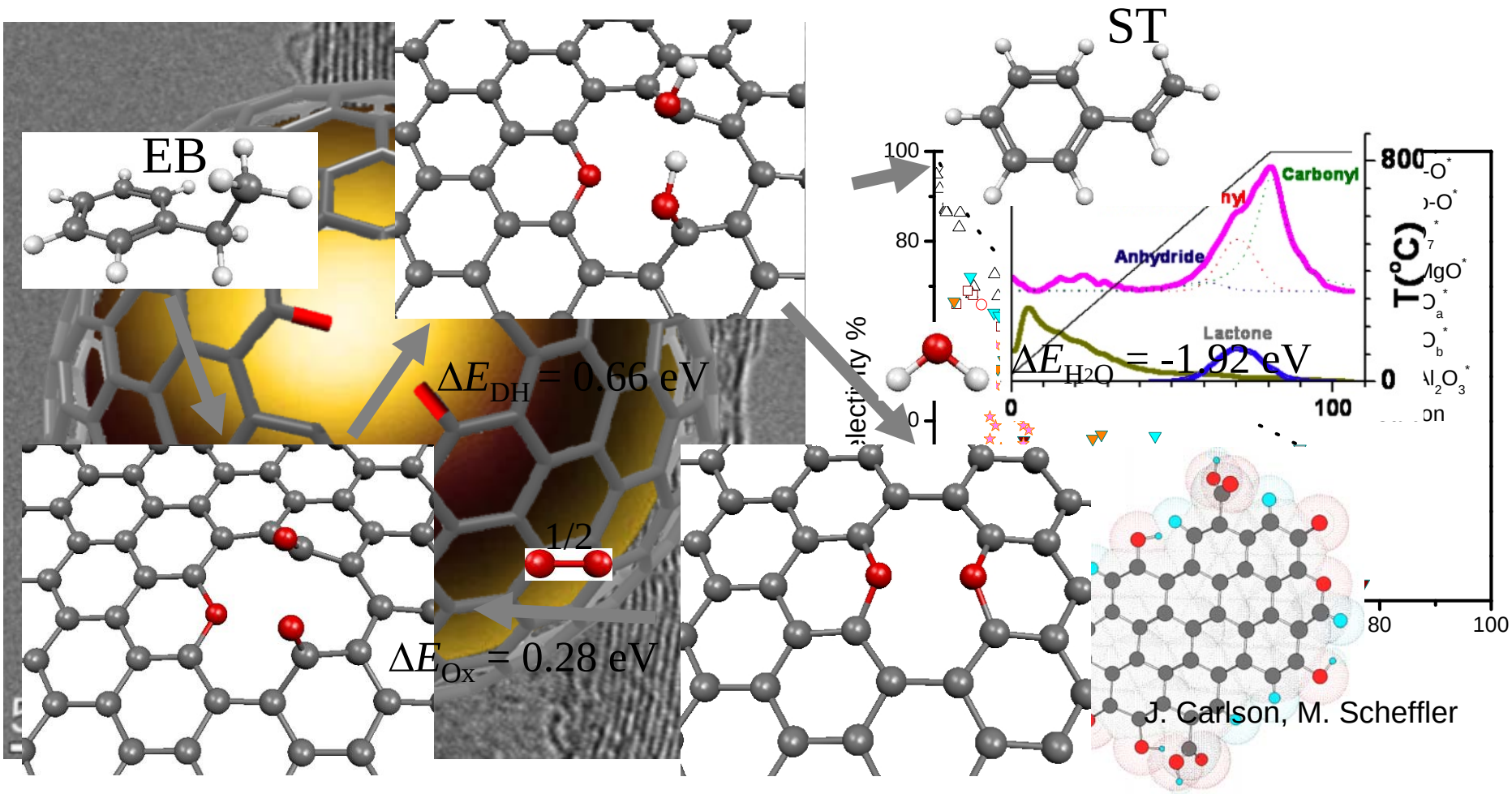
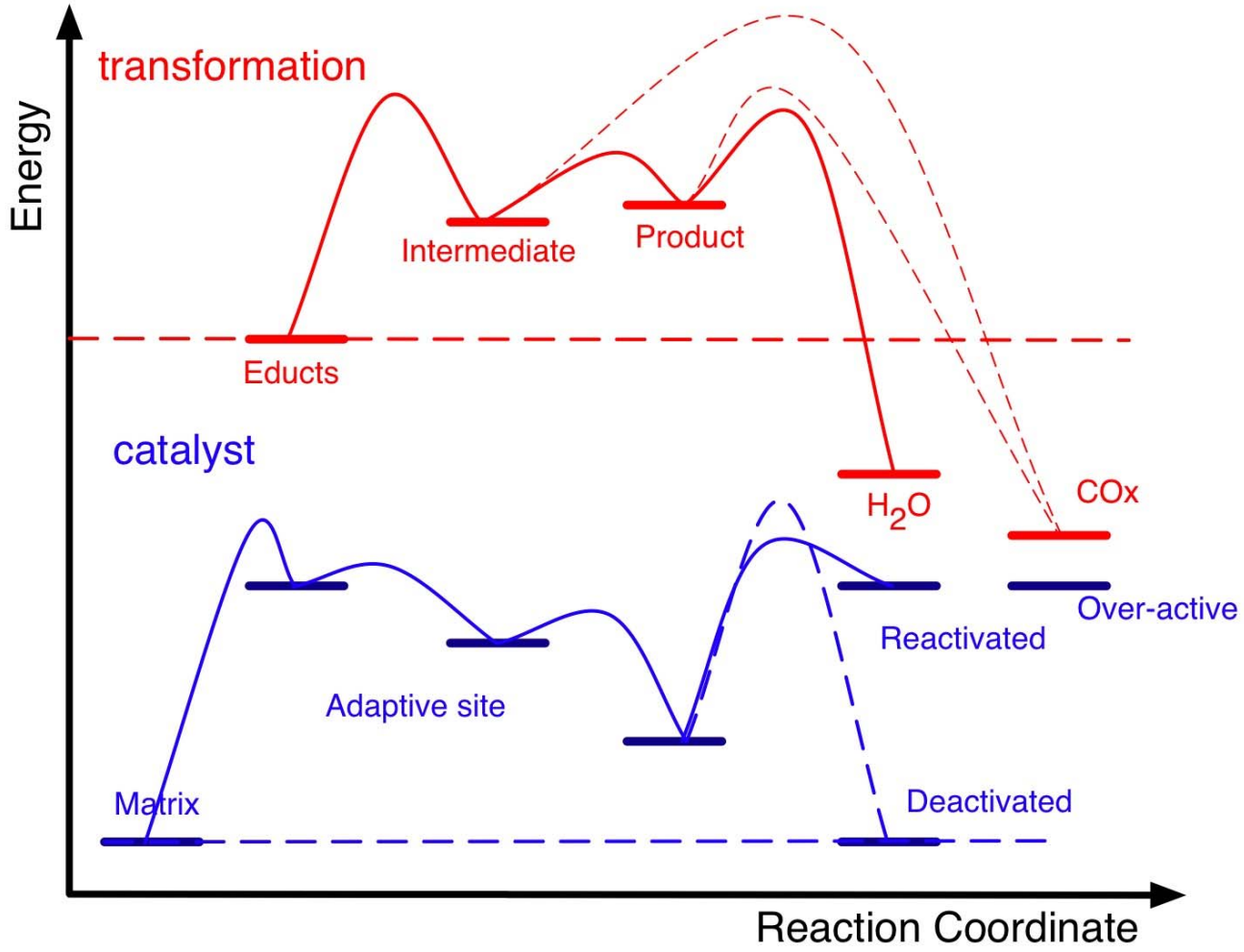
Decouple oxygen reagent from cat structure
Metal-free catalysis for butane ODH



J. Carlson, M. Scheffler

ΔE_{ODH} = -0.98 eV/molecule

Coupling of transformation and material



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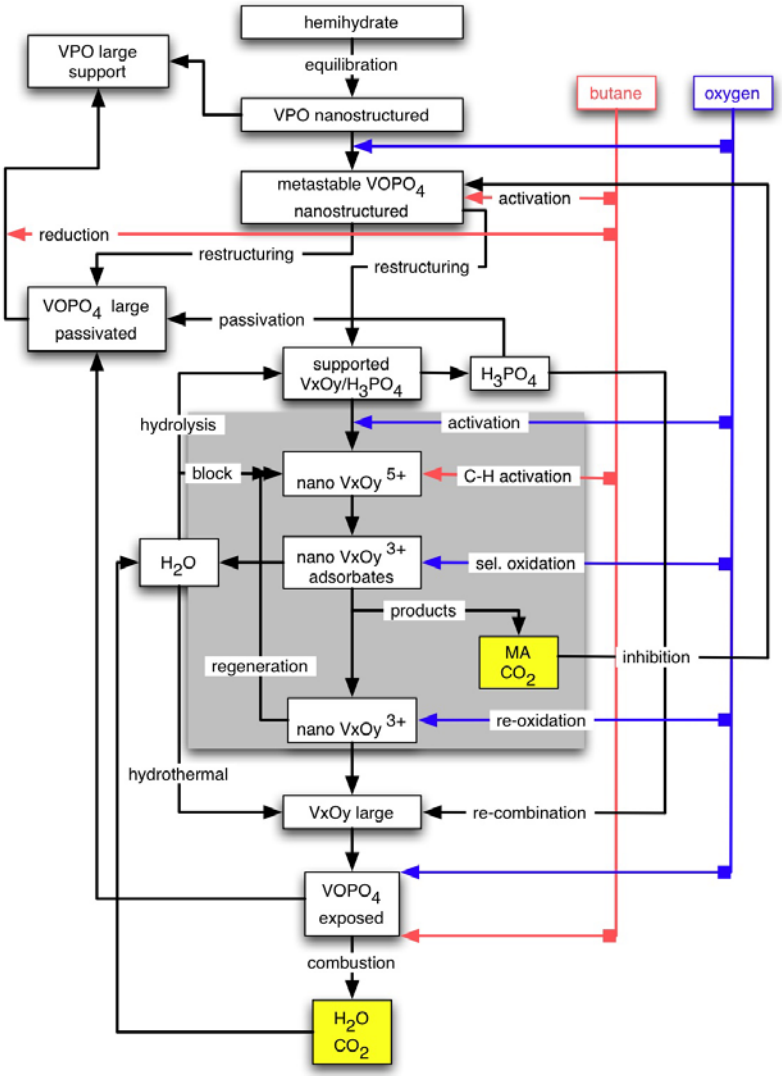
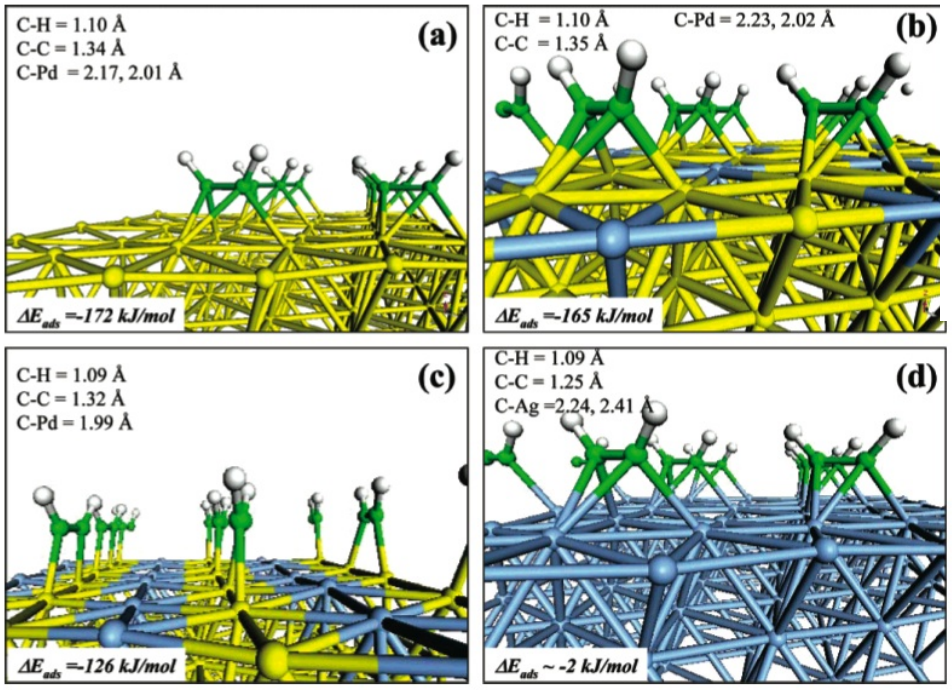
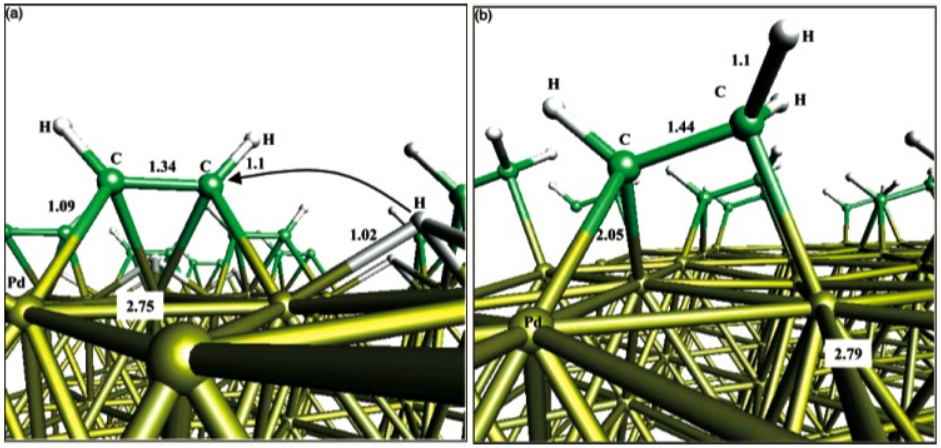
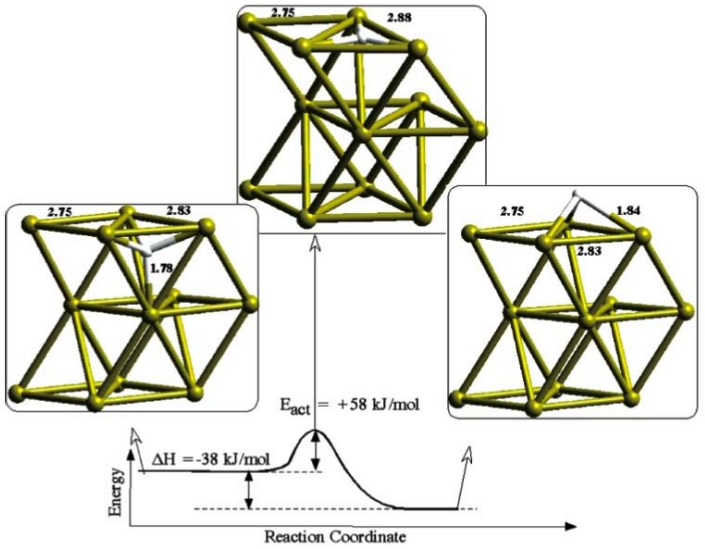
Catalyst dynamics



Reaction pathway: role of H_{sub}







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