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Rathen

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In situ XPS investigations in heterogeneous catalysis

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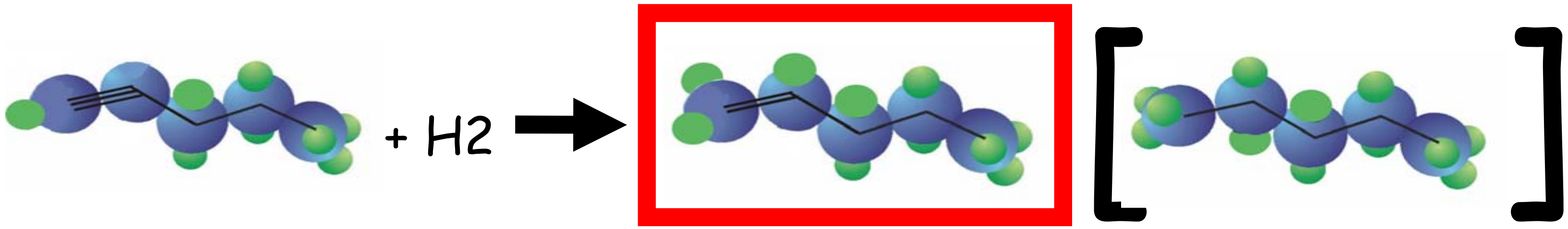
Introduction



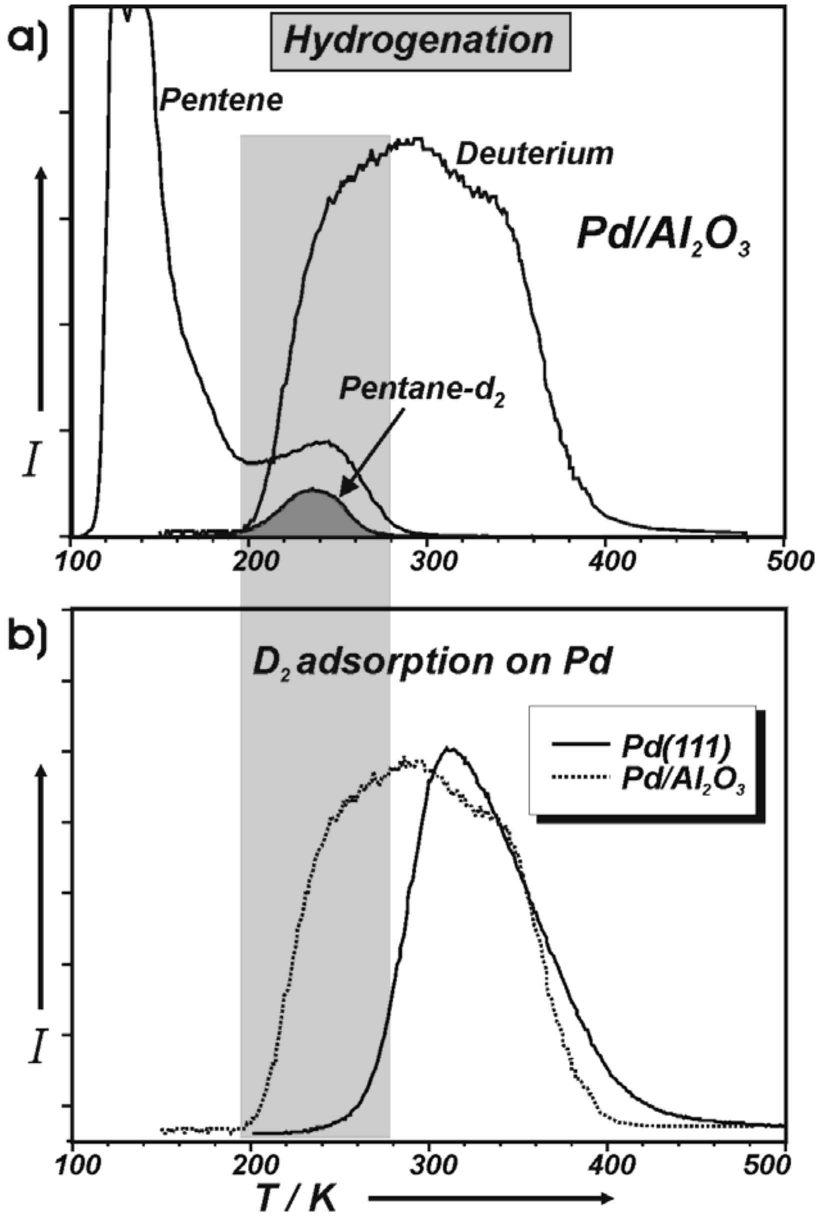
Literature

carbon laydown → selective hydrogenation

"similar" catalysts → different activity & selectivity (structure sensitivity?)

Selectivity issue: what defines selectivity?

Model of overlapping TDS peaks



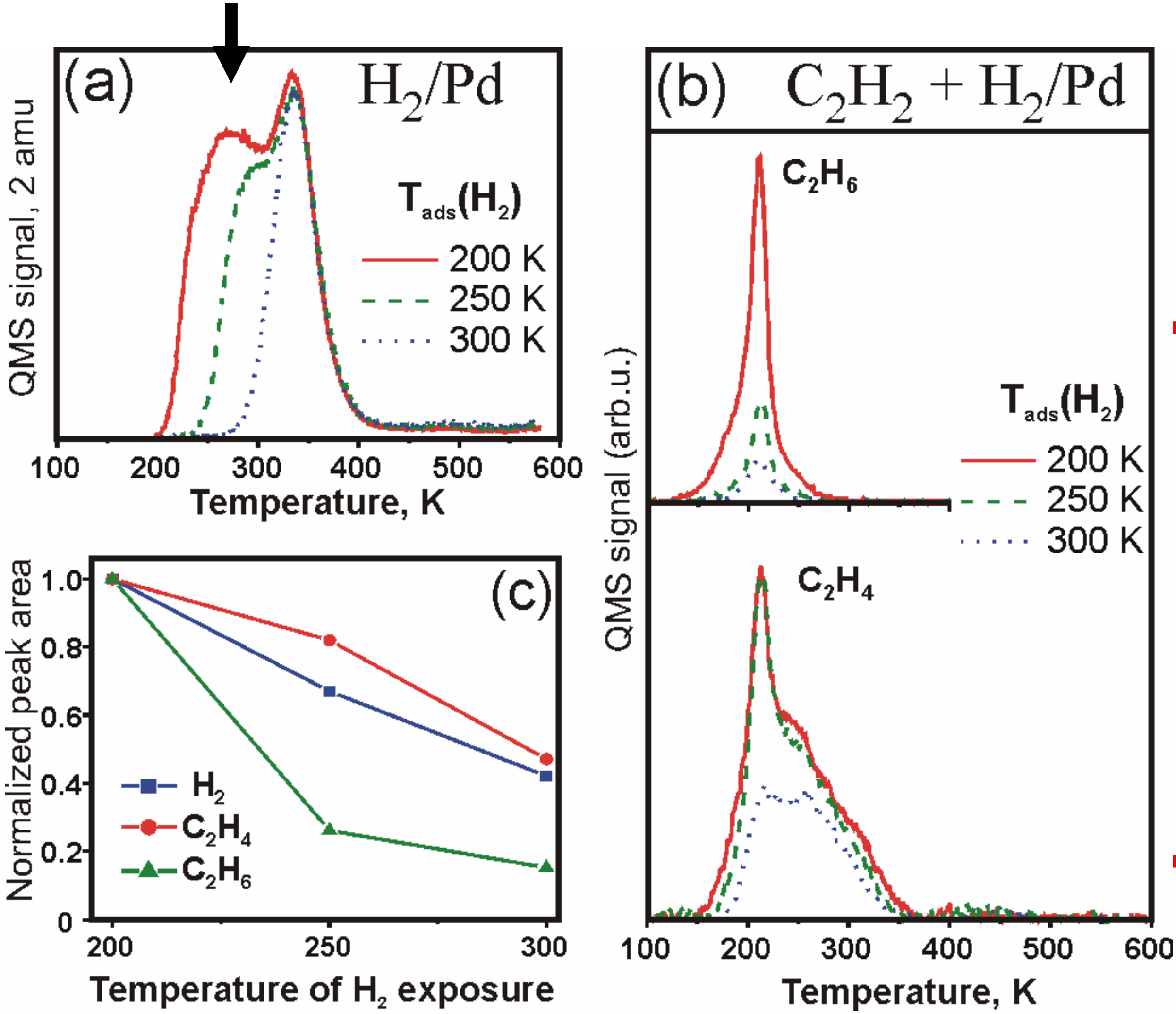
Pentenes to pentane

→ 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)

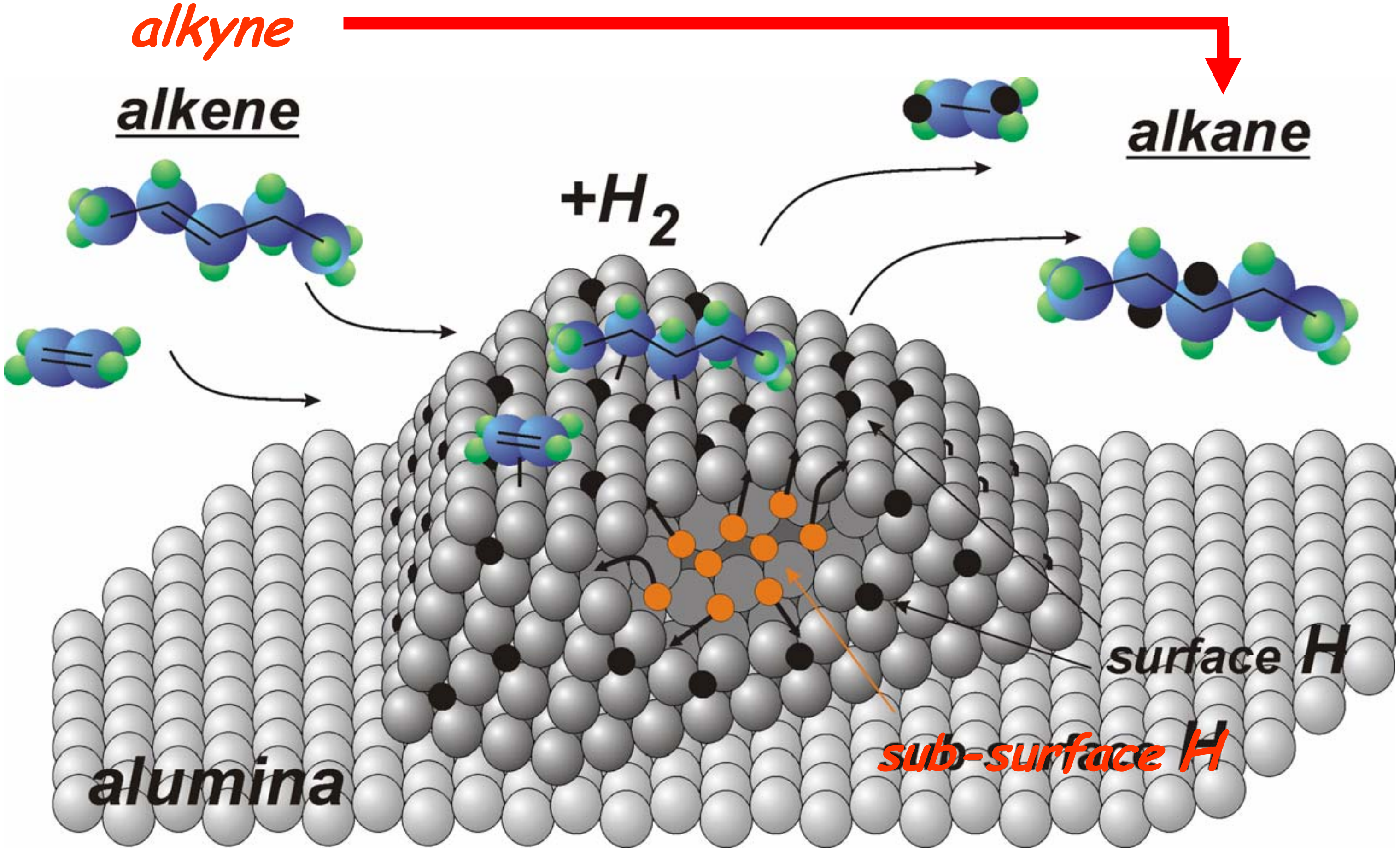


Subsurface H at low T_{ads}

Total hydrogenation decreases strongly without subsurface H

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

Hydrogenation (TDS)



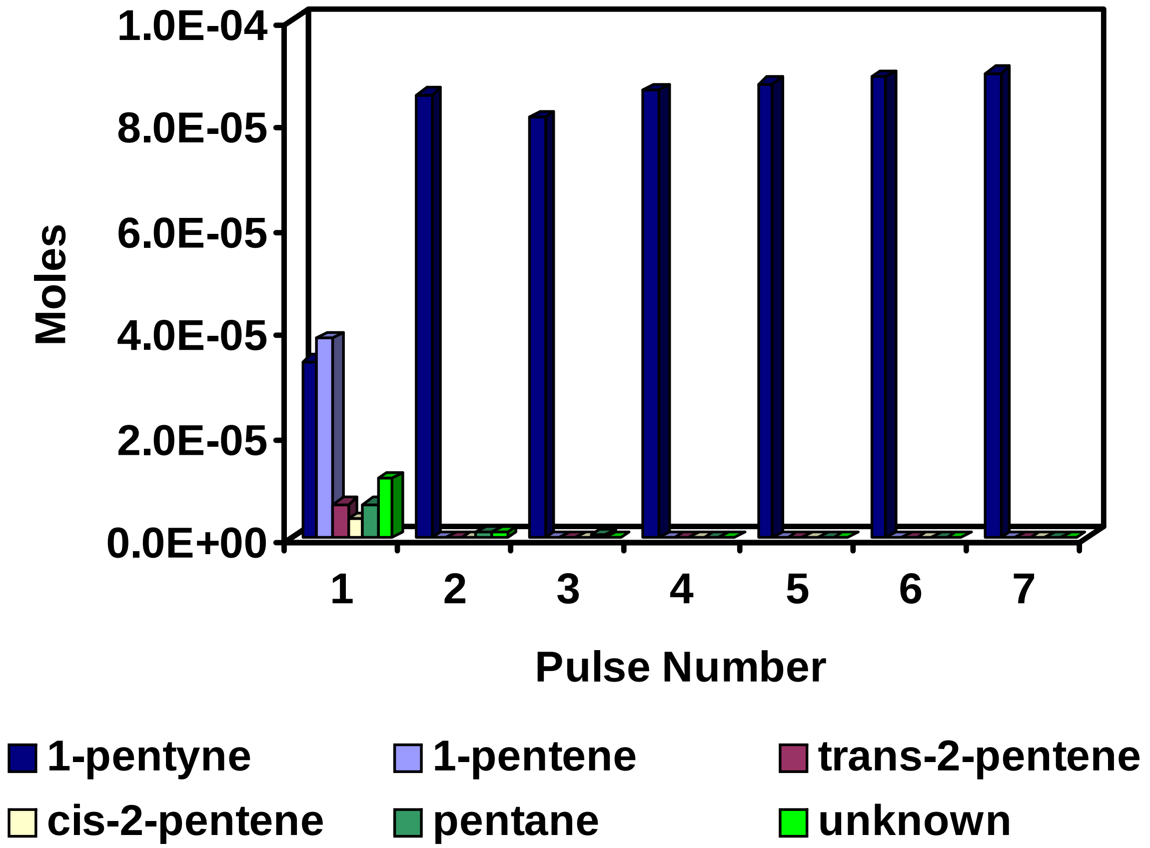
sub-surface H

Summary

1. *Subsurface H*: 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

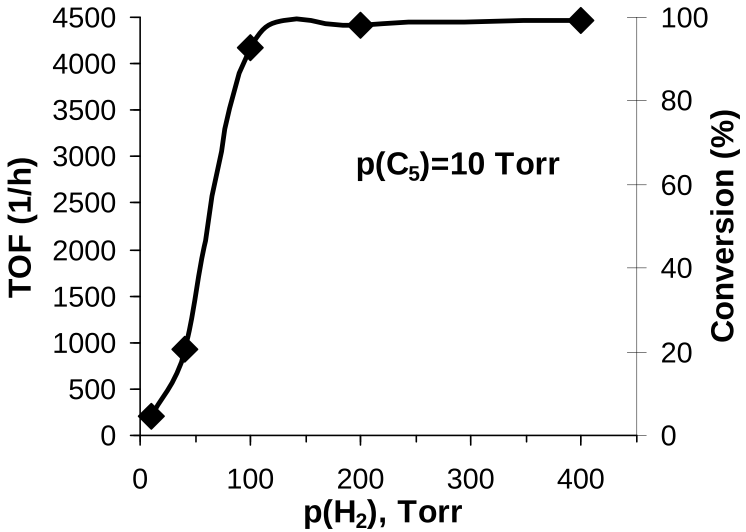
Hneeded/Pdtotal ratio: 13-to-1 Source of H? → Spillover

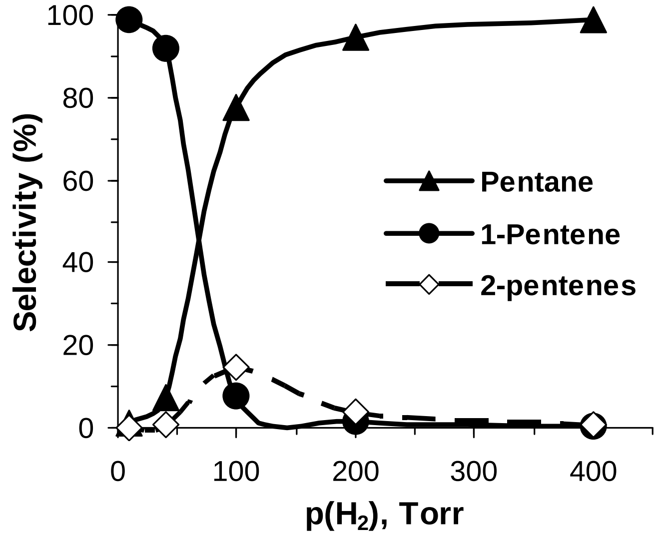
Summary

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

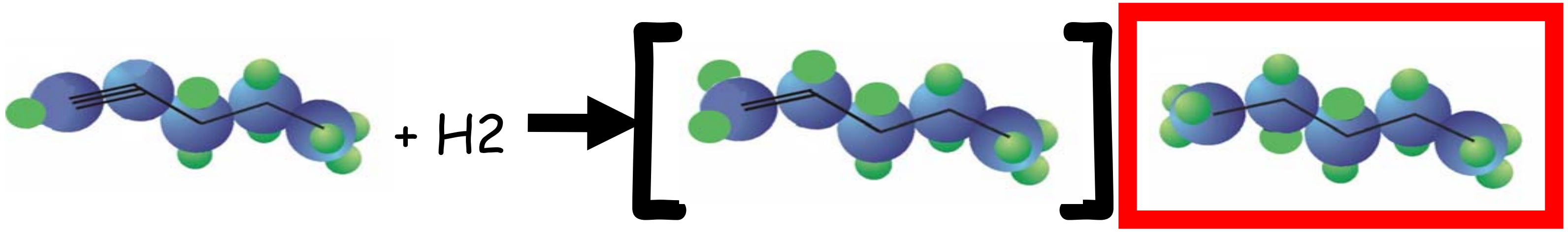
$H_2:C_5 = 4:1$ total hydrogenation

$H_2:C_5 = 3:1$ selective hydrogenation

Summary

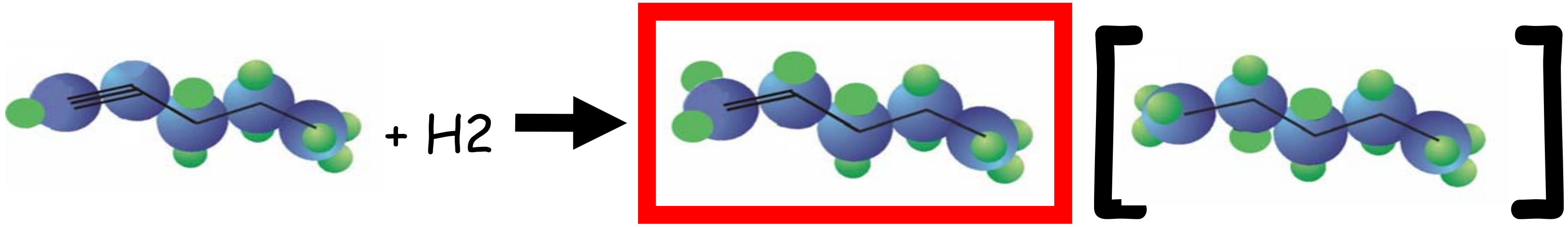
1. *Subsurface H*: effective for alkene-to-alkane but also for alkyne-to-alkane transformation
2. *Surface H*: could be selective (spillover)
3. *Different reaction orders* in the different selectivity regimes & Abrupt changes between regimes

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
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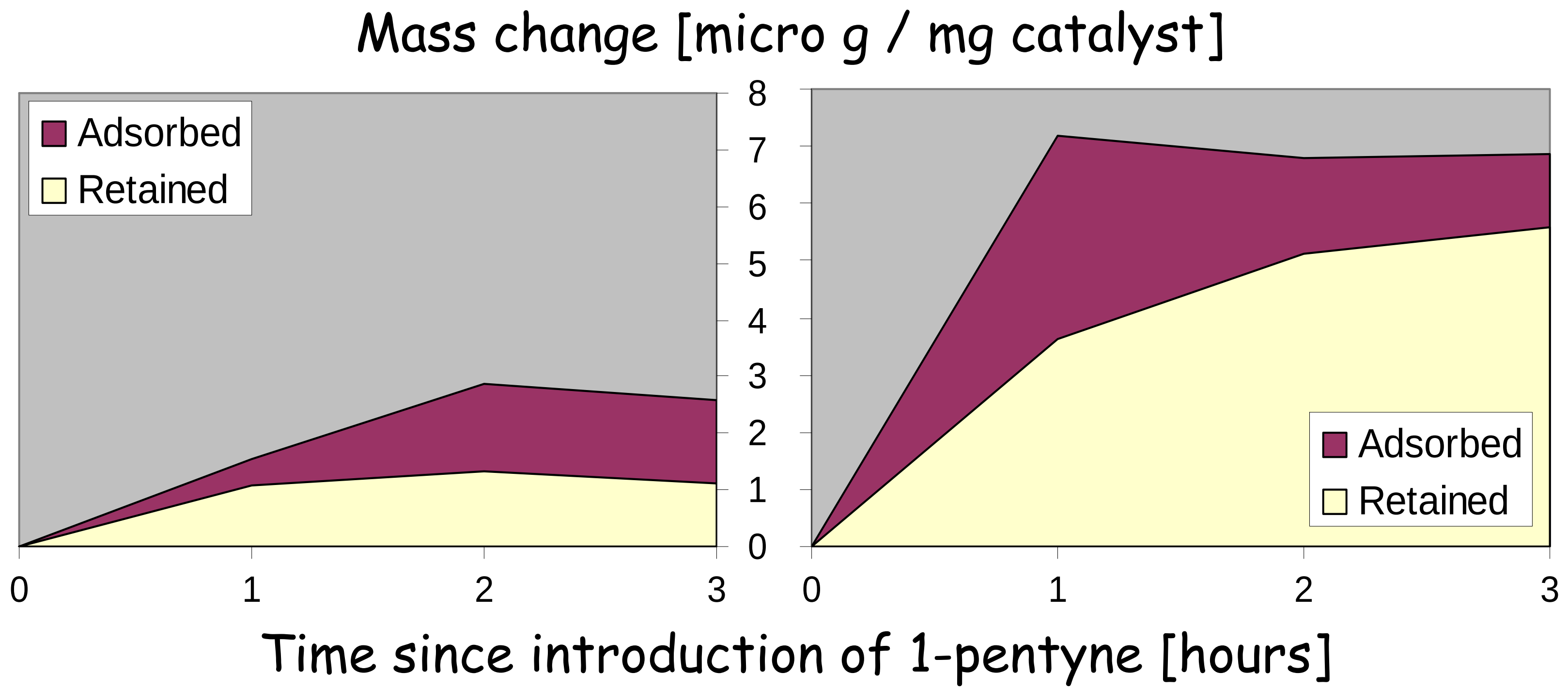
Quartz Wool, 358 K	81.6	17.1	0.2	1.1	-	-	-	-
Quartz Wool, 303 K	89.2	10.6	trace	0.3	-	-	-	-

During TEOM experiment

Pd Black

Reaction with 100% H_2 Reaction with 5% H_2

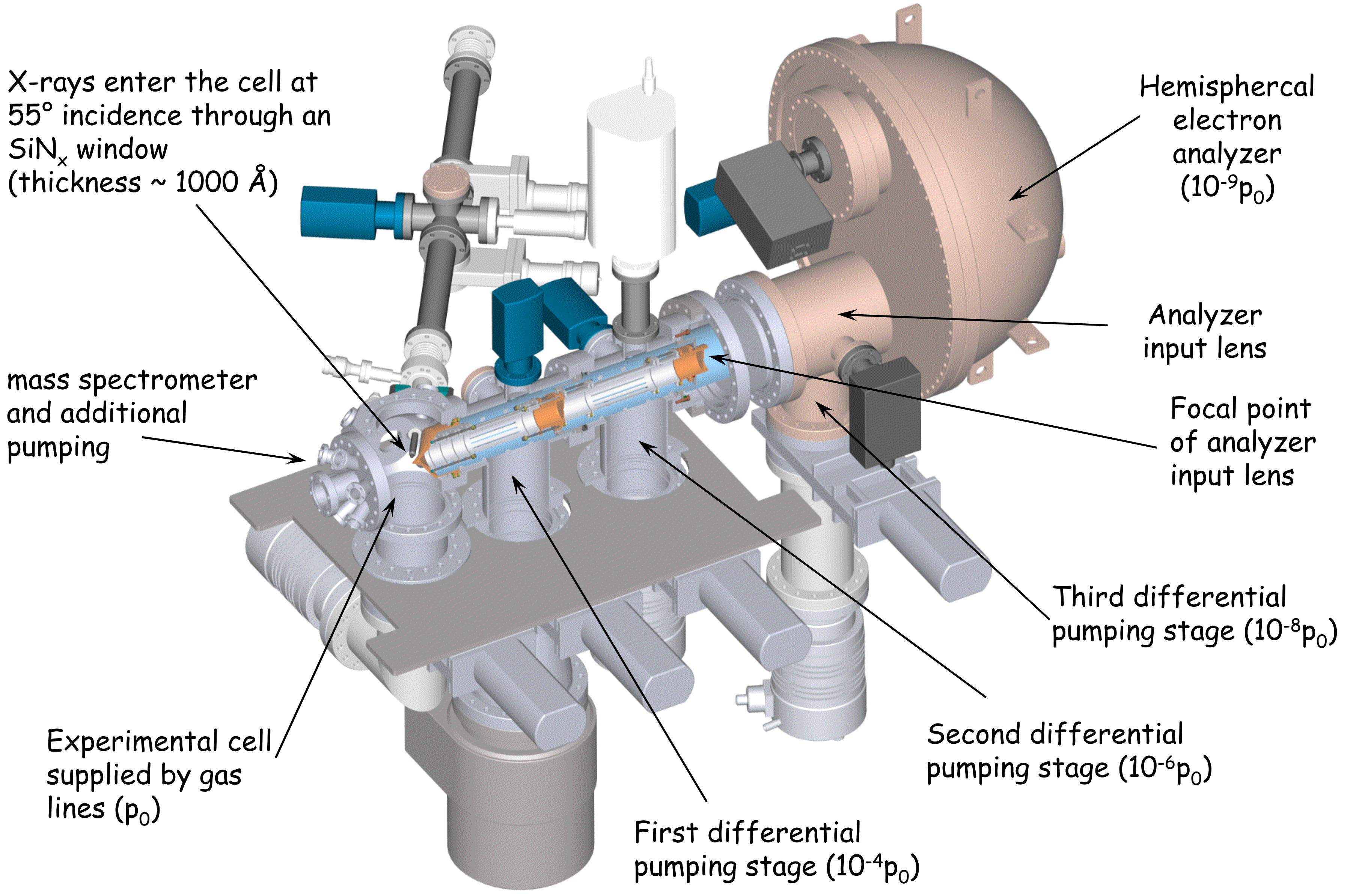


Up to x5 more carbon is retained in the selective hydrogenation regime

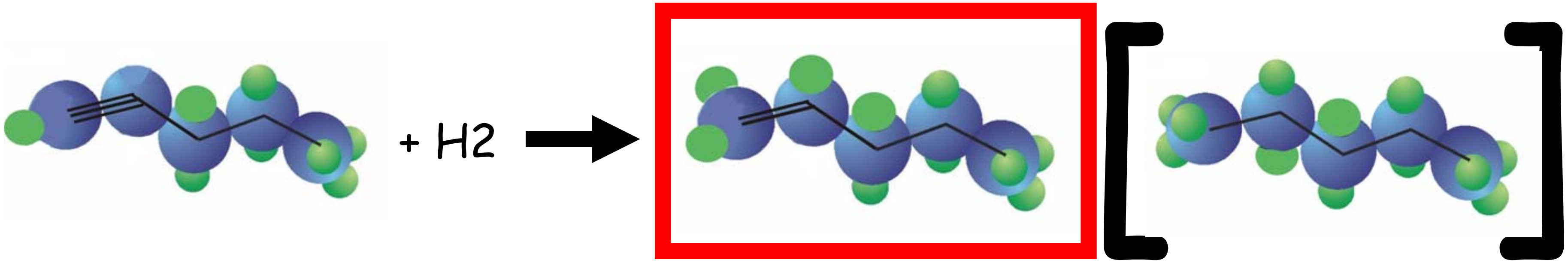
Summary

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



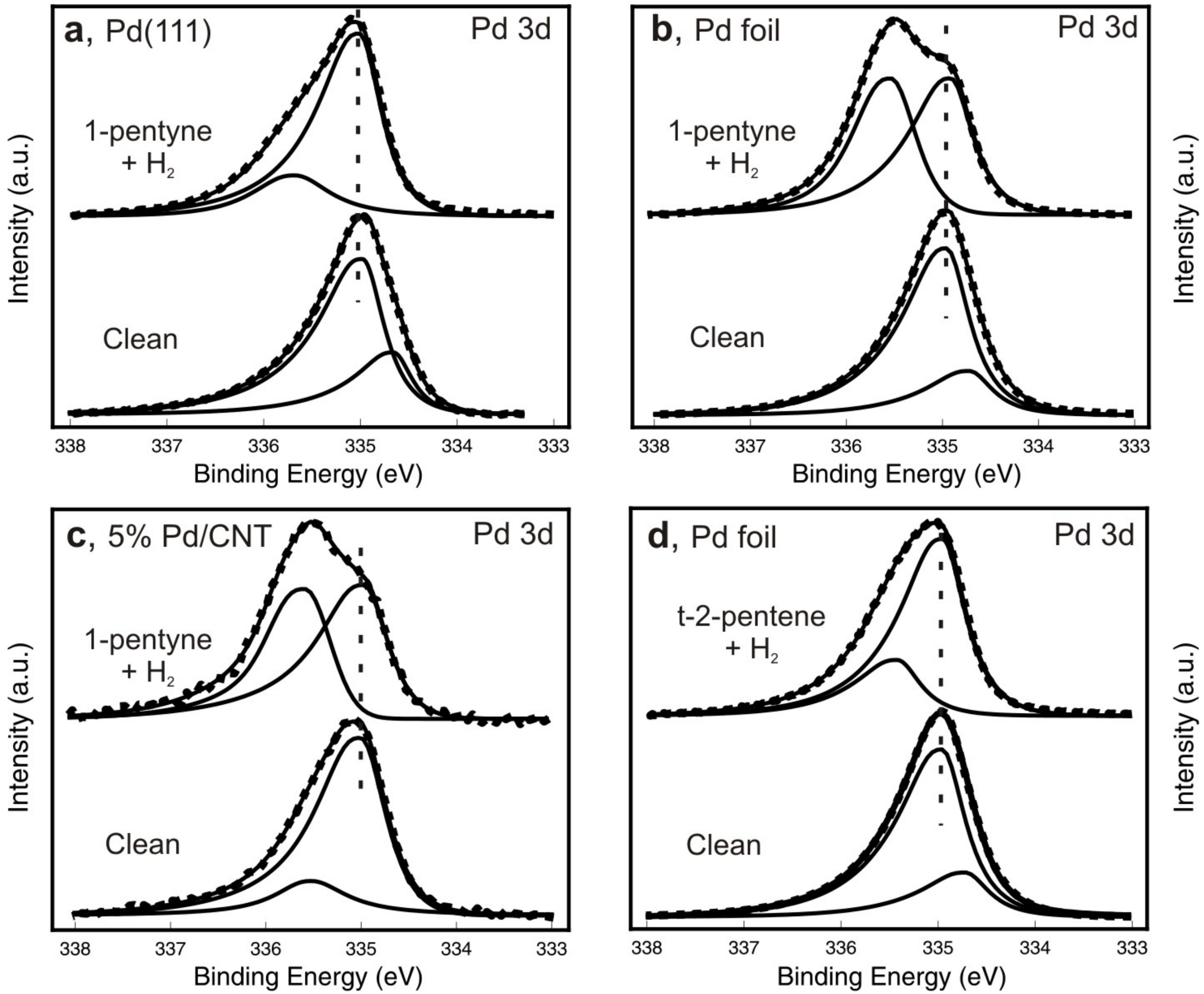
Reaction in the mbar p region (in-situ XPS)



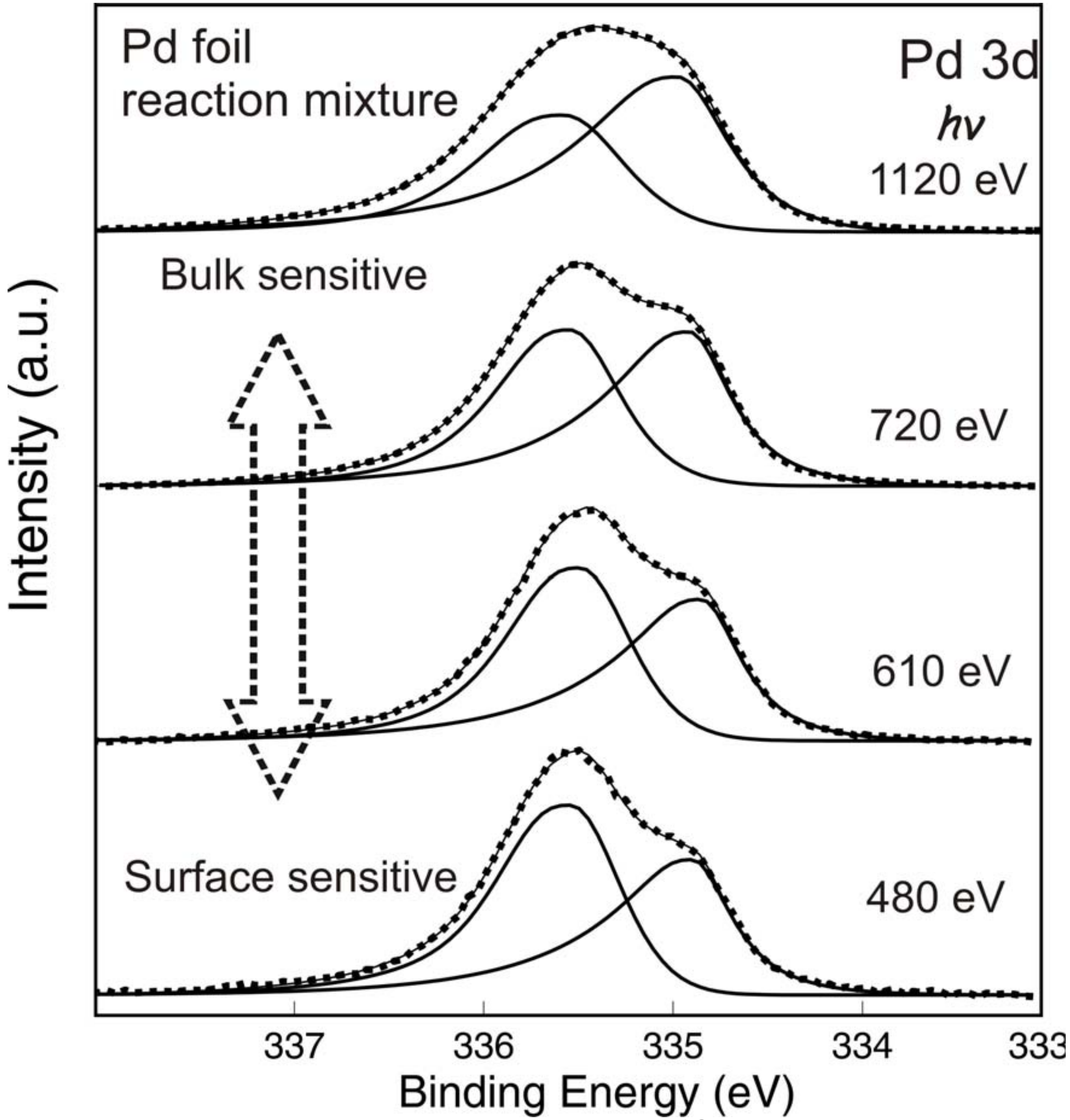
	5% Pd/CNT	3% Pd/Al_2O_3	Pd foil	Pd(111)
Conversion [%]	~ 10	~5	~2.5	<1
Selectivity Pentene [%]	~95	~80	~98	100
Selectivity Pentane [%]	~5	~20	~2	-

Recation conditions: C5/H2 = 1:9, 1 mbar, 358 K

In-situ XPS: Pd 3d (hν: 720 eV)



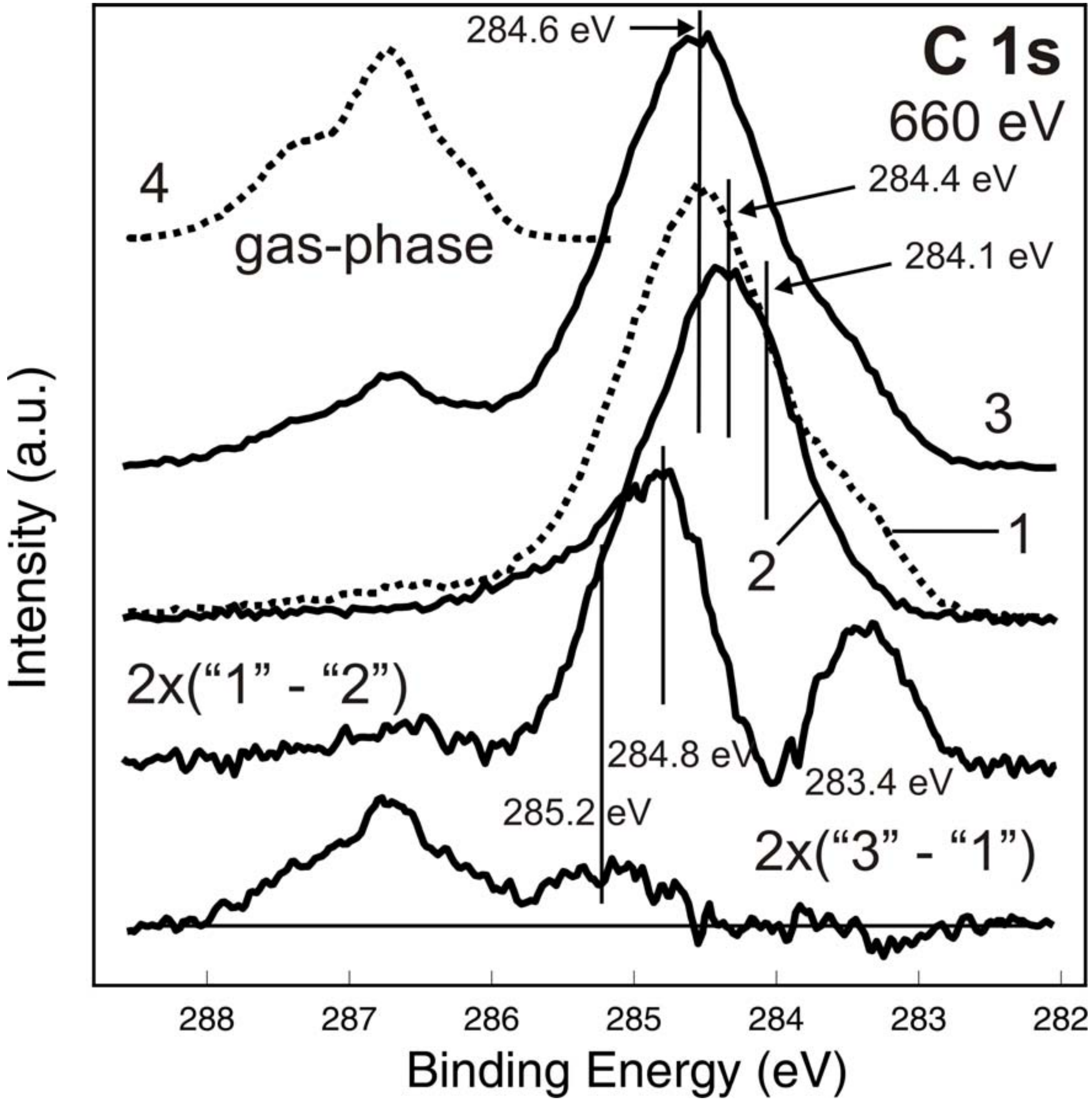
In-situ XPS: Pd 3d depth profiling



Not only adsorbate-induced surface core level shift !

But on-top location!

In-situ XPS: C1s (Switching off experiments)



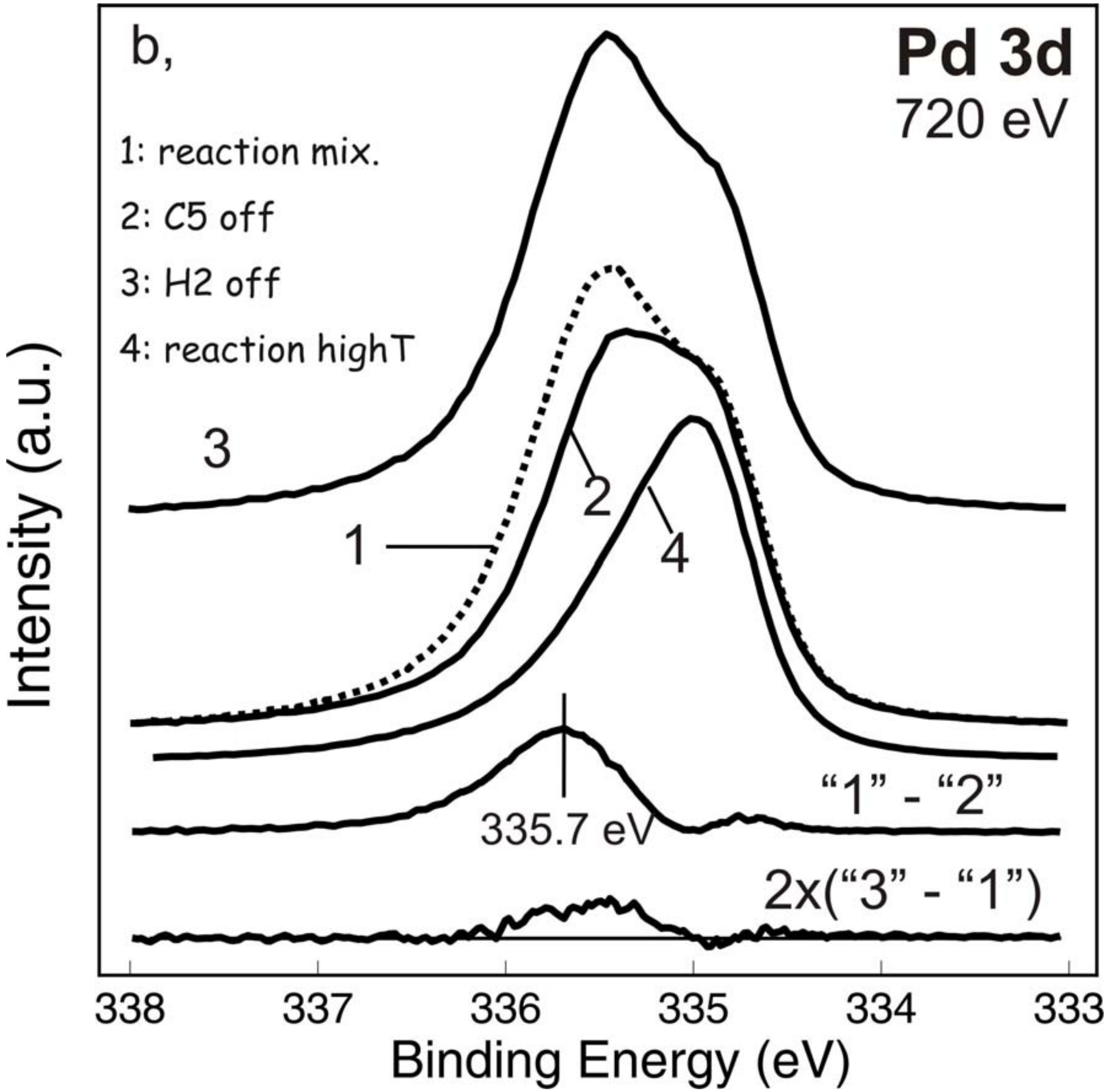
1: reaction mix.

2: C5 off

3: H2 off

4: C5 gas-phase

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



1: reaction mix.

2: C5 off

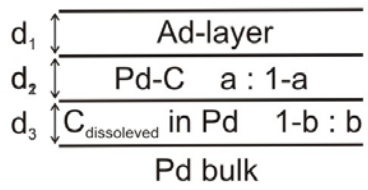
3: H2 off

4: reaction; high T

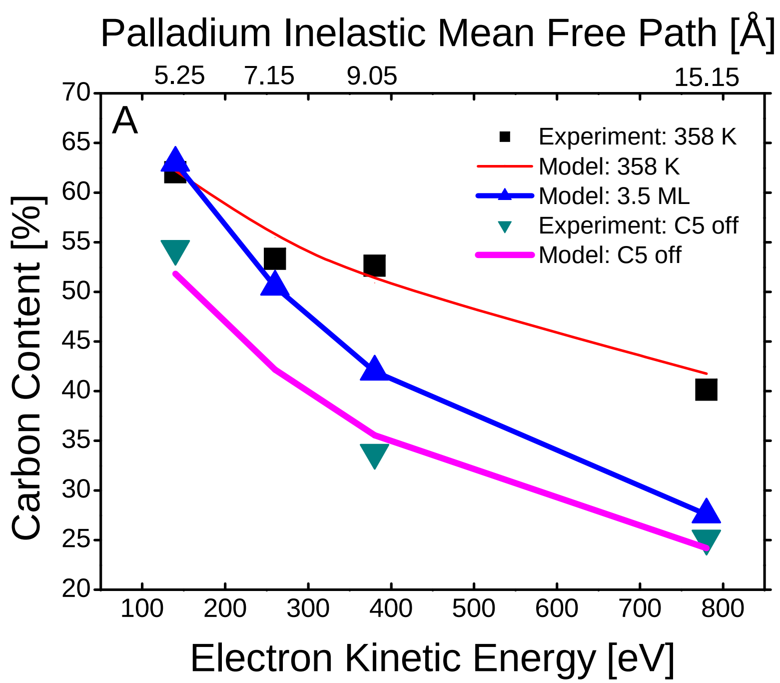
523 K

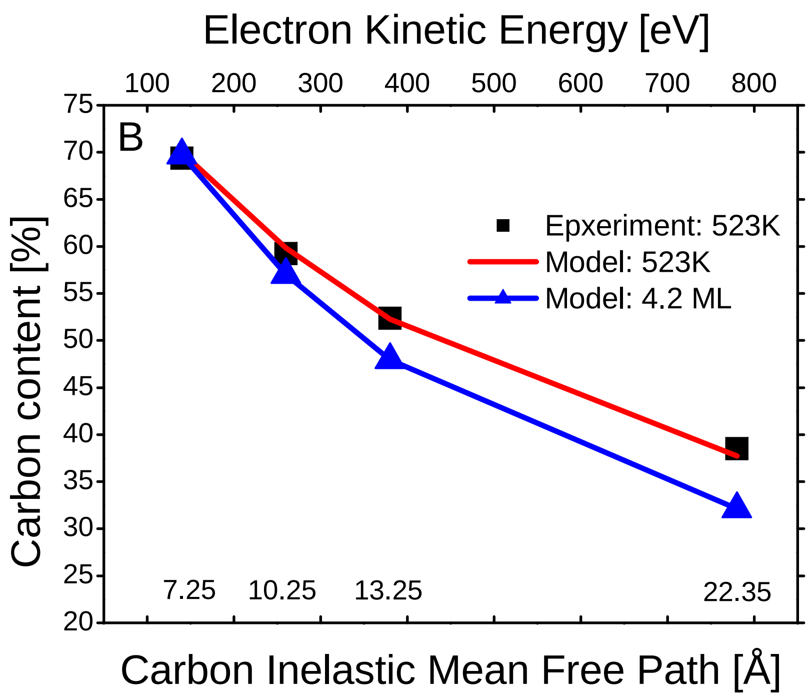
In-situ XPS: Pd vs. C depth profiling

Model



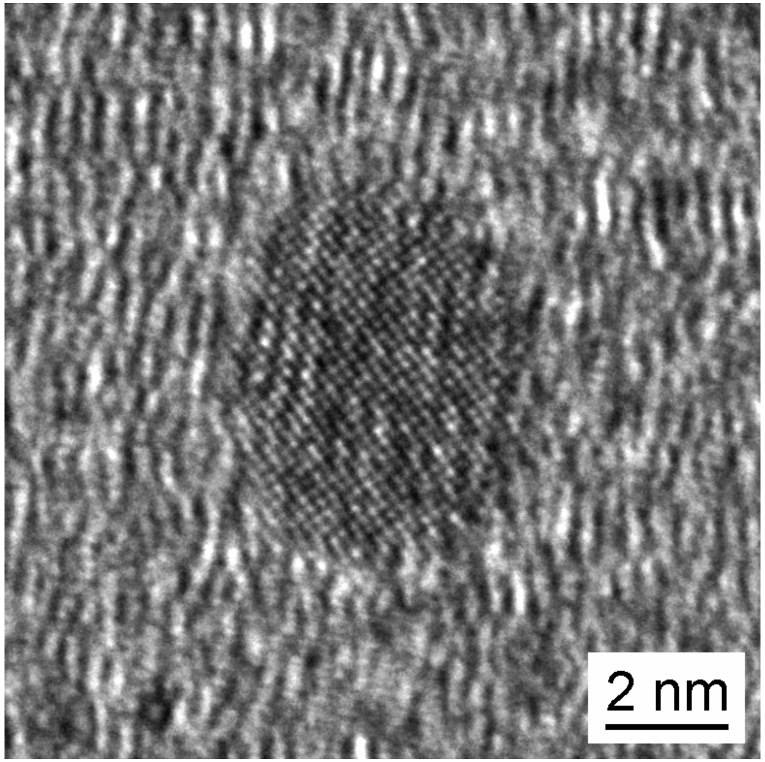
= 0.3 nm
1.4 nm
14 nm

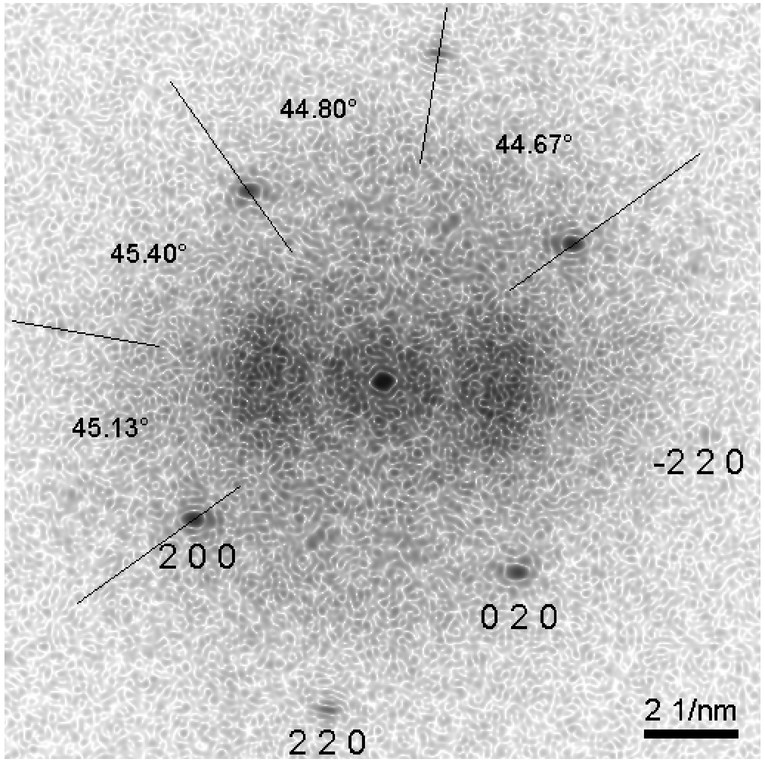




HRTEM: lattice expansion

5% Pd/CNT after reaction





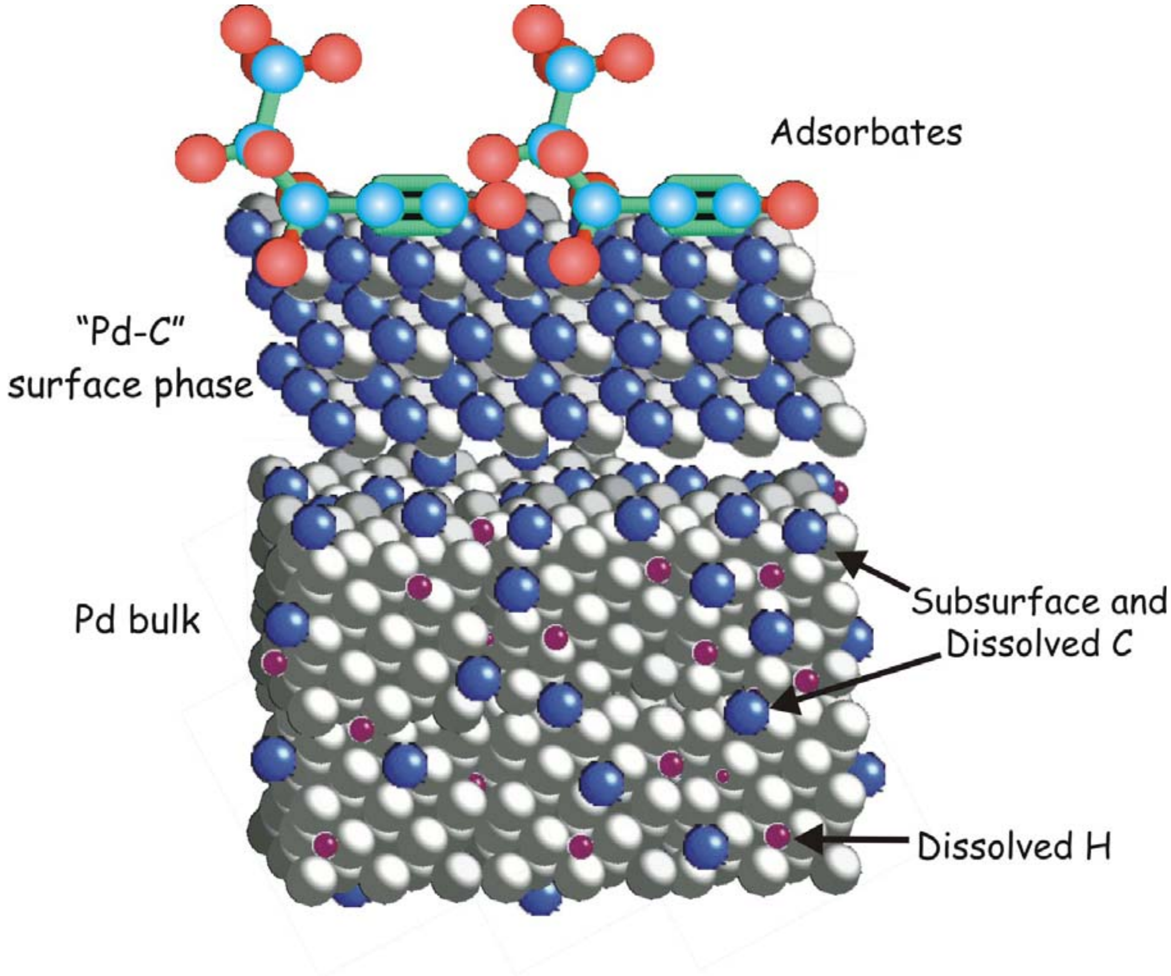
Pd nanoparticle (5nm x 6nm) with typical lattice dilatations, angular distortions are negligible
background: rather disordered graphitic layers of a CNT

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

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 in the early stage of selective pentyne hydrogenation & there is significant amount of *subsurface C* below of it

Model (during the reaction)



Summary

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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

Outlook: In situ XPS / XAS
The future at BESSY

BESSY

ISISS:

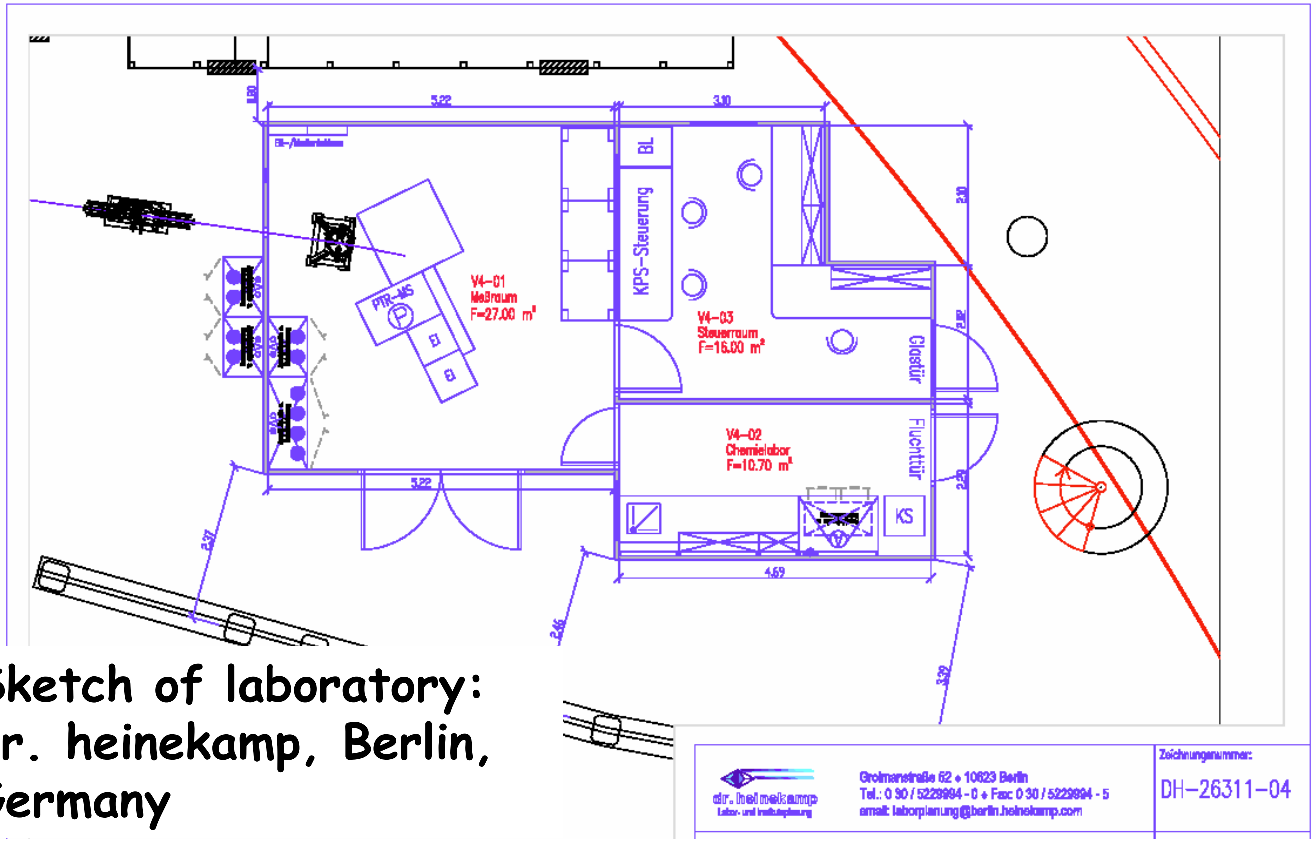
Innovative Station for In Situ Spectroscopy

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 user operation of the beamline: 2007

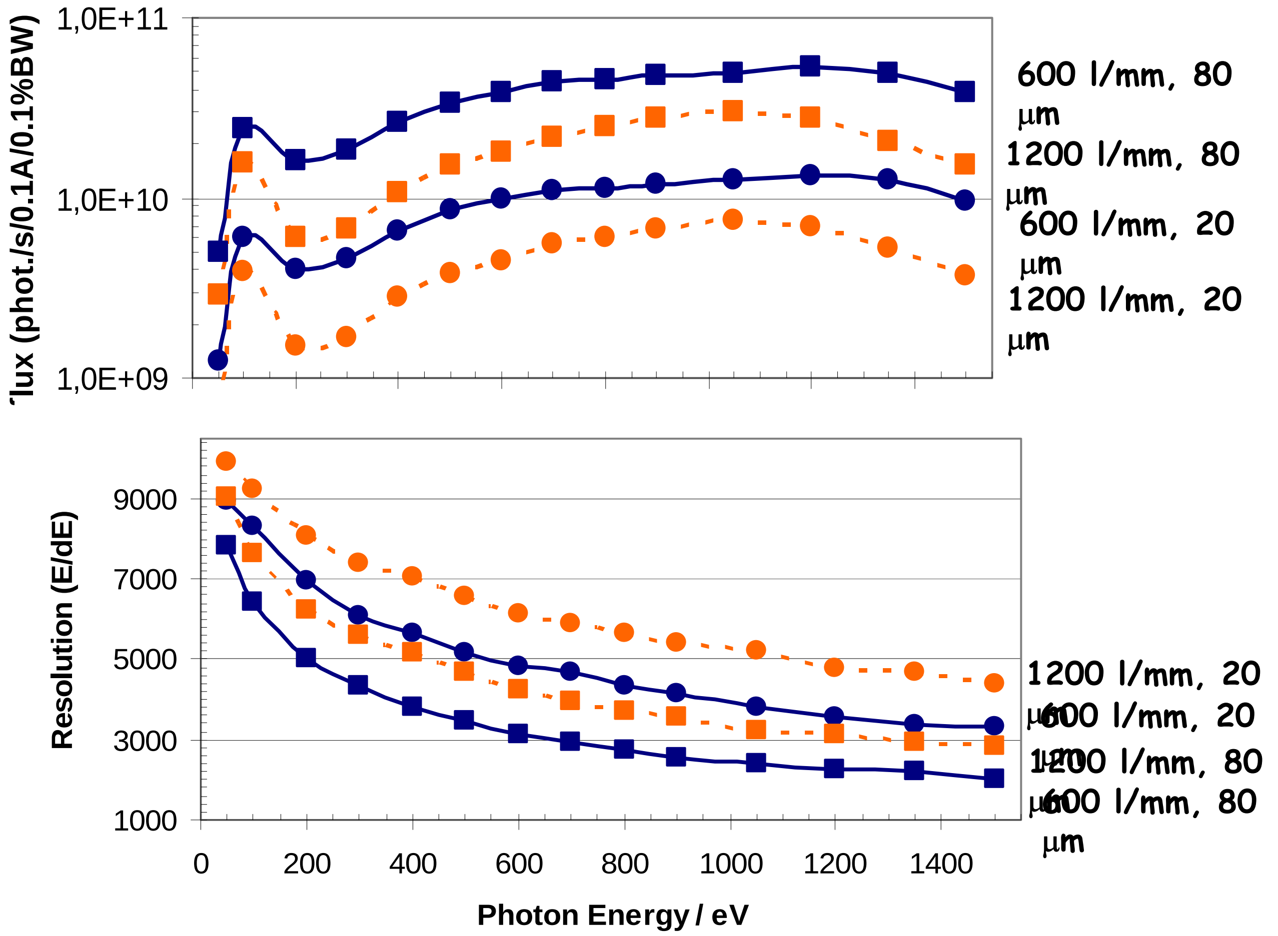
Outlook: In situ XPS / XAS
The future at BESSY

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

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The future at BESSY

Thanks to:

- Detre Teschner, Elaine Vass, Michael Hävecker, Evgueni Kleimenov,,Spiros Zafeiratos, Péter Schnörch, Hermann Sauer, Robert Schlögl (FHI, Dept. AC)
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