Russian-German-Seminar on Catalysis

Bridging The Gap Between Model And Real Catalysis

July 9-12, Novosibirsk-Altai Mountains, Russia

The role of subsurface species in heterogeneous catalytic reactions

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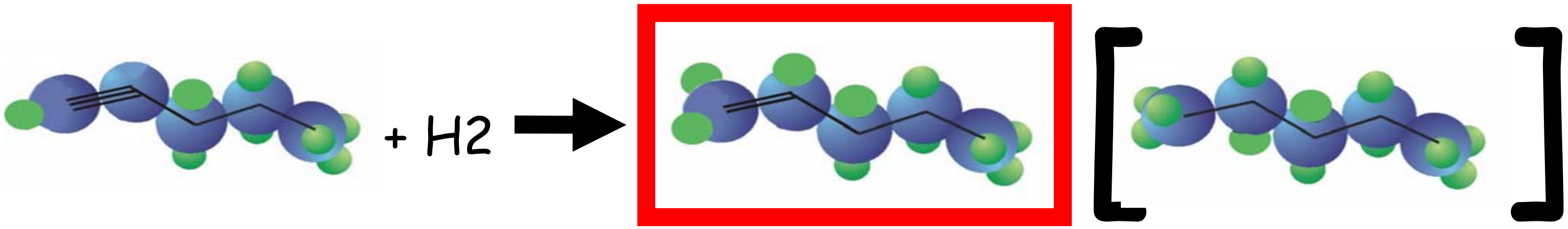
Introduction



Literature

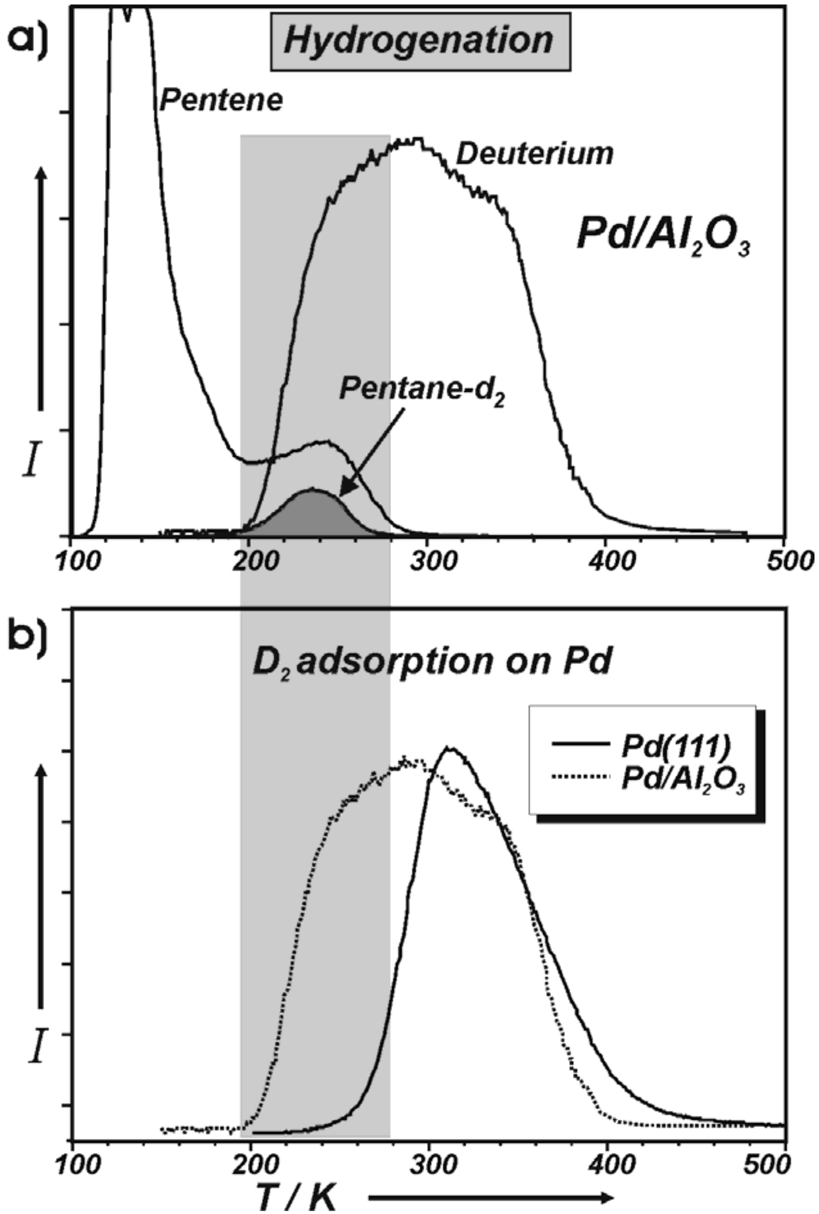
carbon laydown → selective hydrogenation

"similar" catalysts → different activity & selectivity

(structure sensitivity?)

Selectivity issue: what defines selectivity?

Model of overlapping TDS peaks



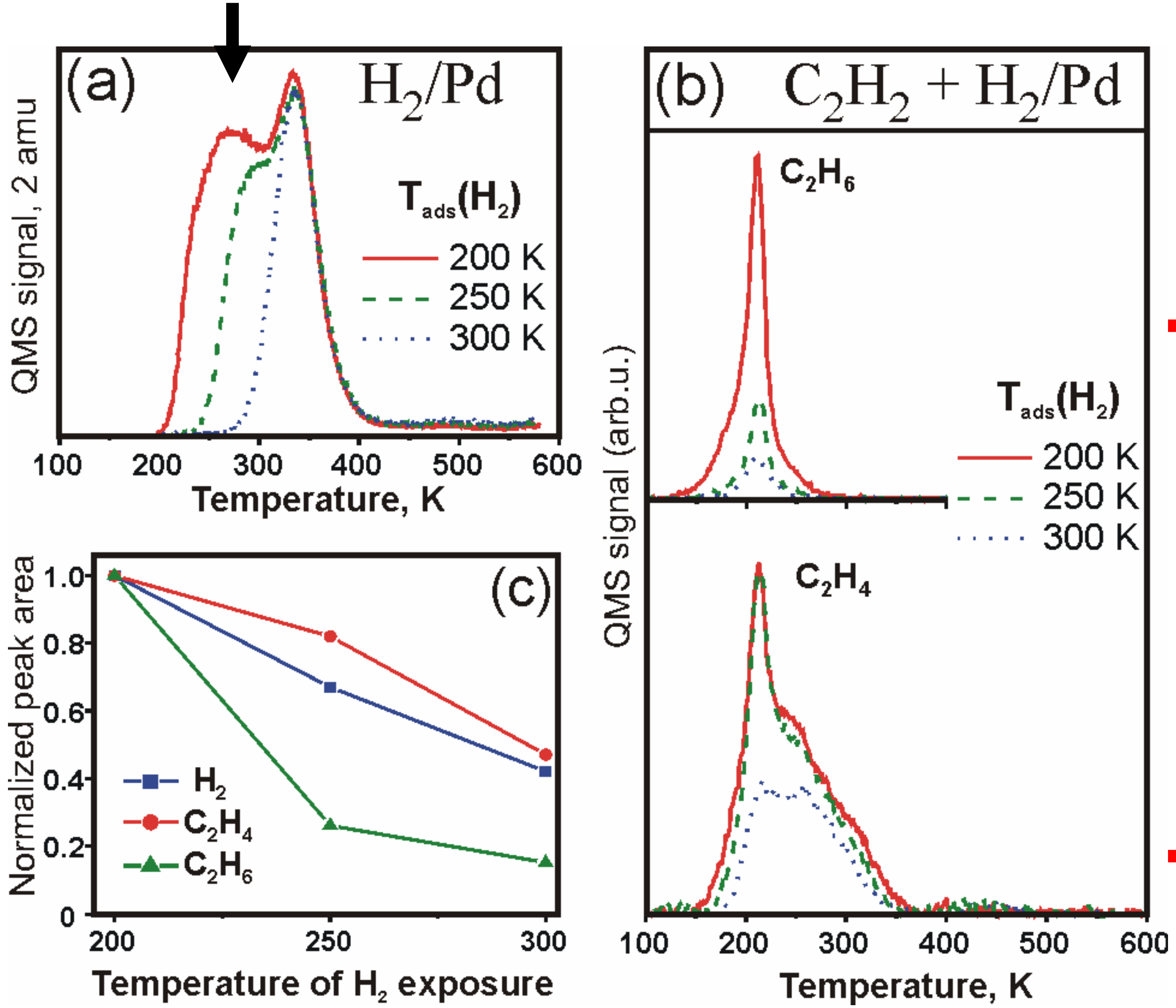
Pentenes to pentane

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

Acetylene hydrogenation (TDS)



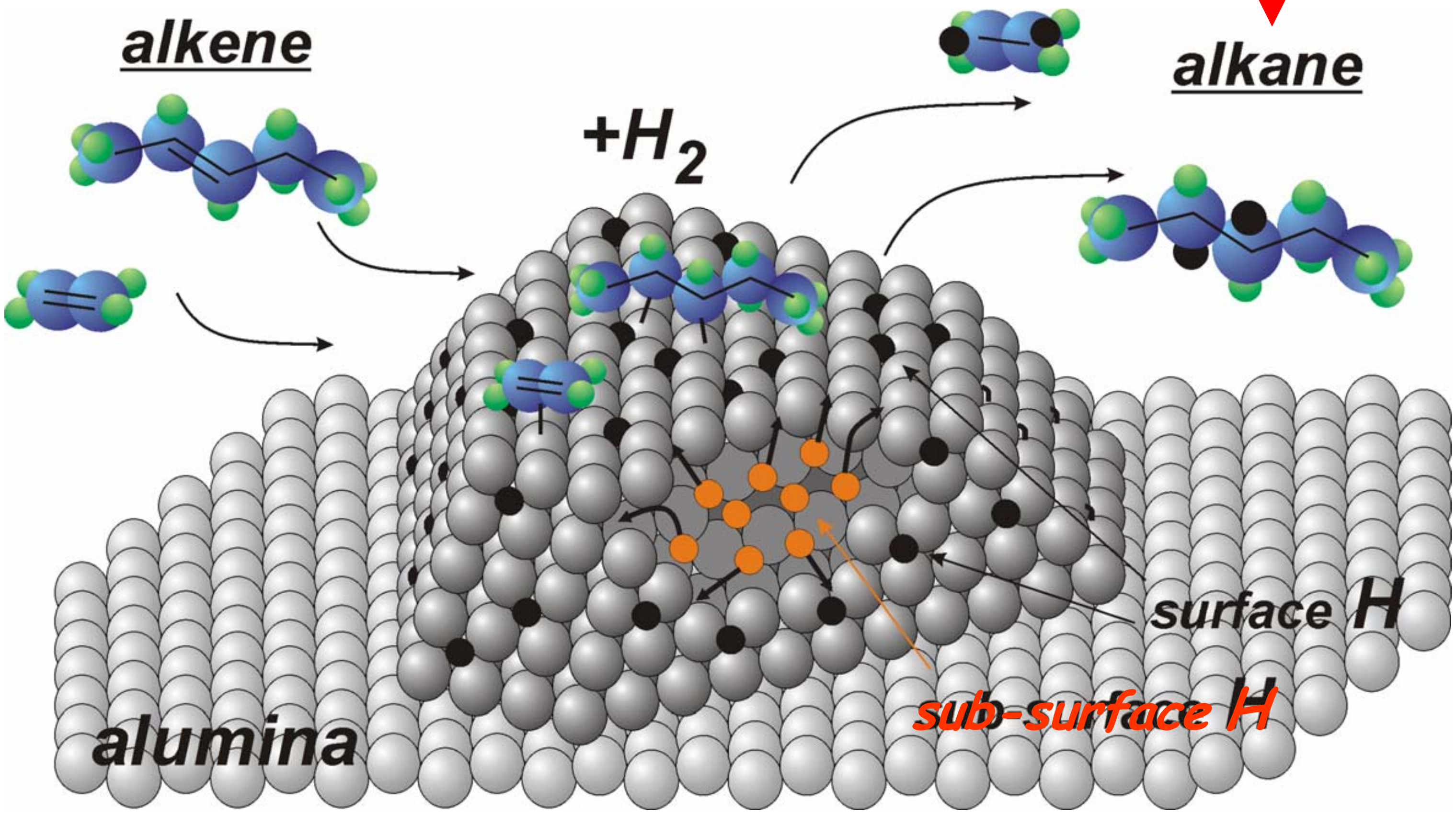
Subsurface H at low T_{ads}

Total hydrogenation decreases strongly without subsurface H

Khan NA, Shaikhutdinov SK, Freund HJ
CATALYSIS LETTERS, 108 (3-4) 159-164, 2006

Hydrogenation (TDS)

alkyne



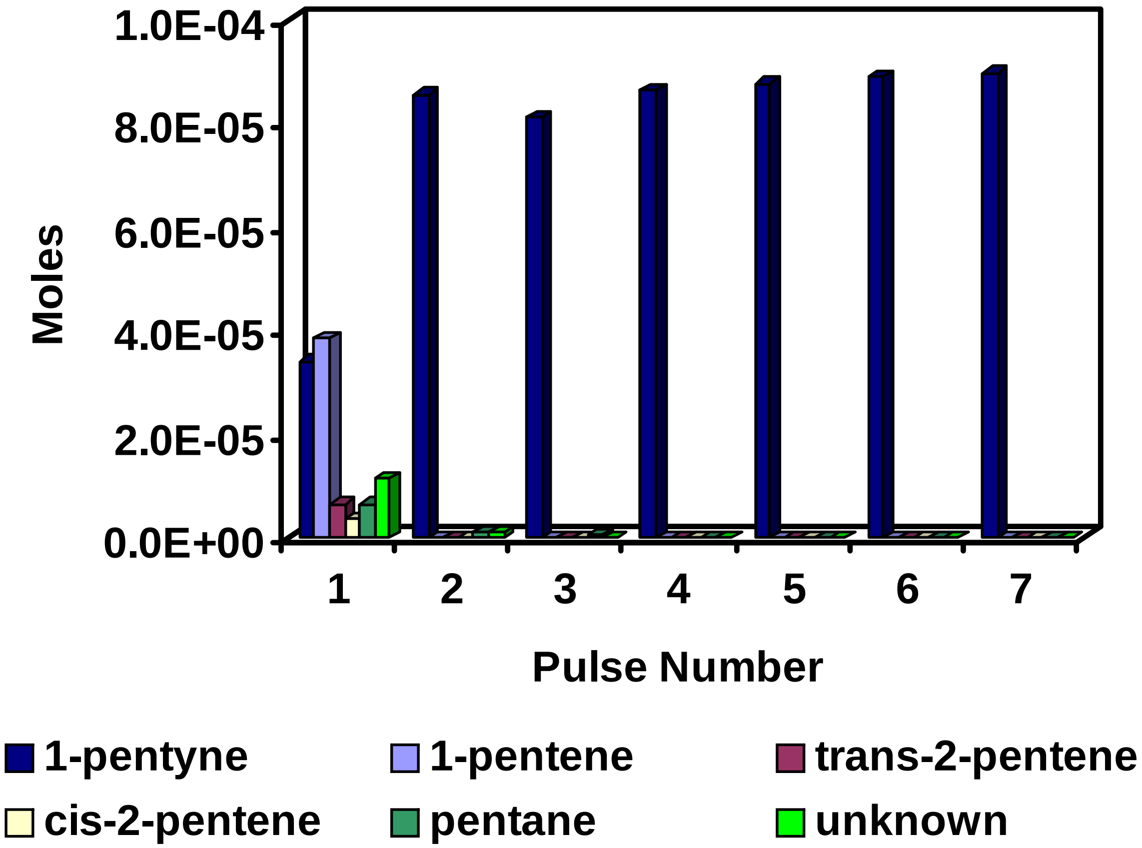
sub-surface H

Summary

1. <u>*Subsurface H*</u>: effective for alkene-to-alkane but also for alkyne-to-alkane transformation

Pulse experiments
1-pentyne Adsorption

(After H_2 pretreatment) $1\%Pd/Al_2O_3$



- First pulse shows activity
- 65% conversion
  - 38.5% 1-pentene
  - 6.5% *trans*-2-pentene
  - 3.5% *cis*-2-pentene
  - 6.5% pentane
  - 11.5% Unknown

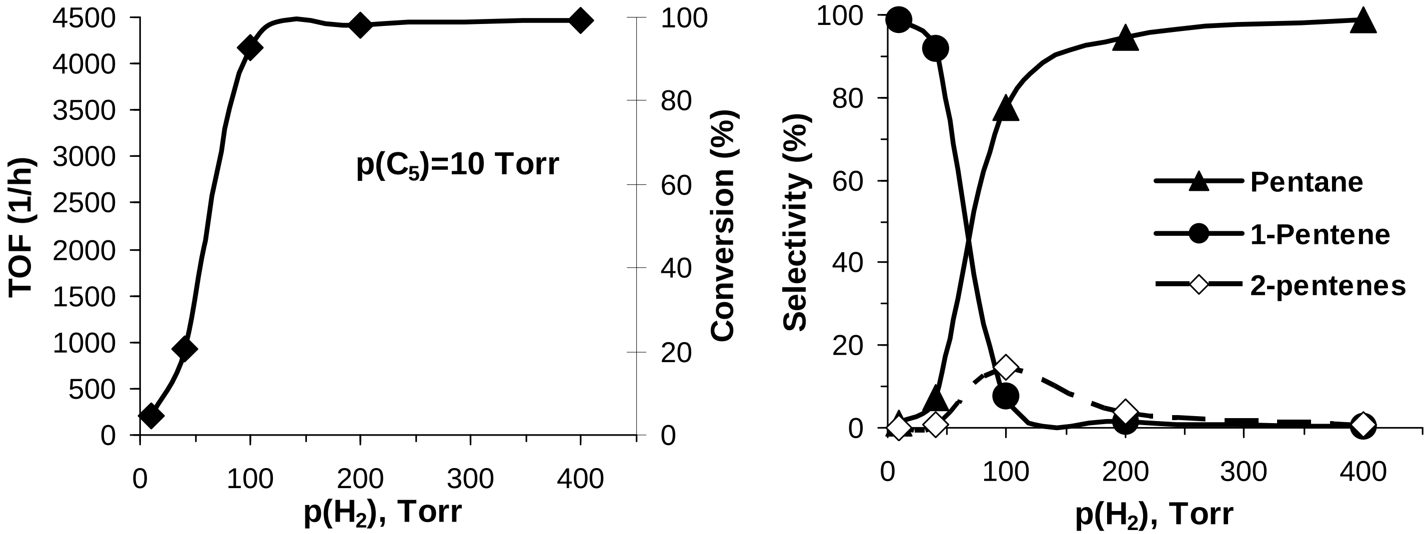
Hneeded/Pdtotal ratio: 13-to-1 Source of H? → Spillover

Summary

1. *Subsurface H*: effective for alkene-to-alkane but also for alkyne-to-alkane transformation
2. *Surface H*: could be selective (spillover)

Hydrogenation

1. 1-Pentyne hydrogenation over 1% Pd/Al_2O_3 in a closed loop-reactor, t=5 min. (after repeated runs at each condition)



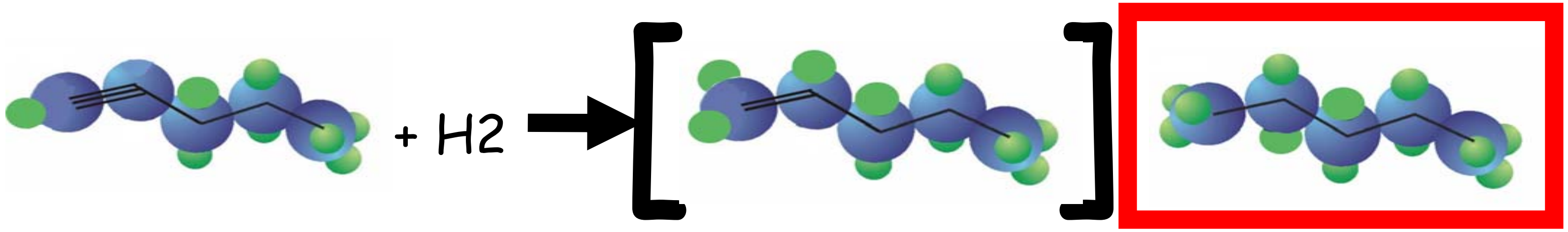
2. 1-Pentyne hydrogenation over 1% Pd/Al_2O_3 in continuous flow

$H_2:C_5$ = 4:1	total hydrogenation
$H_2:C_5$ = 3:1	selective hydrogenation

Summary

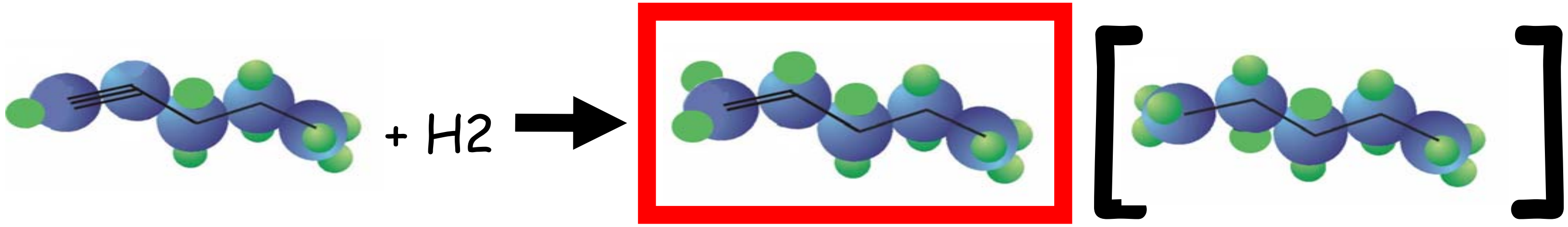
1. *Subsurface H*: effective for alkene-to-alkane but also for alkyne-to-alkane transformation
2. *Surface H*: could be selective (spillover)
3. *Different reaction orders* in the different selectivity regimes & Abrupt changes between regimes

During TEOM experiment



	40 mins				170 mins			
	1-pentyne	1-pentene	2-pentenes	n-pentane	1-pentyne	1-pentene	2-pentenes	n-pentane
Pd/Al_2O_3, 100 % H_2	trace	trace	trace	100	trace	trace	trace	100
Pd Black, 100 % H_2	0.1	trace	0.1	99.8	3.6	0.5	11.3	84.5
Pd Black, 5 % H_2	58.7	40.1	trace	1.2	42.8	54.7	0.2	2.3
Al_2O_3, 100 % H_2	81.1	16.2	0.7	2.0	74.9	22.4	0.7	1.9
Quartz Wool, 358 K	81.6	17.1	0.2	1.1	-	-	-	-
Quartz Wool, 303 K	89.2	10.6	trace	0.3	-	-	-	-

During TEOM experiment



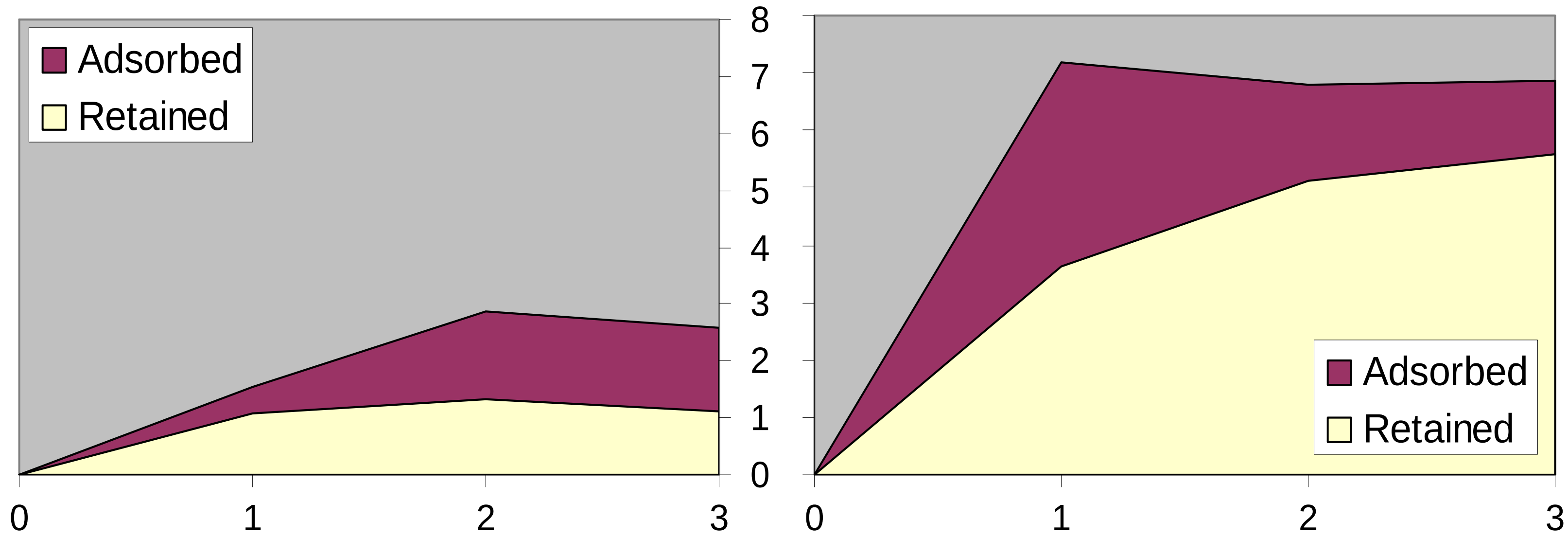
	40 mins				170 mins			
	1-pentyne	1-pentene	2-pentenes	n-pentane	1-pentyne	1-pentene	2-pentenes	n-pentane
Pd/Al_2O_3, 100 % H_2	trace	trace	trace	100	trace	trace	trace	100
Pd Black, 100 % H_2	0.1	trace	0.1	99.8	3.6	0.5	11.3	84.5
Pd Black, 5 % H_2	58.7	40.1	trace	1.2	42.8	54.7	0.2	2.3
Al_2O_3, 100 % H_2	81.1	16.2	0.7	2.0	74.9	22.4	0.7	1.9
Quartz Wool, 358 K	81.6	17.1	0.2	1.1	-	-	-	-
Quartz Wool, 303 K	89.2	10.6	trace	0.3	-	-	-	-

During TEOM experiment

Pd Black

Reaction with 100% H_2 Reaction with 5% H_2

Mass change [micro g / mg catalyst]



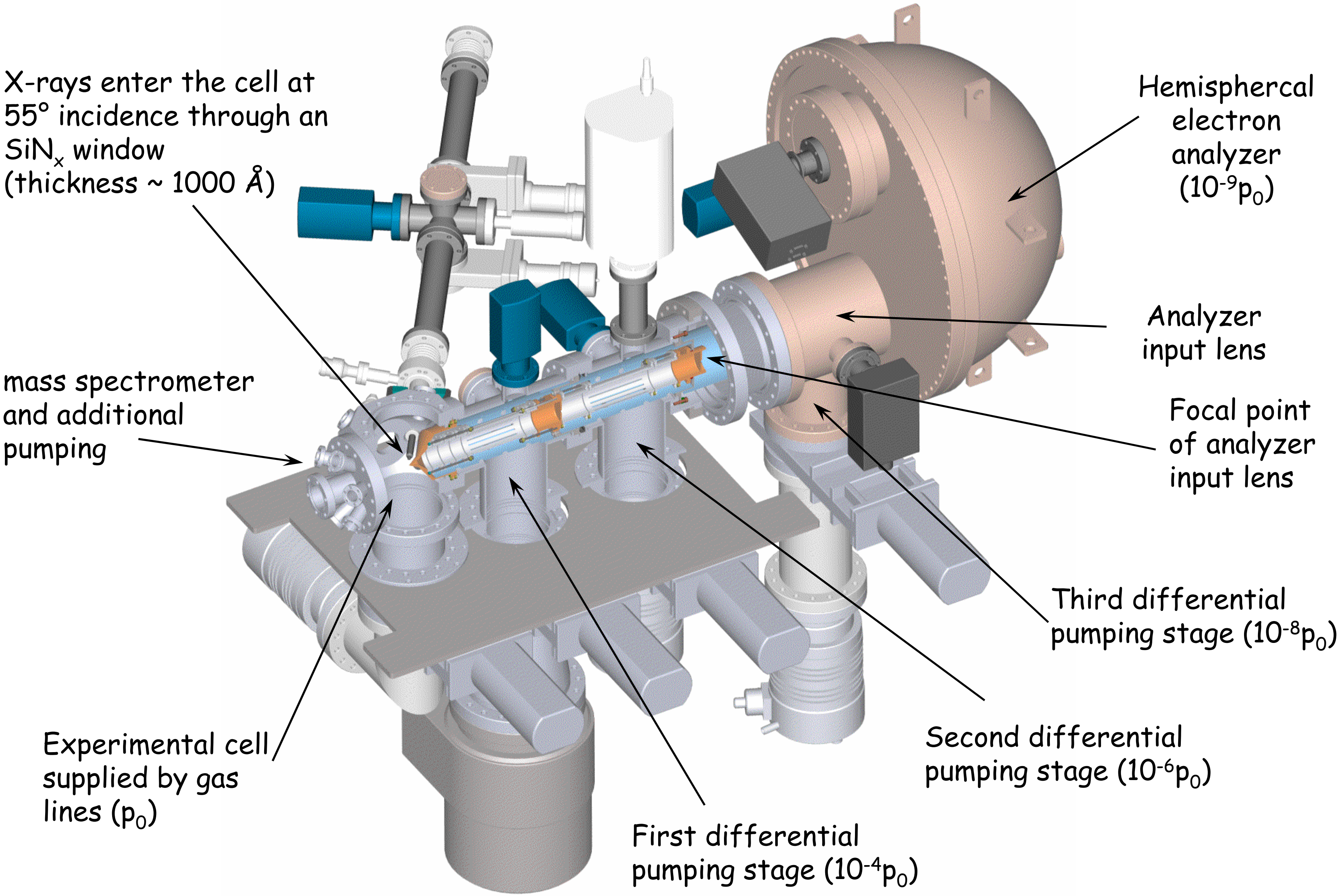
Time since introduction of 1-pentyne [hours]

Up to x5 more carbon is retained in the selective hydrogenation regime

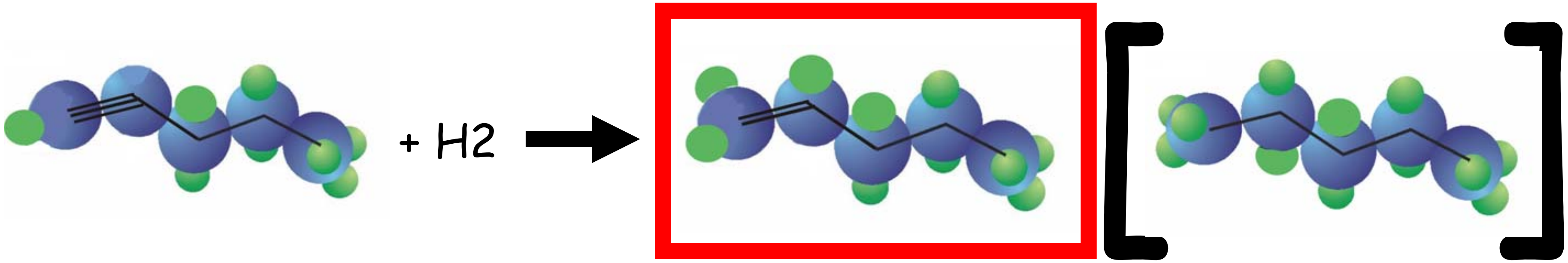
Summary

1. *Subsurface H*: effective for alkene-to-alkane but also for alkyne-to-alkane transformation
2. *Surface H*: could be selective (spillover)
3. *Different reaction orders* in the different selectivity regimes & Abrupt changes between regimes
4. *C uptake* is significantly more in the selective regime

In situ XPS system



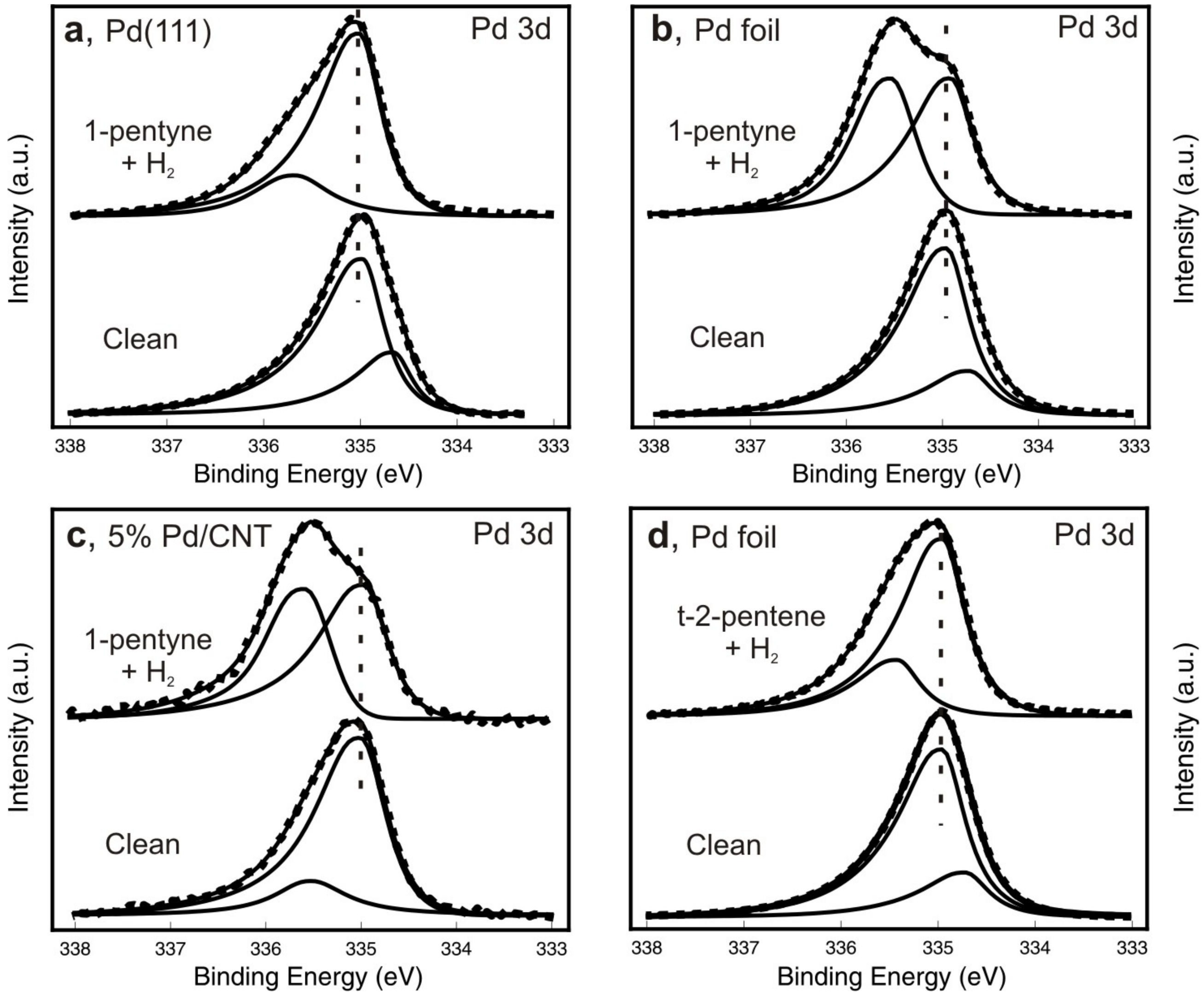
Reaction in the mbar p region (in-situ XPS)



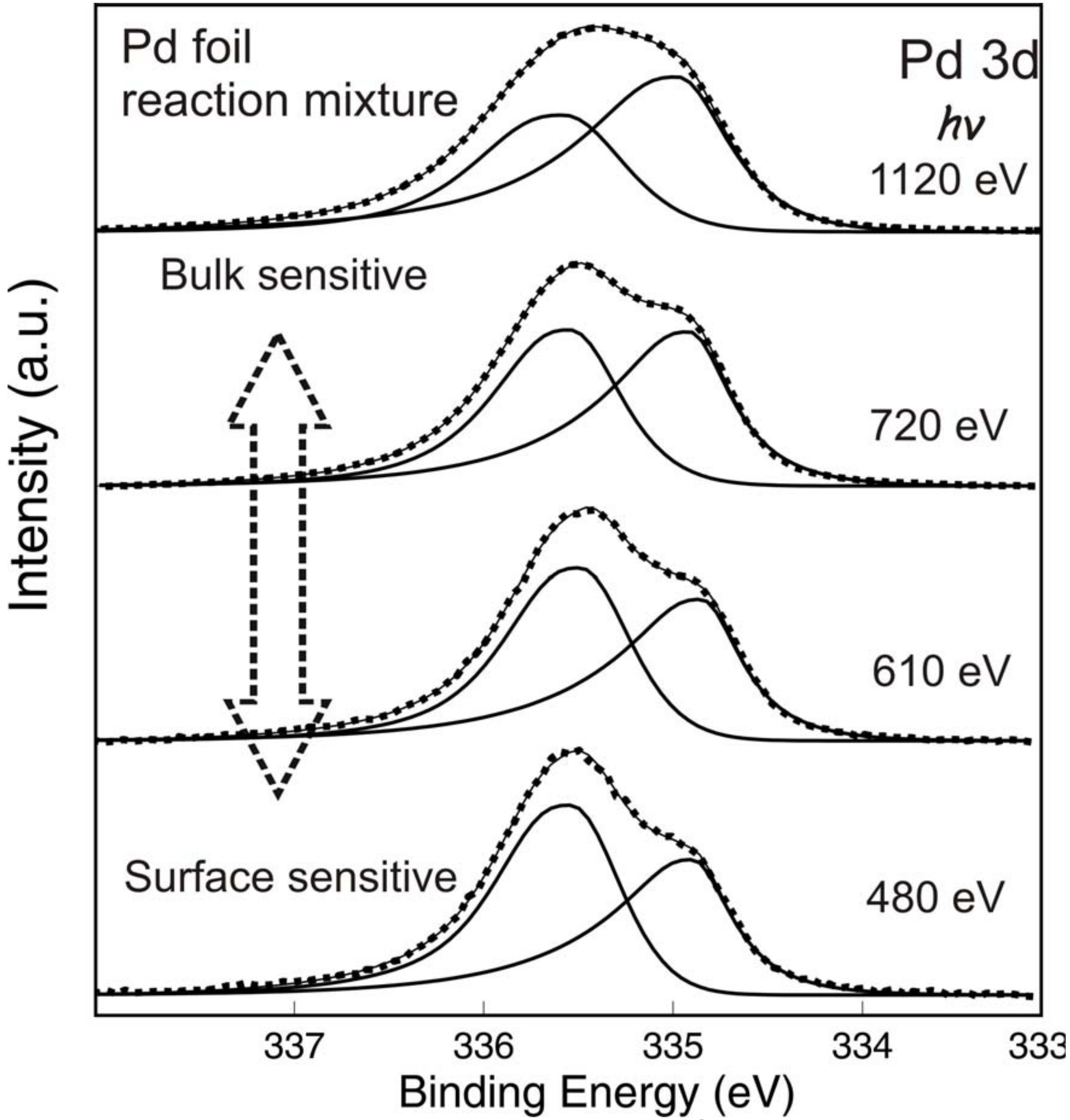
	5% Pd/CNT	3% Pd/Al_2O_3	Pd foil	Pd(111)
Conversion [%]	~ 10	~5	~2.5	<1
Selectivity Pentene [%]	~95	~80	~98	100
Selectivity Pentane [%]	~5	~20	~2	-

Recation conditions: C_5/H_2 = 1:9, 1 mbar, 358 K

In-situ XPS: Pd 3d (hν: 720 eV)



In-situ XPS: Pd 3d depth profiling

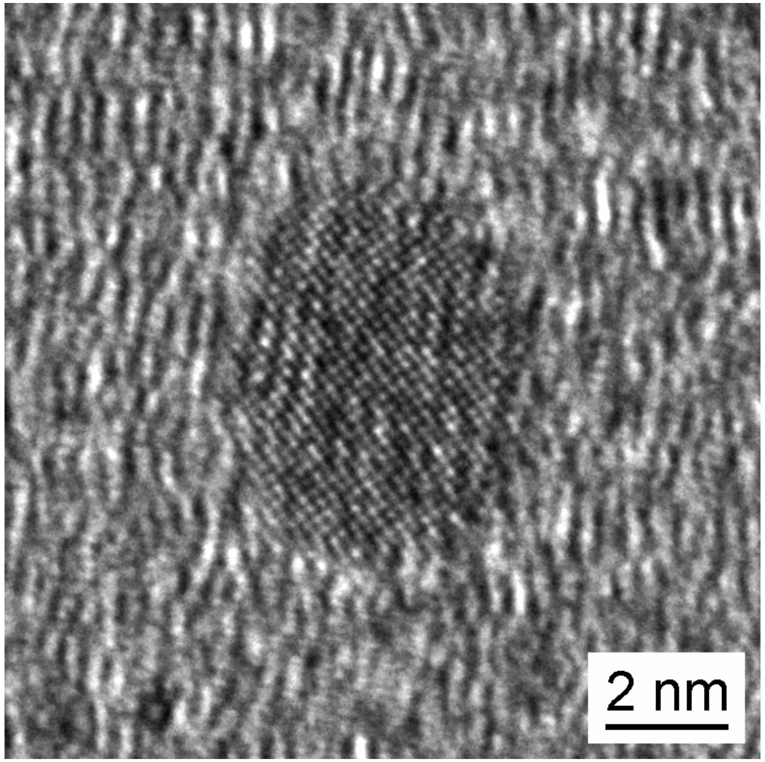


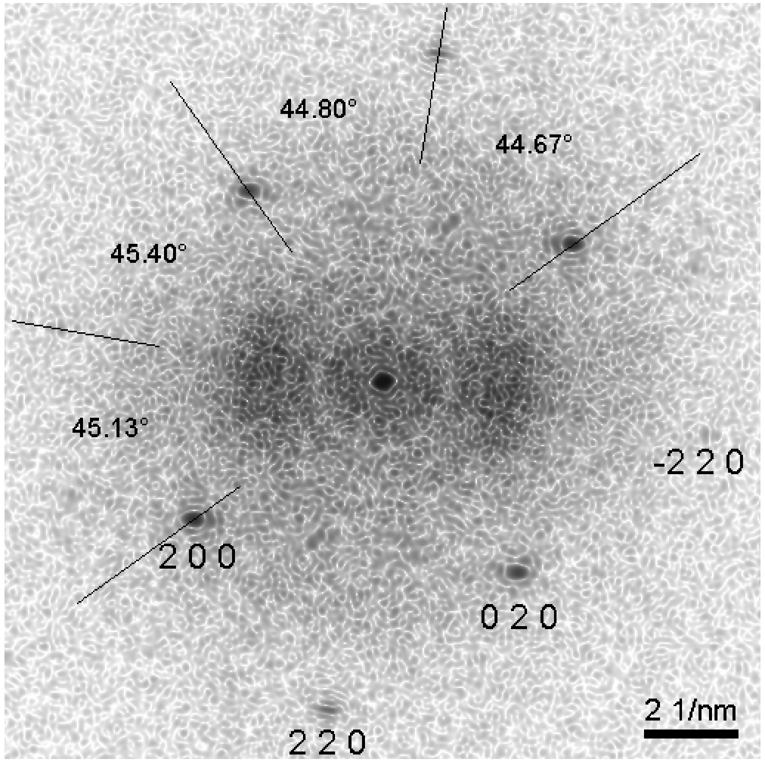
Not only adsorbate-induced surface core level shift !

But on-top location!

HRTEM: lattice expansion

5% Pd/CNT after reaction

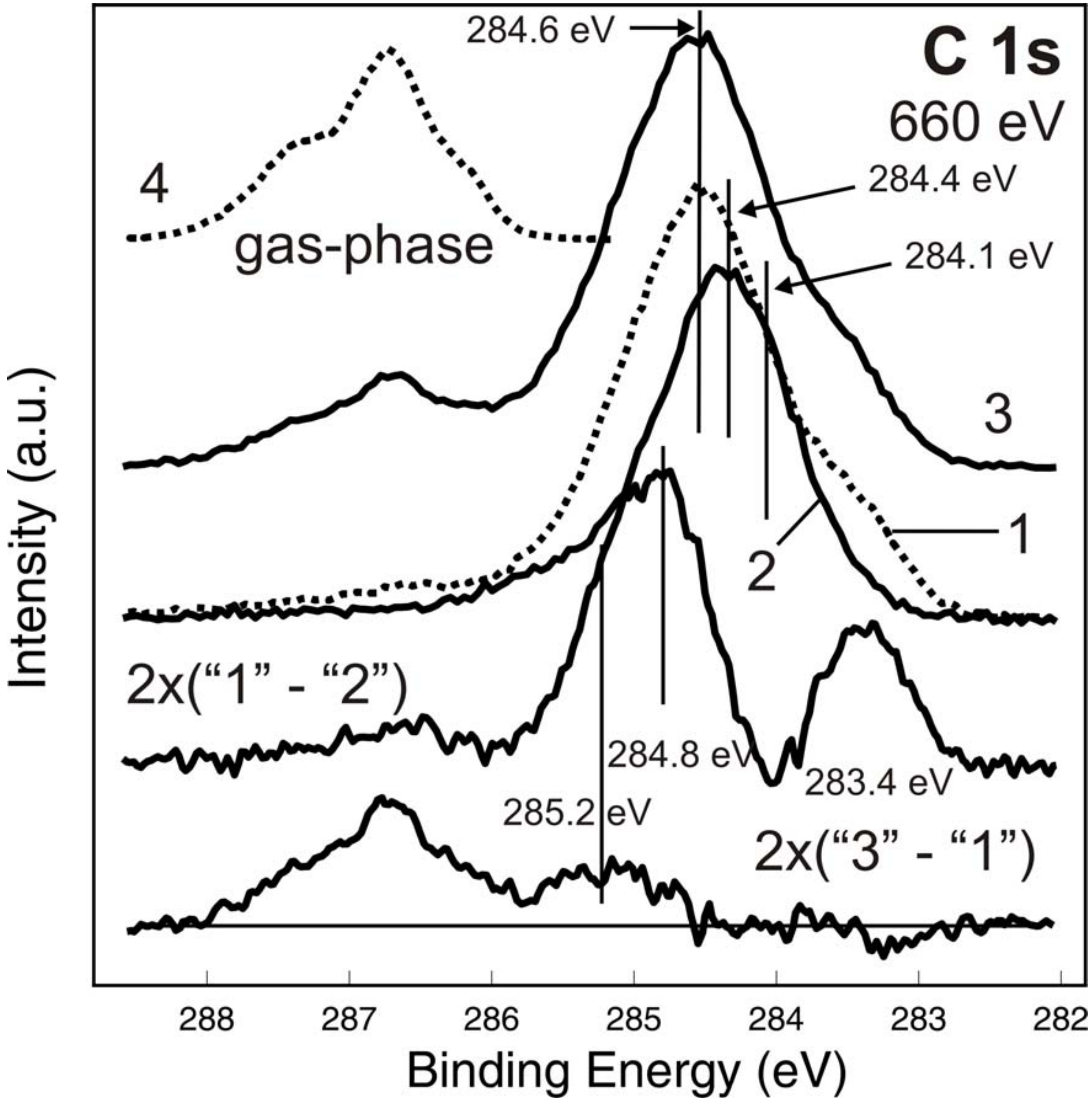




Pd nanoparticle (5nm x 6nm) with typical lattice dilatations, angular distortions are negligible
background: rather disordered graphitic layers of a CNT

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

In-situ XPS: C1s (Switching off experiments)



1: reaction mix.

2: C5 off

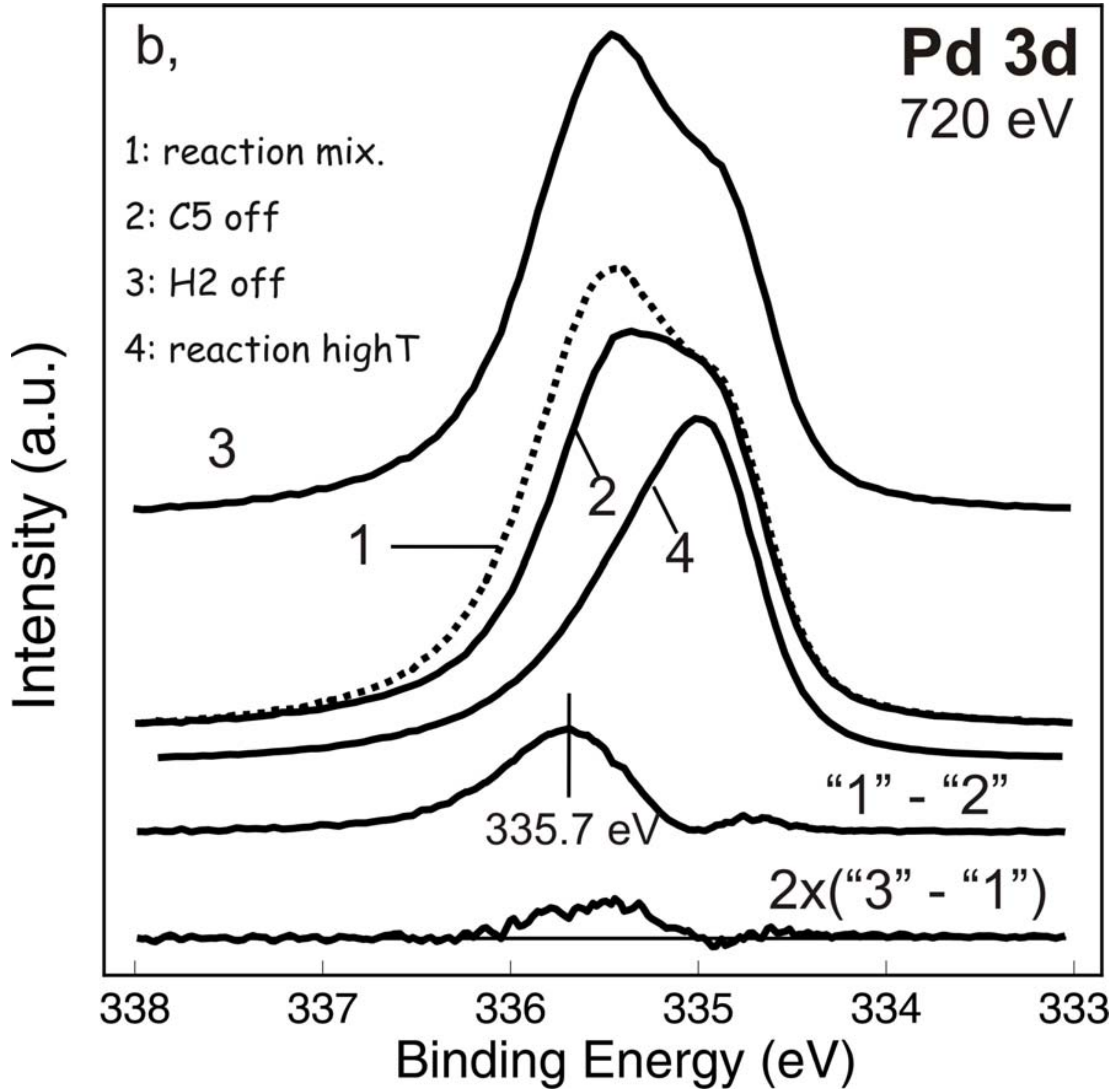
3: H2 off

4: C5 gas-phase

Teschner et al.

J. Catal. 242 (2006) 26-37

In-situ XPS: Pd 3d (Switching off experiments)



1: reaction mix.

2: C5 off

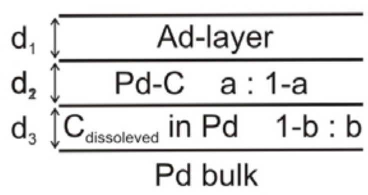
3: H2 off

4: reaction; high T

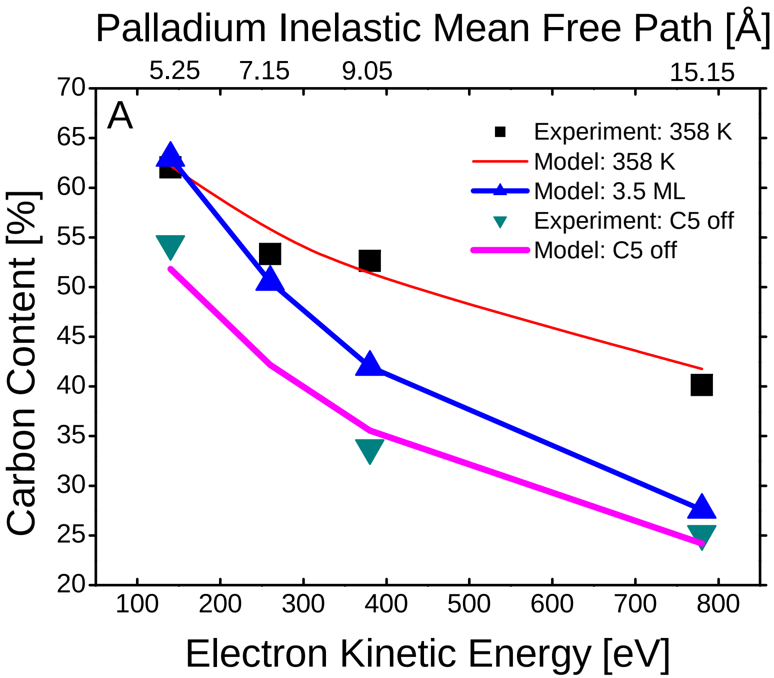
523 K

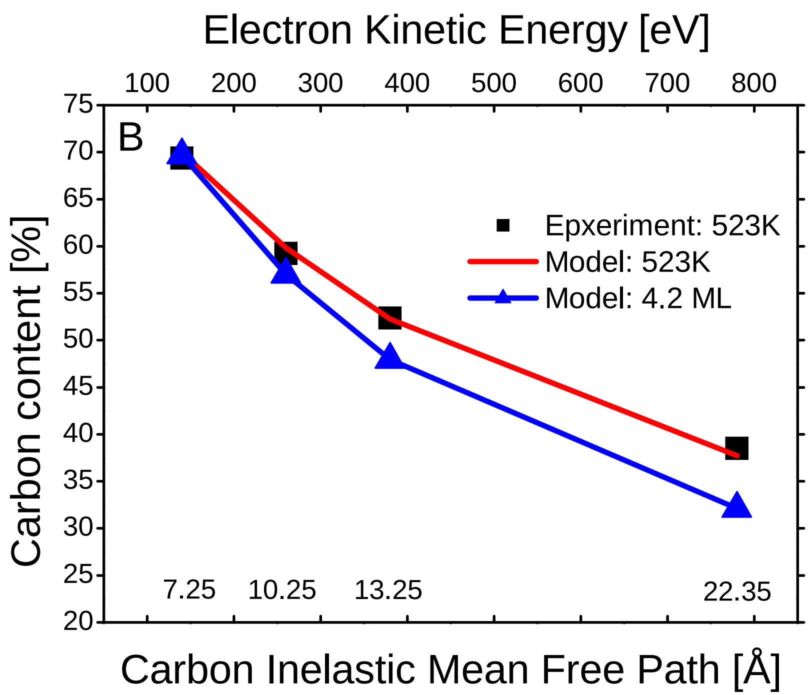
In-situ XPS: Pd vs. C depth profiling

Model

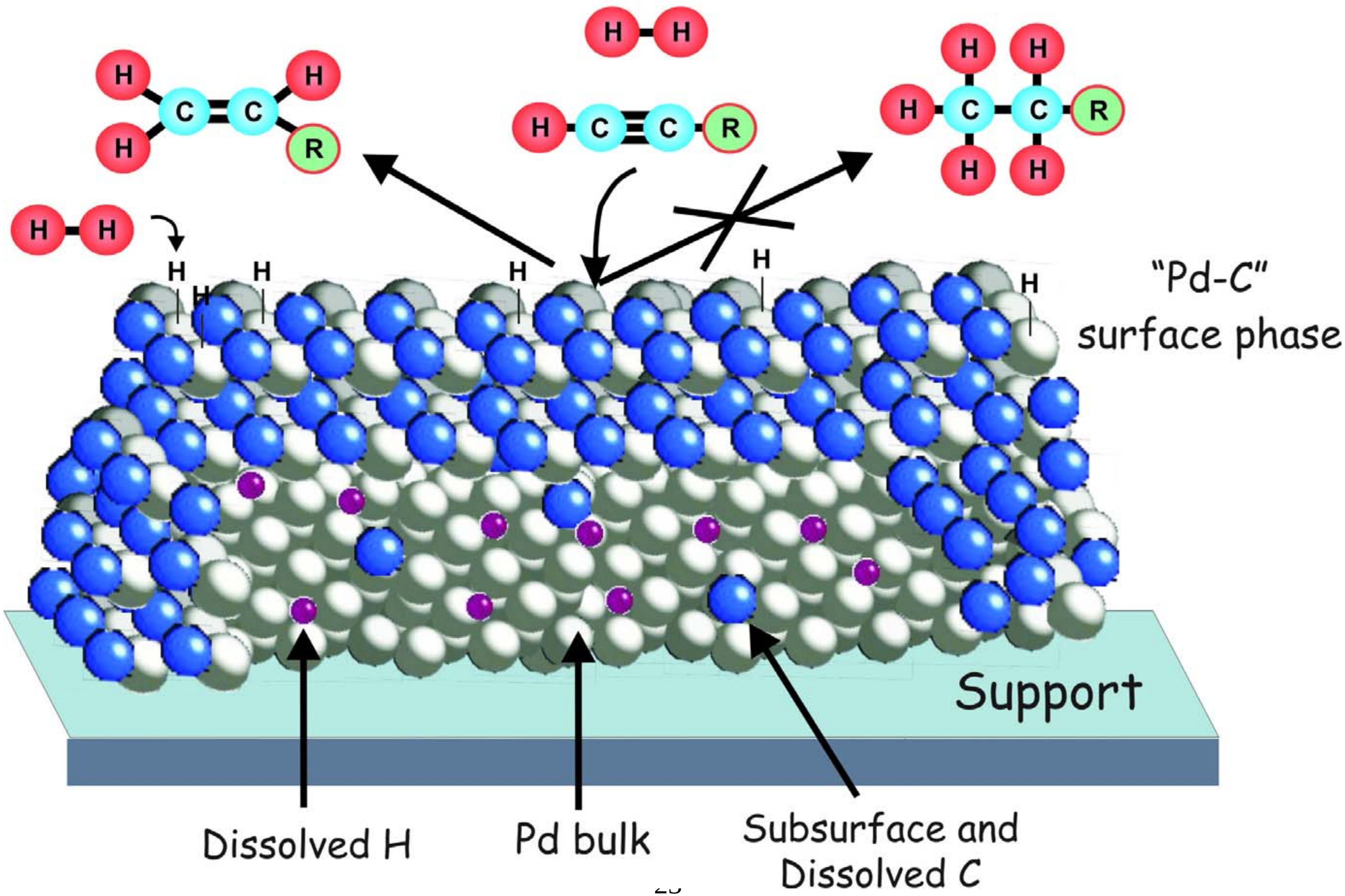


= 0.3 nm
1.4 nm
14 nm





Model

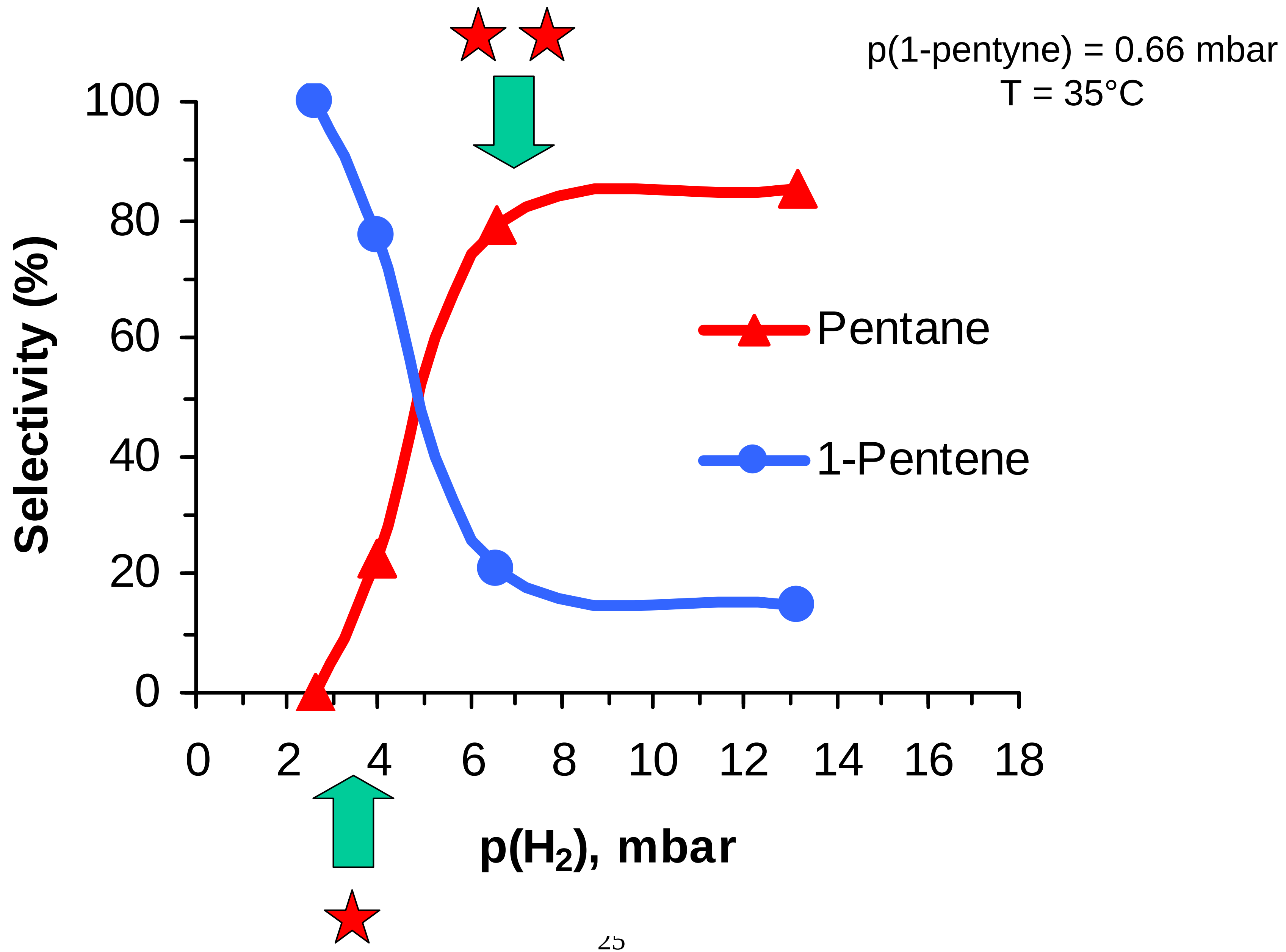


"Pd-C"
surface phase
Support
Dissolved H
Pd bulk
Subsurface and
Dissolved C

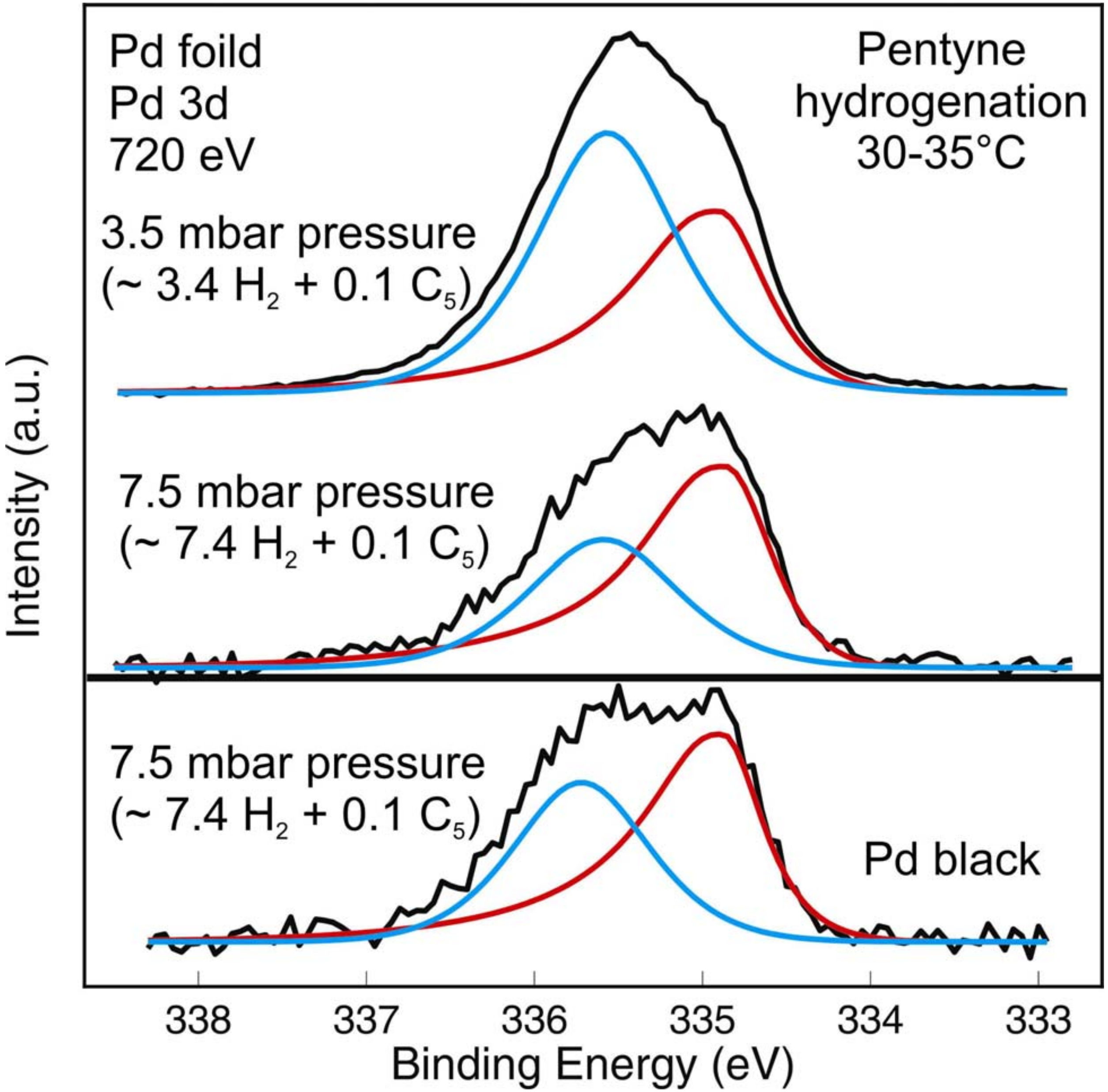
Summary

1. *Subsurface H* : effective for alkene-to-alkane but also for alkyne-to-alkane transformation
2. *Surface H* : could be selective (spillover)
3. *Different reaction orders* in the different selectivity regimes & Abrupt changes between regimes
4. *C uptake* is considerably more in the selective regime
5. *Pd-C surface phase* forms during selective hydrogenation of pentyne & there is significant amount of *subsurface C* below of it
6. Dynamic behaviour of Pd-C and subsurface C

1-pentyne hydrogenation on Pd Black (done in Budapest)

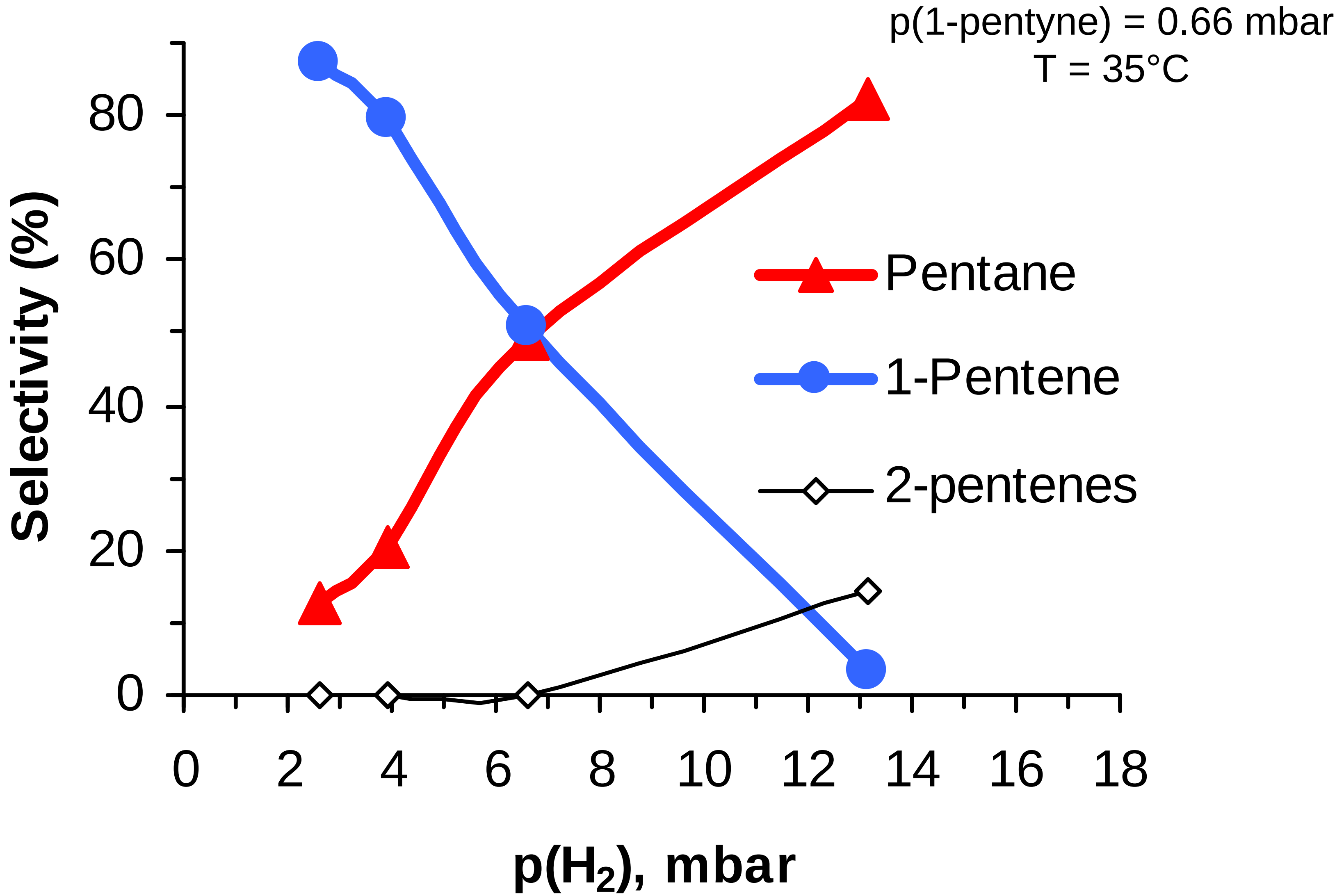


And at Bessy?



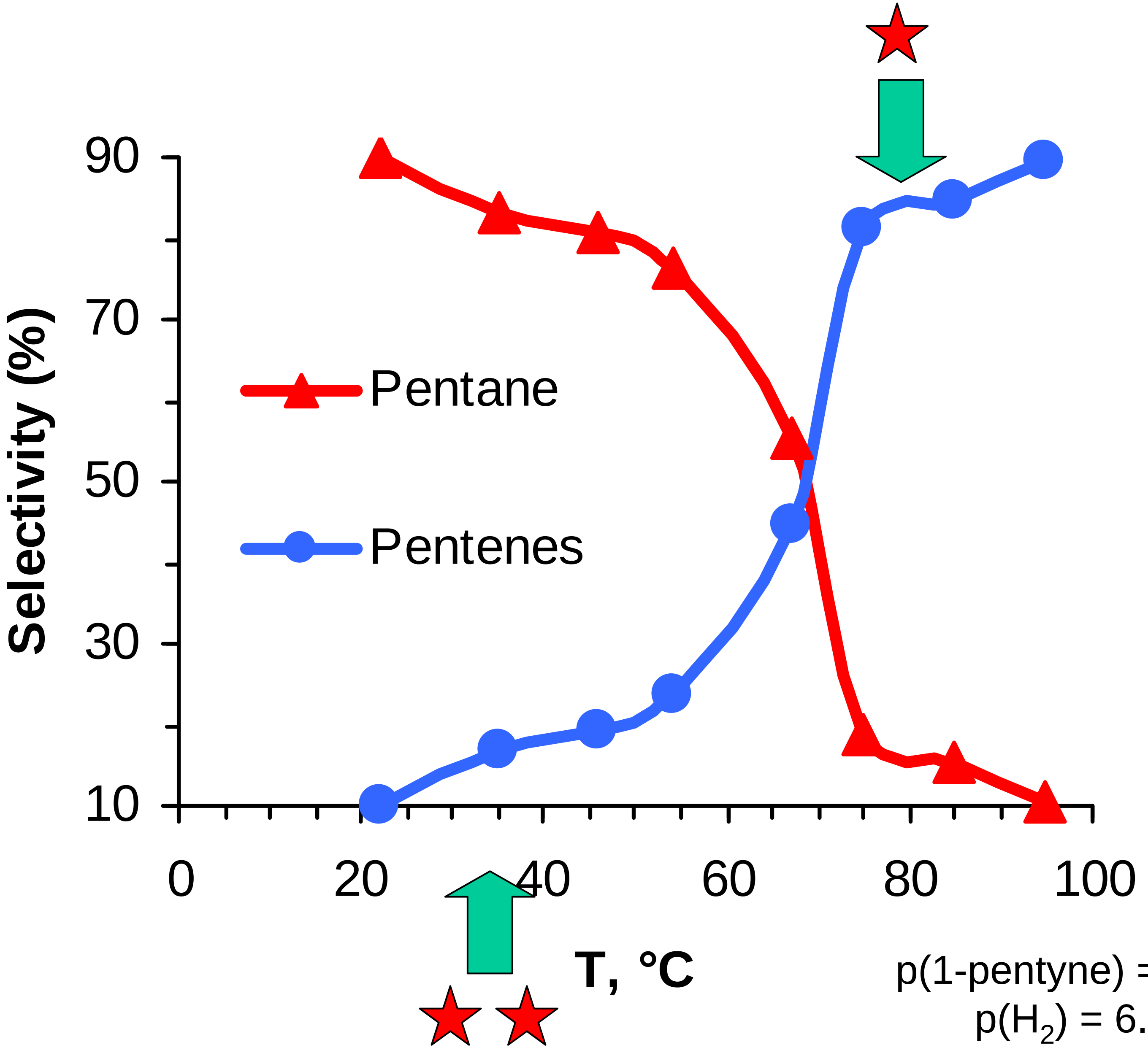
Pd foild
Pd 3d
720 eV
Pentyne
hydrogenation
30-35°C
3.5 mbar pressure
(~ 3.4 H2 + 0.1 C5)
7.5 mbar pressure
(~ 7.4 H2 + 0.1 C5)
7.5 mbar pressure
(~ 7.4 H2 + 0.1 C5)
Pd black
Intensity (a.u.)
338
337
336
335
334
333
Binding Energy (eV)

1-pentyne hydrogenation on 1%Pd/Al_2O_3 (done in Budapest)



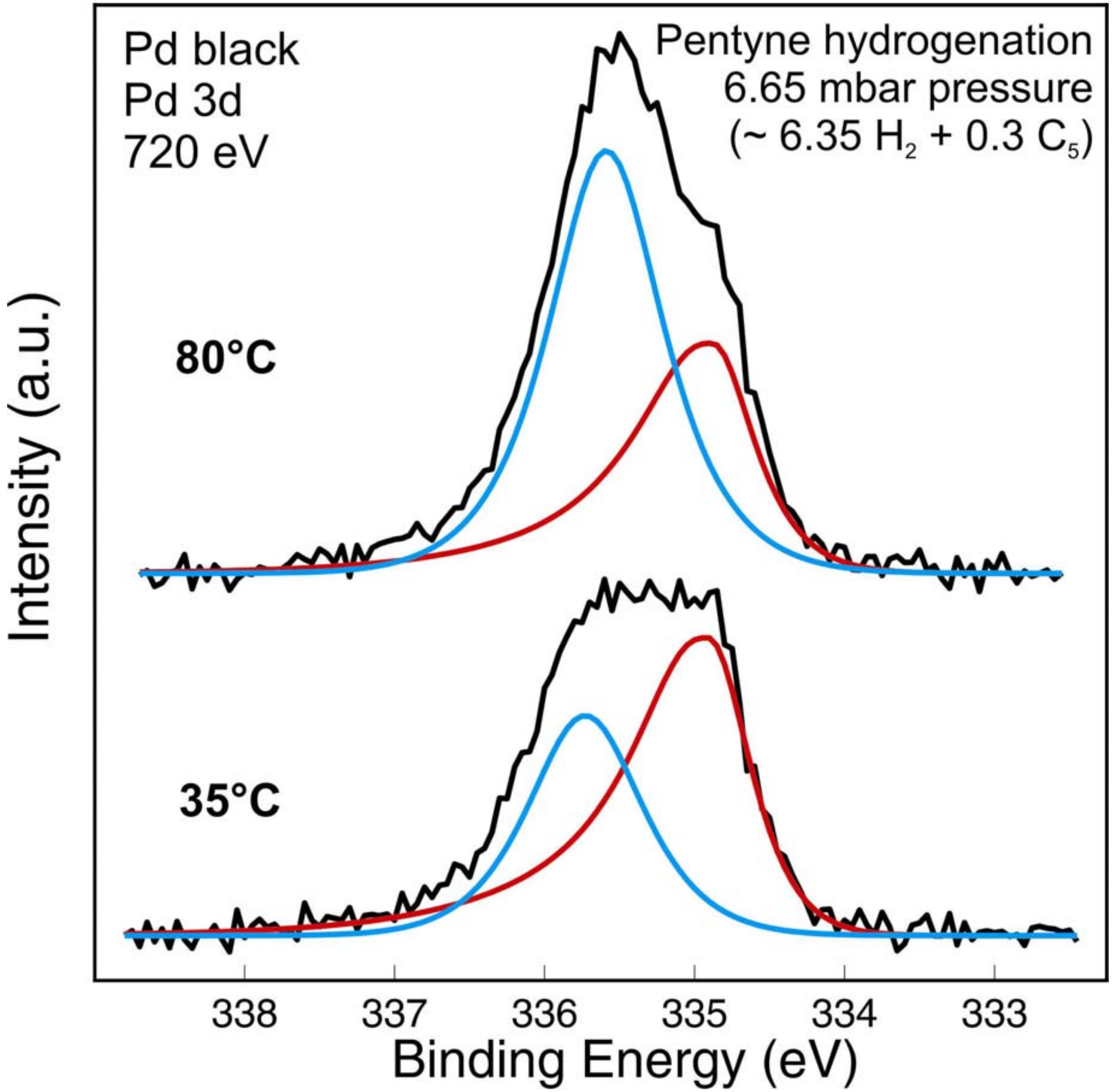
Generally similar trend was observed as with bulk Pd

1-pentyne hydrogenation on Pd Black (done in Budapest)



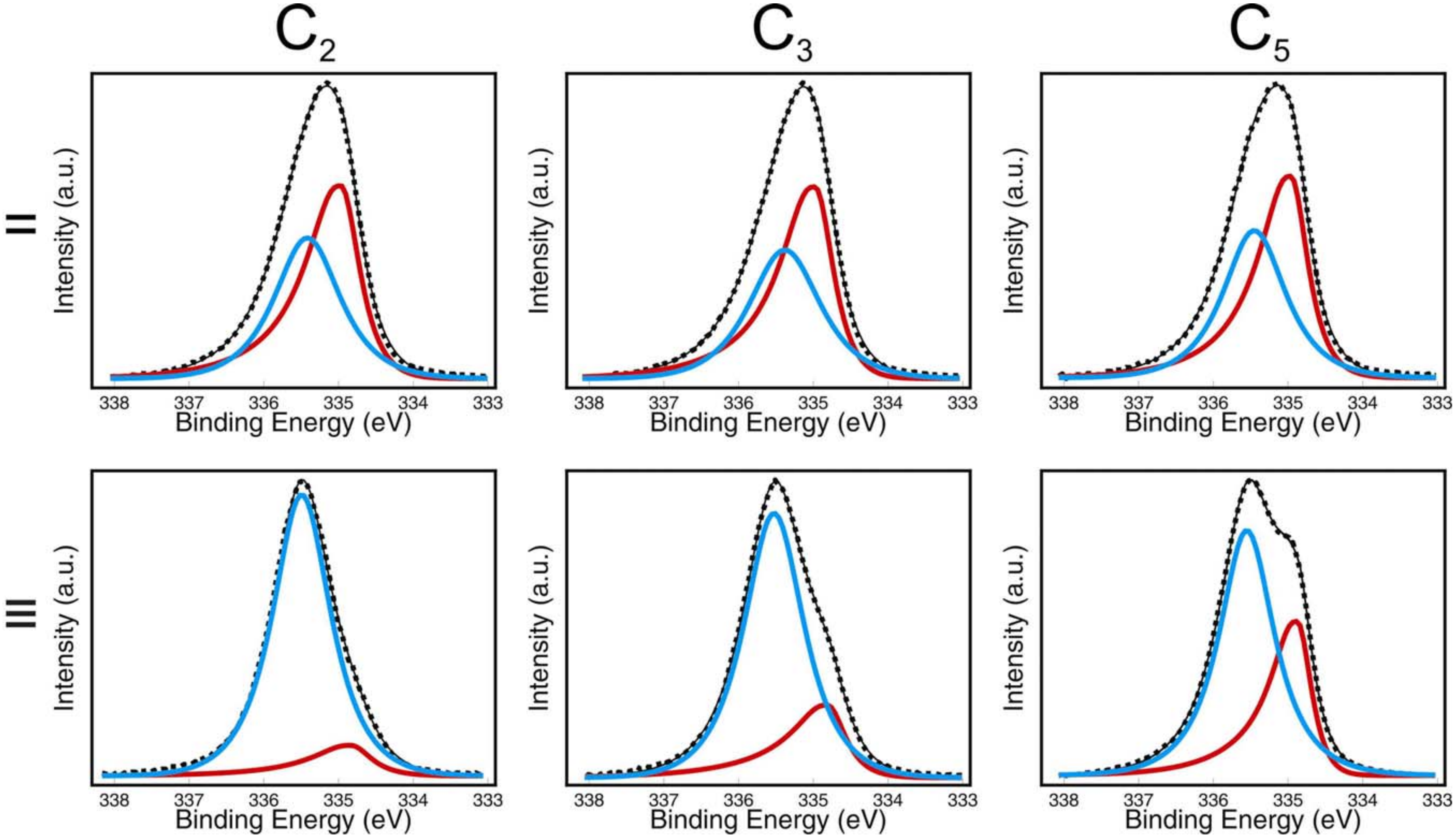
p(1-pentyne) = 0.66 mbar
$p(H_2)$ = 6.6 mbar

And at Bessy?


Pd black
Pd 3d
720 eV
Pentyne hydrogenation
6.65 mbar pressure
(~ 6.35 H2 + 0.3 C5)
80°C
35°C
Intensity (a.u.)
338
337
336
335
334
333
Binding Energy (eV)

Alkene and alkyne hydrogenation at BESSY

Pd foil, ~70°C, 1mbar (0.1 mbar C_xH_y + 0.9 mbar H_2)



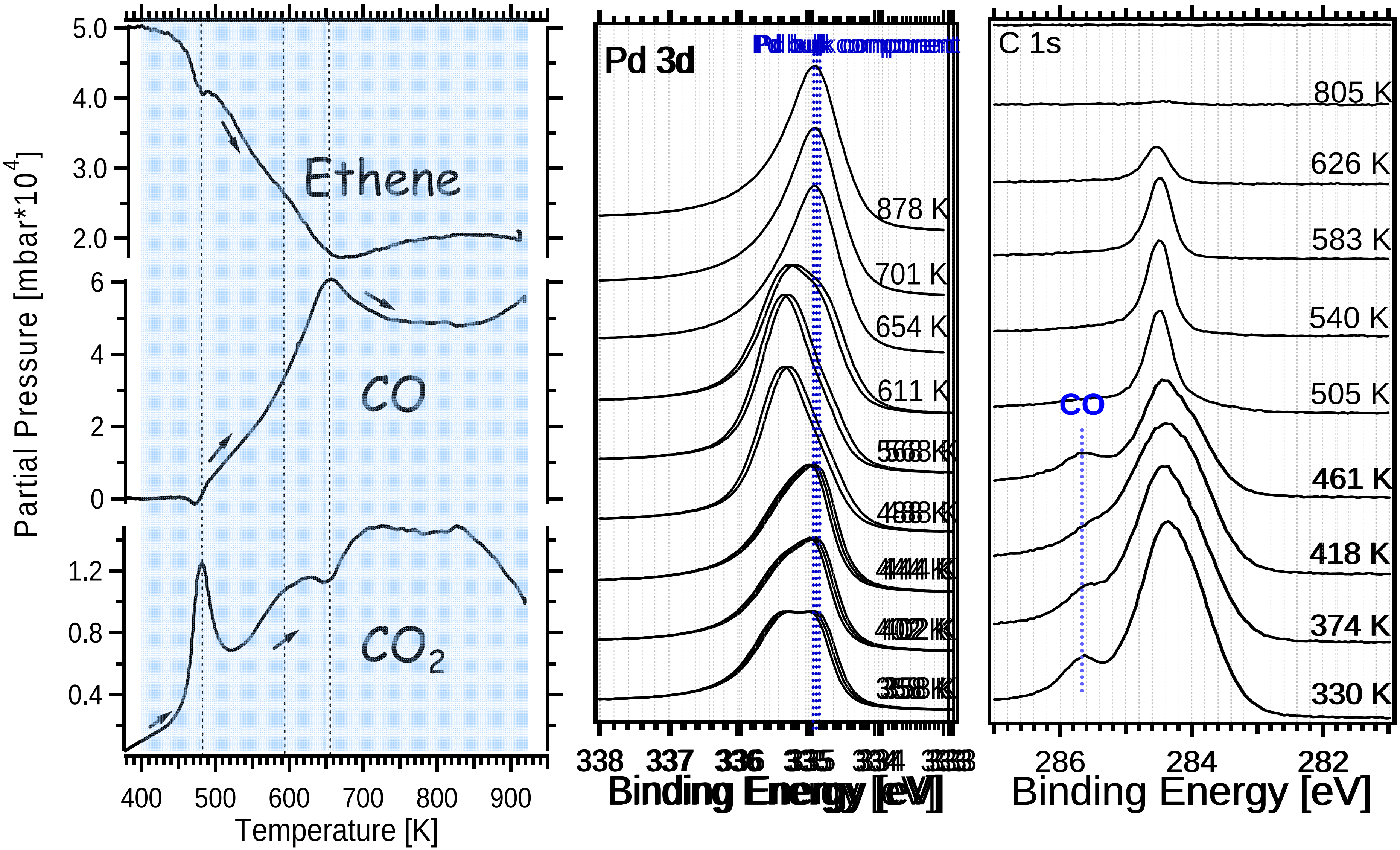
Summary

- Alkene → Alkane: no Pd-C formation
- Alkyne → Alkane: no Pd-C formation
- Alkyne → Alkene: Pd-C formation

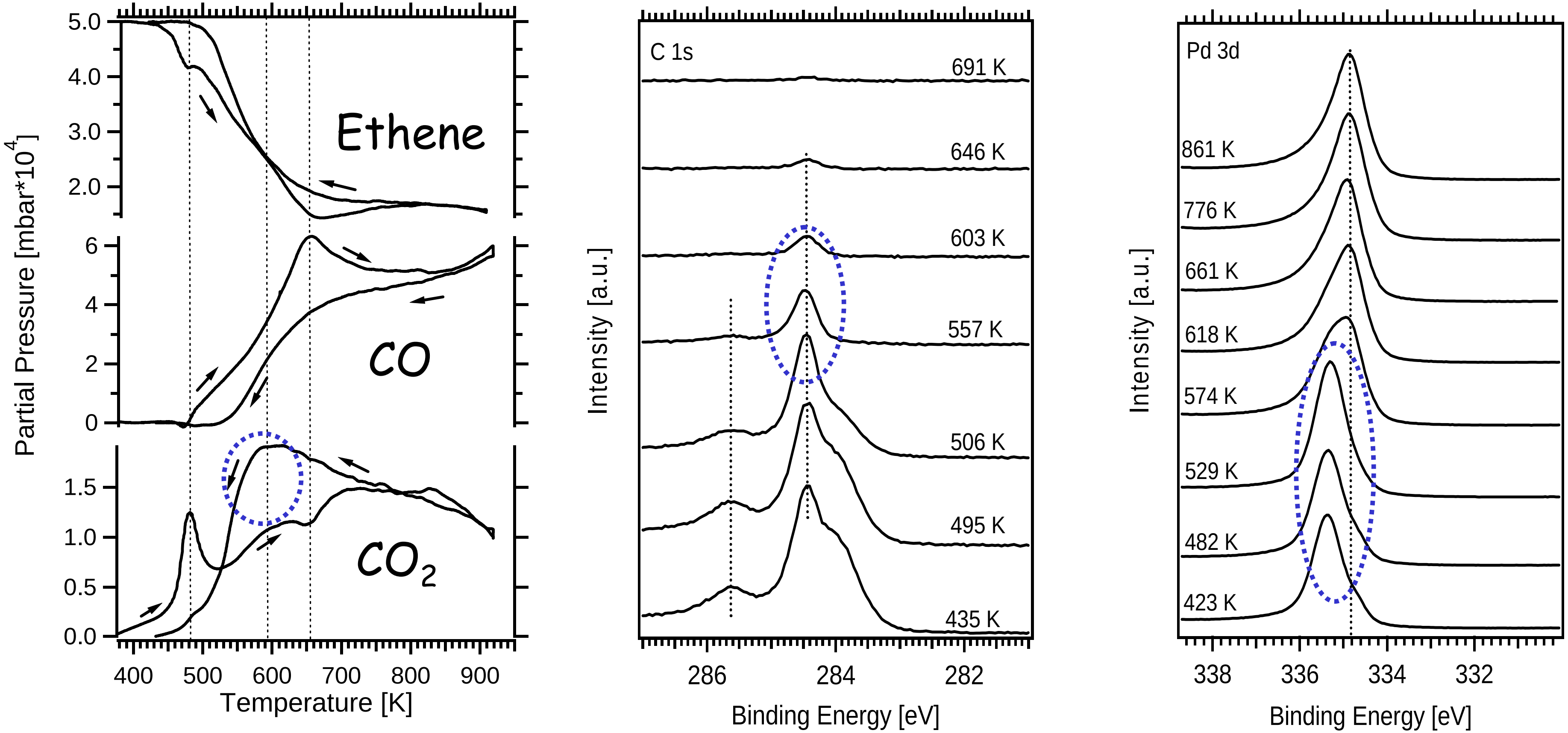
Pd-C surface phase controls selectivity

- In situ measurements: 2*10-3 mbar

$C_2H_4:O_2=1:3$, heating ramp $10K*min^{-1}$



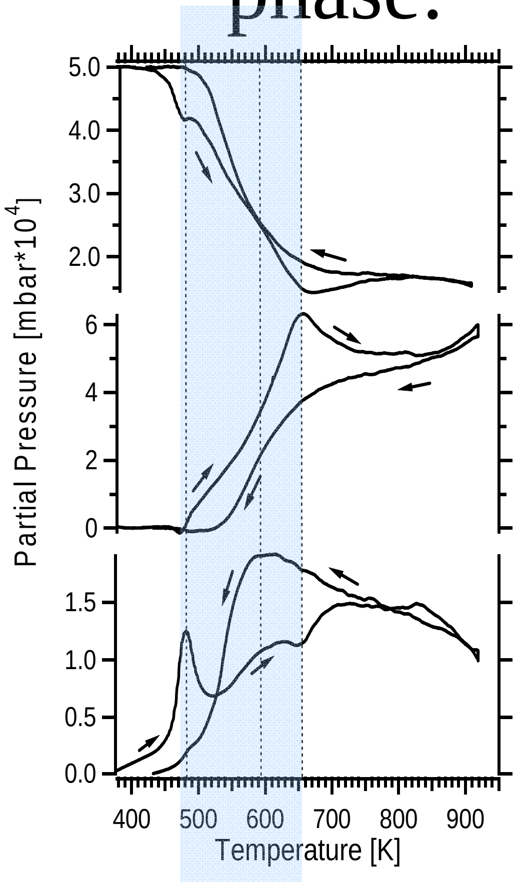
- In situ measurements:



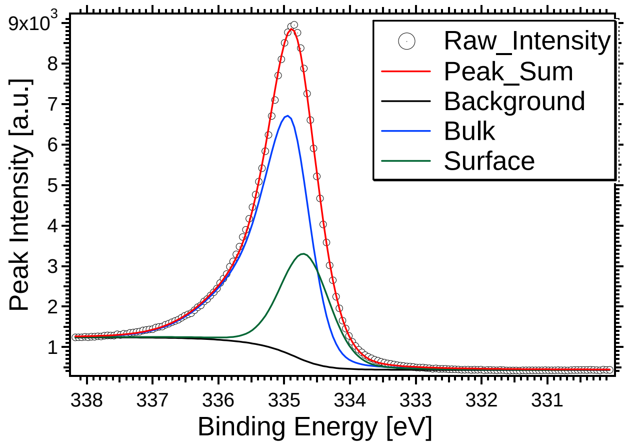
During the oxidation a carbon containing phase is formed and changes the selectivity from CO_2 towards CO

- Detailed analysis of this carbon containing phase:

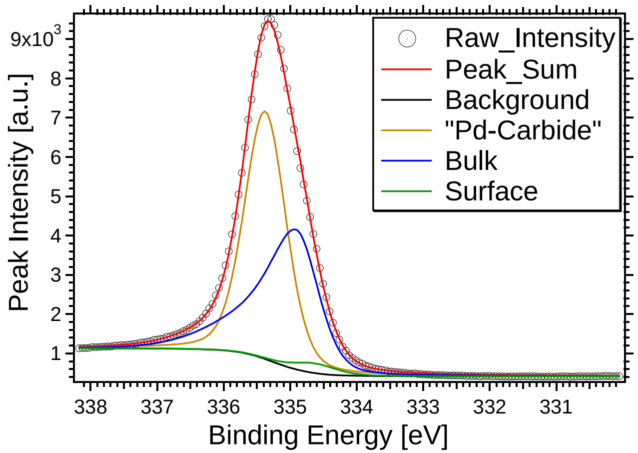
Peak deconvolution [1]



850 K: Metal



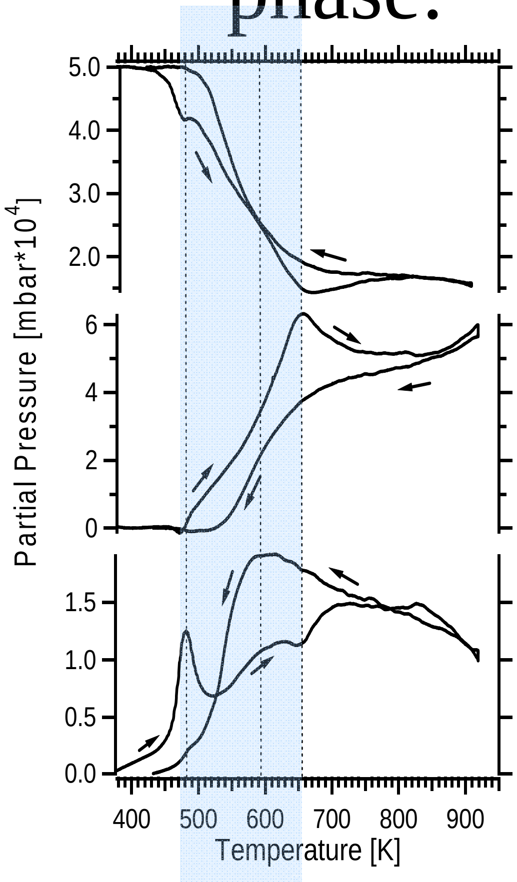
550 K: Pd_xC_y



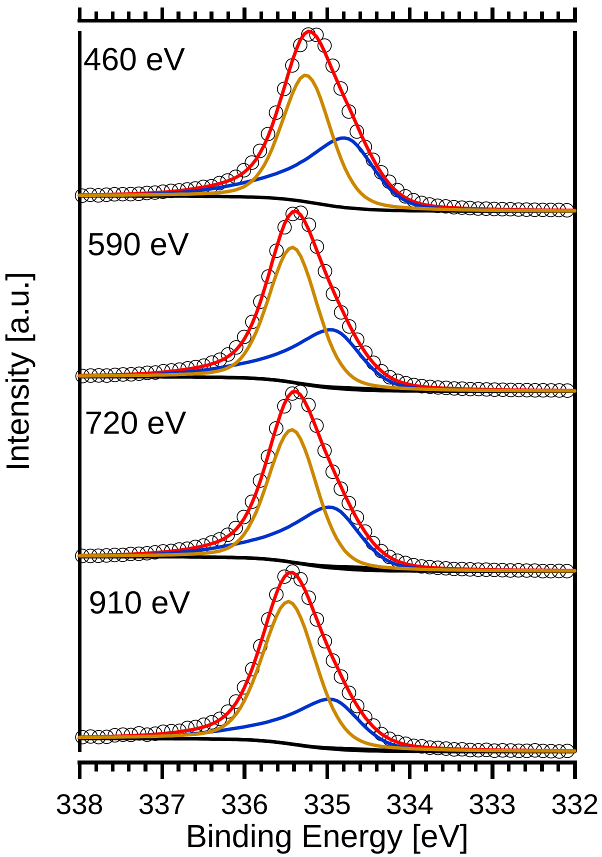
An additional peak which we attribute to Pd_xC_y can clearly be identified at a BE of 335.34 eV.

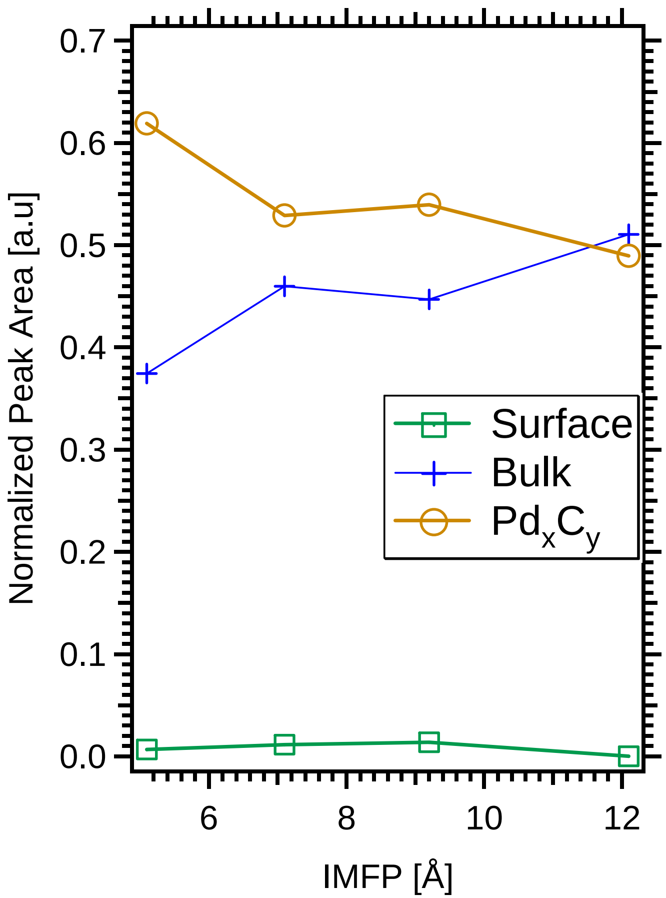
[1] J. N. Andersen,et al. Phys. Rev. B 50 1994 17525

- Detailed analysis of this carbon containing phase:



Depth profiles:





Conclusions

- During ethene oxidation the incorporation of carbon leads to a non metallic Pd-C phase.
- The new, highly symmetric $Pd3d_{5/2}$ peak was observed. The depth profiles indicate that this new phase is not only limited to the surface.
- The appearance of this phase is accompanied by strongly enhanced CO selectivity

Outlook: In situ XPS / XAS
The future at BESSY

BESSY ISISS:

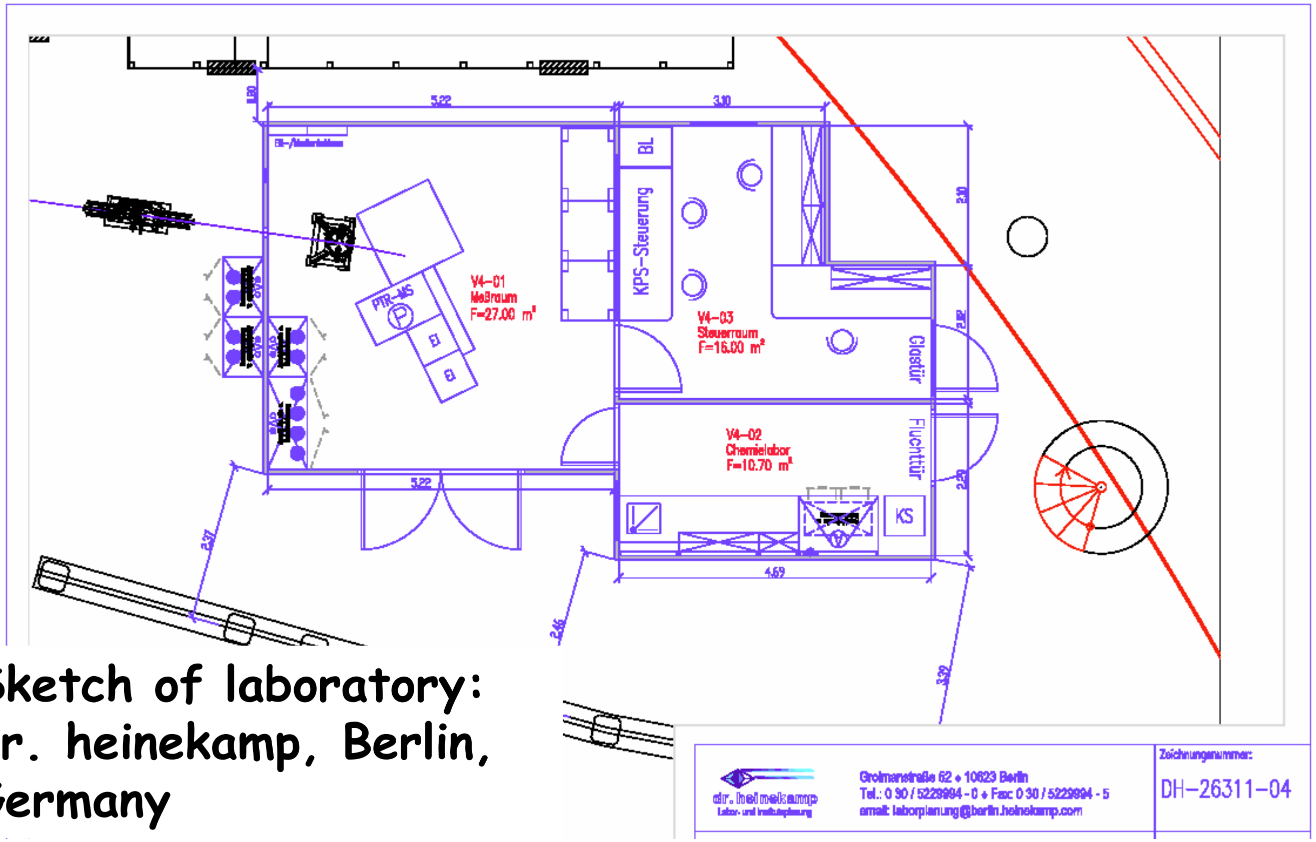
Innovative Station for In Situ Spectroscopy

A project of BESSY and the Dep. Inorganic Chemistry, Fritz-Haber-Institut

- Installation of a beamline exclusively used for in situ spectroscopy in the soft X-ray range
- Installation of infrastructure optimized for these kind of experiments on site (e.g. chemical lab, gas supply, gas analytics)
- Later, further implementation of other in situ spectroscopy techniques: multi wavelength Raman, UV-Vis, fluorescence yield ?!
- Start of operation of the beamline: 2007

Outlook: In situ XPS / XAS
The future at BESSY

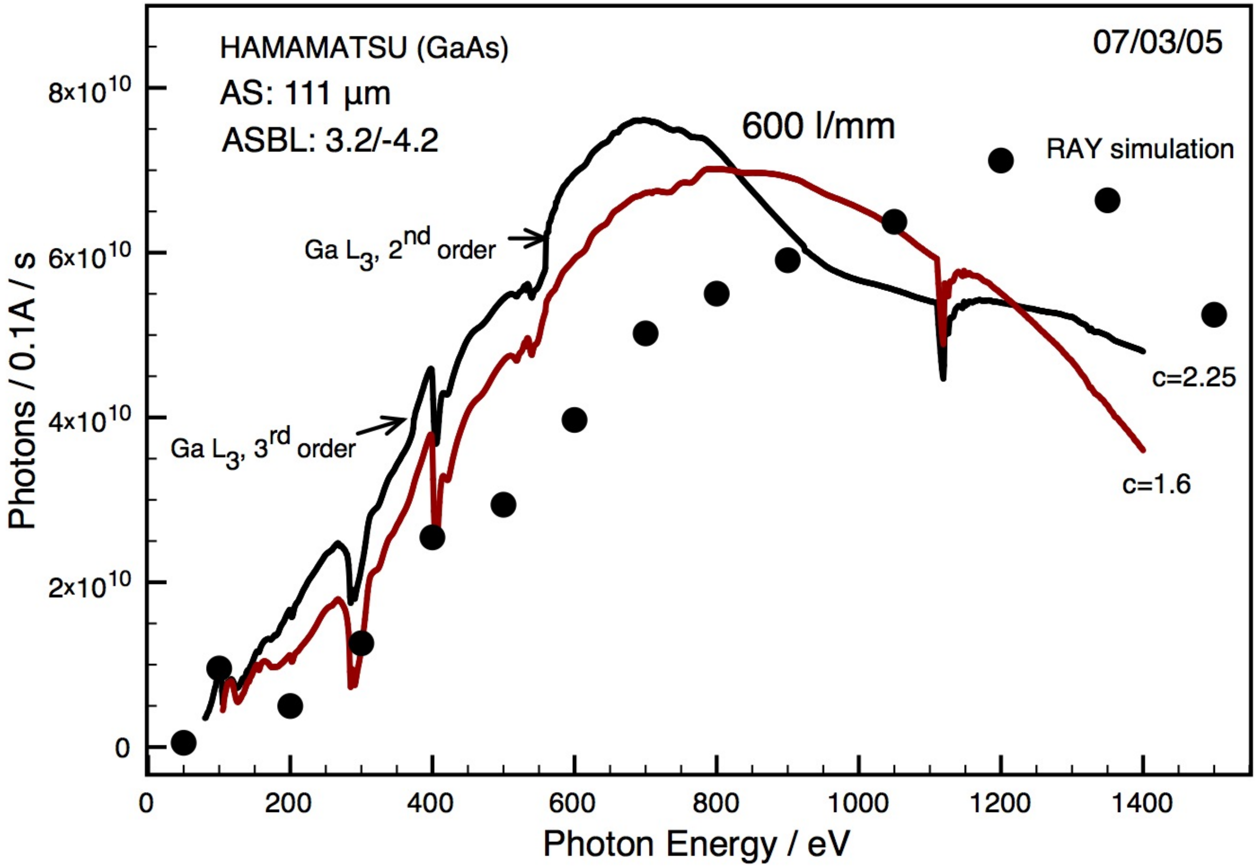
ISISS:



Sketch of laboratory:
dr. heinekamp, Berlin,
Germany

Outlook: In situ XPS / XAS
The future at BESSY

Outlook: In situ XPS / XAS
The future at BESSY



Outlook: In situ XPS / XAS
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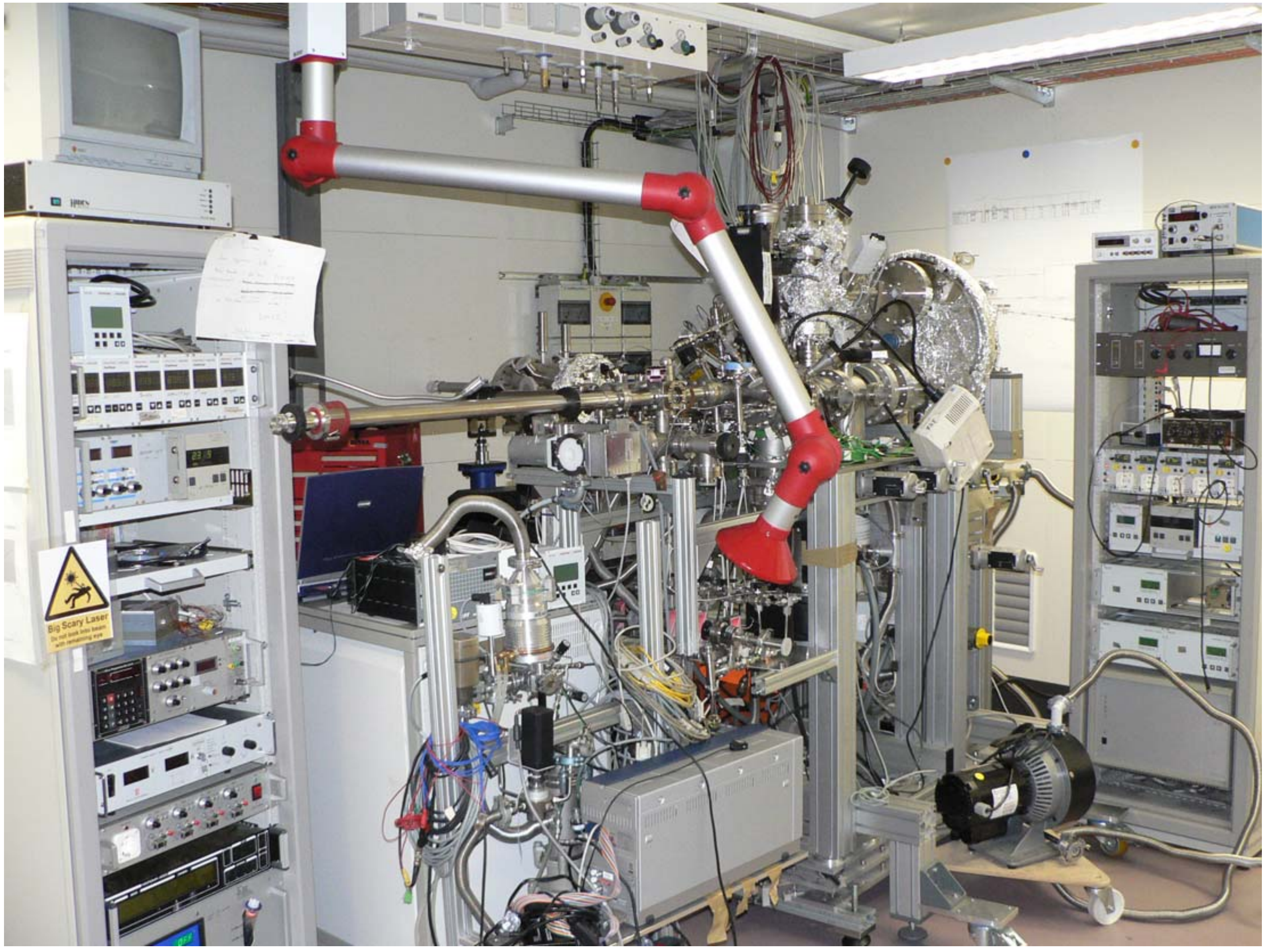
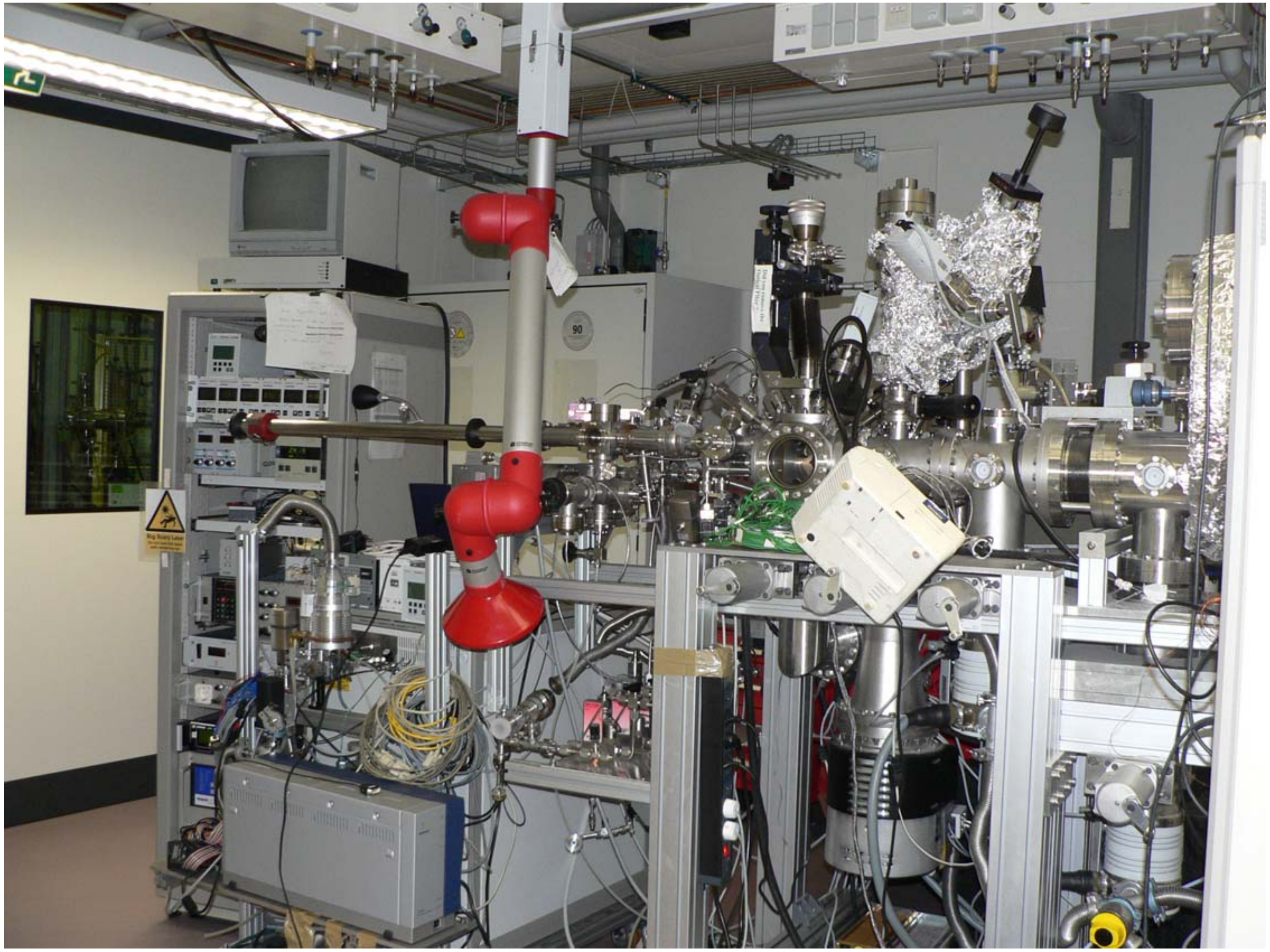


Outlook: In situ XPS / XAS
The future at BESSY



Outlook: In situ XPS / XAS
The future at BESSY

Thanks to:

- Mounir Chamam, Attila Wootsch (Institute of Isotops, Budapest)
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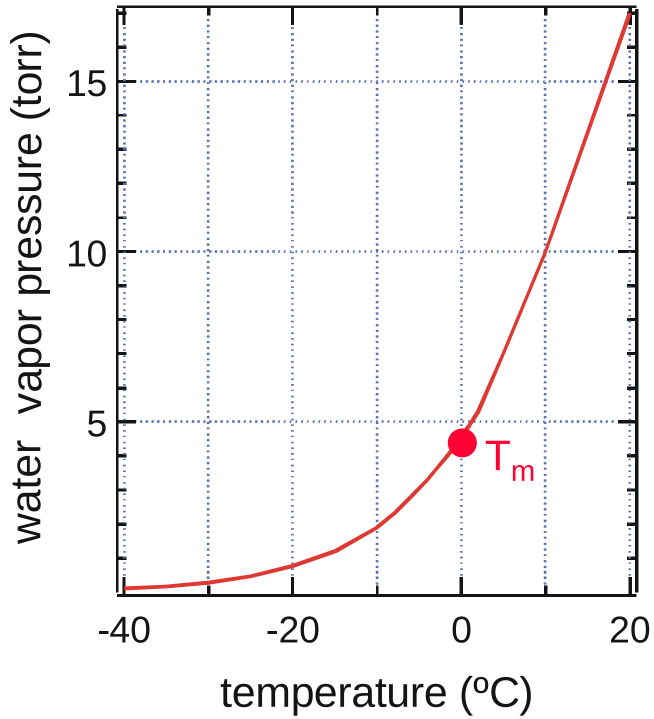
- B. Klötzer, W.Unterberger, K. Hayek (University Innsbruck, Dept. Physical Chemistry)
- B. Aszalos-Kiss, D. Zemlianov (Purdue University)
- F. Senf, R. Follath, W. Braun, J. Blume, J. Schmidt, G. Reichardt, O. Schwarzkopf (BESSY)

Why in situ XPS ?

- Many processes cannot be investigated in UHV: "Pressure Gap"
  - **environmental chemistry**
  - **catalysis**
  - corrosion
  - electrochemistry
  - biological samples



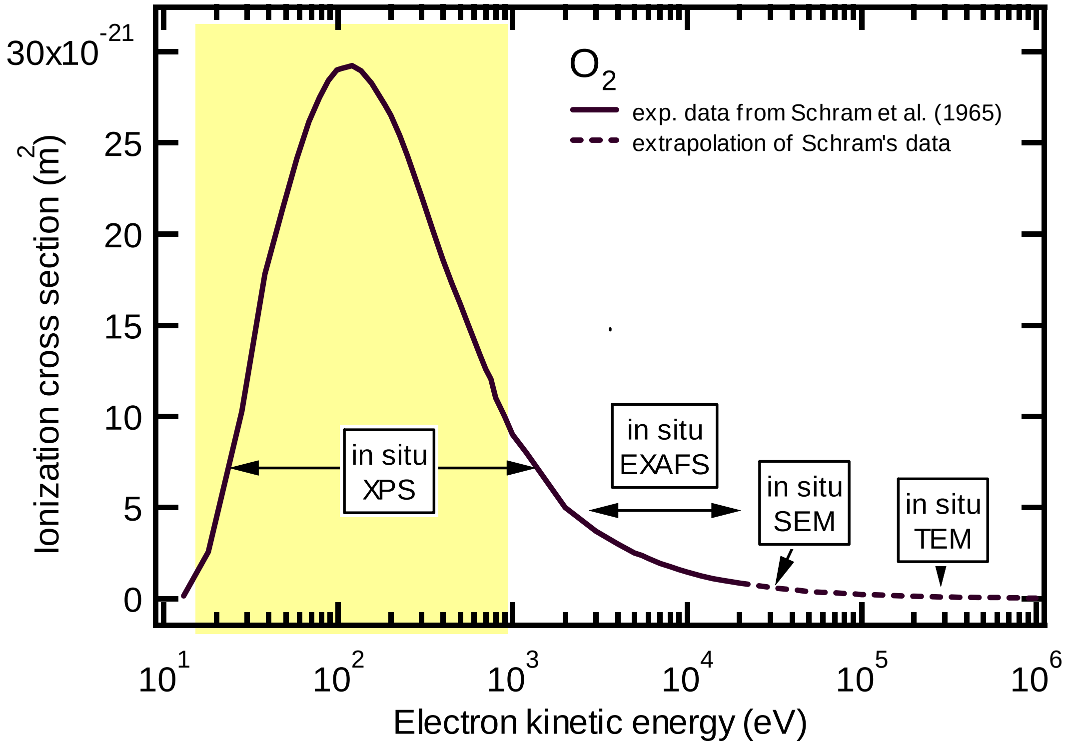
- Very few methods can investigate the solid-gas interface at high pressures
  - non-linerar optics (SFG, SHG)
  - scanning probe microscopies
  - X-ray diffraction

- Photoelectron spectroscopy is very powerful
  ⇒ Goal: XPS at pressures of at least 5 torr

In situ XPS: obstacles

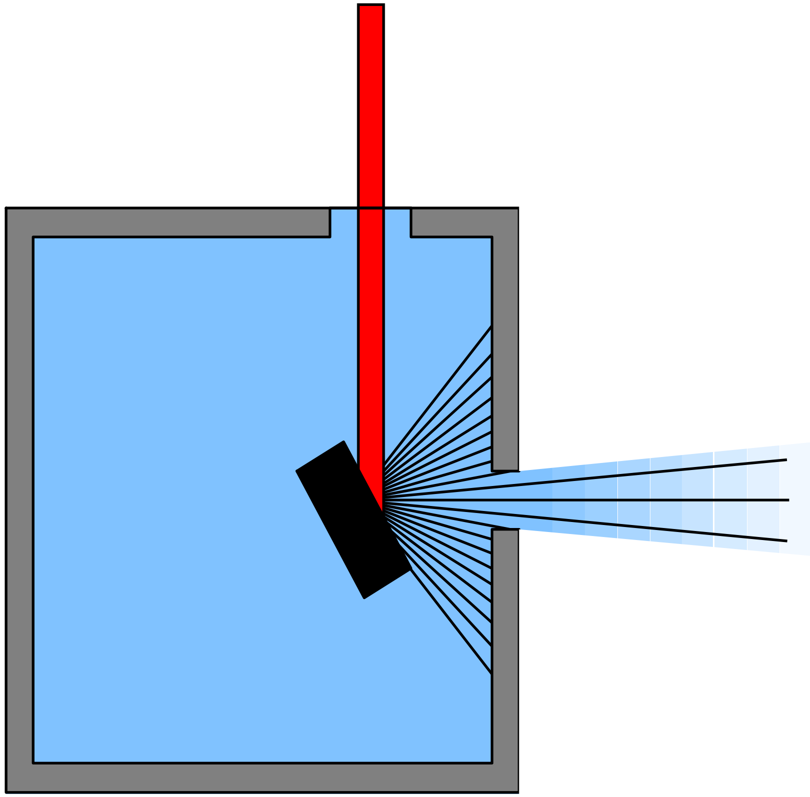
Fundamental limit:

elastic and inelastic scattering of electrons in the gas phase



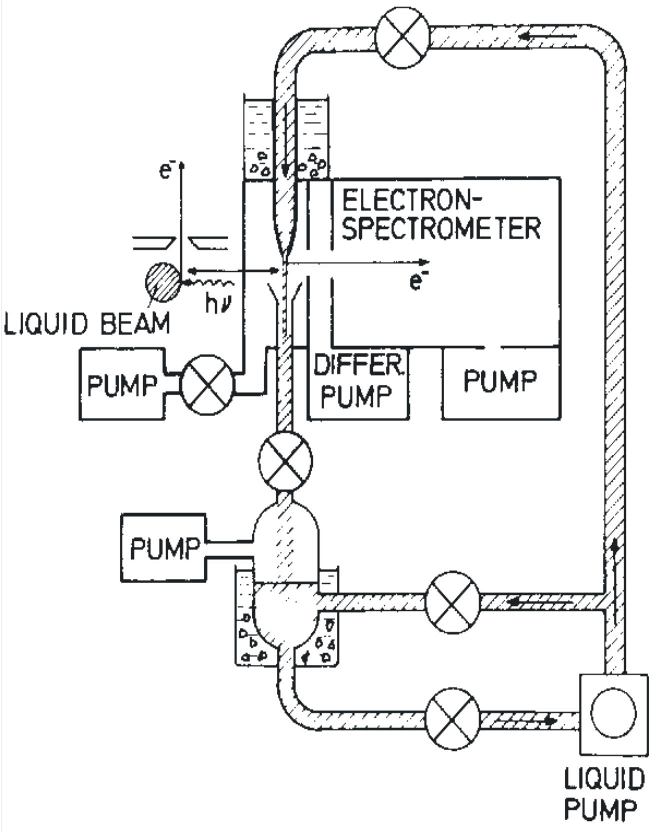
Technical issues:
- Differential pumping to keep analyzer in high vacuum
- Sample preparation and control in a flow reactor

In situ XPS: basic concept



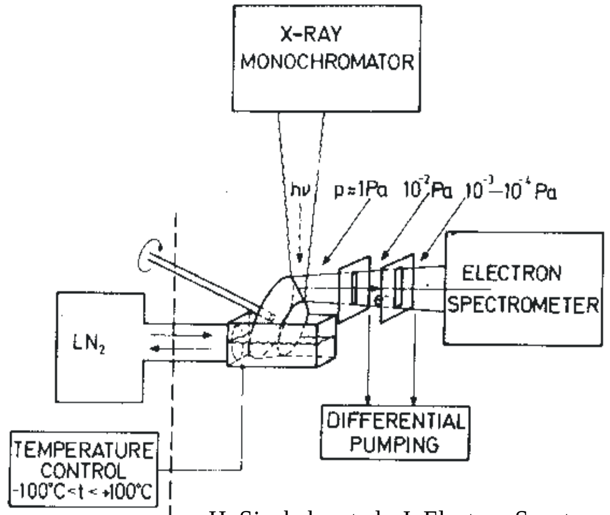
- Photons enter through a window
- Electrons and a gas jet escape through an aperture to vacuum

In situ XPS instruments: previous designs



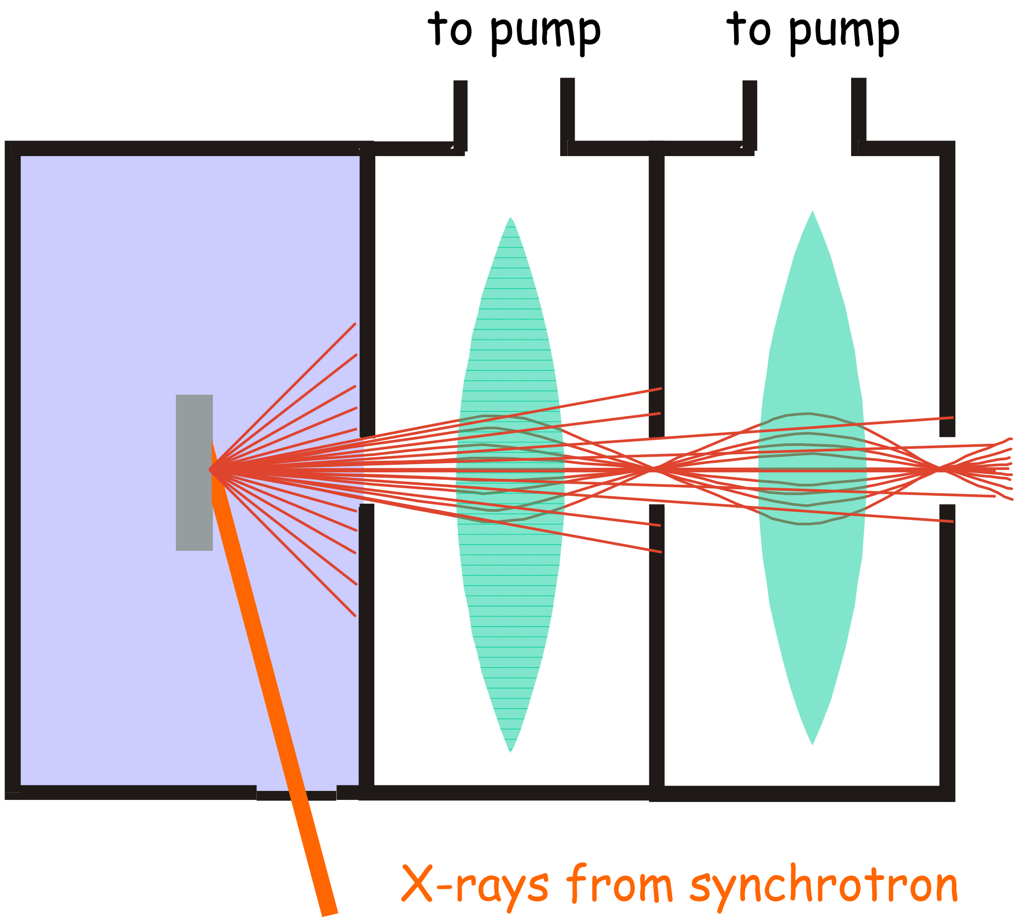
H. Siegbahn et al., J. Electron Spectrosc. Relat. Phenom. **2**, 319 (1973)

- H. Siegbahn et al. (1973-)
- M.W. Roberts et al. (1979)
- M. Faubel et al. (1987)
- M. Grunze et al. (1988)
- P. Oelhafen (1995)



H. Siegbahn et al., J. Electron Spectrosc. Relat. Phenom. **24**, 205 (1981)

In situ XPS using differentially pumped electrostatic lenses



D.F. Ogletree, H. Bluhm, G. Lebedev, C.S. Fadley, Z. Hussain, M. Salmeron, Rev. Sci. Instrum. 73 (2002) 3872.

Close-up of sample-first aperture region

Gas phase composition can
be measured by XPS.
gas phase signal:
1 torr·mm ~ a few monolayers