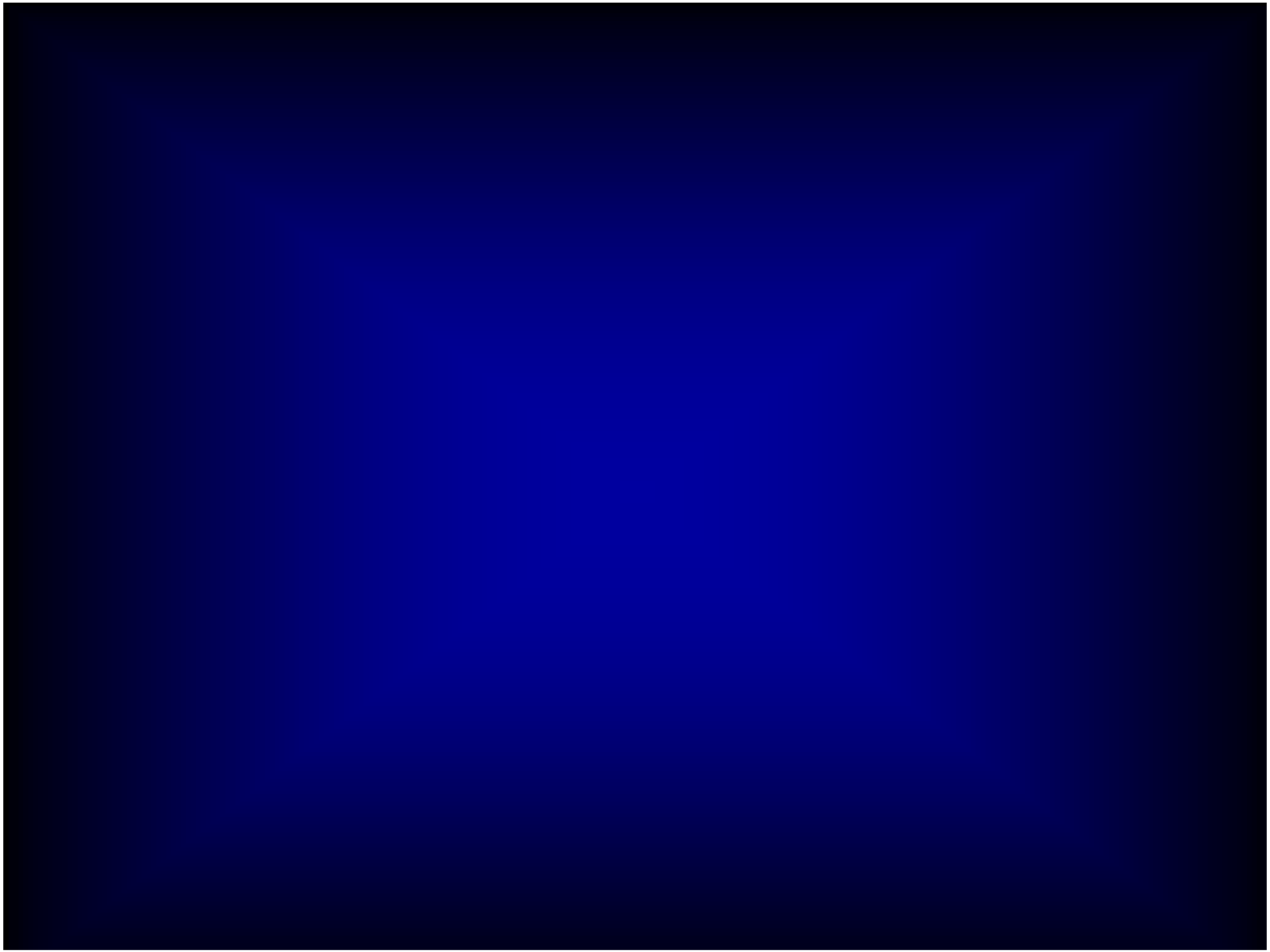


M. Armbrüster, K. Kovnir, R. Giedigkeit, J. Grin, MPI CPFS

Robert Schlögl
Fritz-Haber-Institut der MPG

Pd and its Intermetallics in Heterogeneous Catalysis

FUNDAMENTALS

The function of a catalyst: The single crystal approach

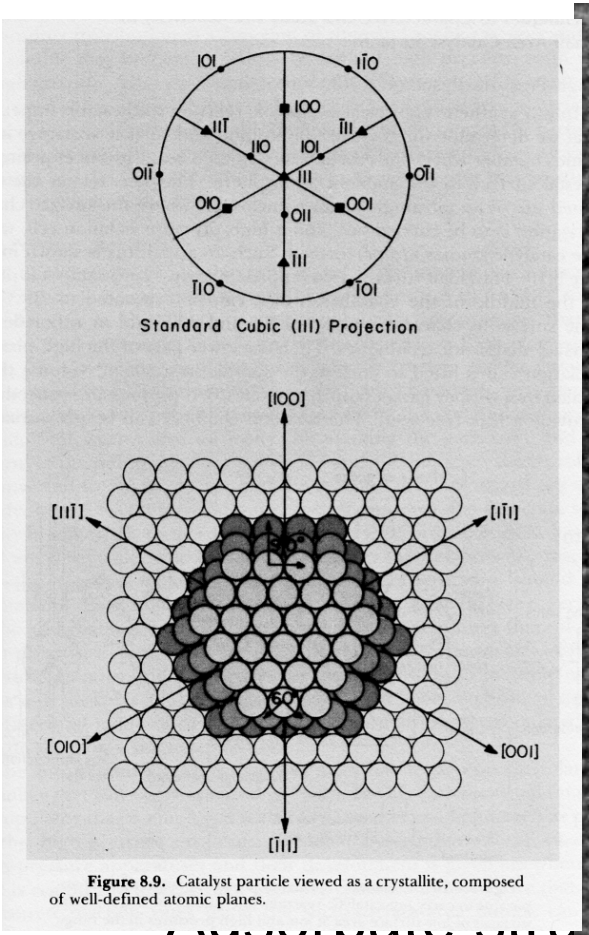
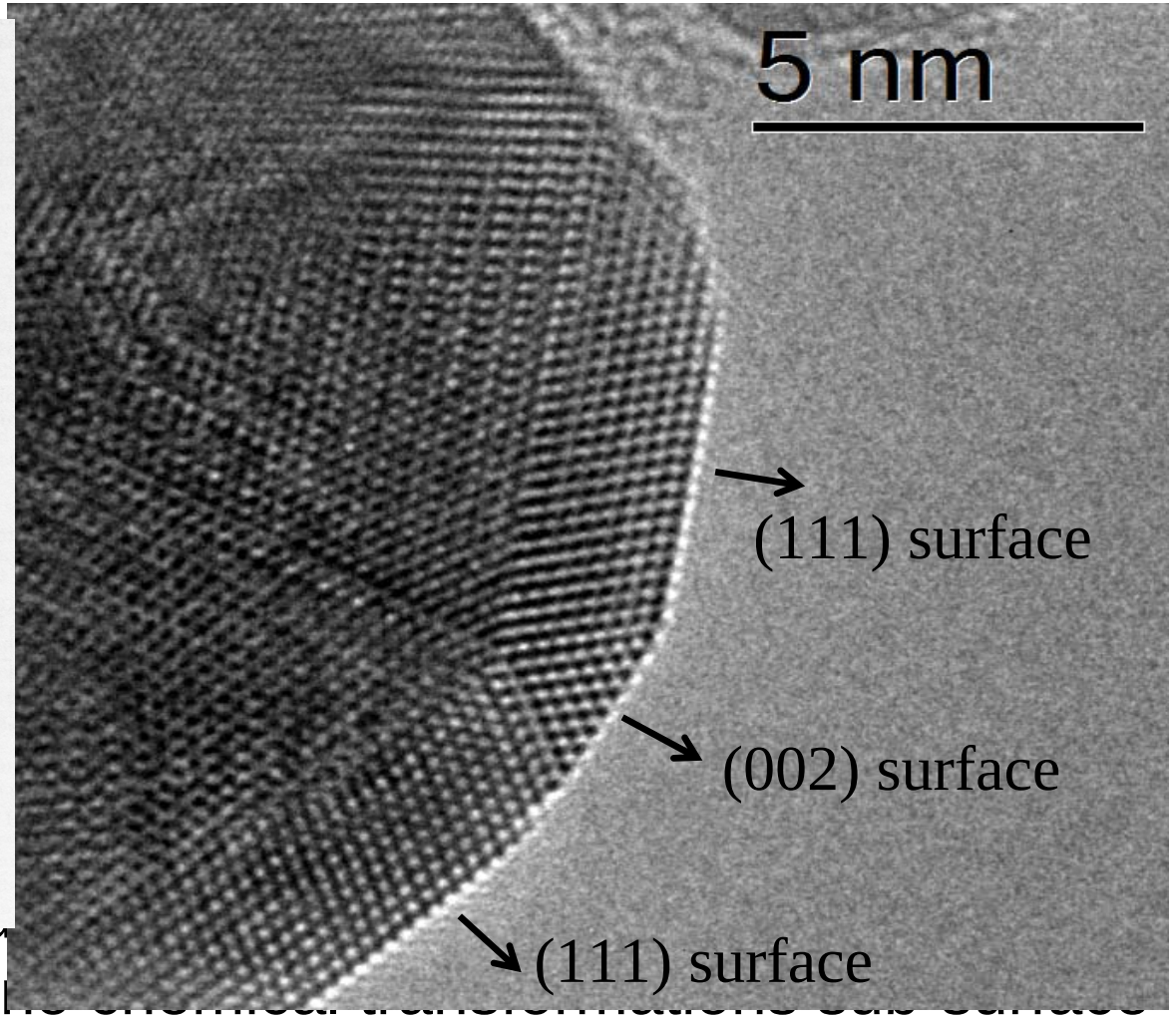


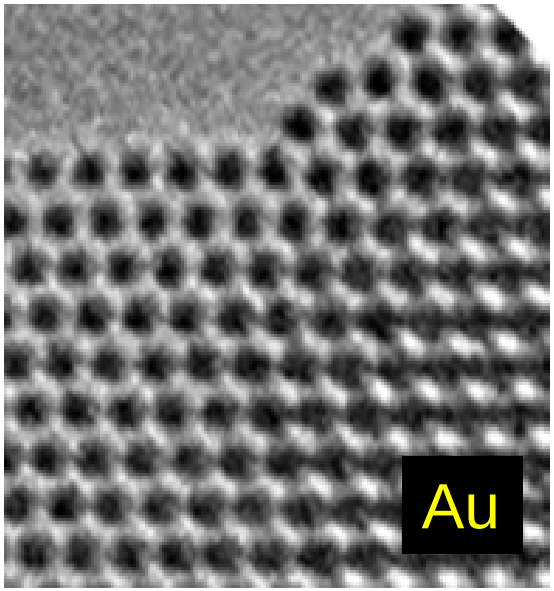
Figure 8.9. Catalyst particle viewed as a crystallite, composed of well-defined atomic planes.

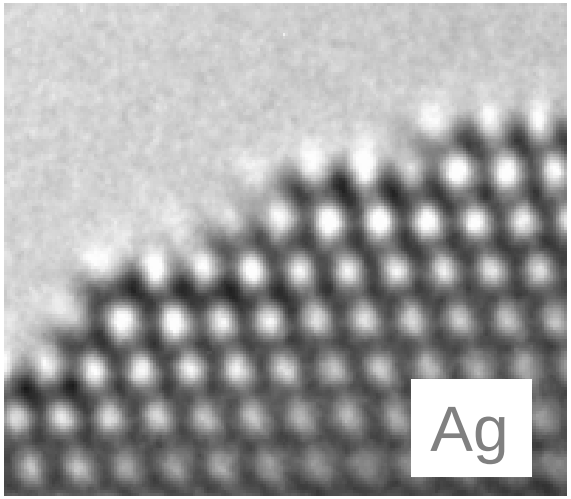
Somorjai 1981

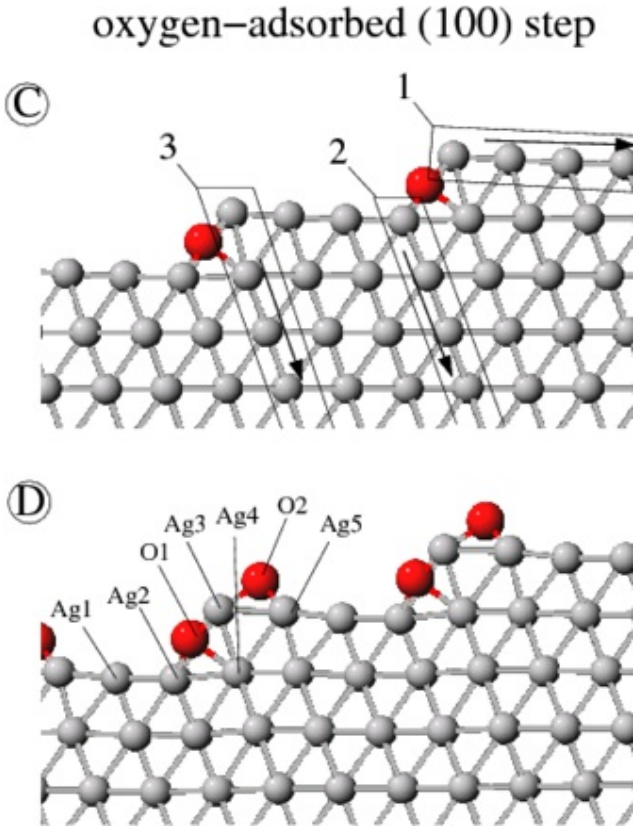


Bulk is "irrelevant",

Defects: Oxo-philicity







T. Jakob
M. Scheffler

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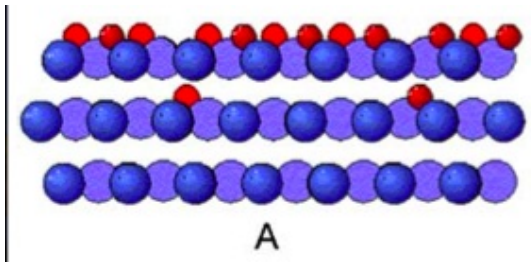
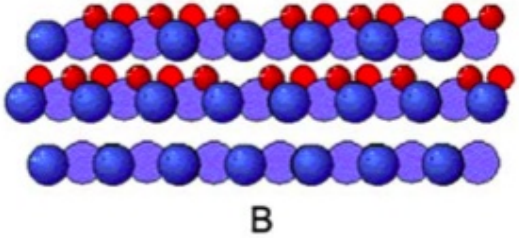
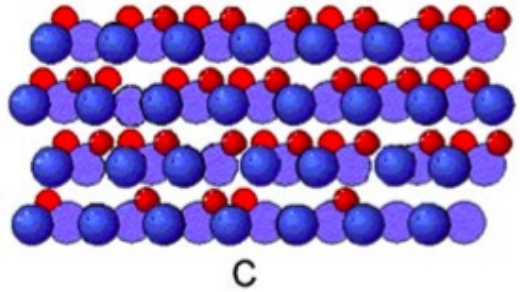
Metastable sub-surface species



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

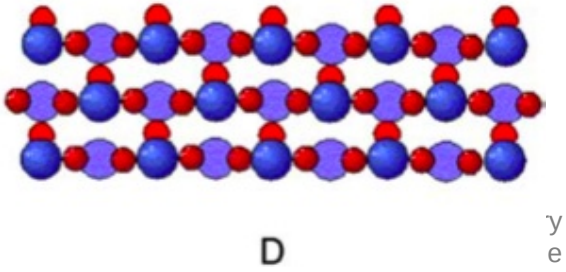
At slightly elevated potential: “trilayer” (theory)





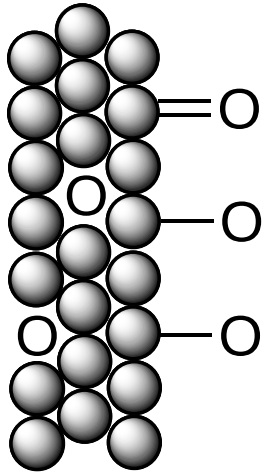
At potentials bejond the “pressure gap”: sub-oxide, sub-surface oxide, TSO (HP-XPS)

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



Di-oxygen as oxidant

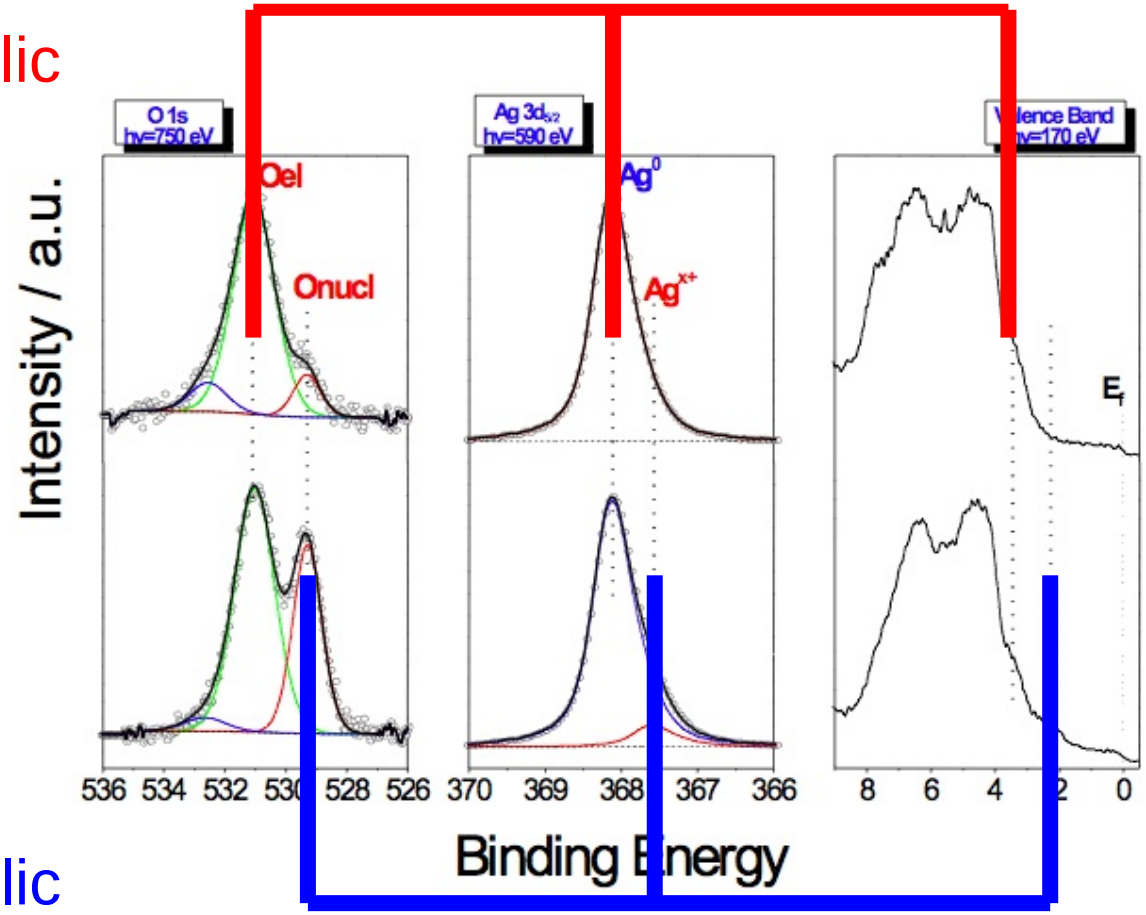
- Atomic chemisorbed oxygen (created typically in UHV) is amphoteric in redox properties: at “virtual pressure” → sub-surface
- Sub-surface oxygen is not reactive but
  - Polarizes the surface for adsorption
  - Restructures the surface by incorporation (autocatalytic)
  - Segregates to the surface as O nucleo
  - Polarizes atomic oxygen into O electro
- Electrophilic oxygen
  - Oxidizes functional substrates (CO, olefines)
  - Creates all oxygenate organic molecules
- Nucleophilic oxygen
  - Activates C-H bonds into functional substrates
  - Creates basicity and binds water (OH)
  - Protonates via OH oxygenates



With metals

Multifunctional oxygen

electrophilic



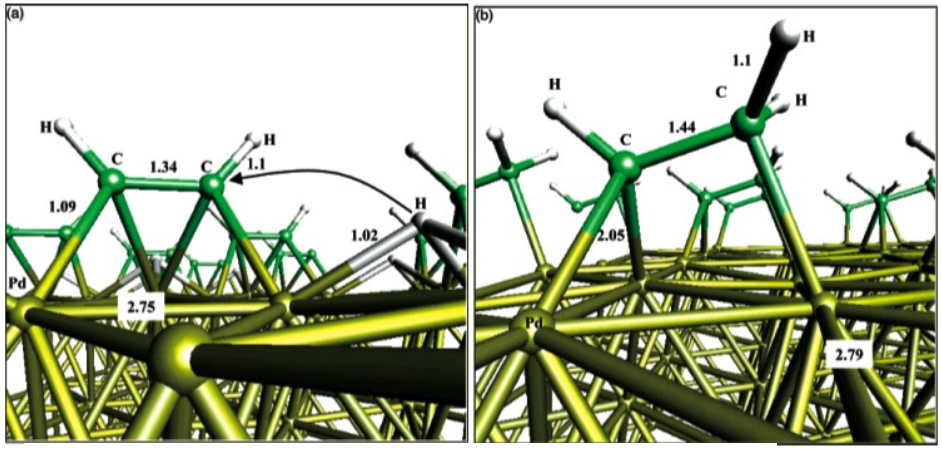
nucleophilic

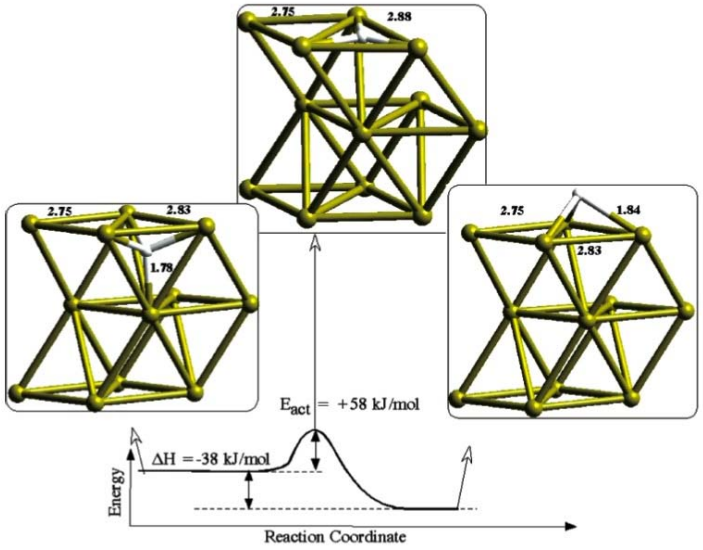
Analogy: Protonic vs hydridic hydrogen?

Hydrogenation Catalysis

- A widely used yet often poorly selective catalyst for hydrogenation reactions is Pd metal as nano-particles on supports.
- Selectivity controlled by additives (poorly reproducible).
- Concept: Size of active site controls selectivity.
- Concept: sub-surface “hydride” is relevant or detrimental.

Reaction pathway: role of H_{sub}



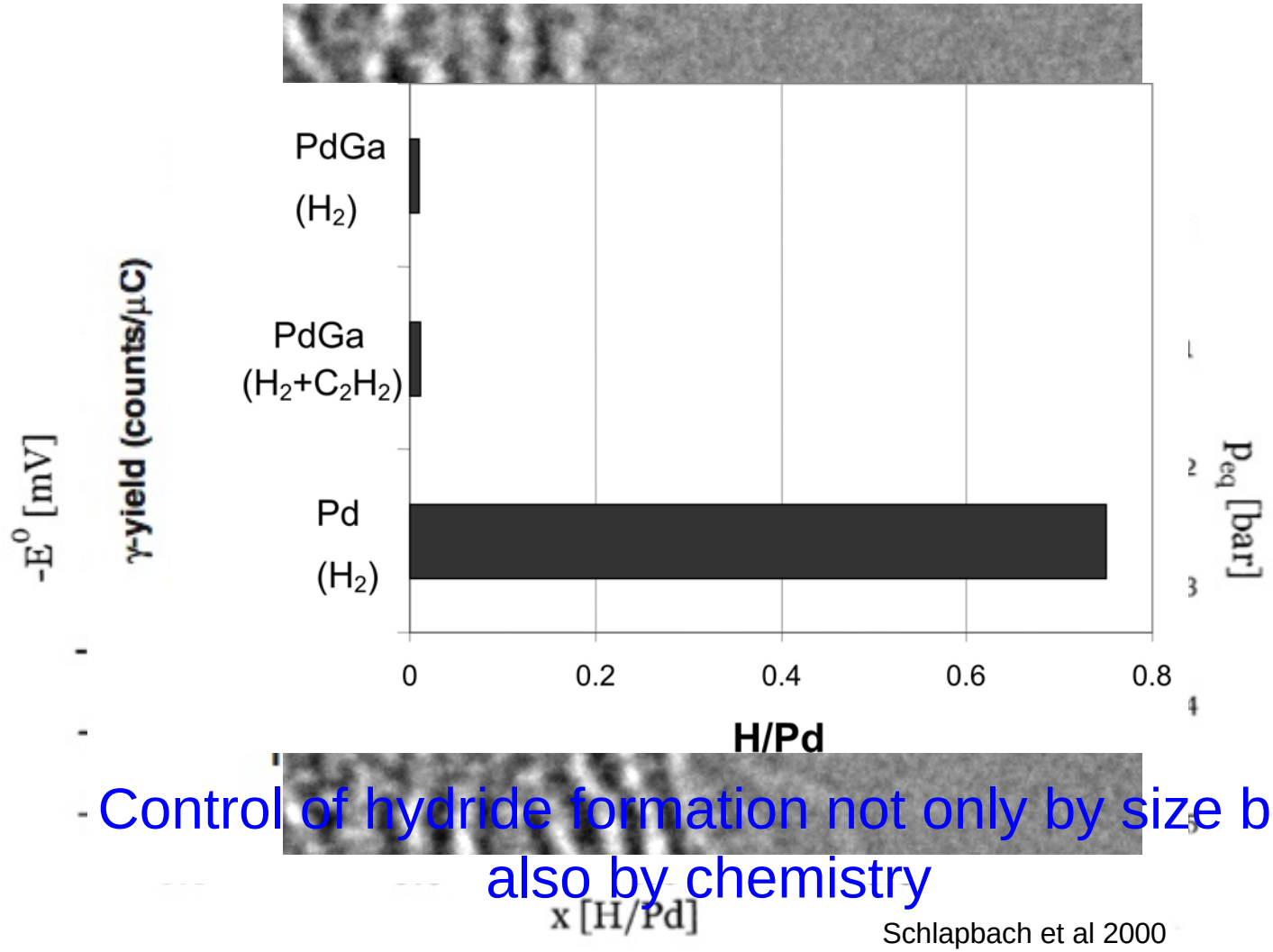


Active site: 6 Pd atoms:
Rate controlled by equal chemical potentials of [H] and [substrate].

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

M. Neurock, 2003, 2005

Pd-H in nanoparticles



Control of hydride formation not only by size but also by chemistry

Schlapbach et al 2000
Eastman et al , 1993

Nano Pd in fluid phase oxidation

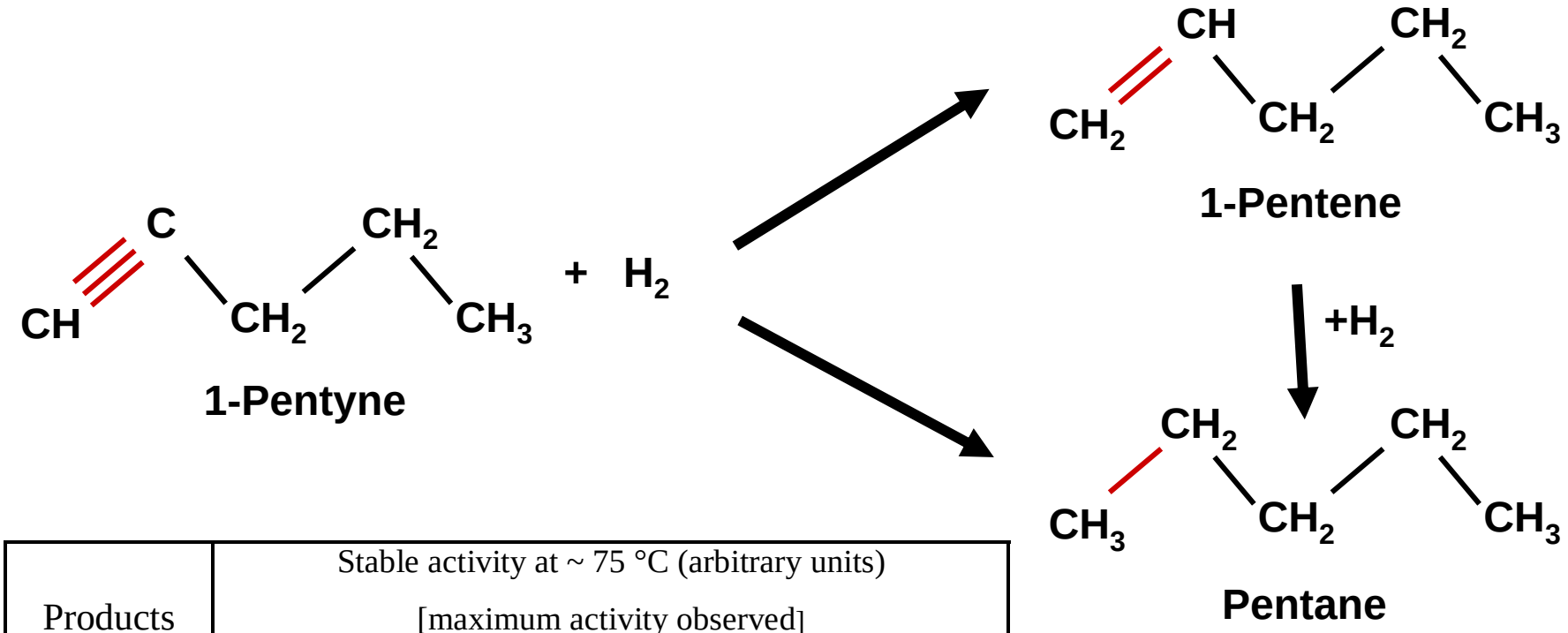
Alcohol	Time Reaction (h)	Conversion		Selectivity to aldehyde	
		Pd CNTs	Pd N-CNTs	Pd CNTs	Pd N-CNTs
Benzyl alcohol	2	16	96	>99	>99
1-phenylethanol	2	25	99	>99* *ketone	>99* *ketone
Cinnamyl alcohol	2	10	78	74	77
2-octen-1-ol	2	14	81	34	42
1-octanol	8	3	14	54	58

Benzyl benzoate

Structure controls reactivity:
Size as proxy?

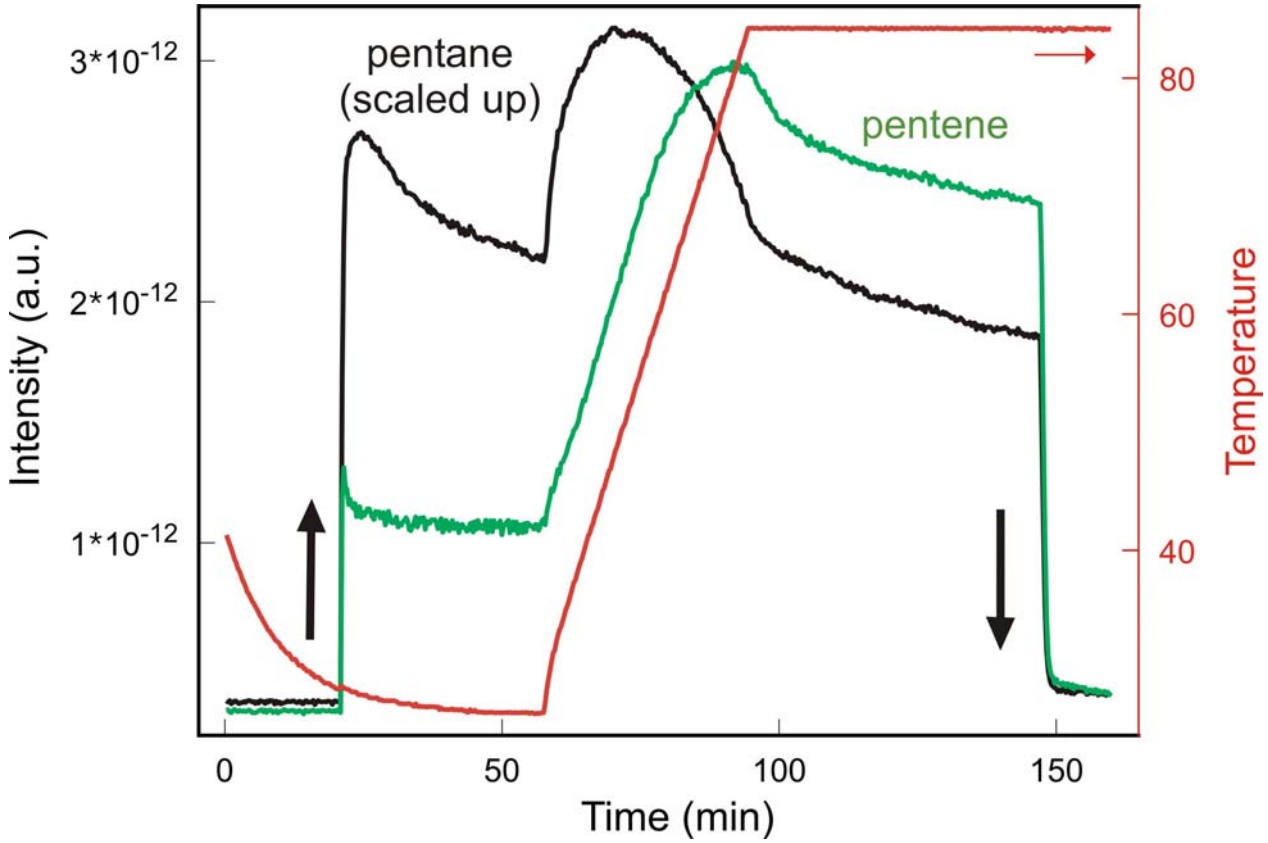
Metal (?)
Hydrogenation Catalysts

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

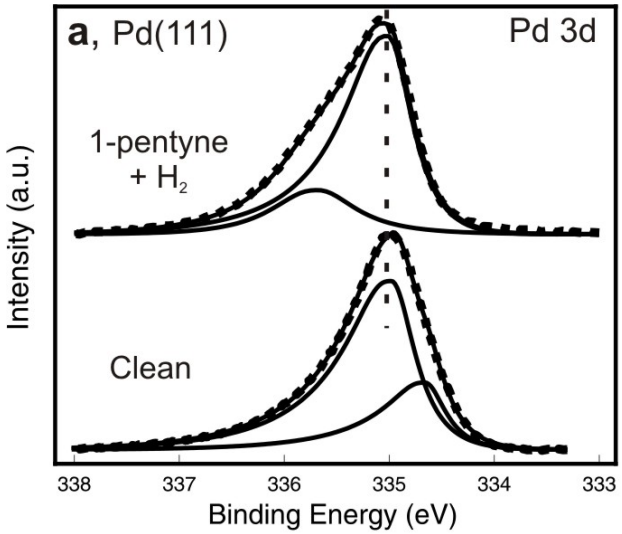
A consecutive reaction



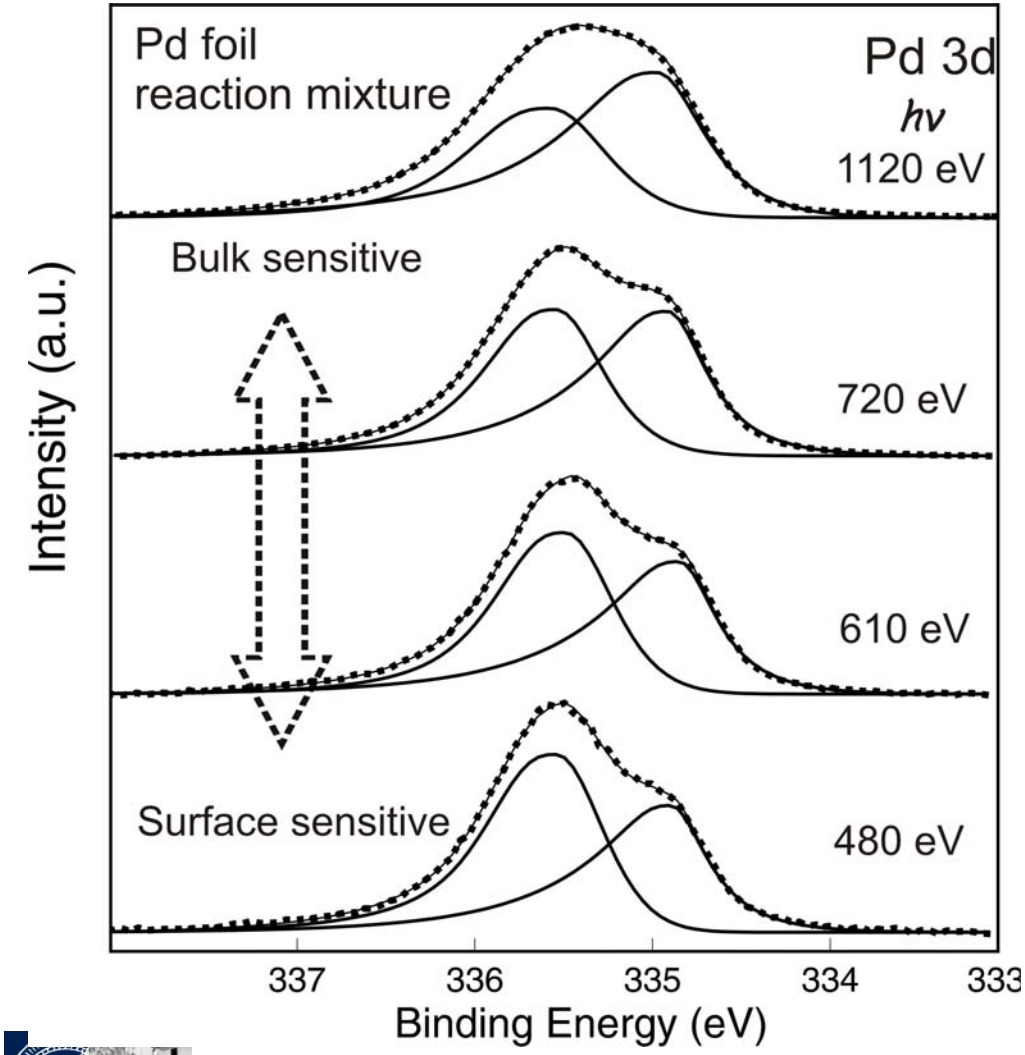
Deep hydrogenation
before
selective hydrogenation

0.03 mbar pentyne
0.85 mbar H2

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

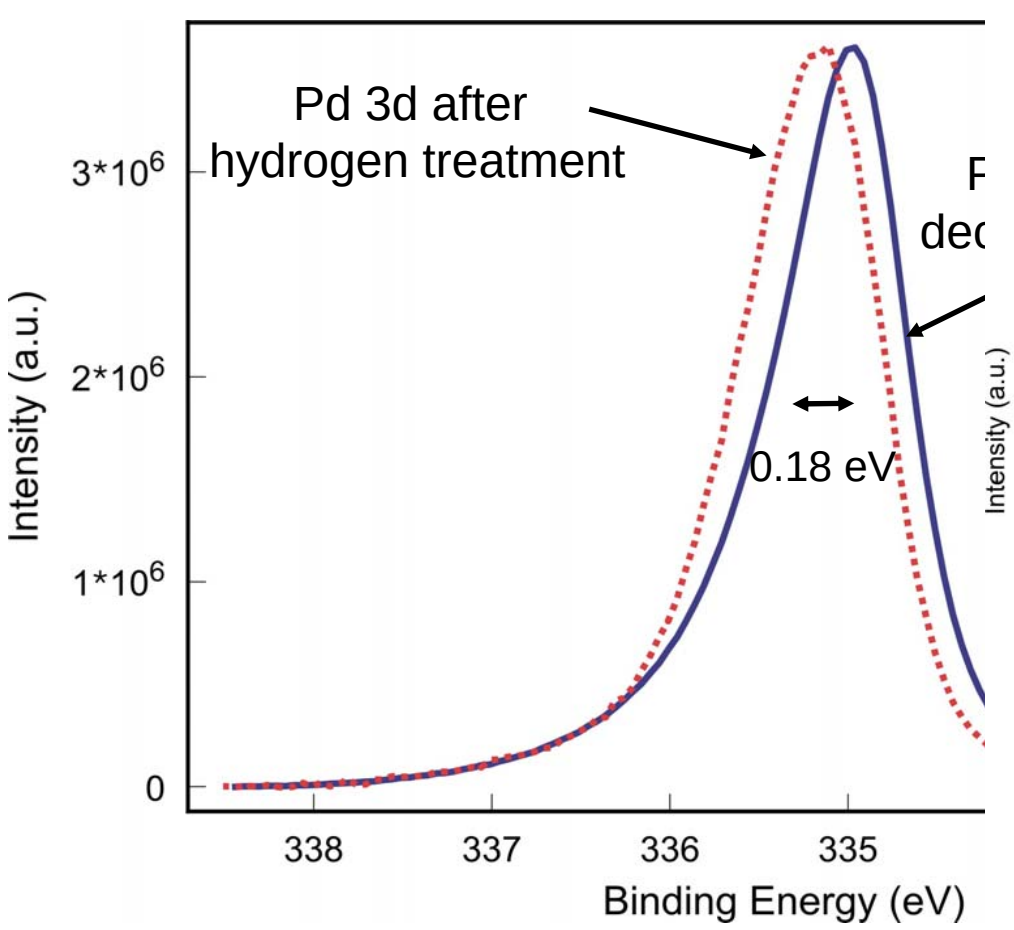


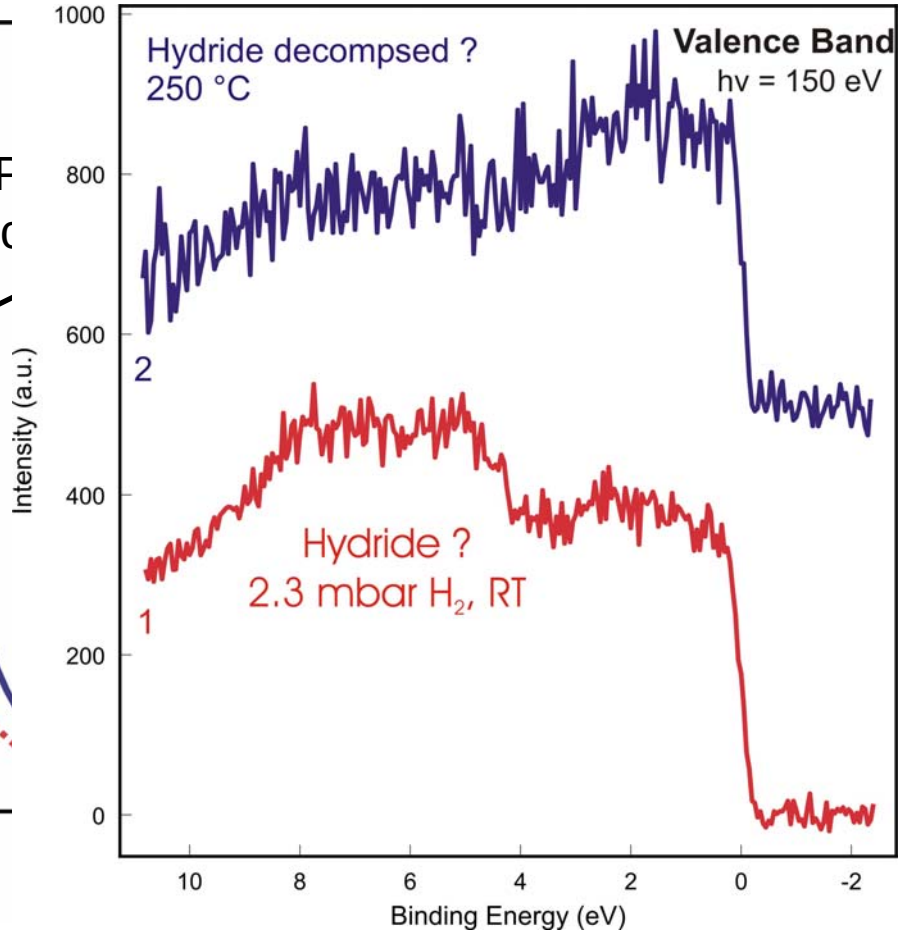
In-situ XPS: Pd 3d depth profiling



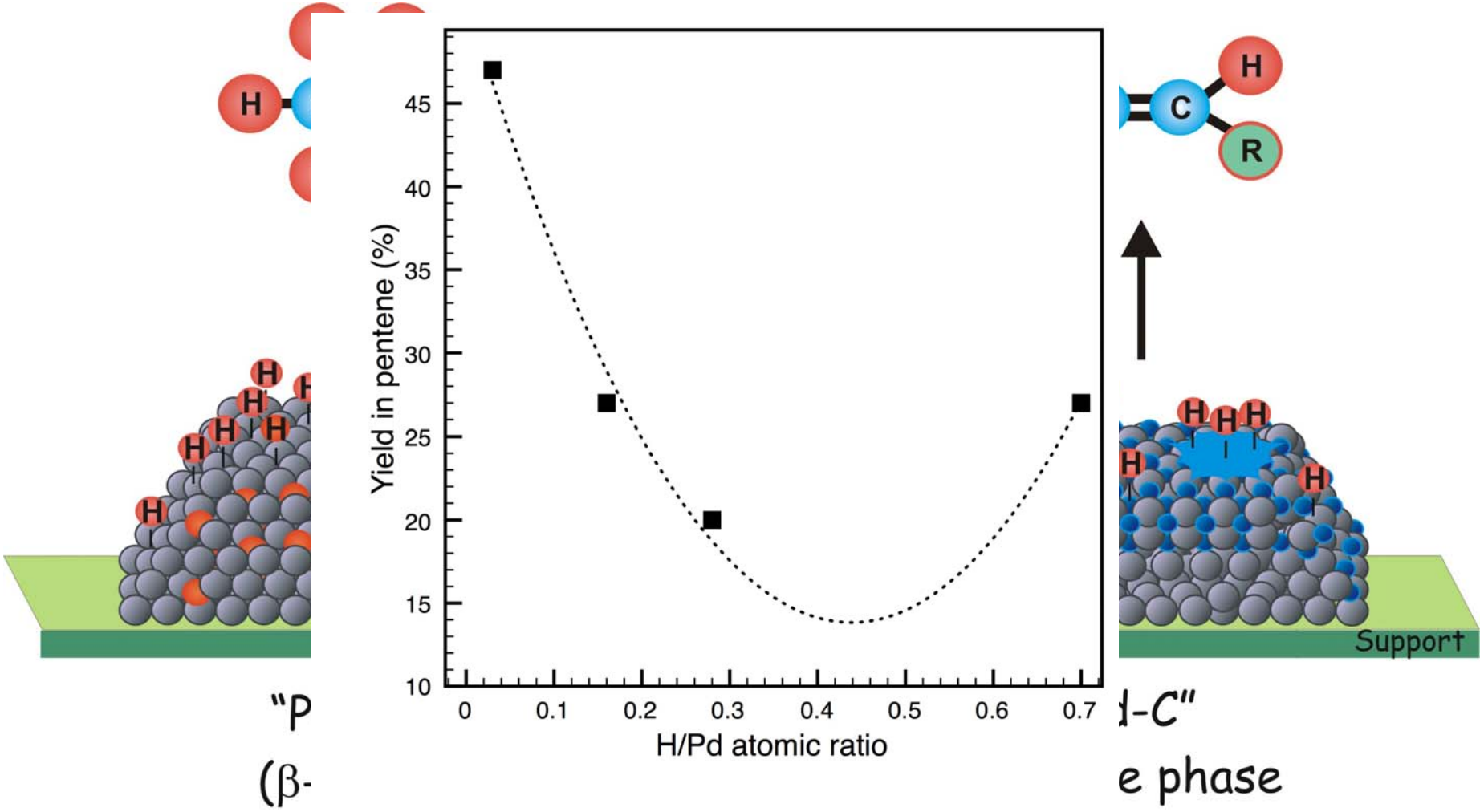
unambiguous localisation of carbon-induced component in the surface-near region

Sub-surface H vs. sub-surface C

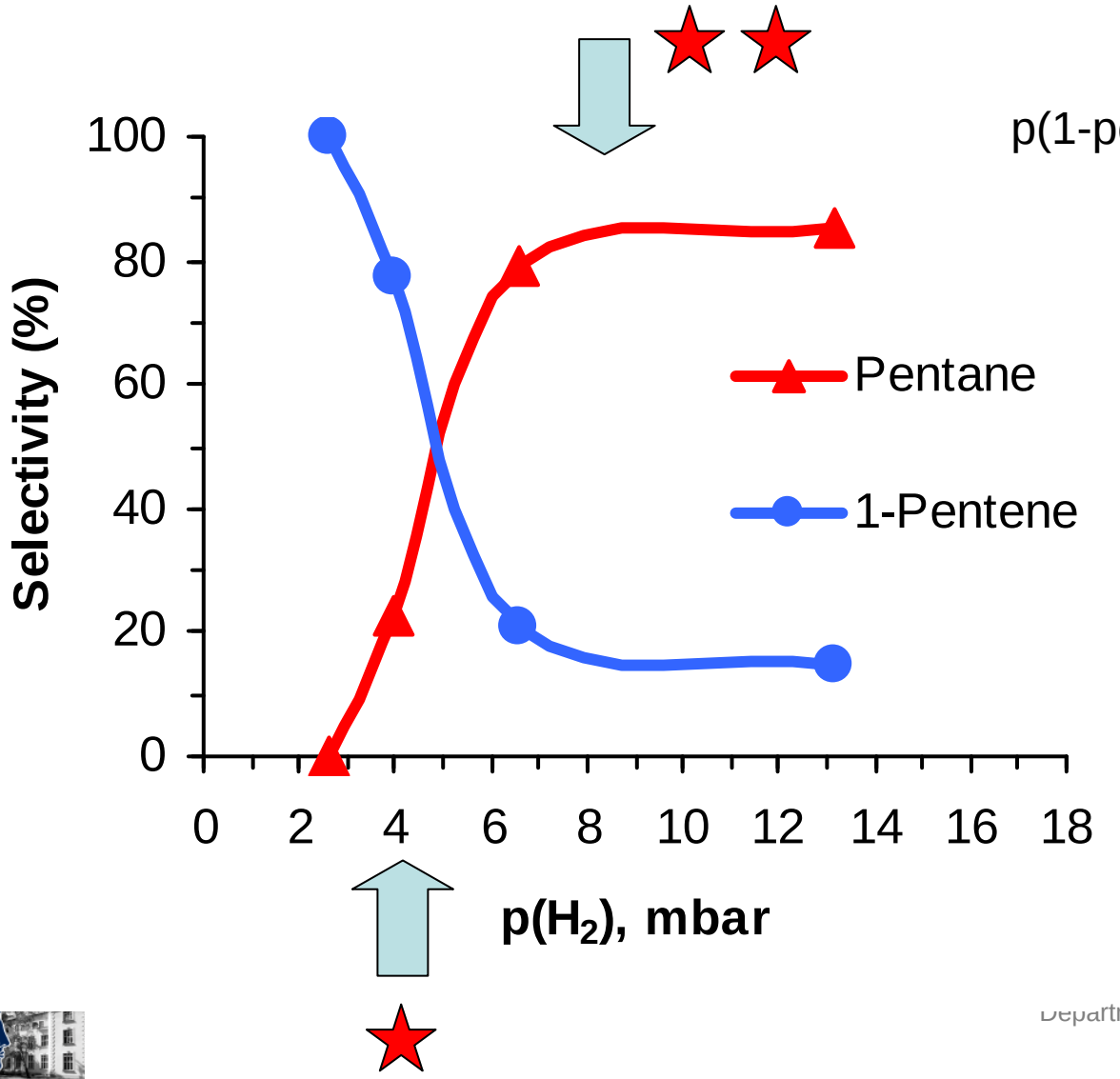




Selectivity control



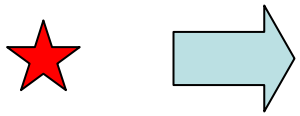
Pressure gap: reaction

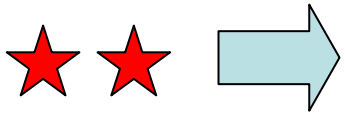


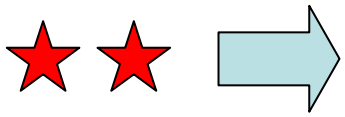
p(1-pentyne) = 0.66 mbar
T = 35°C

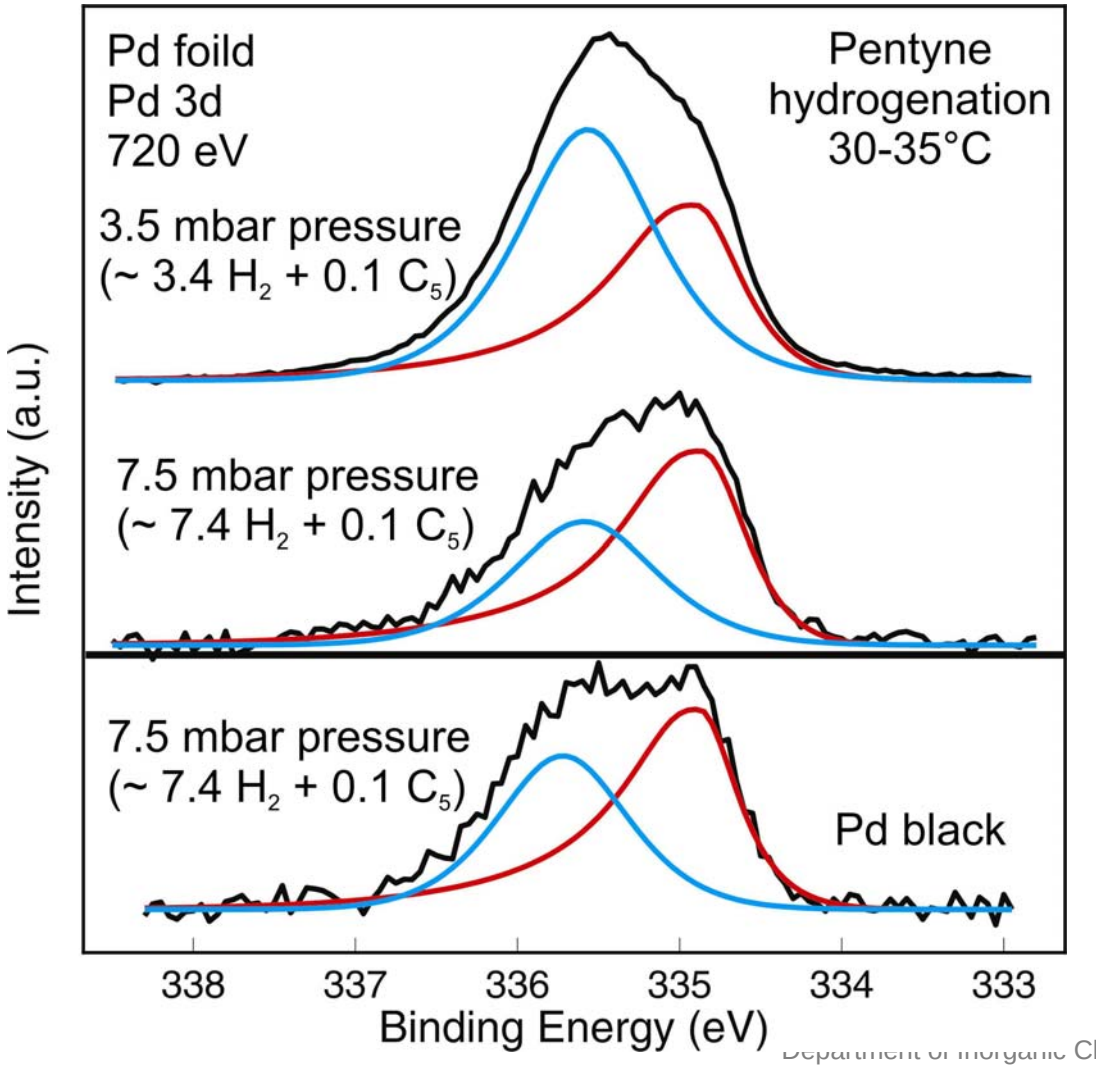
Unsupported Pd black

Pressure gap: origin

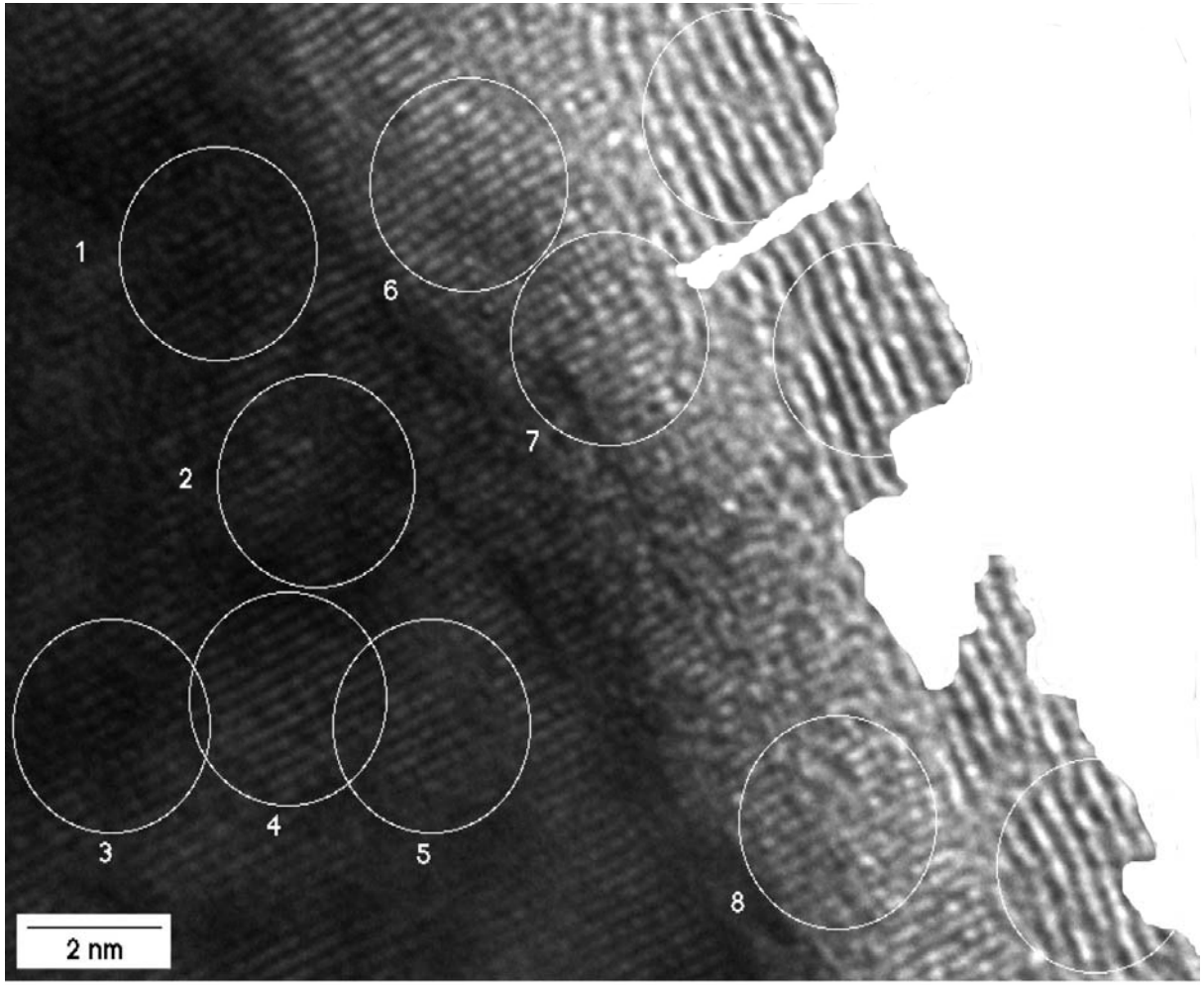


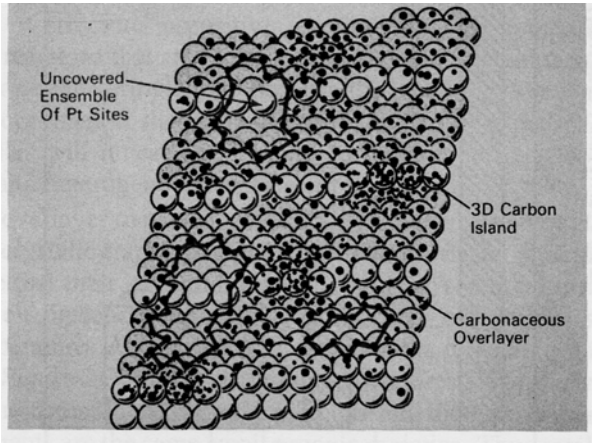






Real structue: the role of nanostructuring

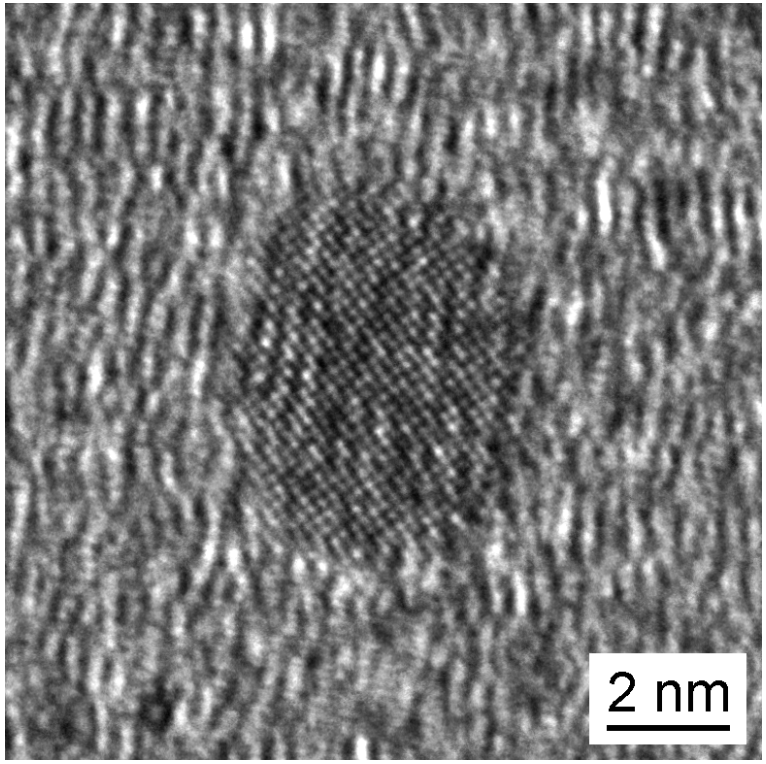


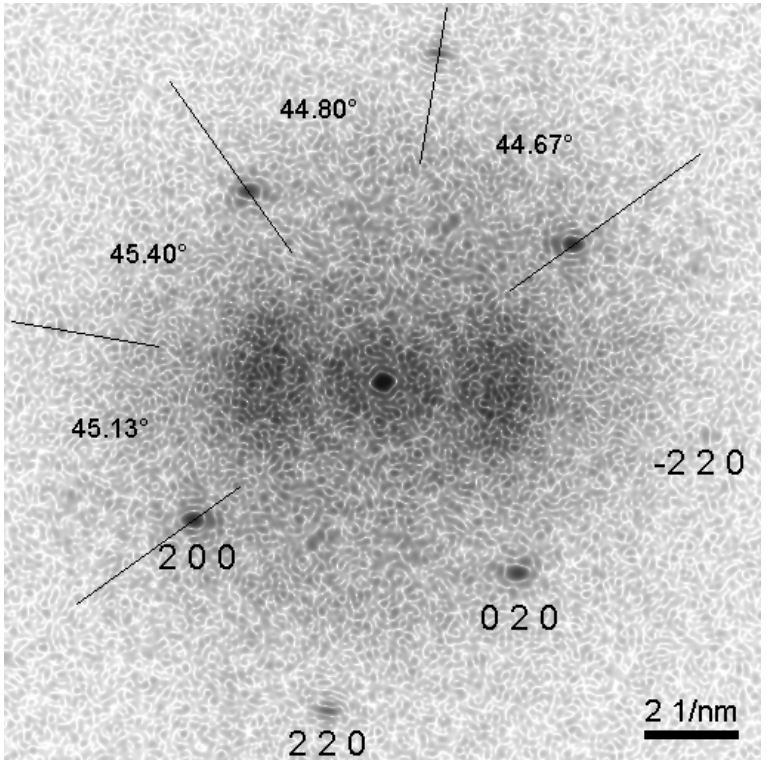


Somorjai 1994

Hydrogen dissolution under carbon!

“Structure sensitivity”





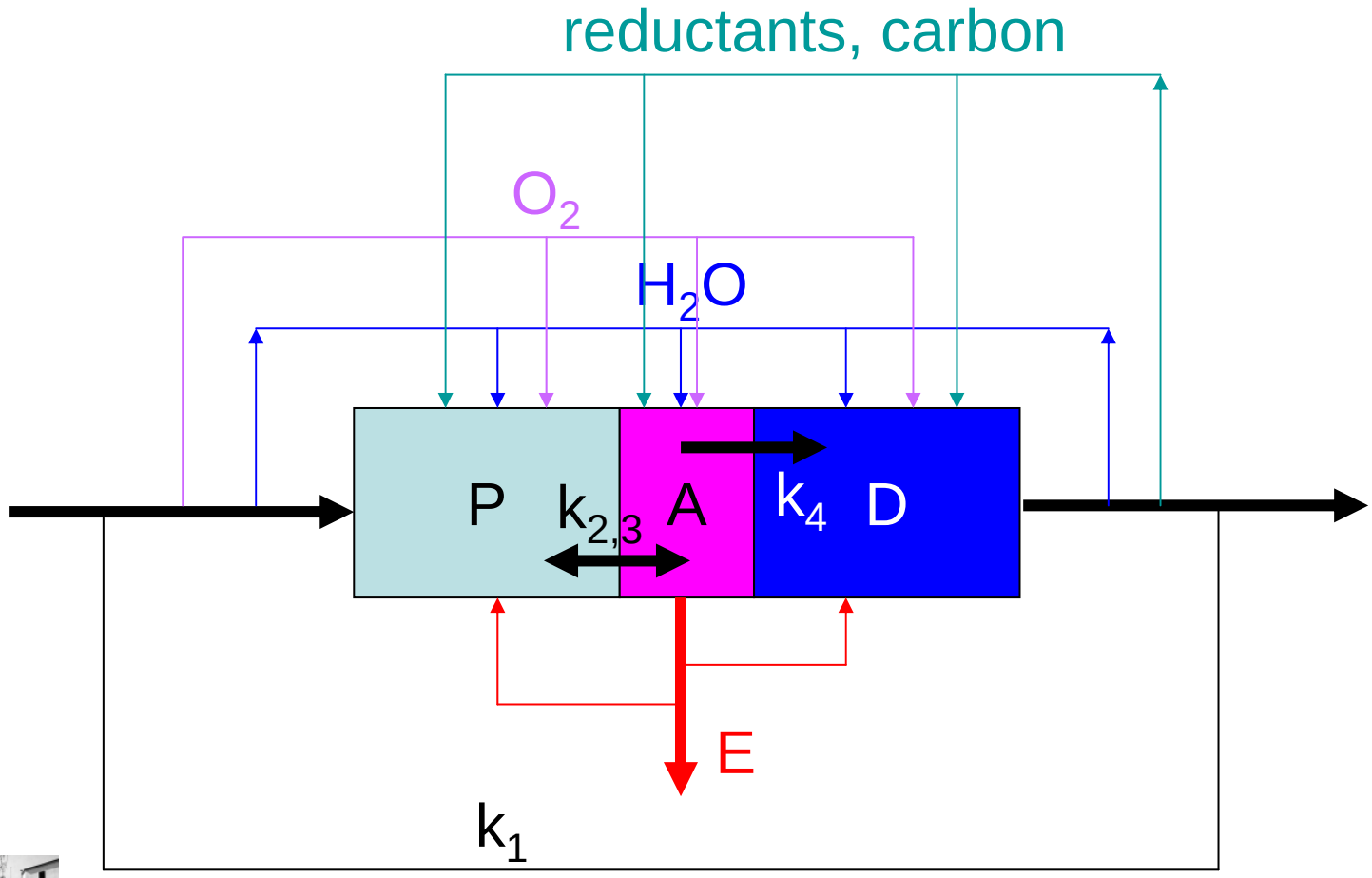
5% Pd/CNT after reaction

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

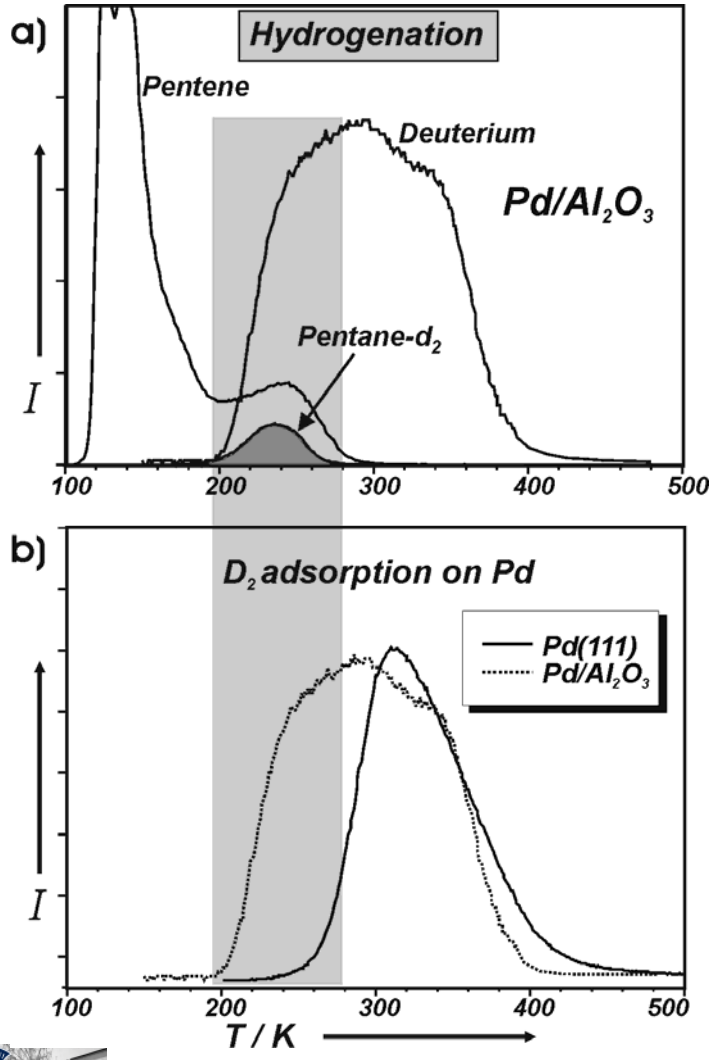
FIRST SUMMARY

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

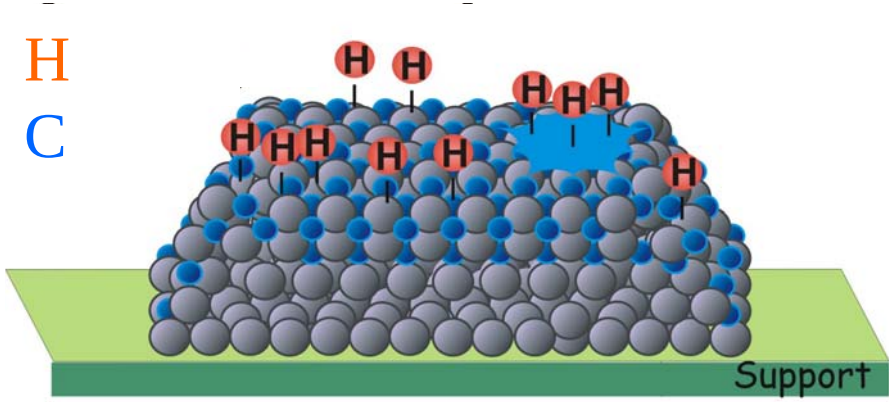
Hydrogenation in the presence of subsurface H [Pd particles]

No hydrogenation without subsurface H [Pd(111)]

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

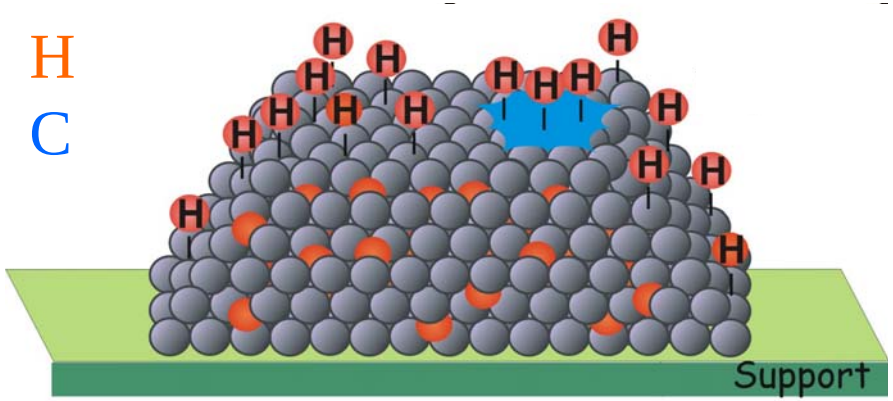
Summary

Alkyne → Alkene:



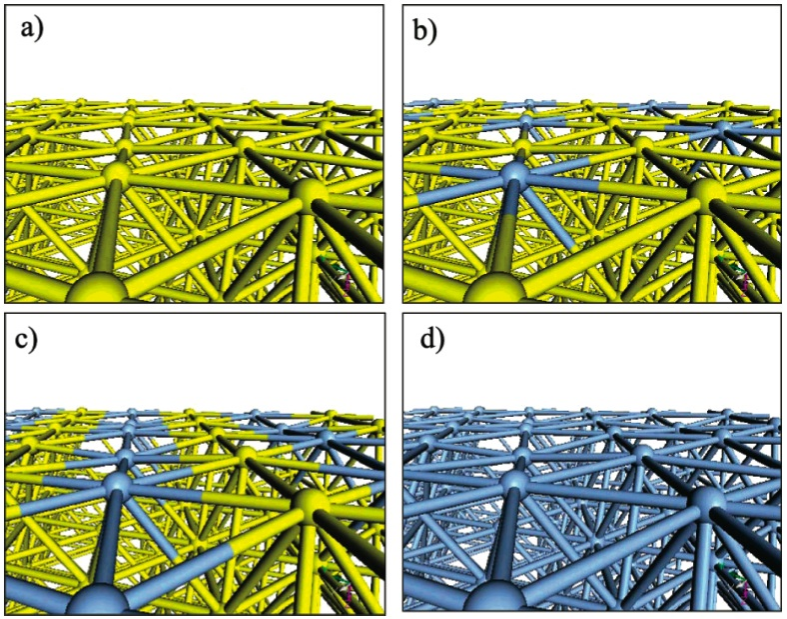
Alkene → Alkane:

Alkyne → Alkane:

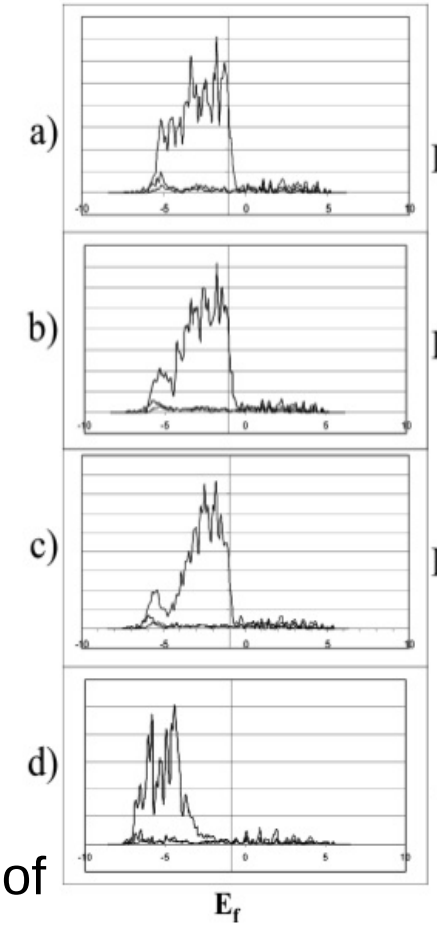


Alloys and Intermetallics: Two different classes of metals as Catalysts

Alloy Systems



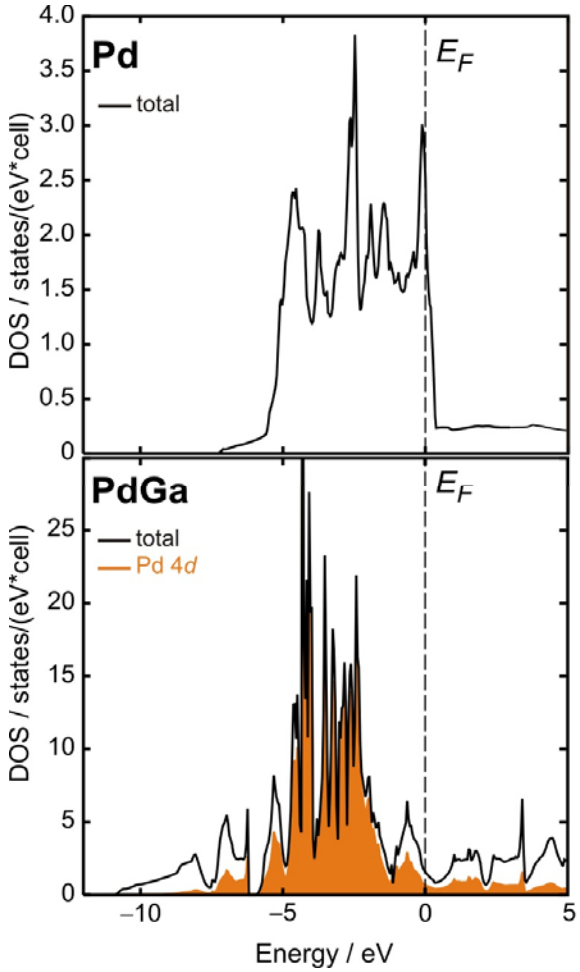
M. Neurock, 2003, 2005

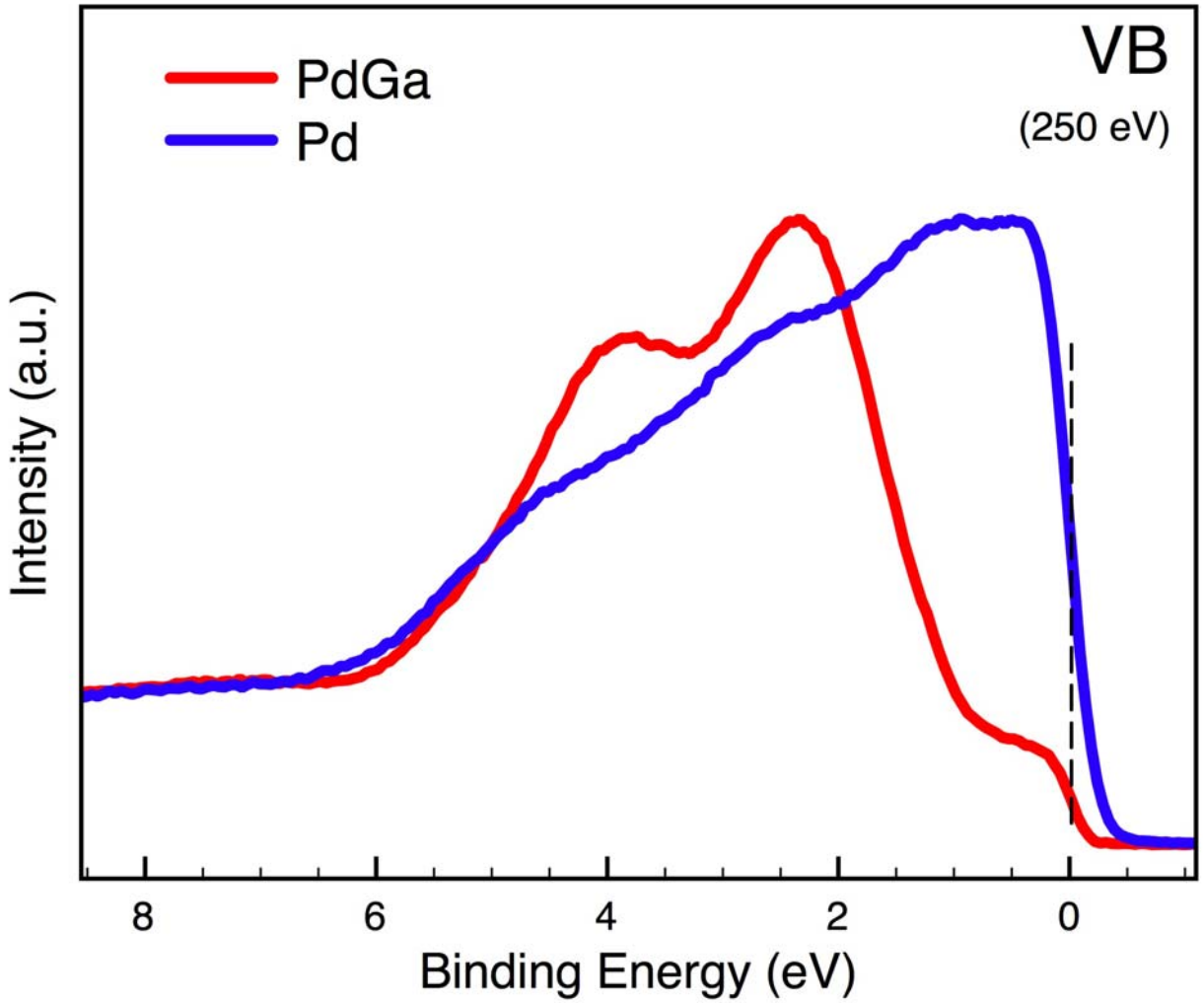


	d-band center (eV)
Pd(111)	-2.35
$Pd_{75}Ag_{25}$/Pd(111)	-2.42
$Pd_{50}Ag_{50}$/Pd(111)	-2.40
Ag(111)	-4.34

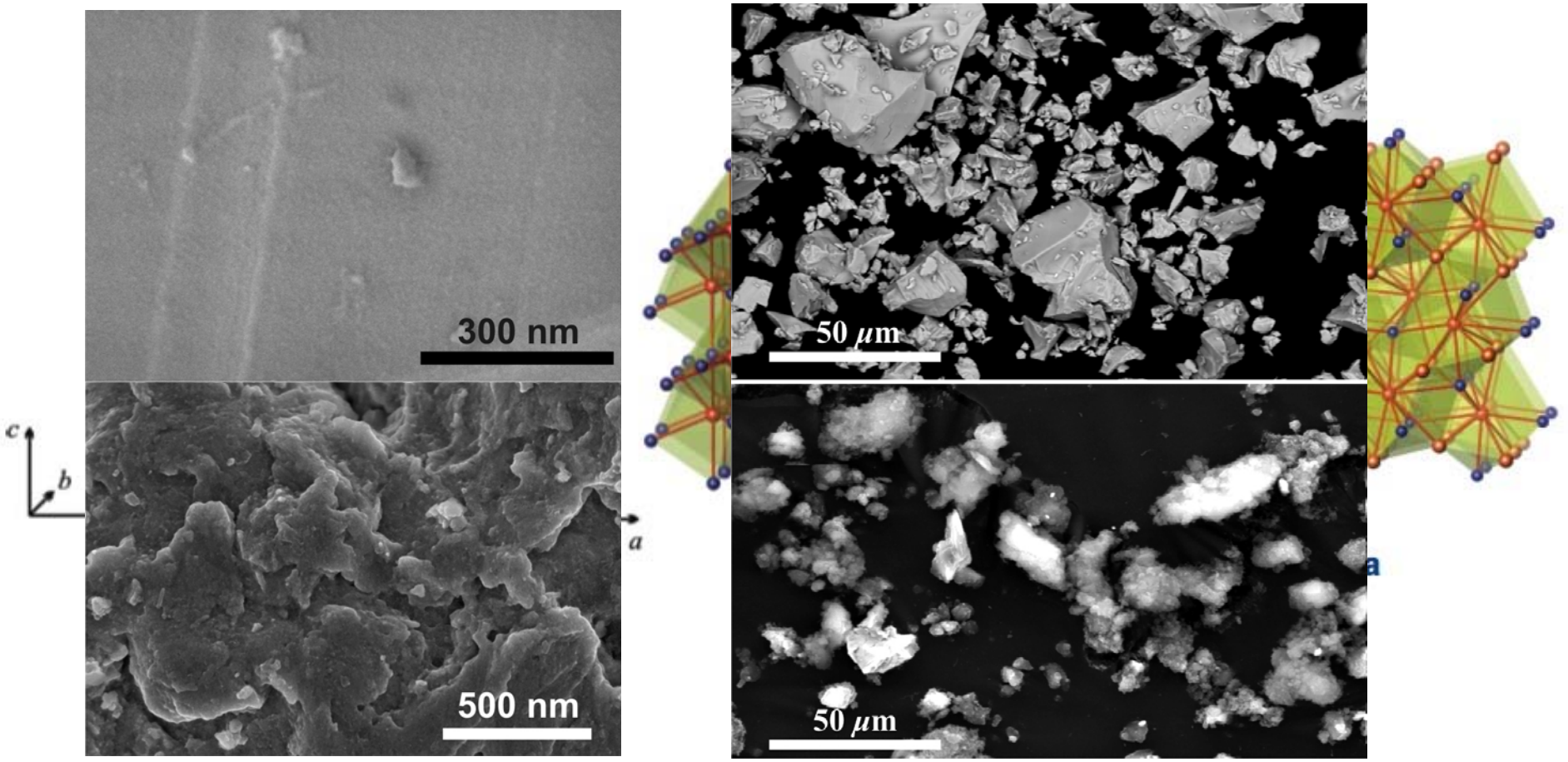
Combined benefits of site isolation and of electronic structure modification

Intermetallics: kovalent interaction





Structures and termination



Chemical etching for activation

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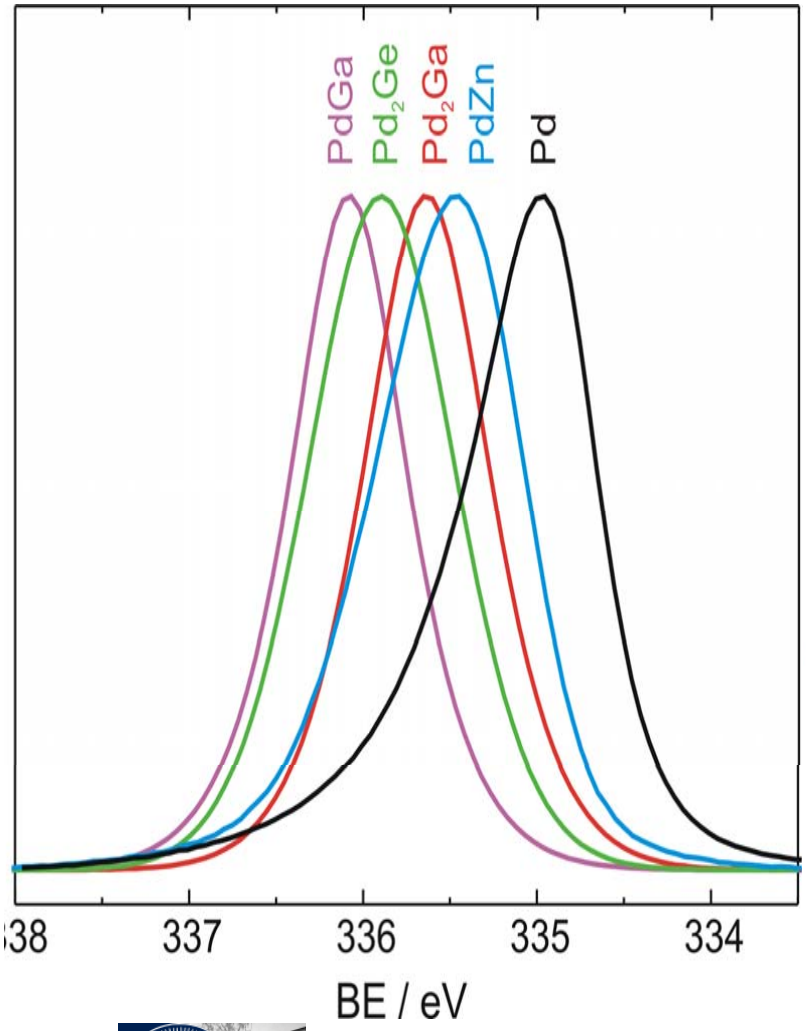
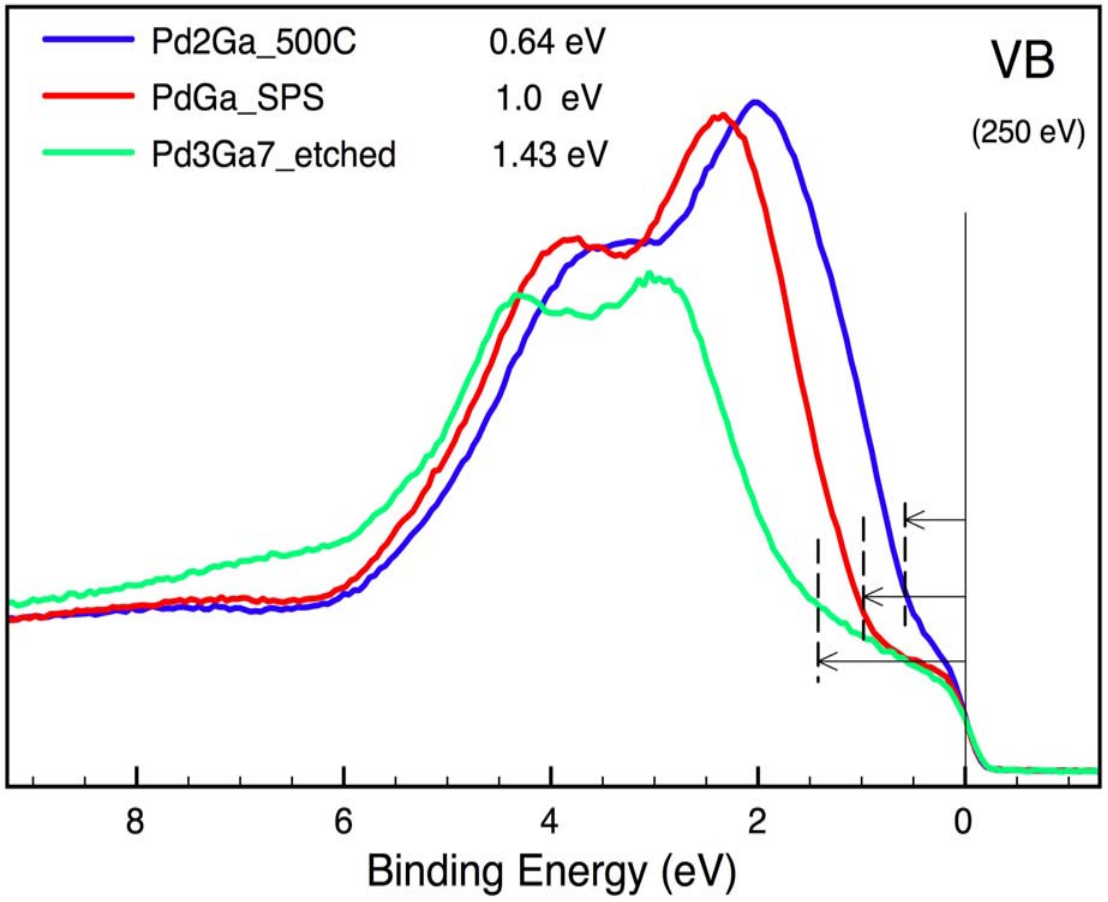
Opportunities

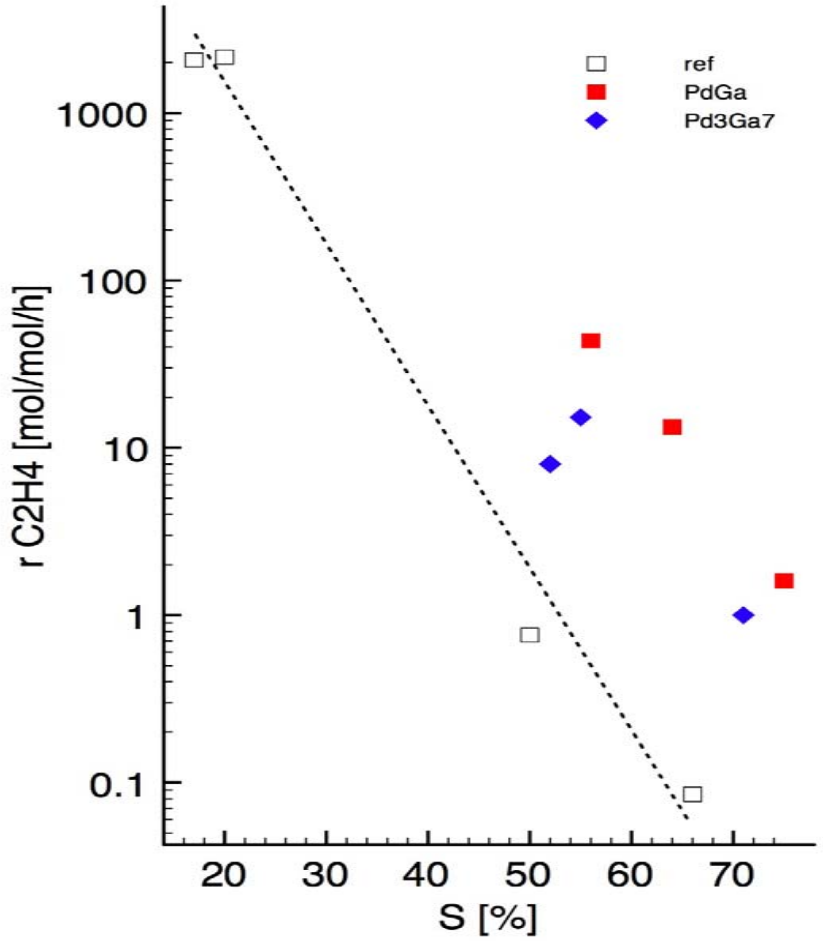
- Alloys are chemically unstable and segregate: rapid loss of site-isolating effect.
- Alloys exhibit only weak modifications of electronic structure: strong influence of local geometry, (ensemble effect).
- Concept: use intermetallics:
  - Covalent metal-metal interaction: High structural stability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

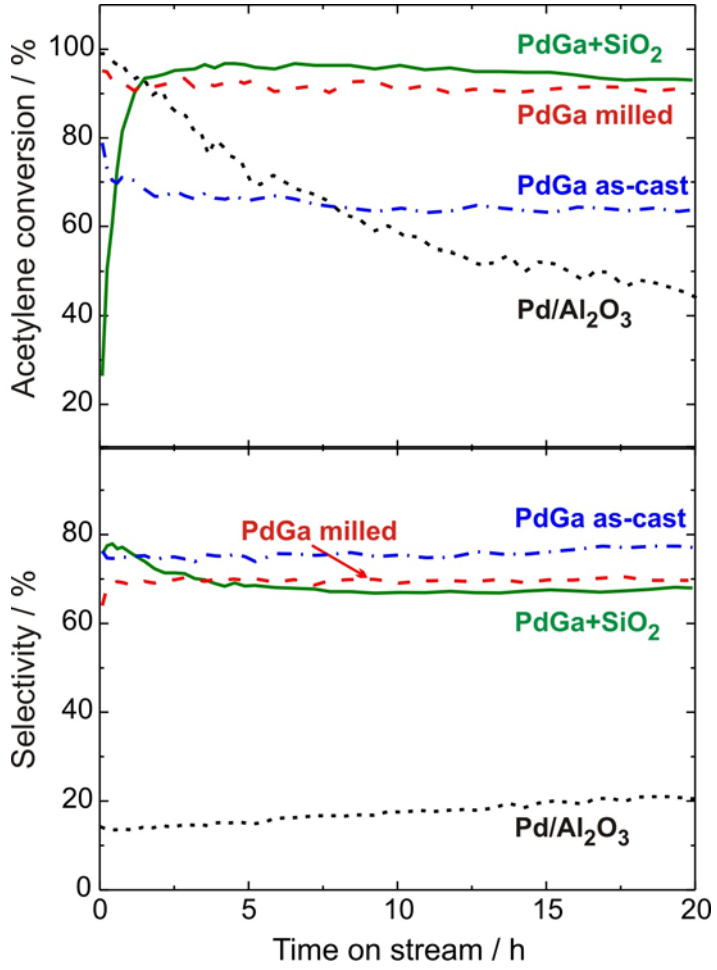
A family of compounds with quite different properties





PdGa: a designer system





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Reaction in C3-yne hydrogenation

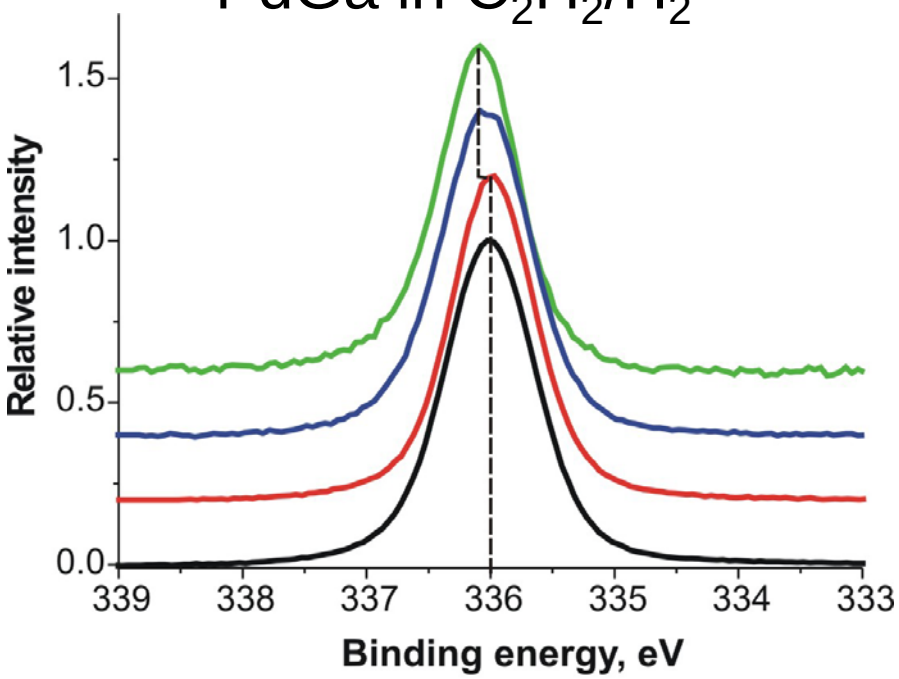
Experiment	H/Pd	Catalytic conditions	Conversion Selectivity
in H_2	0.024±123%	-	-
C3-Mix	0.048±58%	1.2 ml/min C_3H_4 36 ml/min C_3H_6 12 ml/min H_2 91 / 60 °C	X: >99.99% S(C_3H_6): 75 / 83% S(C_3H_8): 17 / 10% S(C_6): 7%
in N_2	0.06±48%	-	-

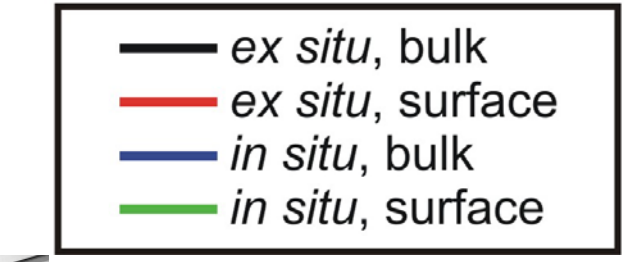
1. -5 °C: Starts unselective: ~50% C_3H_8 and C_3H_6 in the product stream
2. -5 °C: Gets selective: ~66% C_3H_4 conversion
3. -4 °C: Starts producing C_3H_8 again
4. -2 °C: ~67% C_3H_8 and 33% C_3H_6 in the product stream

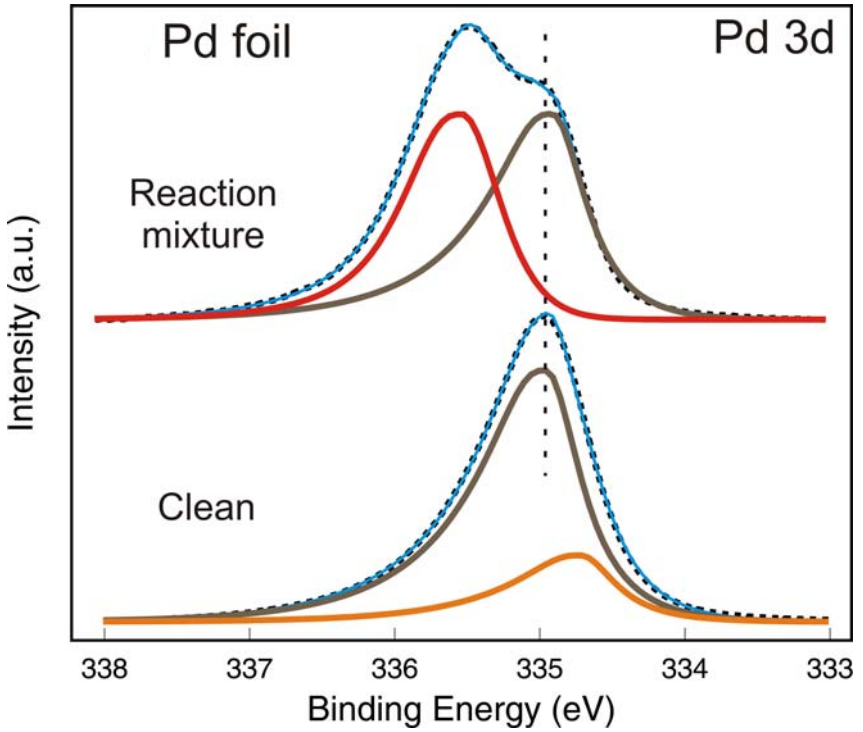
Experiment	H/Pd	Catalytic conditions	Conversion Selectivity
in H_2	0.75±6%	-	-
C3-Mix	0.8±5%	1.2 ml/min C_3H_4 12 ml/min C_3H_6 12 ml/min H_2 ~-5 °C	

A stable sub-surface regime

PdGa in C_2H_2/H_2



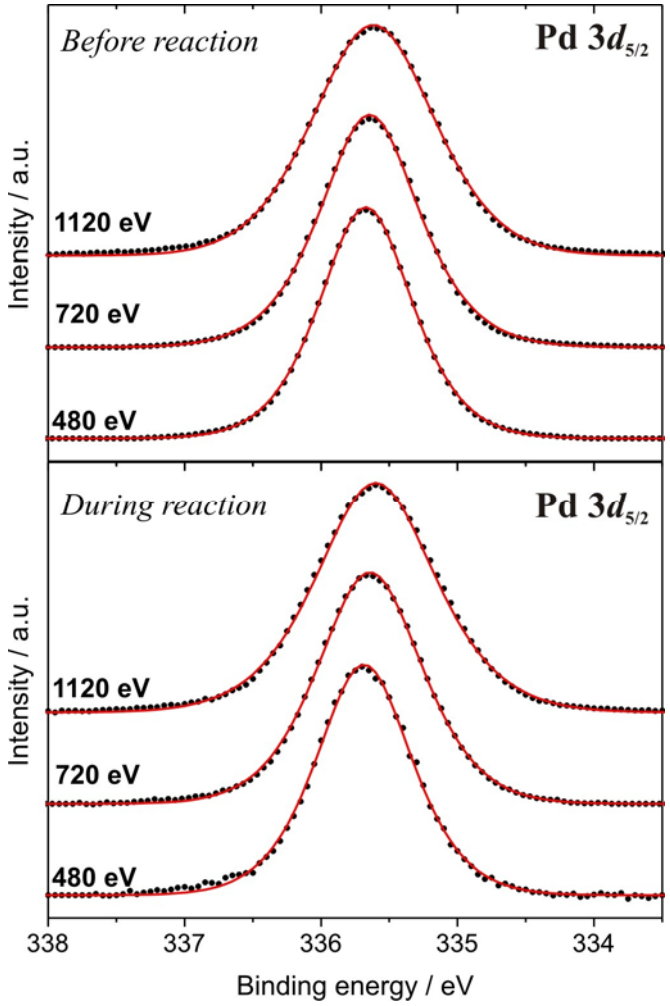


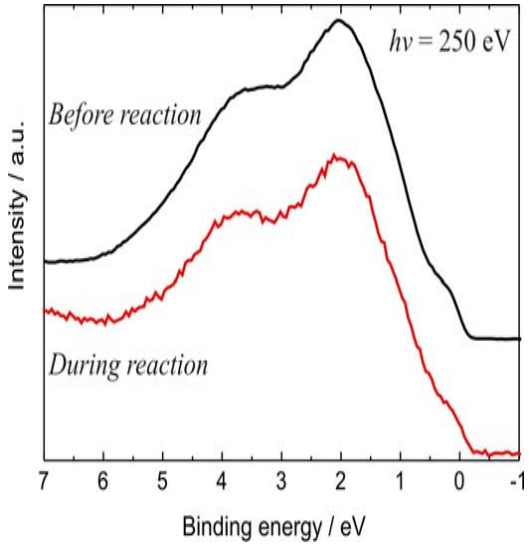


D. Teschner et al., J. Catal. ***2006****, 242 26.*

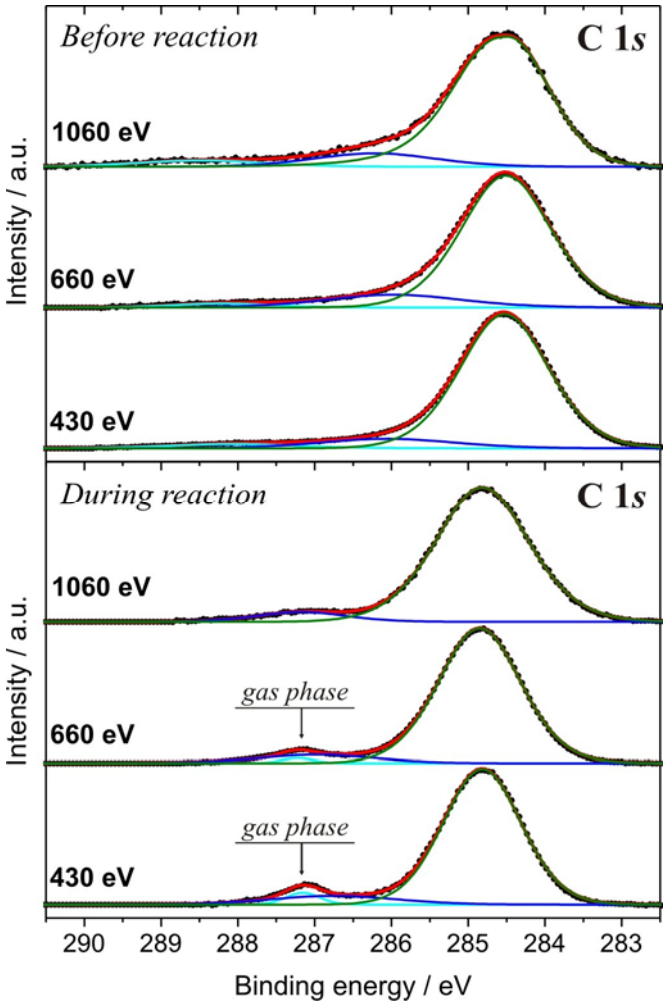
Pd in alkyne/H_2

Pd_2Ga





Depth (nm)	PdGa at% C	Pd_2Ga at% C
3.8	0.4	2.3
2.3	0.8	6.0
1.4	2.0	24.1



stable bulk but surface condensation

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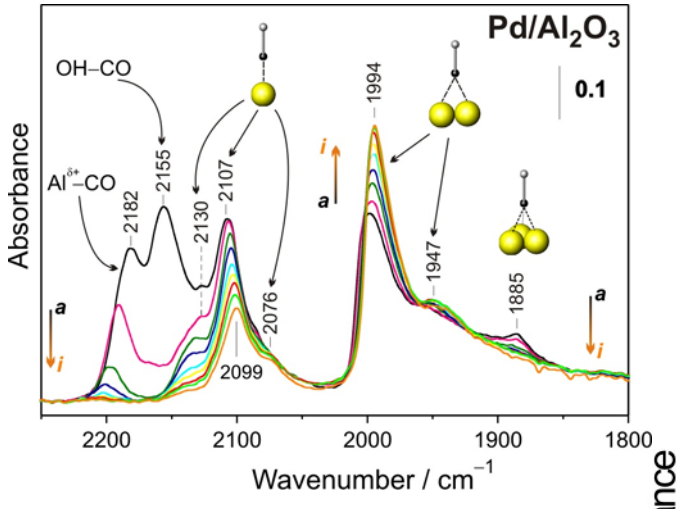
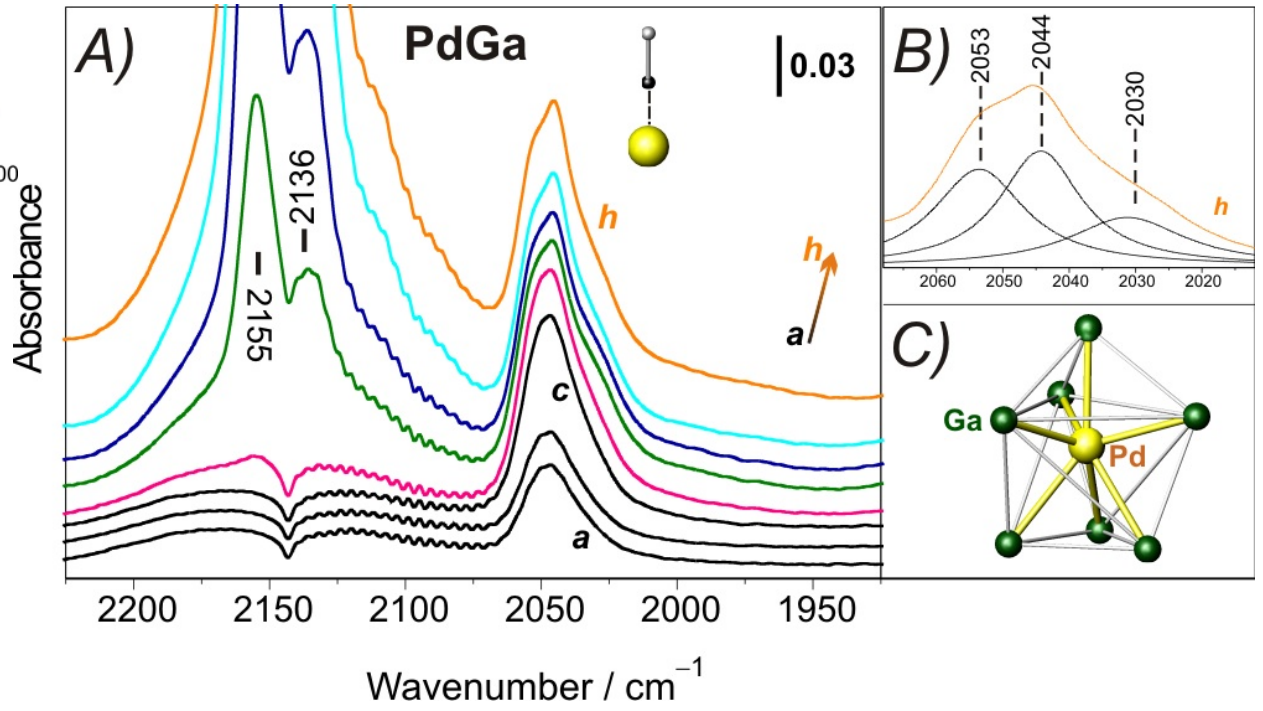
Site isolation: experimental



Adsorption, evacuation and cooling

CO adsorption in FTIR



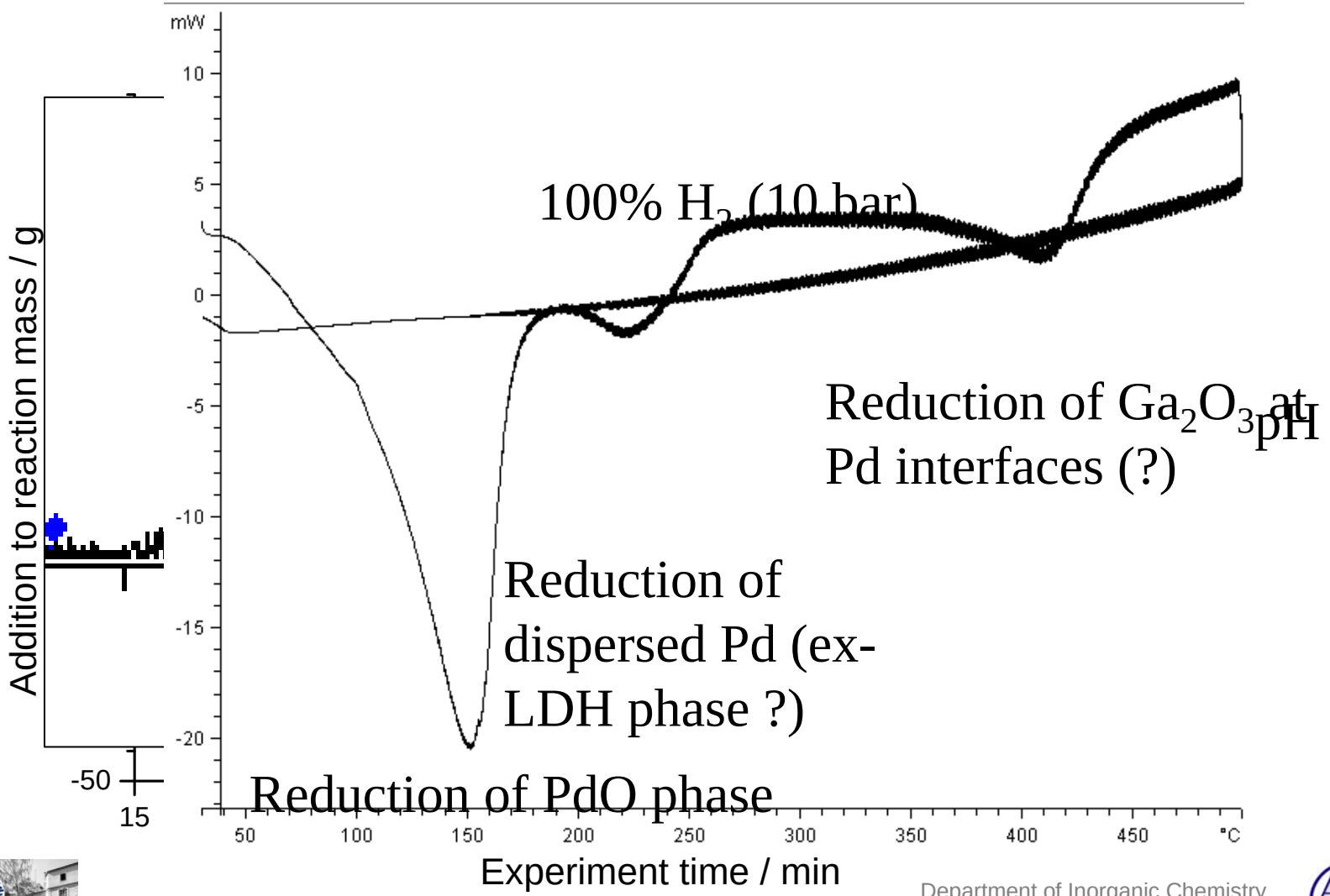
Adsorption and cooling

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.

Nanostructured and supported: PdGa on hydrotalcite



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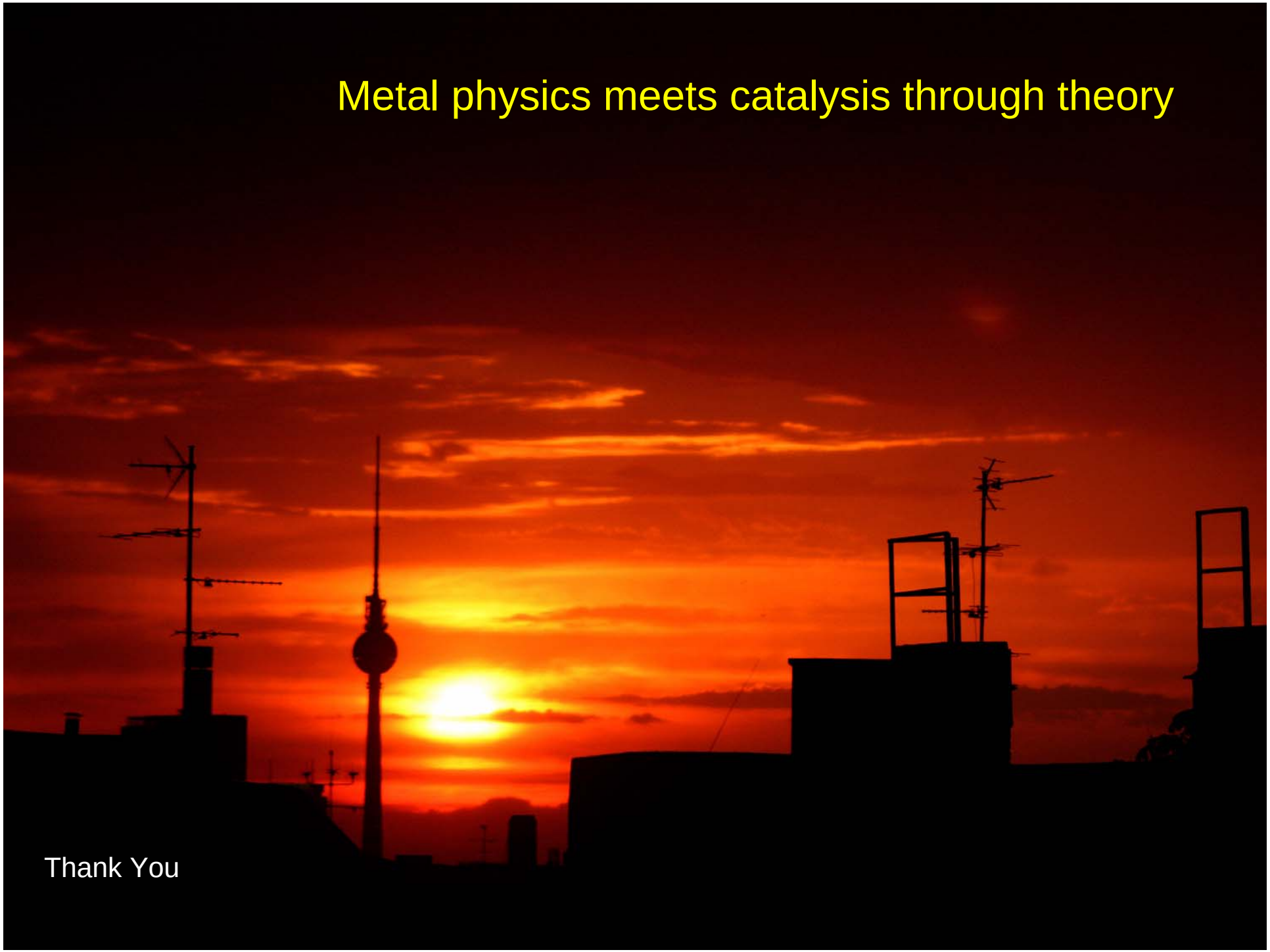
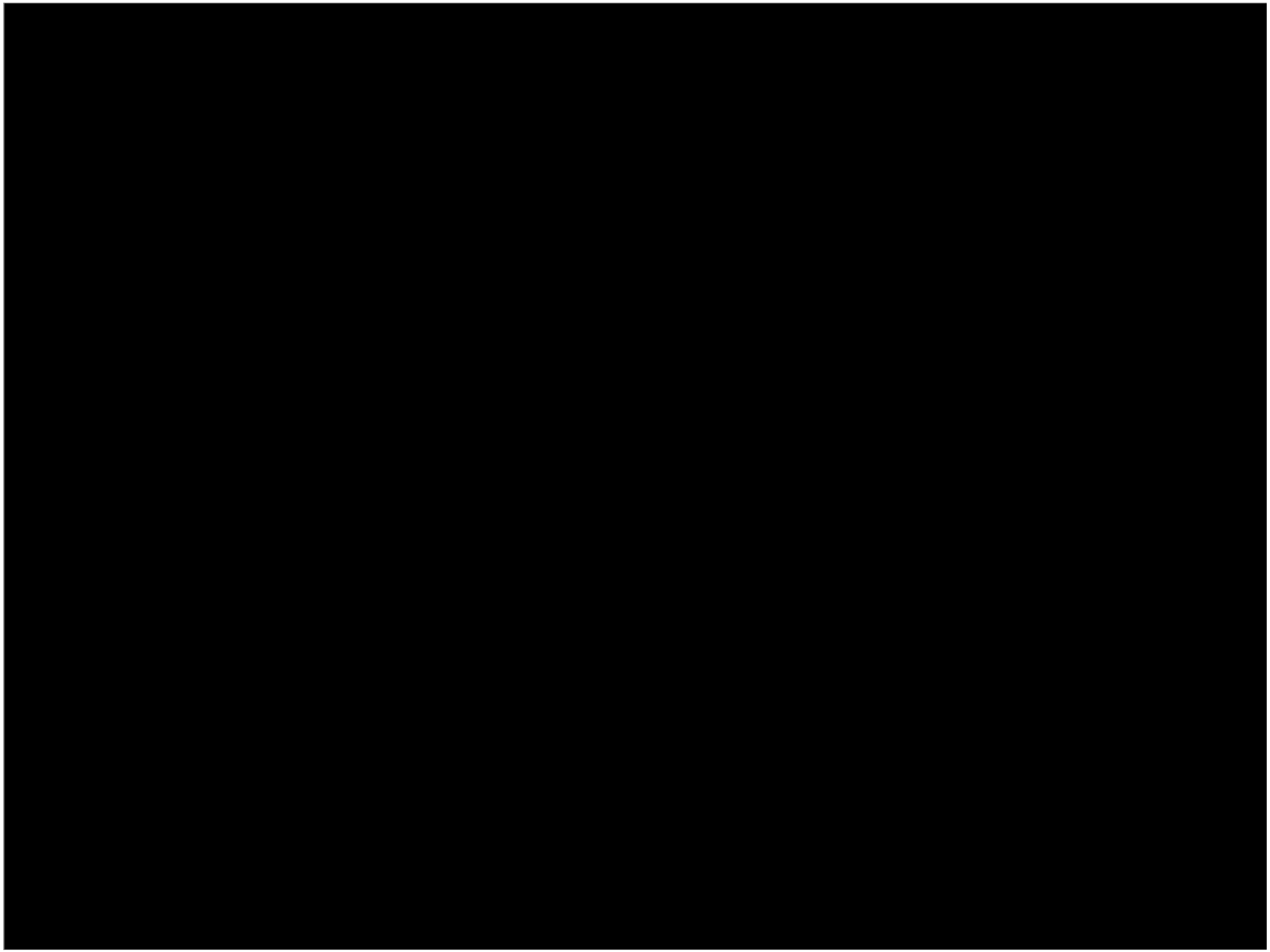
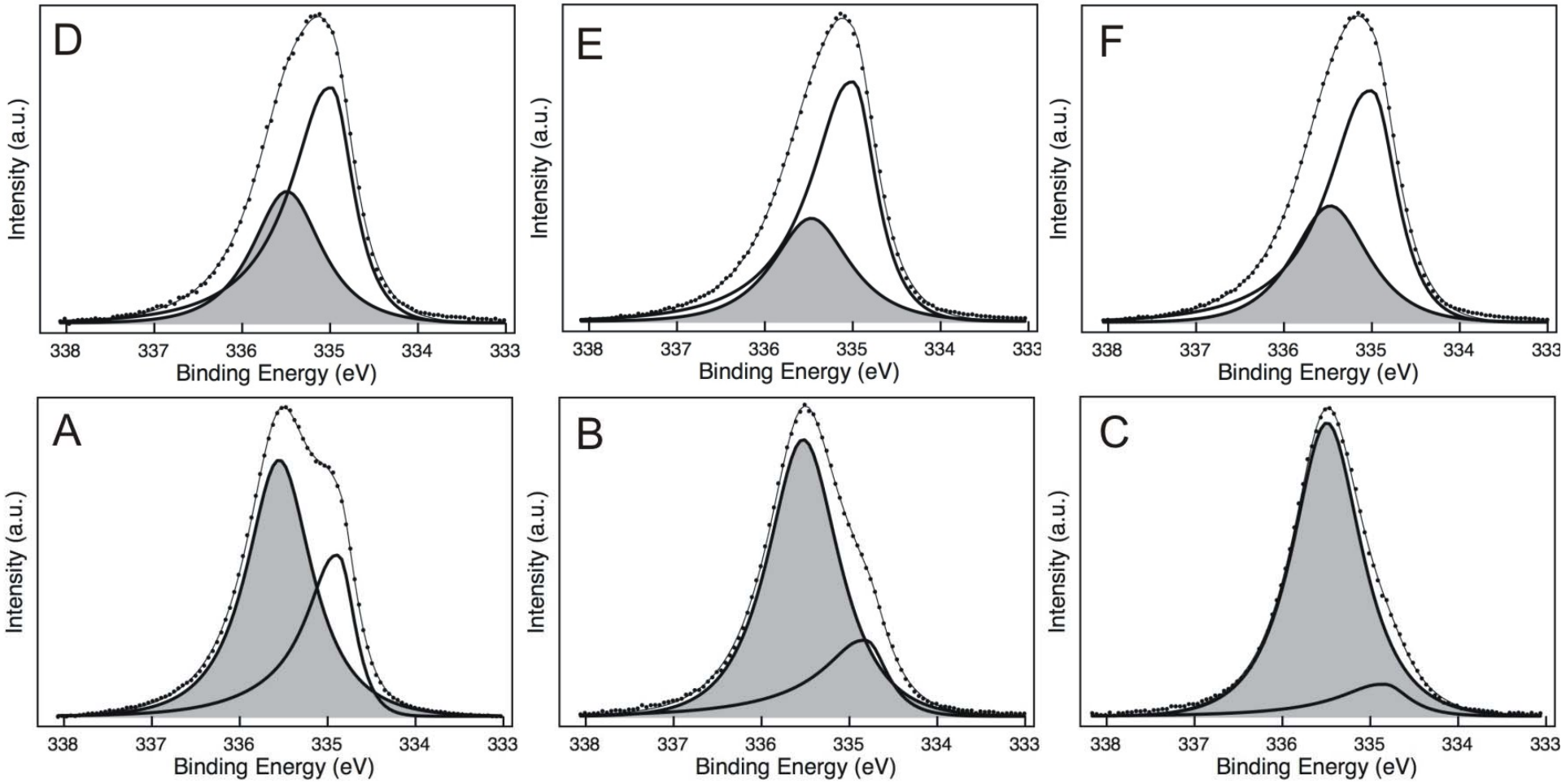
Outlook

- 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.

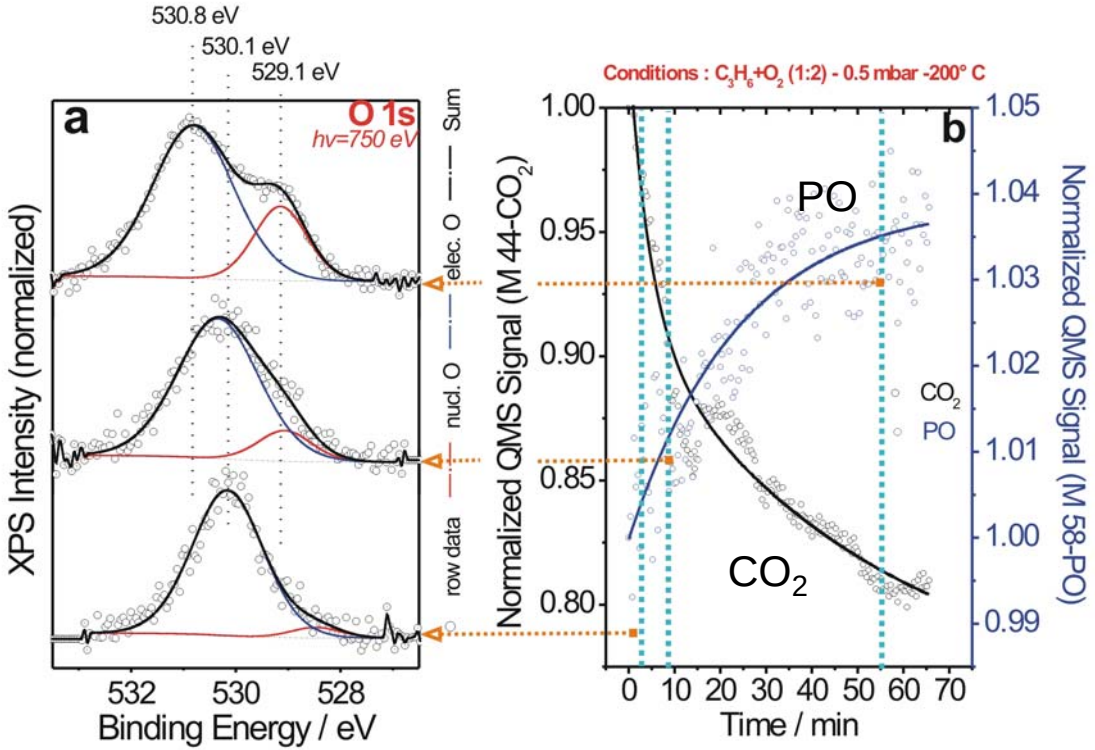

Metal physics meets catalysis through theory
Thank You



Alkene and alkyne hydrogenation at the synchrotron
Pd foil, ~70°C, 1 mbar (0.1 C_xH_y + 0.9 H_2)



Structure-function correlation in Ag: PO formation



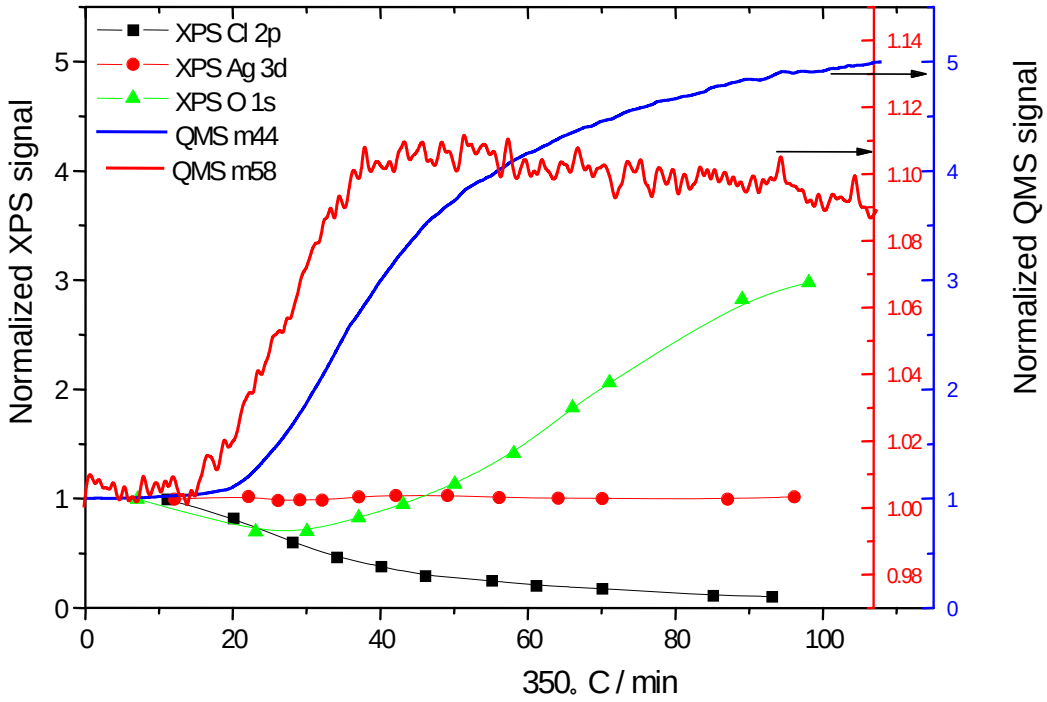
Auto-formation of selective electrophilic oxygen by gradual intercalation of sub-surface oxygen in Ag

Ag nano, 473 K, 0.5 mbar, 1:2 C_3H_8:O_2
Total oxygen content “0.2 ML”

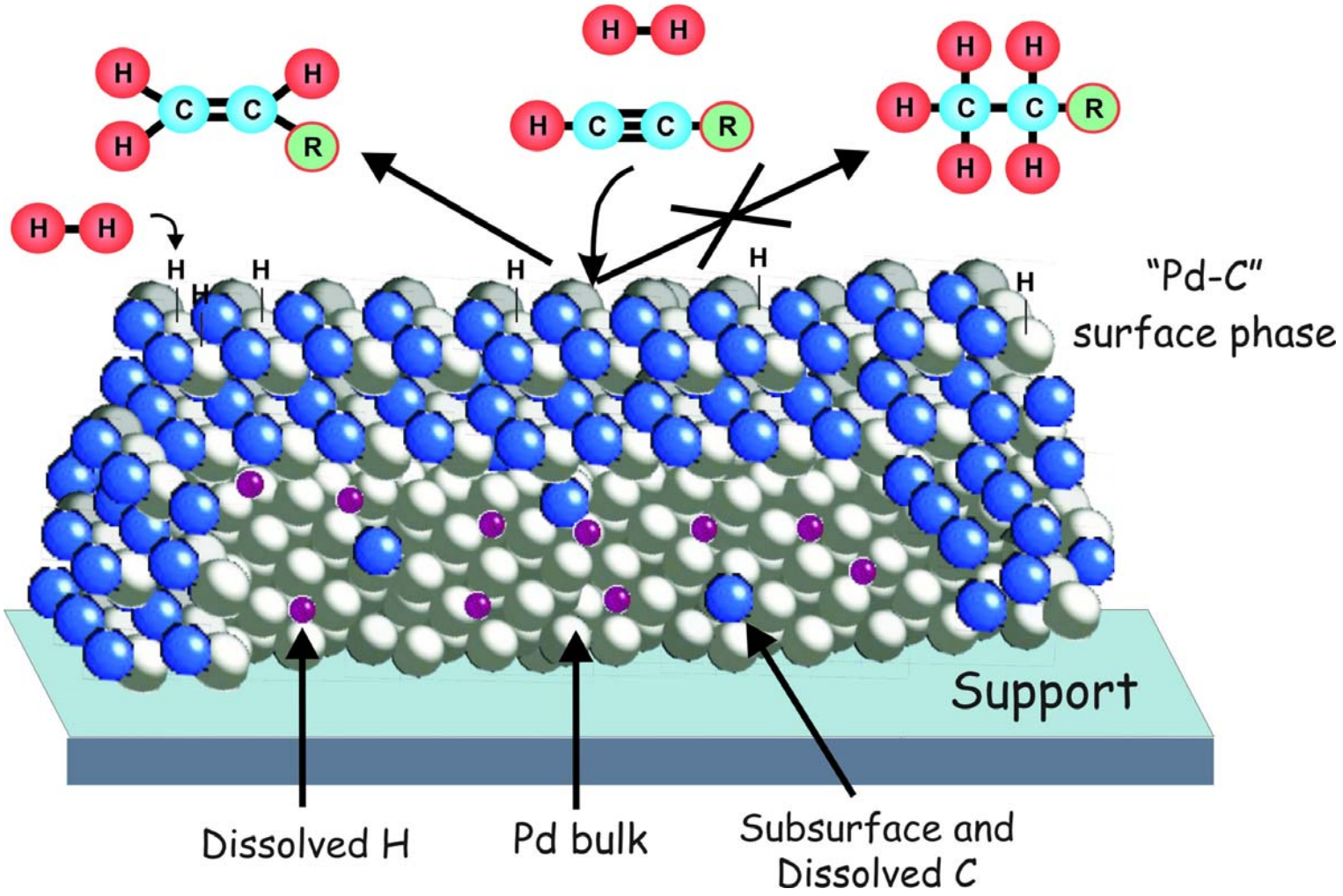
The function of a promoter

Chlorine is an effective but not sustained promoter

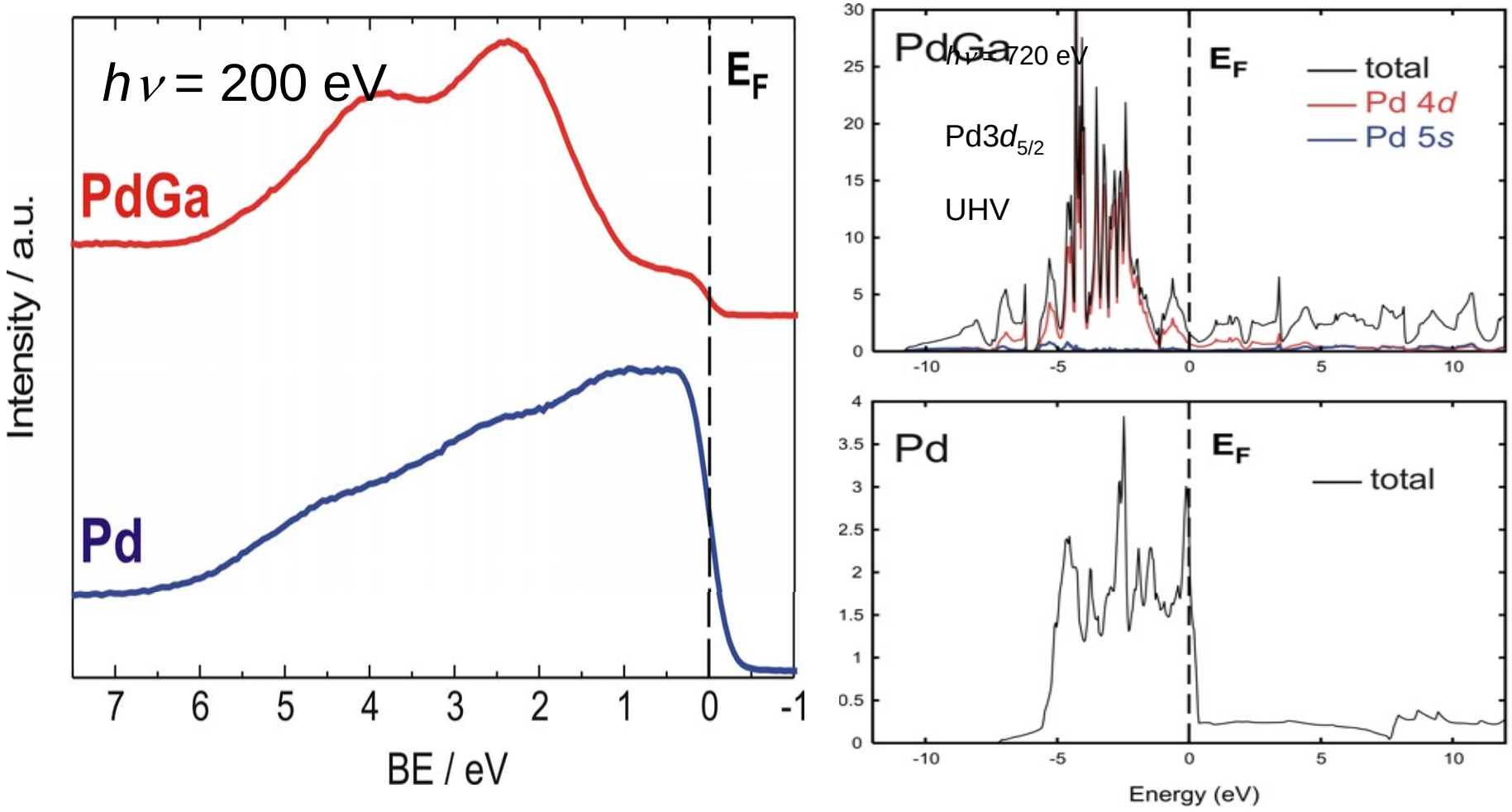
Chlorine is covered under fresh Ag surface: after 45 min tos: loss of promotion



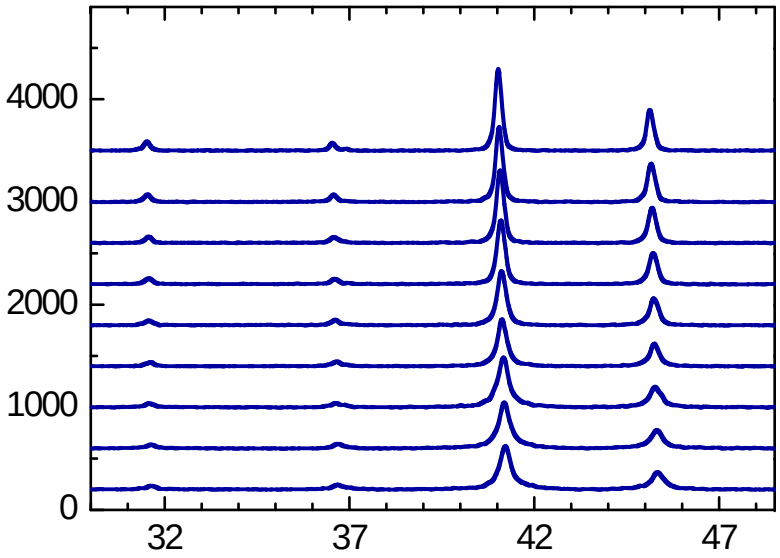
The Model

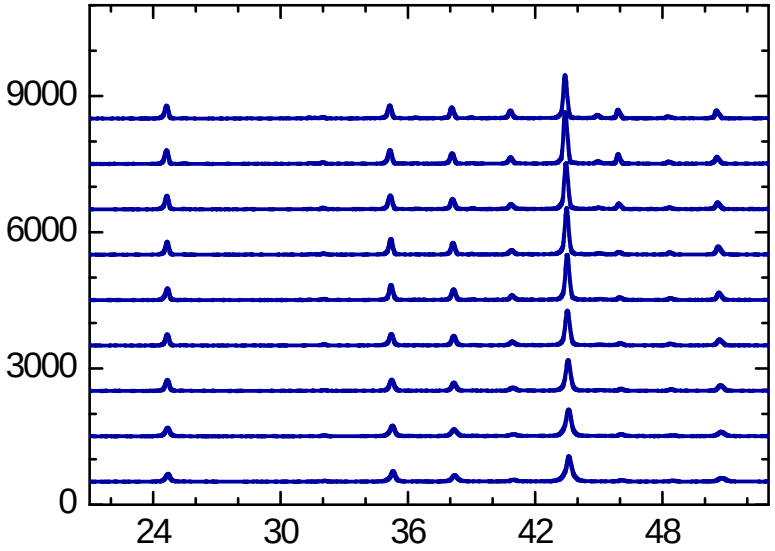

"Pd-C"
surface phase
Support
Dissolved H
Pd bulk
Subsurface and
Dissolved C

Meet the challenge: Intermetallics of Pd



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

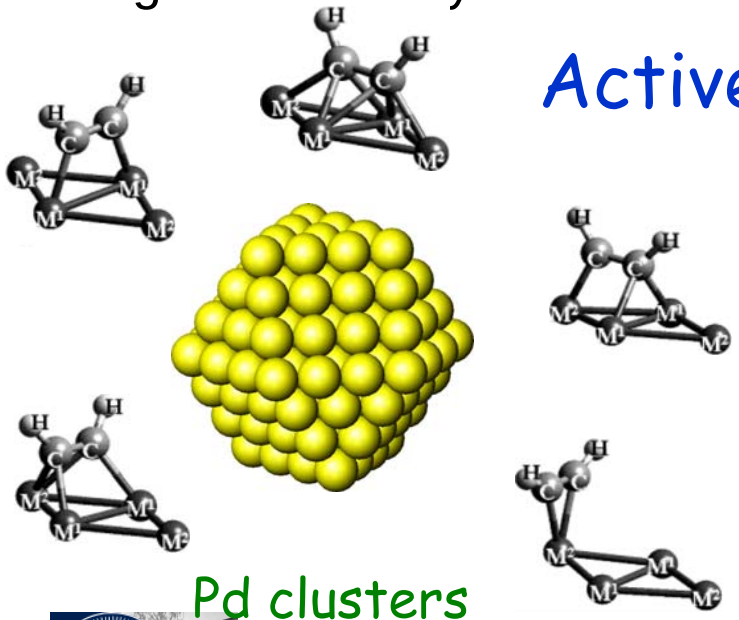
Pd-Ga intermetallics:

PdGa and Pd_3Ga_7

✓ activity

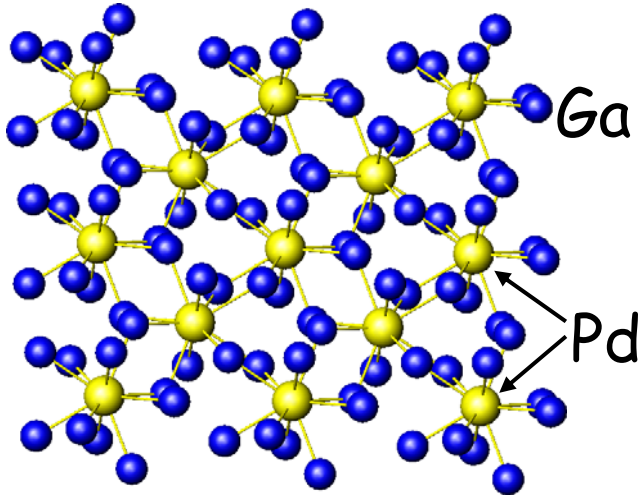
✓ selectivity

✓ long-time stability



Active sites

Pd clusters



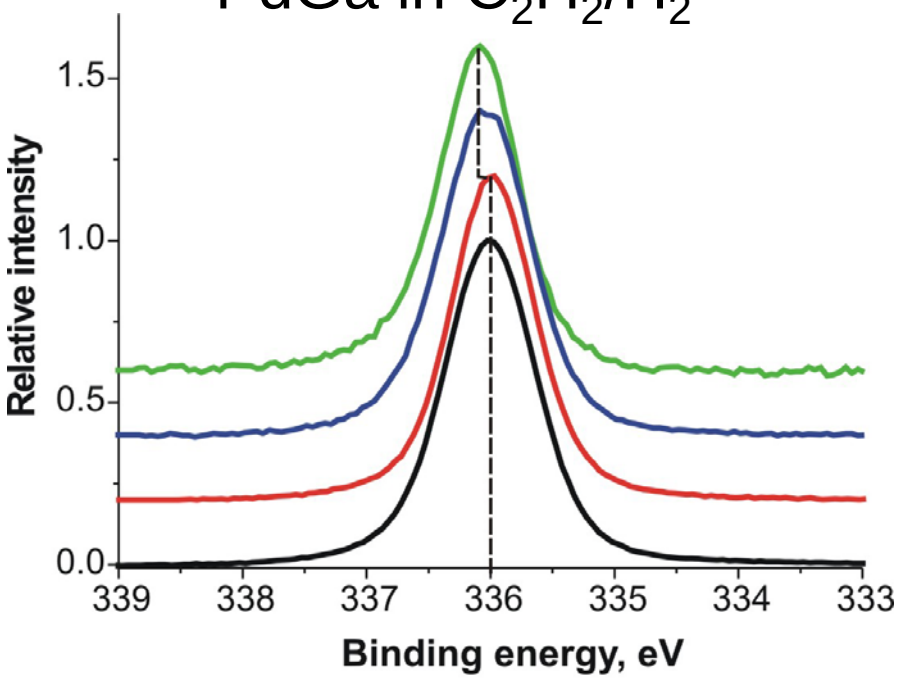
Isolated Pd atoms

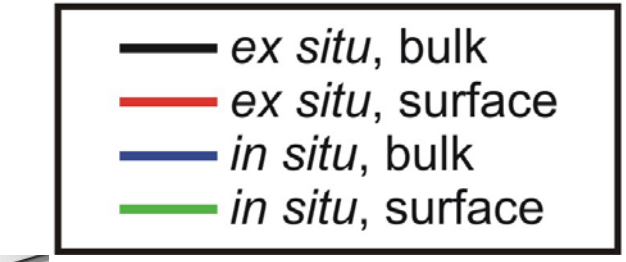
Consequences

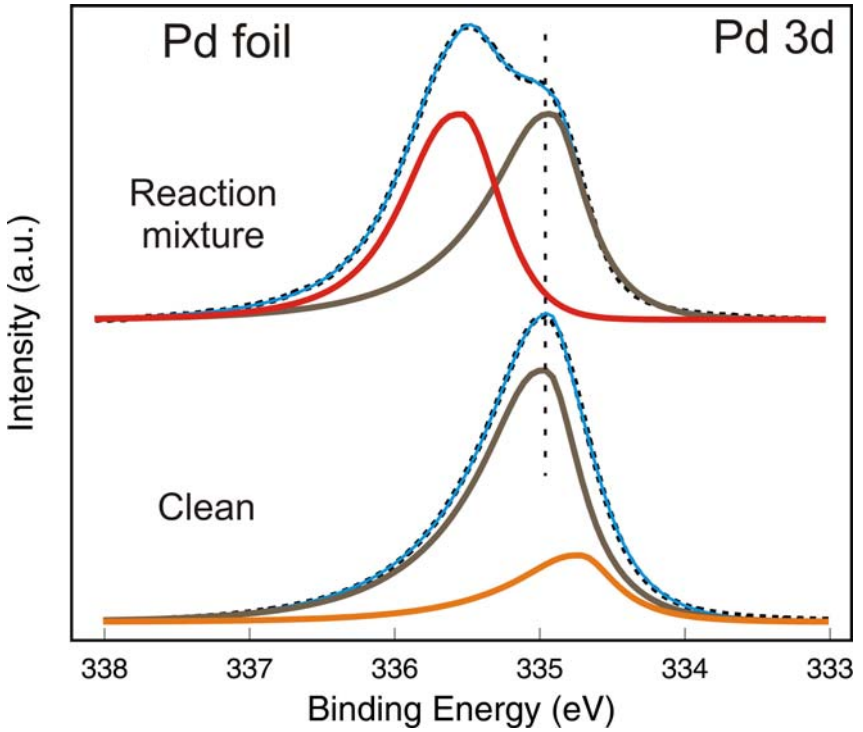
- Well-ordered extended (model) materials slow down activation and stay often non-reactive (gaps);
- Except for kinetically non-demanding reactions (single step processes);
- Where they also reach only moderate performance.
- High performance catalysis needs addition of complexity:
  - Nanostructuring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

The reactions

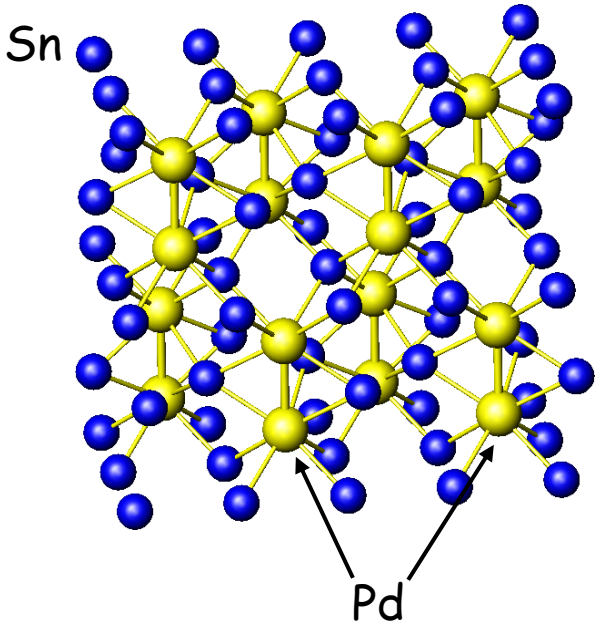
Selective hydrogenation of C-C triple bonds in medium-sized molecules to olefins:
Key step in vitamin and pharmaceutical synthesis

Extremely critical reaction conditions
Severe stability problems

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

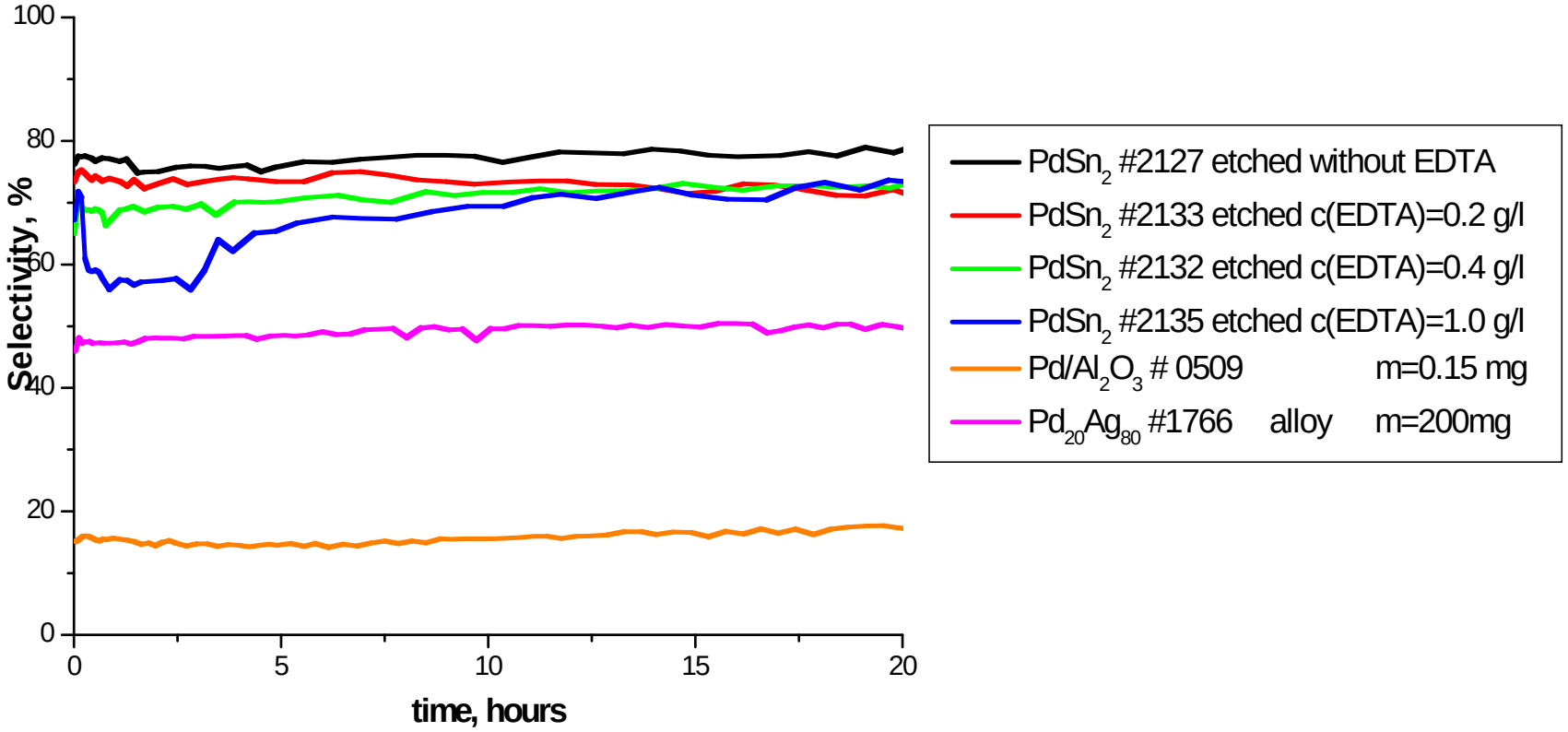
Flexibility of concept?

$PdSn_2$



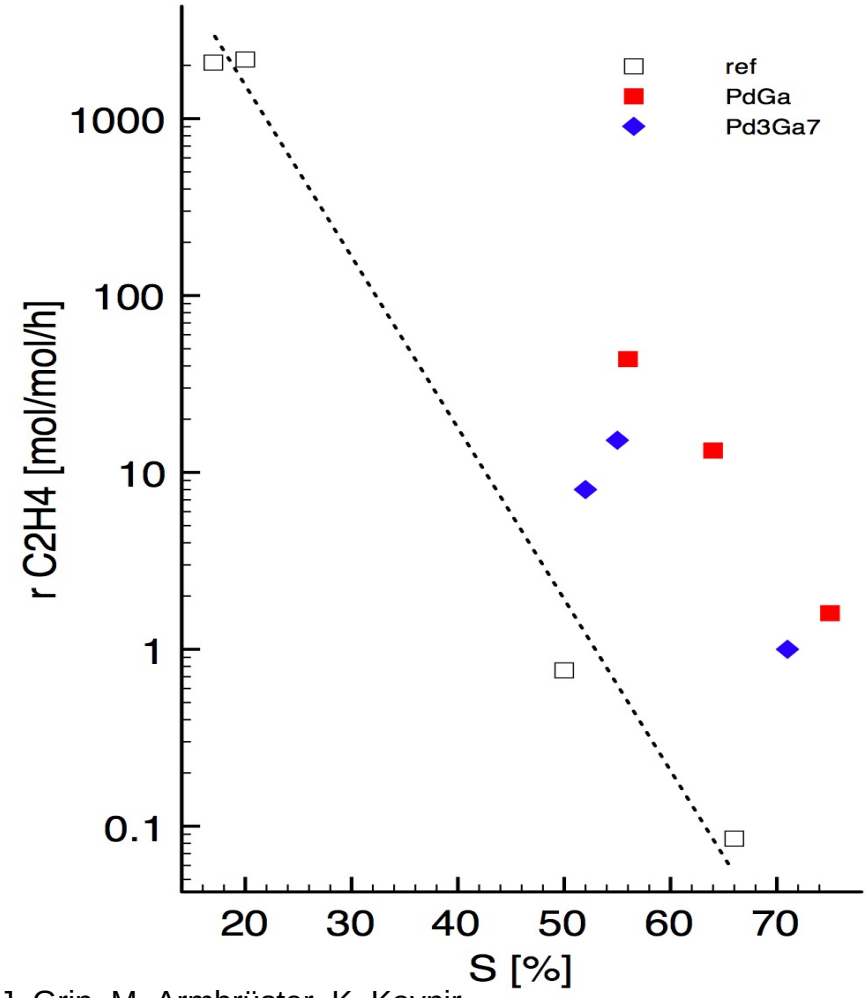
Sample	*Etching solution*	*Conversion after 1 hour*	*Conversion after 3 hour*
# 2039	100mg of sample, no etching	4 %	–
# 2040	saturated EDTA	15%	10%
# 2041	EDTA/NH_3, pH=10.3	21%	15%
# 2042	EDTA/NH_3/H_2O_2, pH=10.5	> 10%	–
# 2049	EDTA/NaOH, pH=12.8	25%	12%
# 2051	EDTA/NaOH, pH=13.3	43%	20%
# 2015	EDTA/NaOH,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

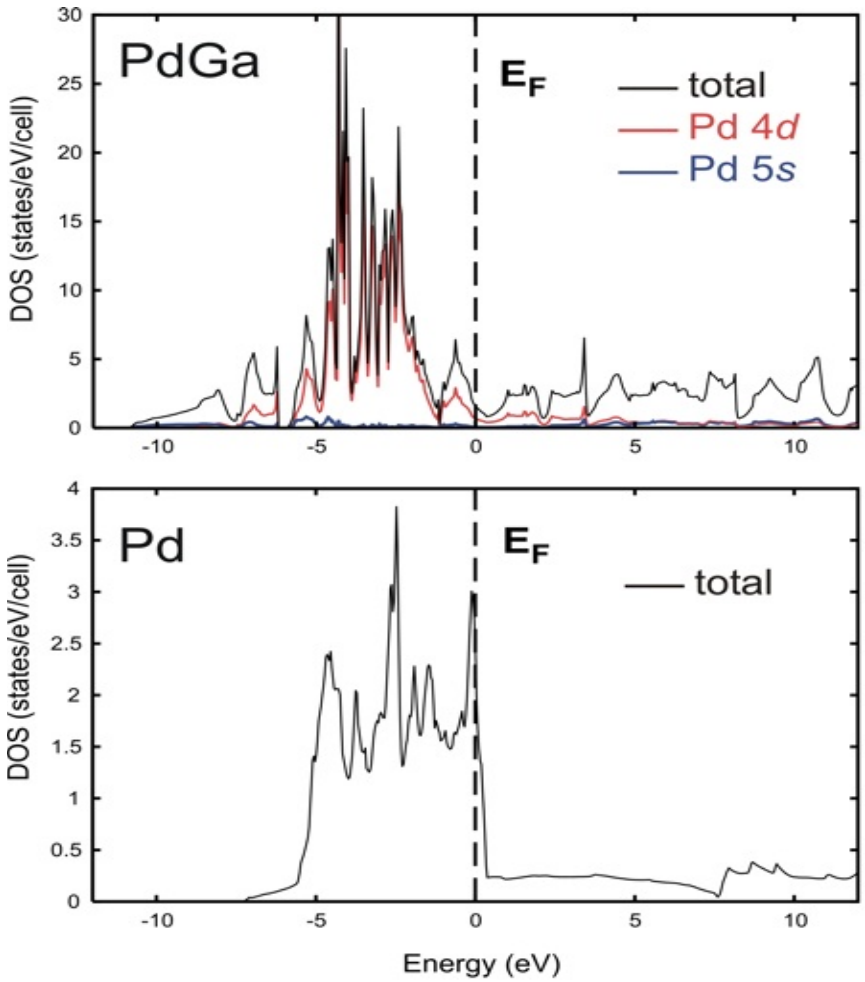
Good active sites but solid state dynamics?



85 mg after washing with EDTA at pH 13

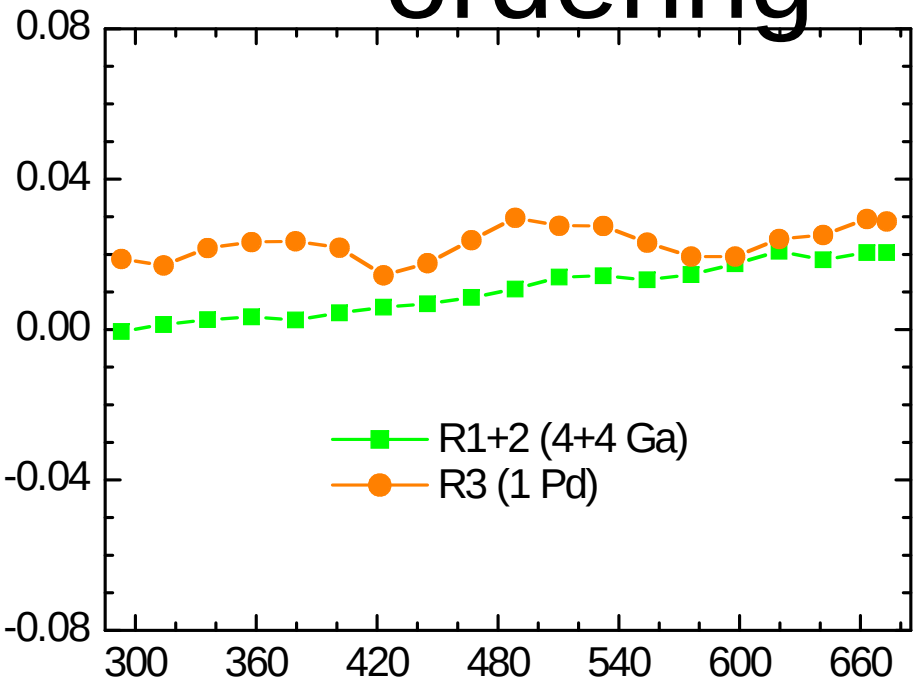
Proof of concept: new hydrogenation systems

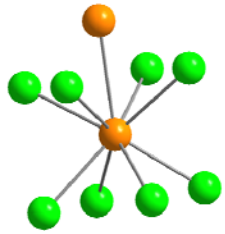




J. Grin, M. Armbrüster, K. Kovnir

Structural stability: no modification of local ordering





Pd_3Ga_7

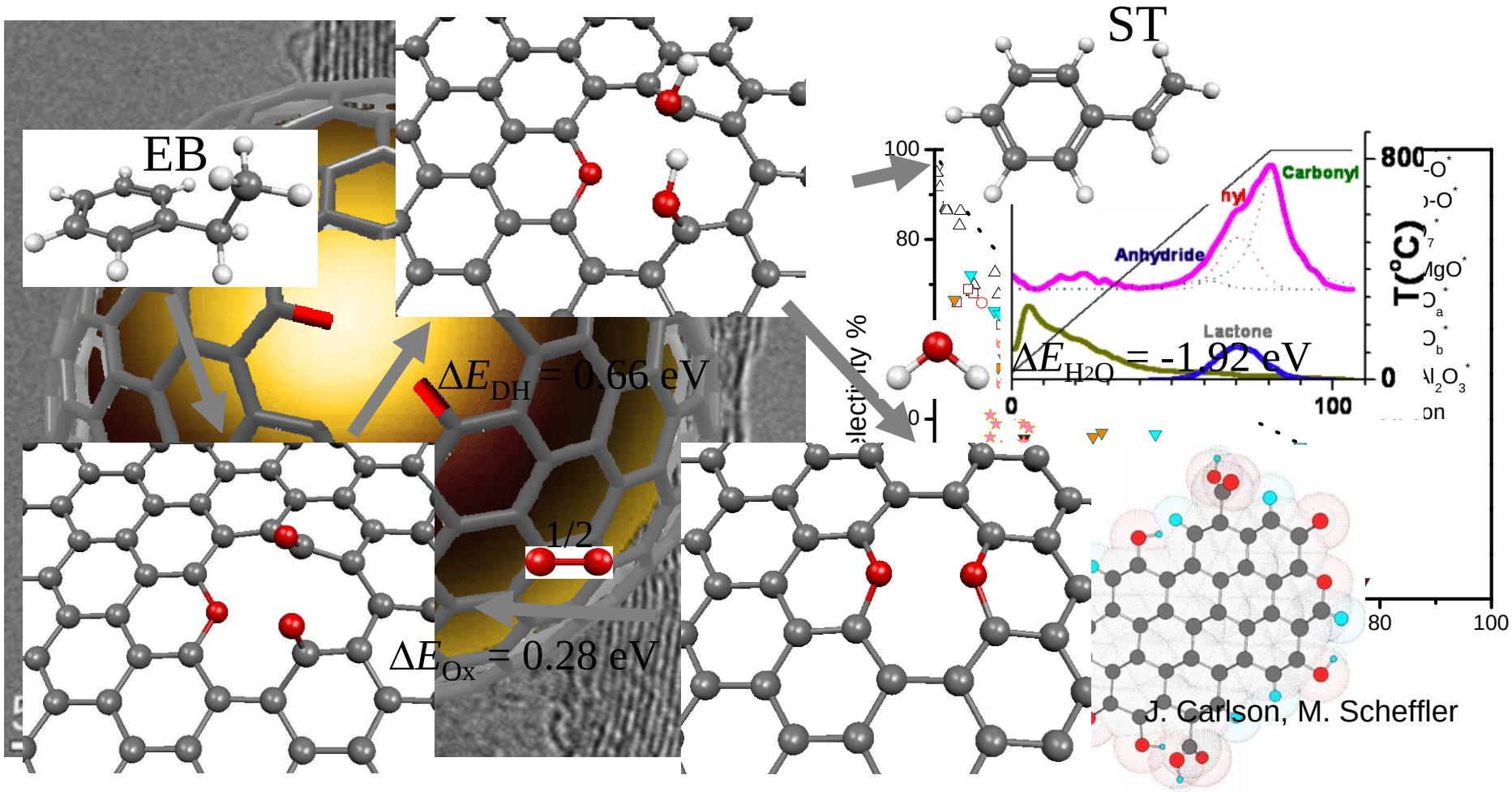
EXAFS analysis

Pd_3Ga_7 in 10% C_2H_2 + 20% H_2

Active sites in a high performance catalyst

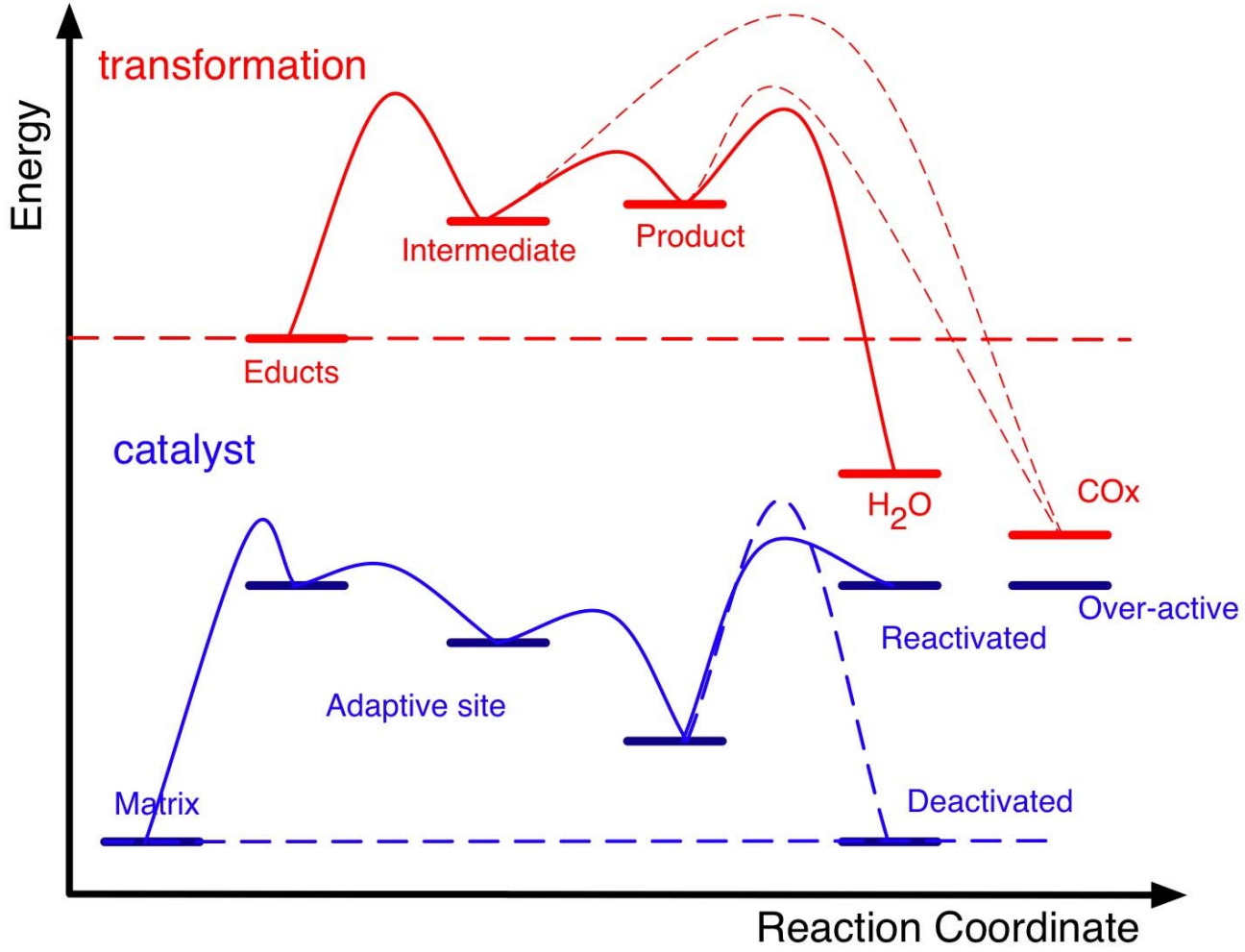
- An active heterogeneous catalyst contains adaptive sites for reaction.
- They adapt their structure according to the local chemical potential and guarantee selective operation on progressively more reactive adsorbates.
- The complex structure of the precursors is required to fix the chemical potential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

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

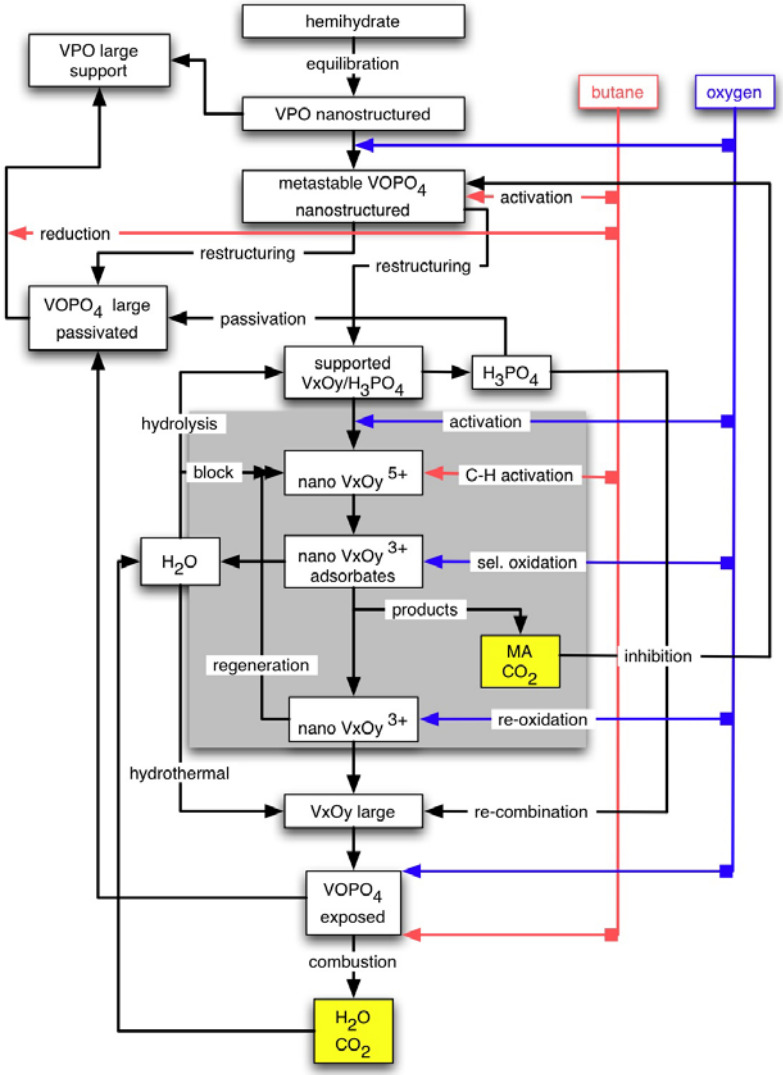


$$\Delta E_{ODH} = -0.98 \text{ eV/molecule}$$

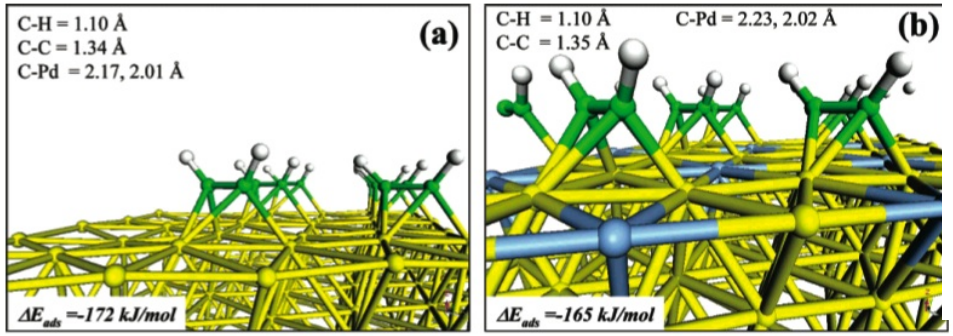
Coupling of transformation and material

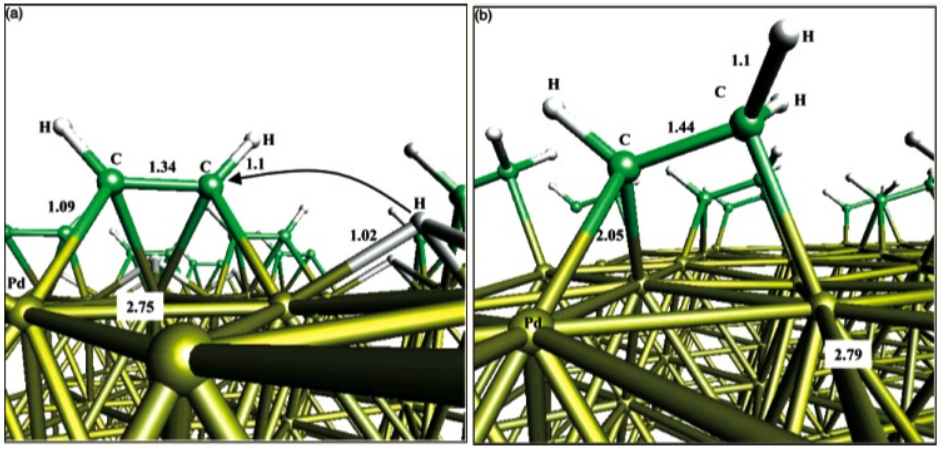


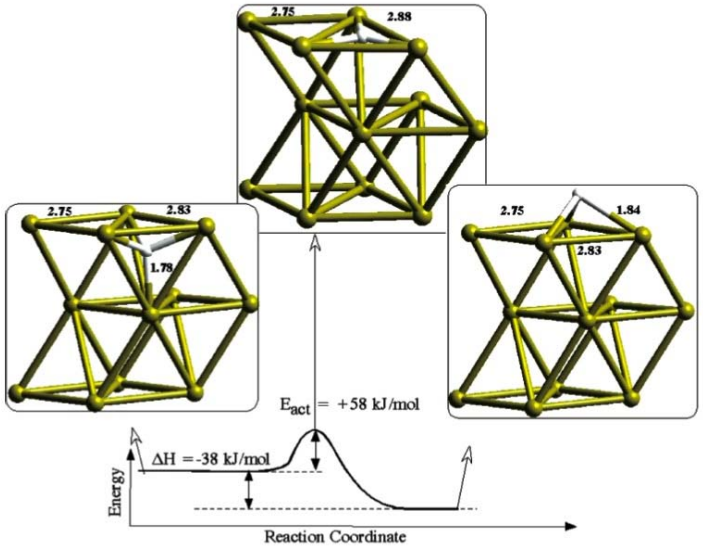
Catalyst dynamics



Reaction pathway: role of H_{sub}







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