The influence of subsurface carbon on the selectivity in the hydrogenation reaction of 1-pentyne over Pd catalysts

FHI; Dep. of Chemical Physics

INSTITUTE *of* ISOTOPE

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Contributors

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Athena: ADVANCED TECHNOLOGY IN CATALYTIC CHEMISTRY AND ENGINEERING FOR NOVEL APPLICATIONS

OBJECTIVE

TO BE ABLE TO ADD OR REMOVE HYDROGEN OR OXYGEN TO A GIVEN MOLECULE WITH HIGH ACTIVITY AND SELECTIVITY.

THE UNIVERSITY OF BIRMINGHAM

UNIVERSITY OF CAMBRIDGE

UNIVERSITY of GLASGOW

Hydrogenation

Dehydrogenation

Selective Oxidation

UniS University of Surrey Guildford

CARDIFF UNIVERSITY PRIFYSGOL CAERDYDD

AC FHI

Max-Planck-Gesellschaft

Fritz-Haber-Institute

Department of Chemical Physics RESEARCH GROUPS

JM Johnson Matthey + EPSRC

www.chem.gla.ac.uk/athena/

Introduction

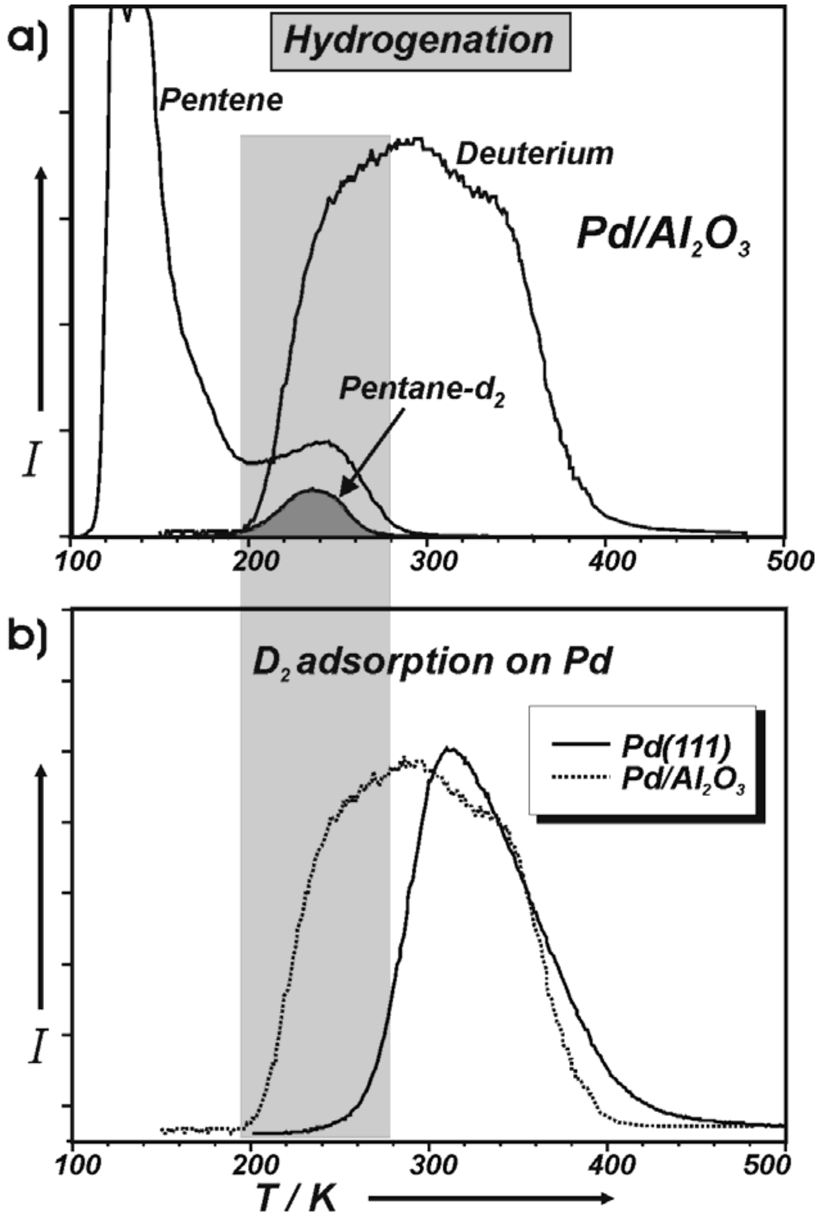
Literature

carbon laydown $\rightarrow$ selective hydrogenation

"similar" catalysts $\rightarrow$ different activity & selectivity (structure sensitivity?)

Selectivity issue: what defines selectivity?

Model of overlapping TDS peaks



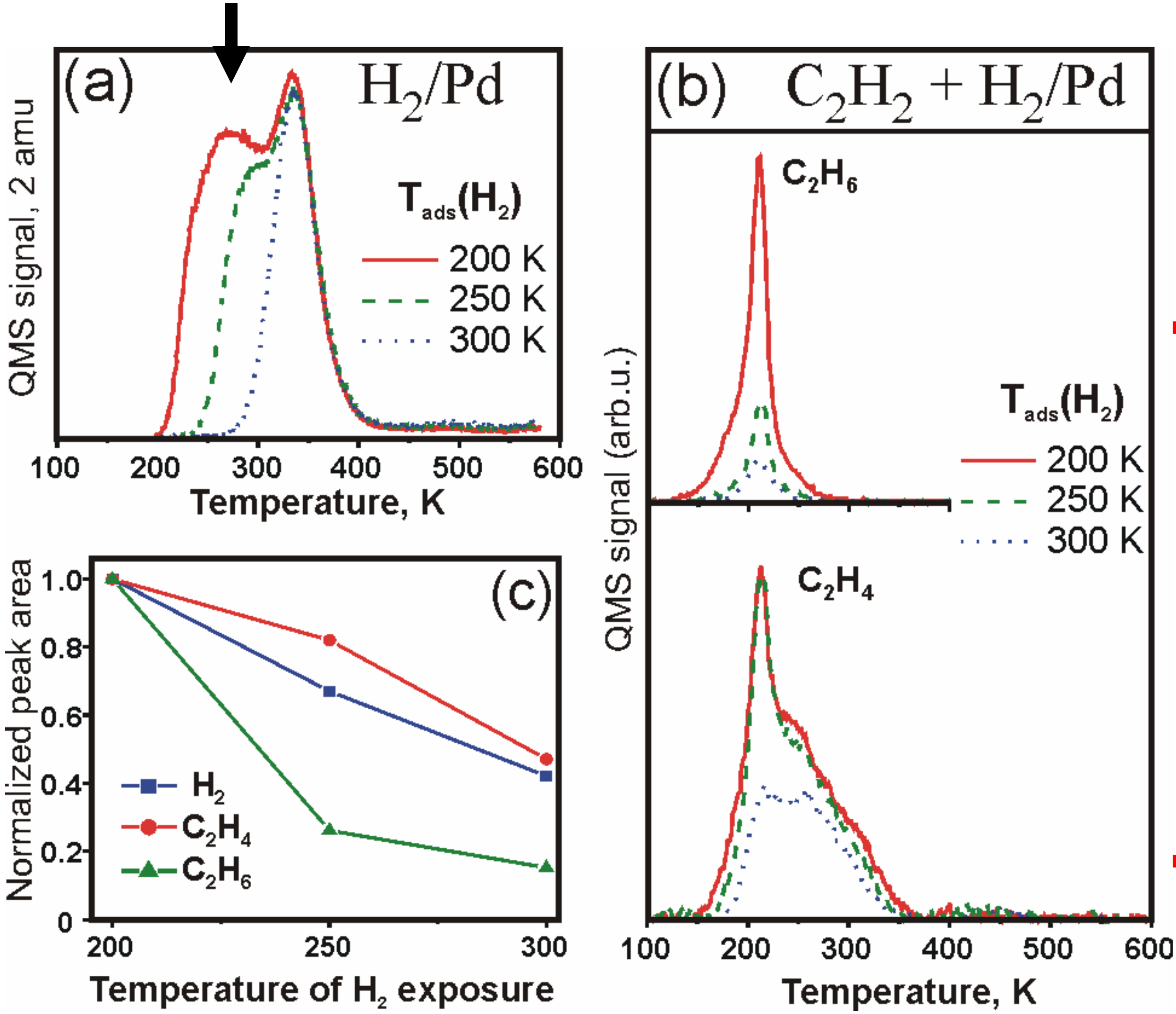
Pentenes to pentane

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)

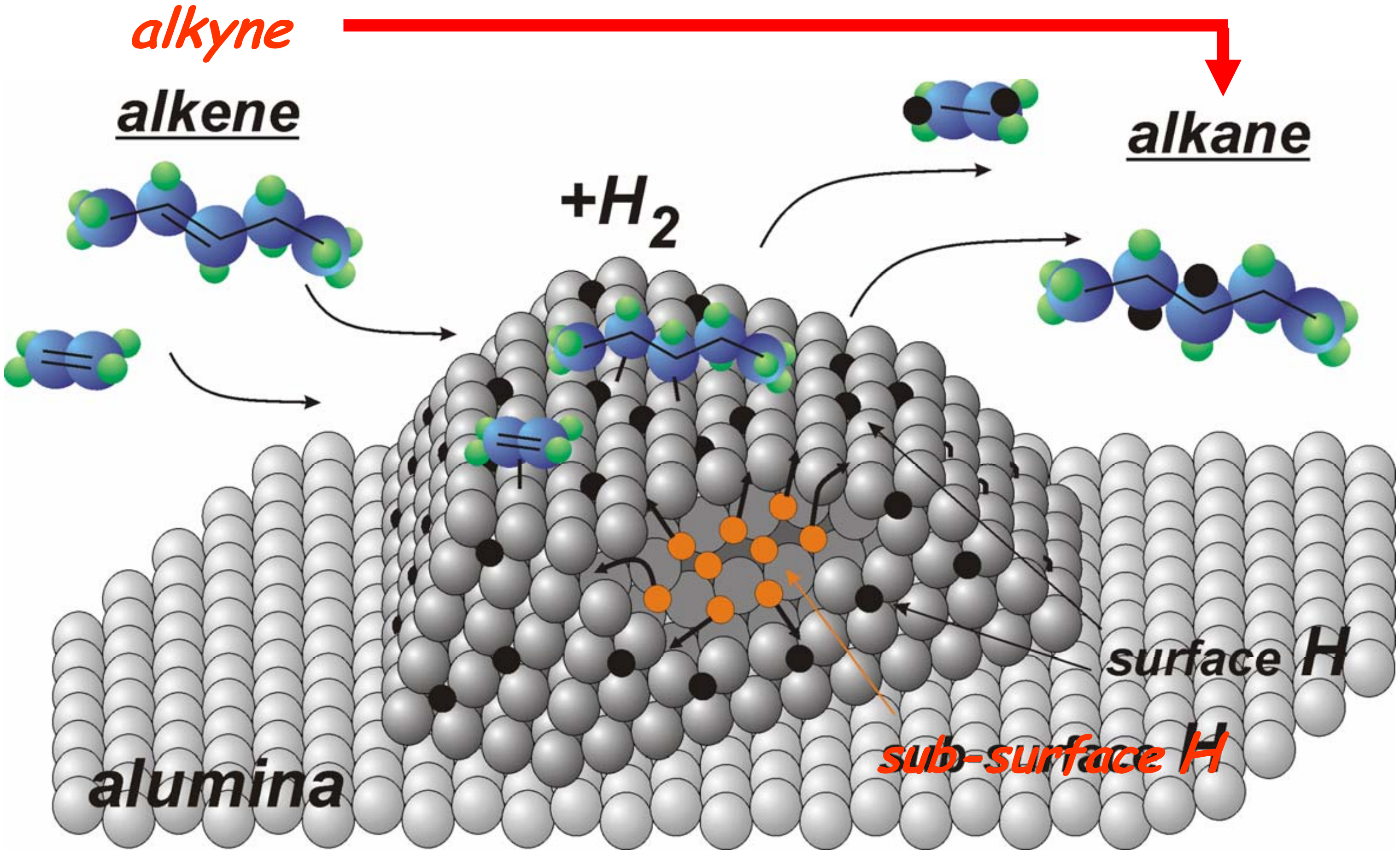


Subsurface H at low T_{ads}

Total hydrogenation decreases strongly without subsurface H

Kahn NA, Shaikhutdinov SK, Freund HJ
CATALYSIS LETTERS
in press.

Hydrogenation (TDS)



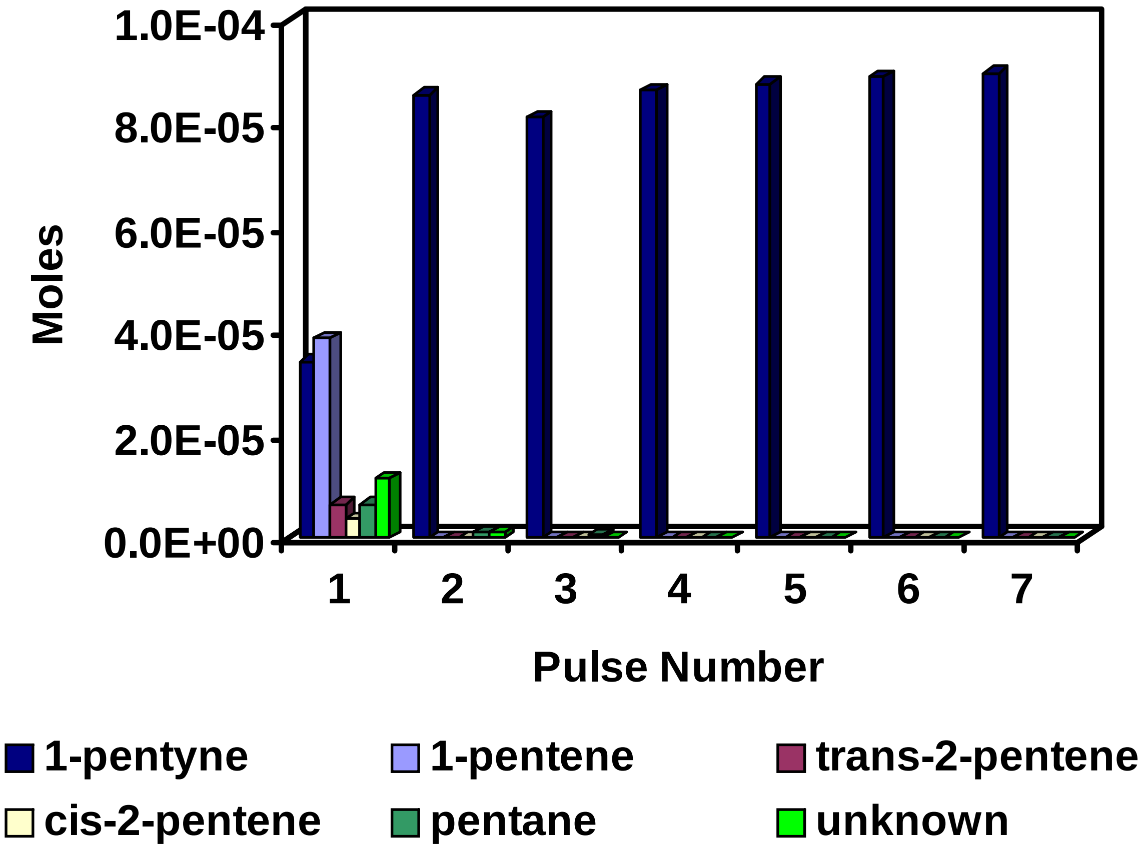
sub-surface H

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**

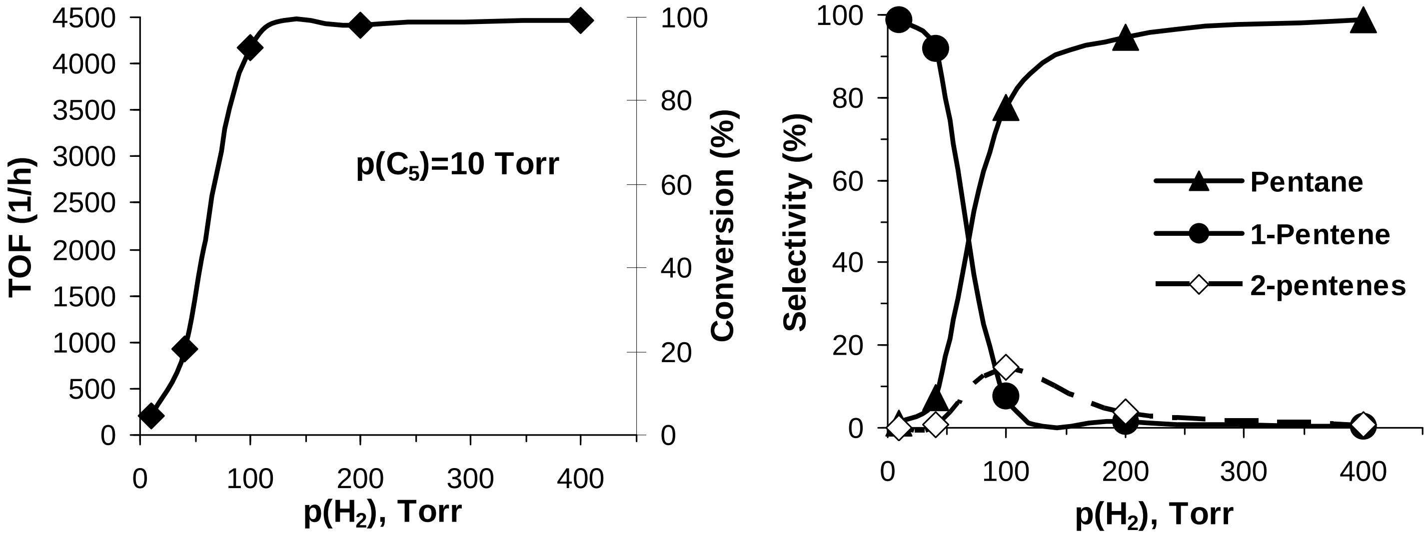
H_{needed}/Pd_{total} ratio: 13-to-1 Source of H? → Spillover

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

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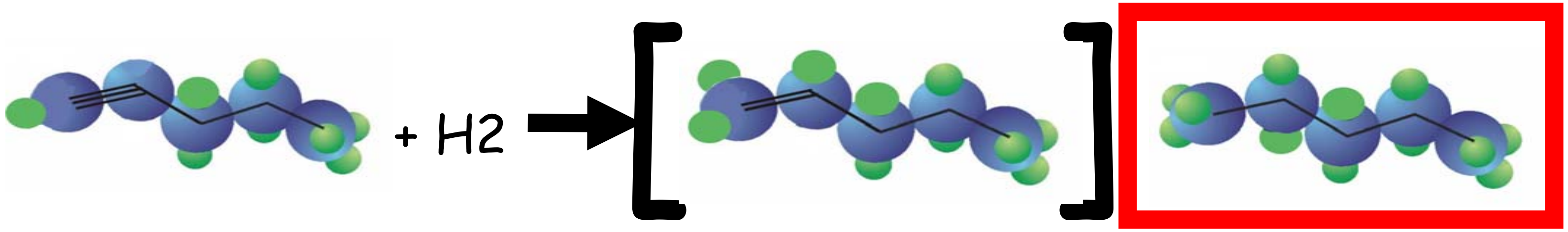
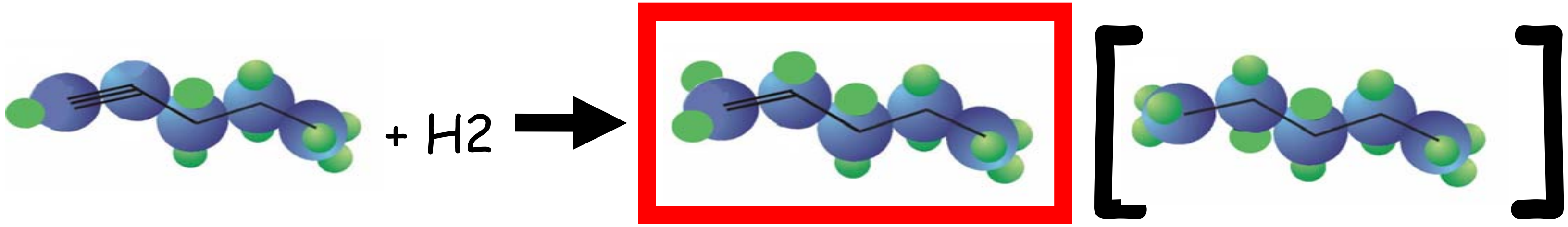
2. *Surface H*: could be selective (spillover)
3. *Different reaction orders* in the different selectivity regimes & Abrupt changes between regimes

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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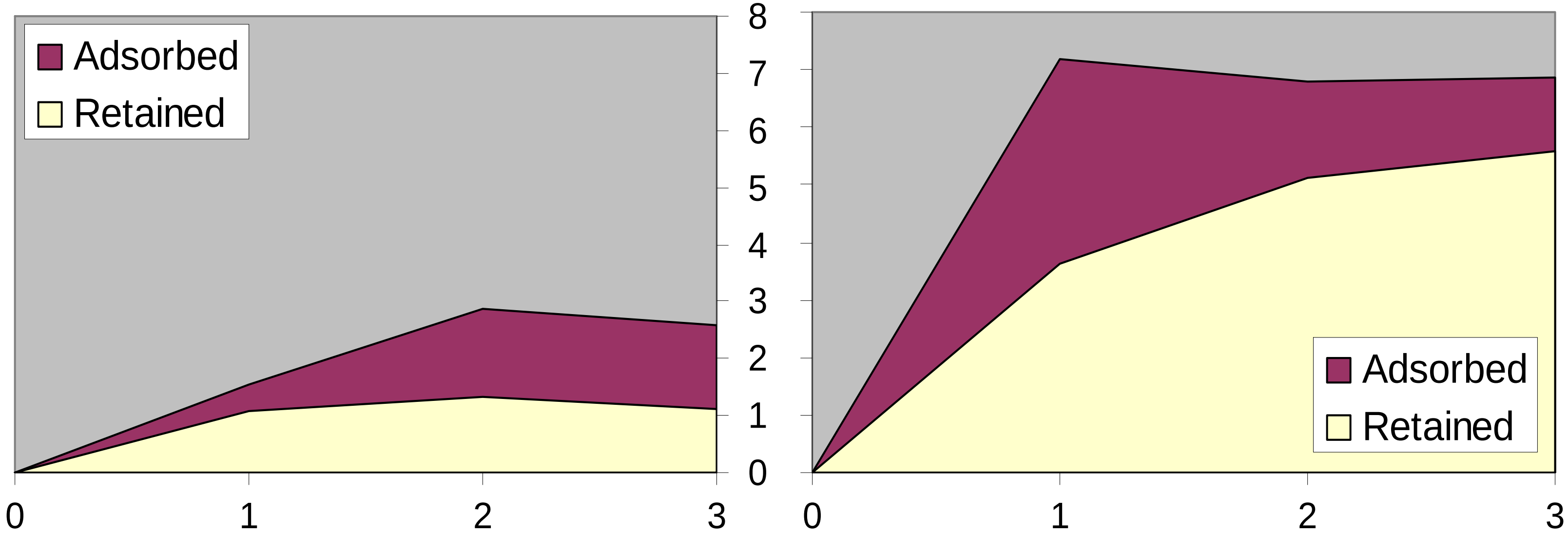
Quartz Wool, 303 K	89.2	10.6	trace	0.3	-	-	-	-

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

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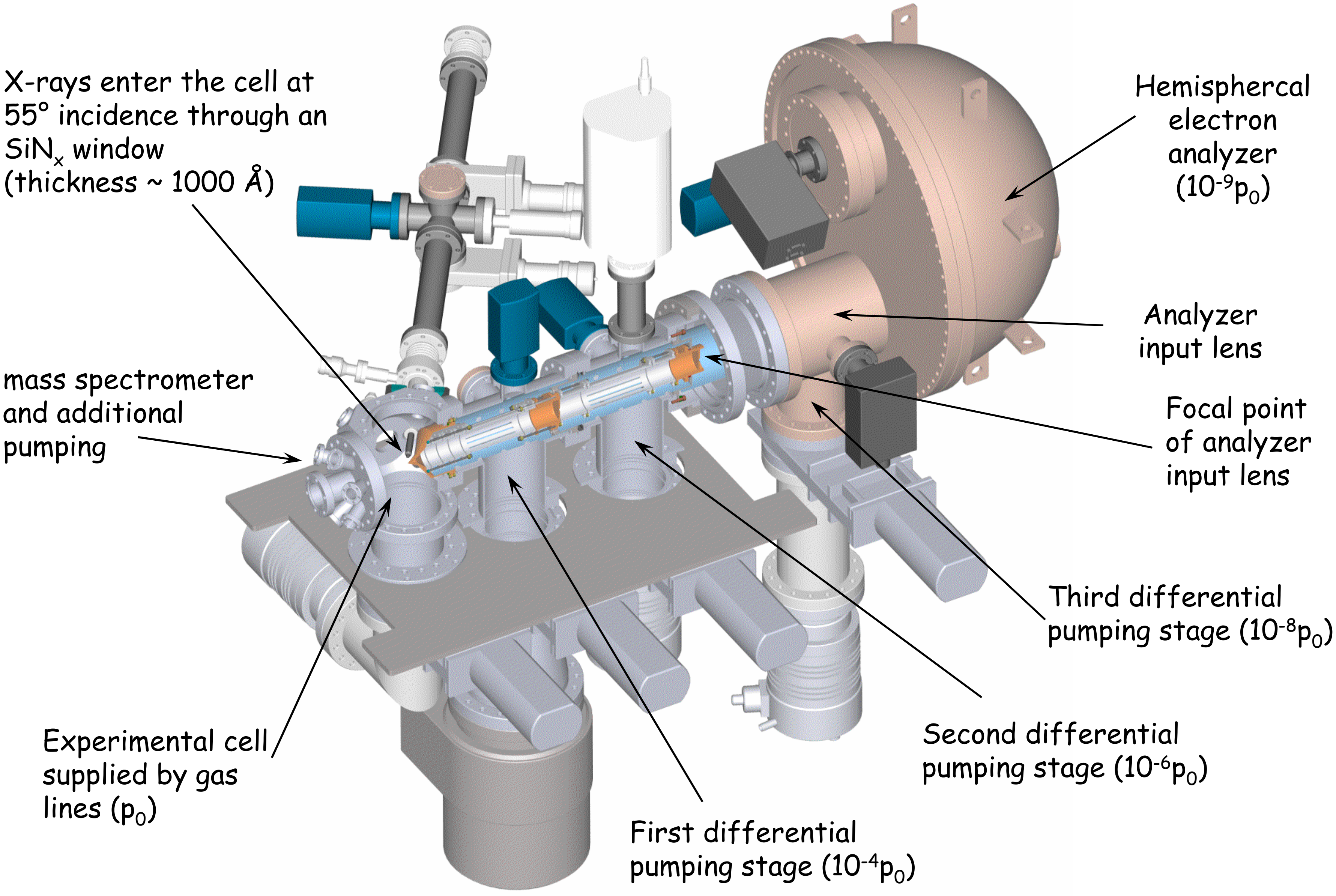
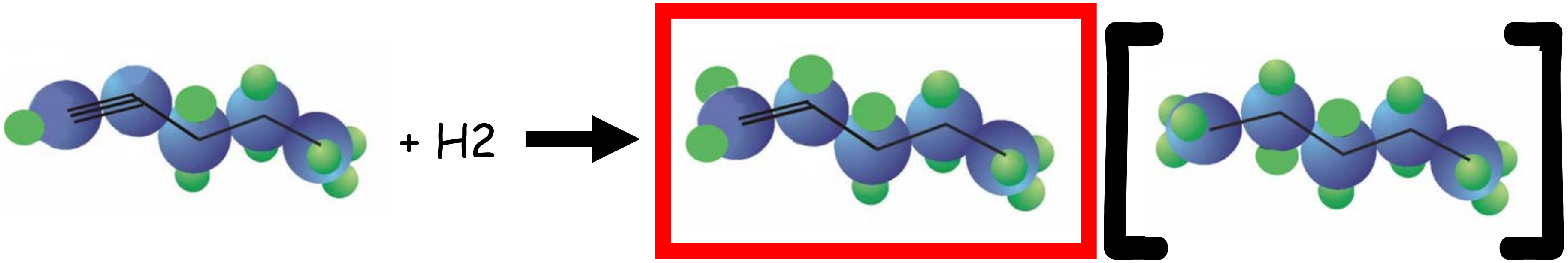
2. *Surface H*: could be selective (spillover)
3. *Different reaction orders* in the different selectivity regimes & Abrupt changes between regimes
4. *C uptake* is significantly more in the selective regime

In situ XPS system



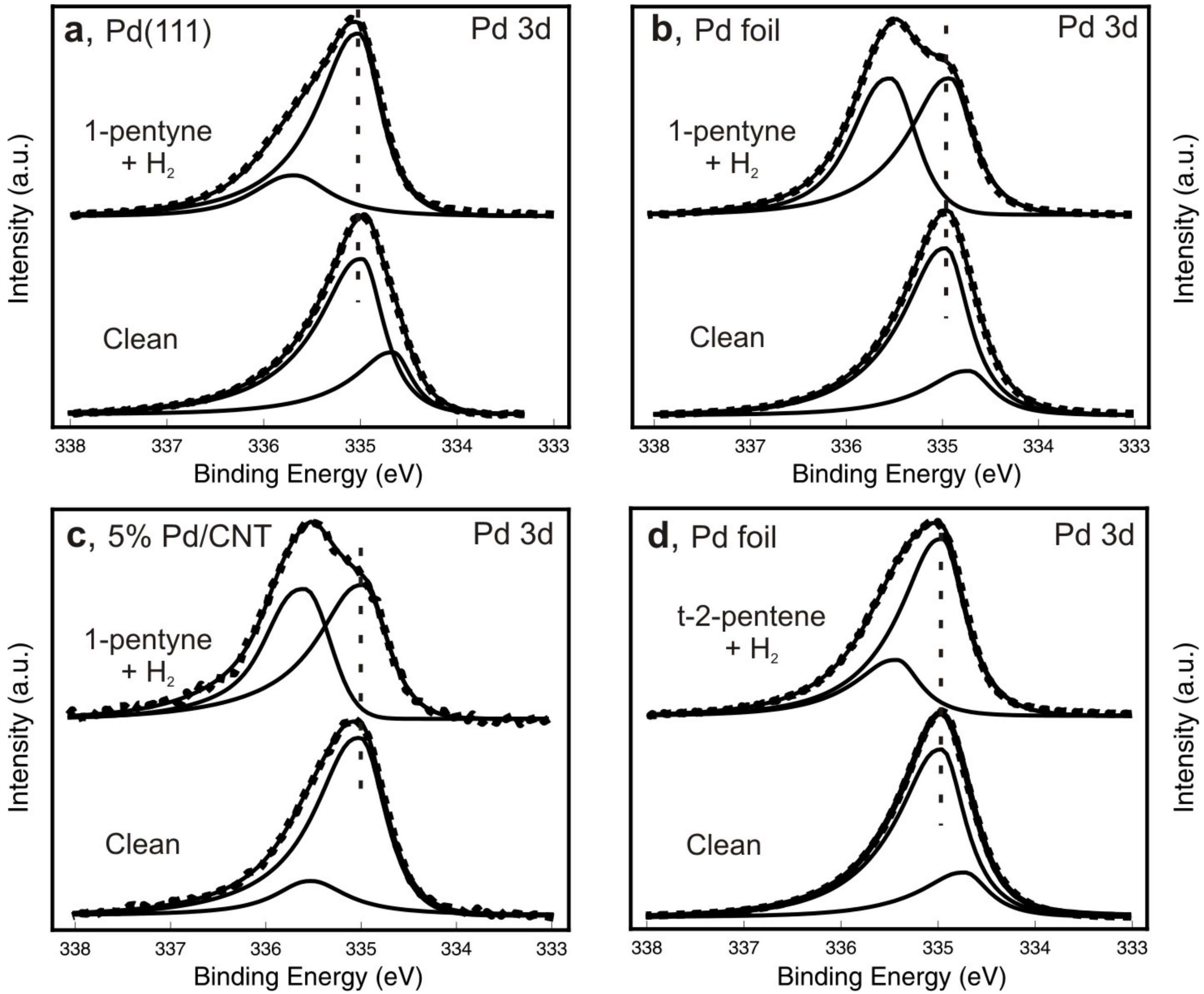
Reaction in the mbar p region (in-situ XPS)



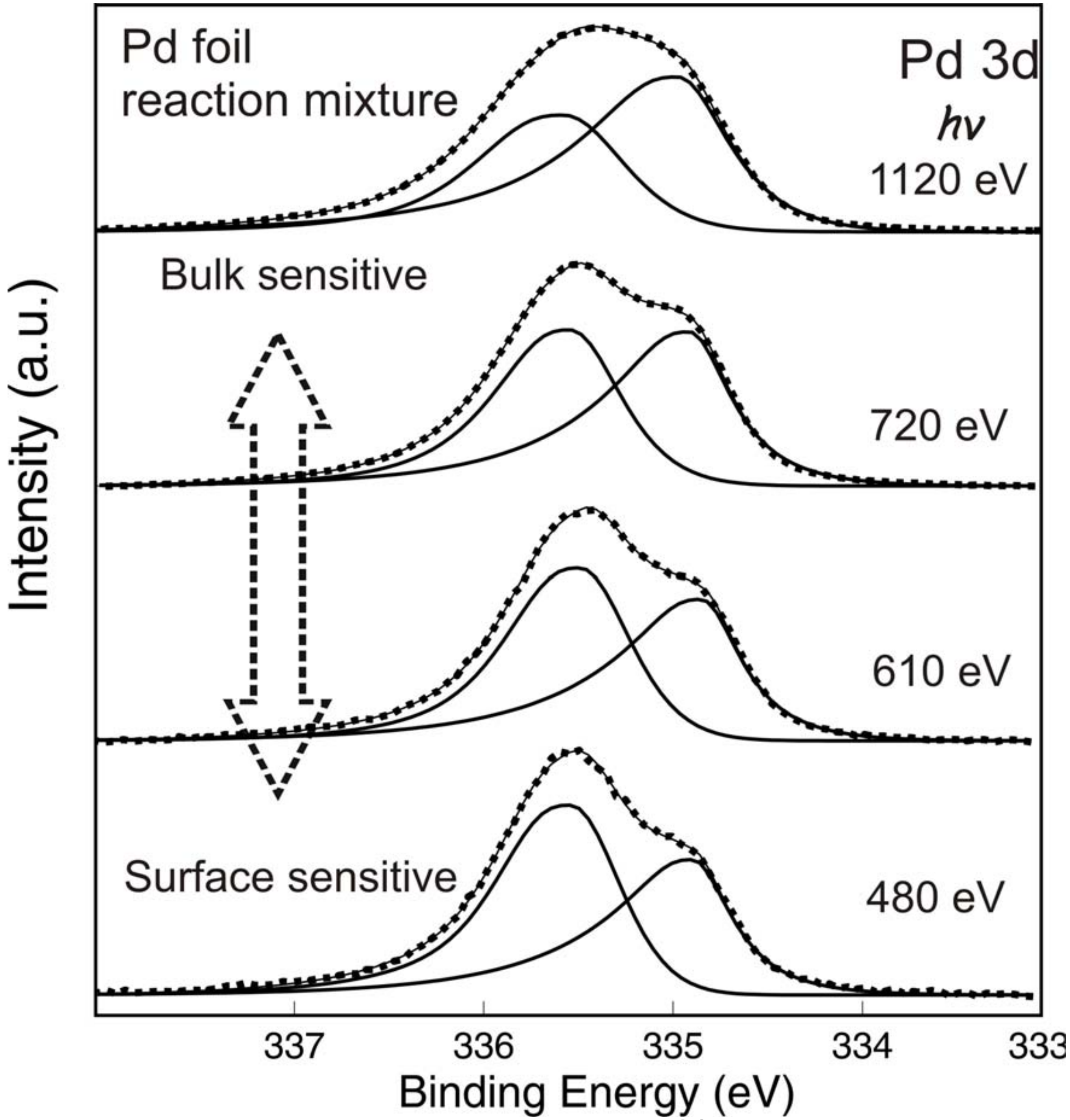
	5% Pd/CNT	3% Pd/Al_2O_3	Pd foil	Pd(111)
Conversion [%]	~ 10	~5	~2.5	<1
Selectivity Pentene [%]	~95	~80	~98	100
Selectivity Pentane [%]	~5	~20	~2	-

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

In-situ XPS: Pd 3d (hν: 720 eV)



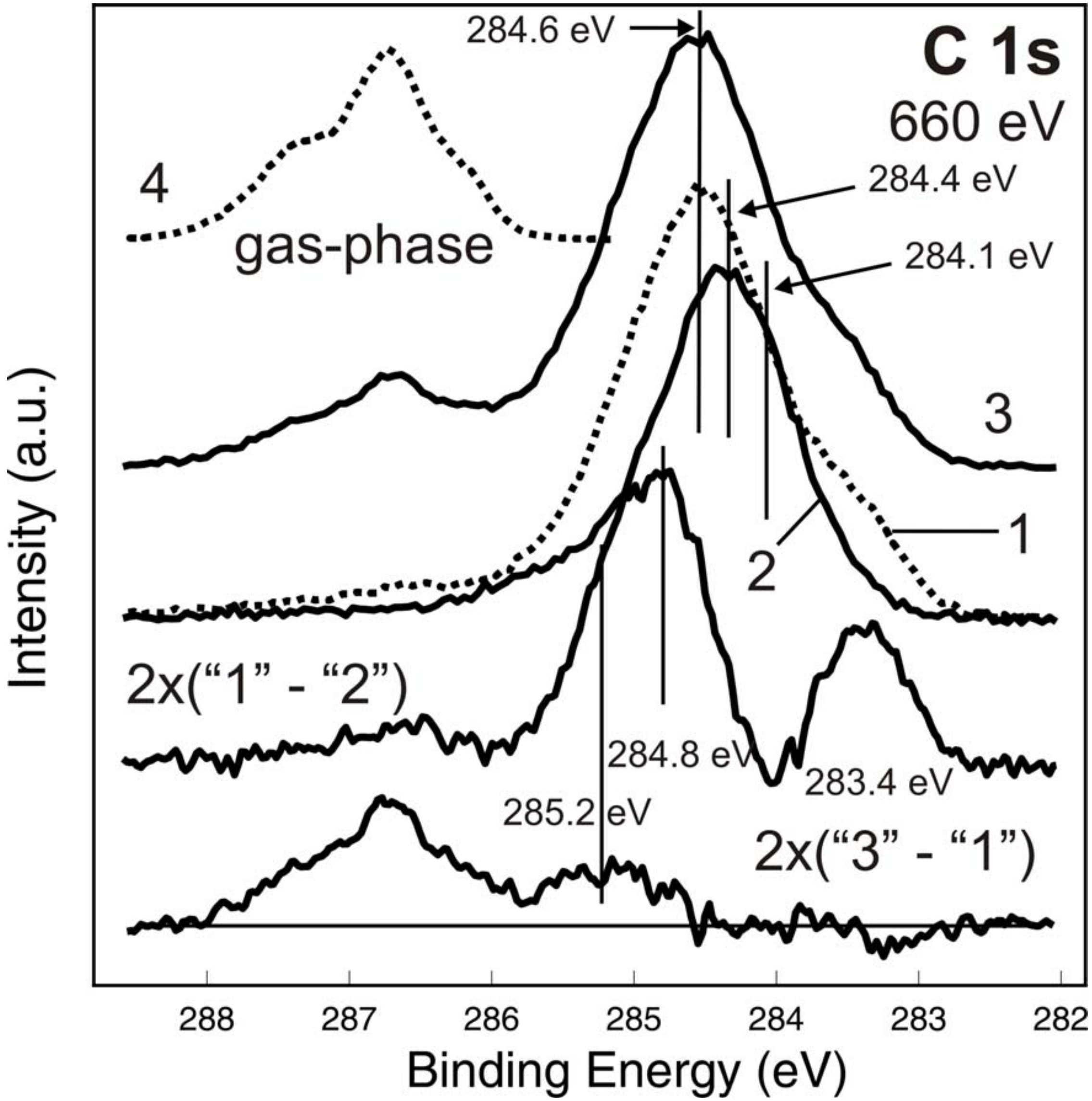
In-situ XPS: Pd 3d depth profiling



Not only adsorbate-induced surface core level shift !

But on-top location!

In-situ XPS: C1s (Switching off experiments)



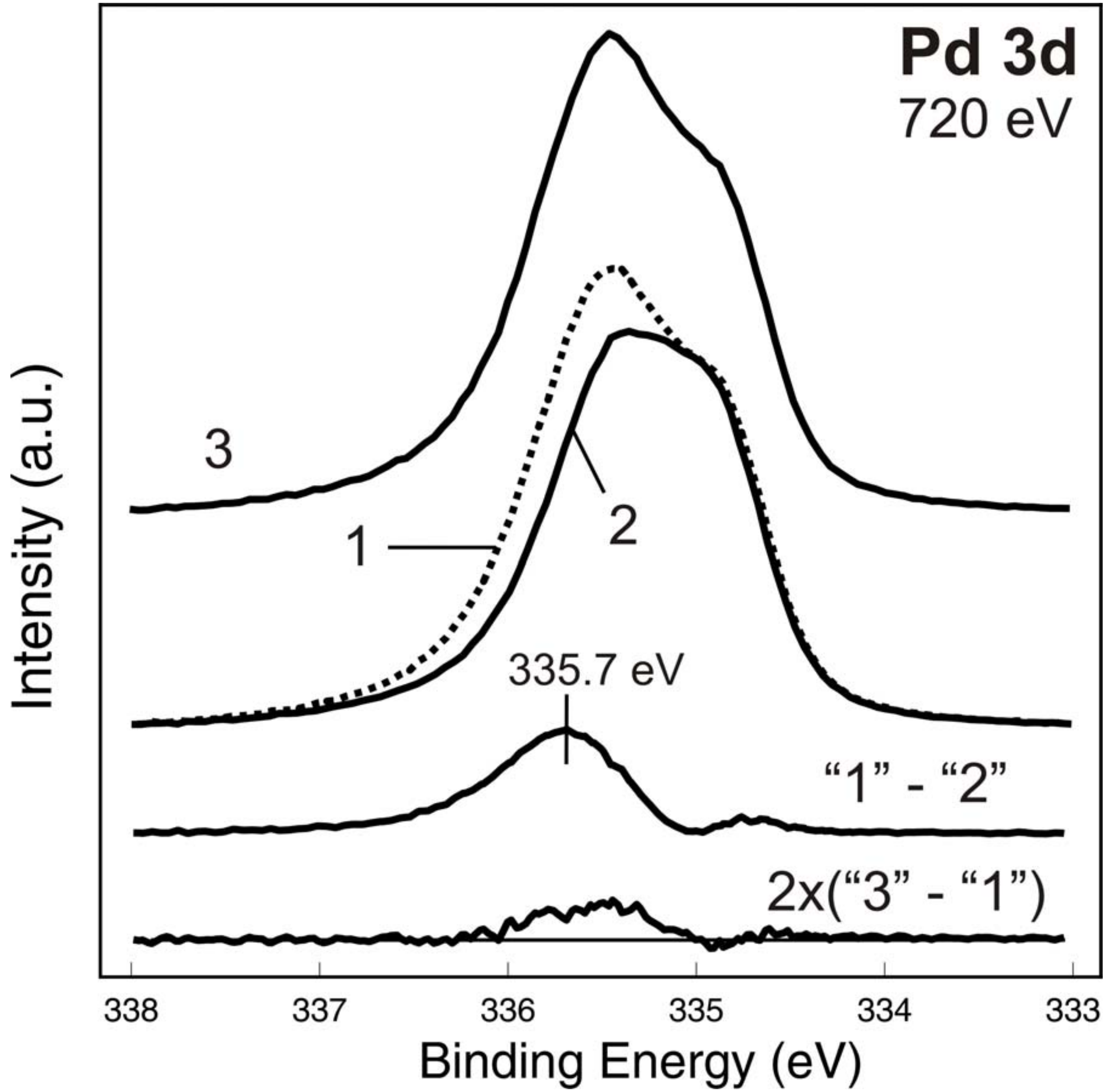
1: reaction mix.

2: C5 off

3: H2 off

4: C5 gas-phase

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

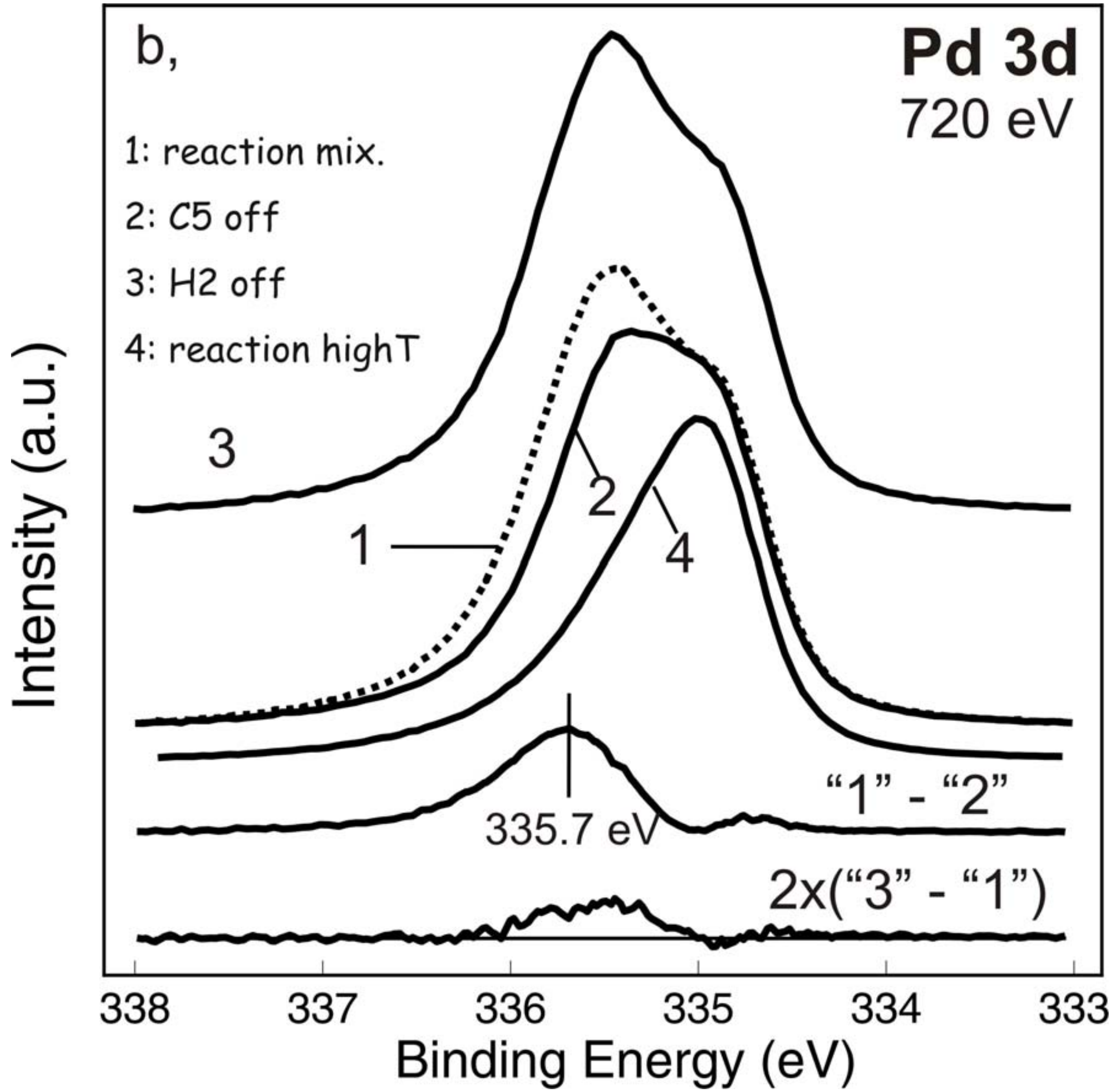


1: reaction mix.

2: C5 off

3: H2 off

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



1: reaction mix.

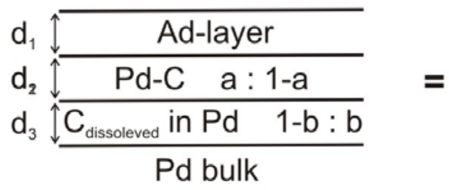
2: C5 off

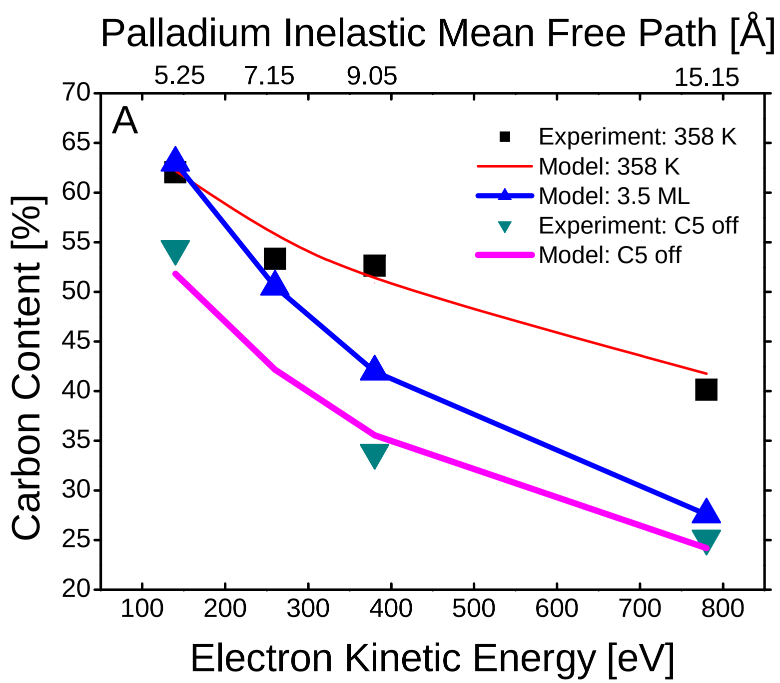
3: H2 off

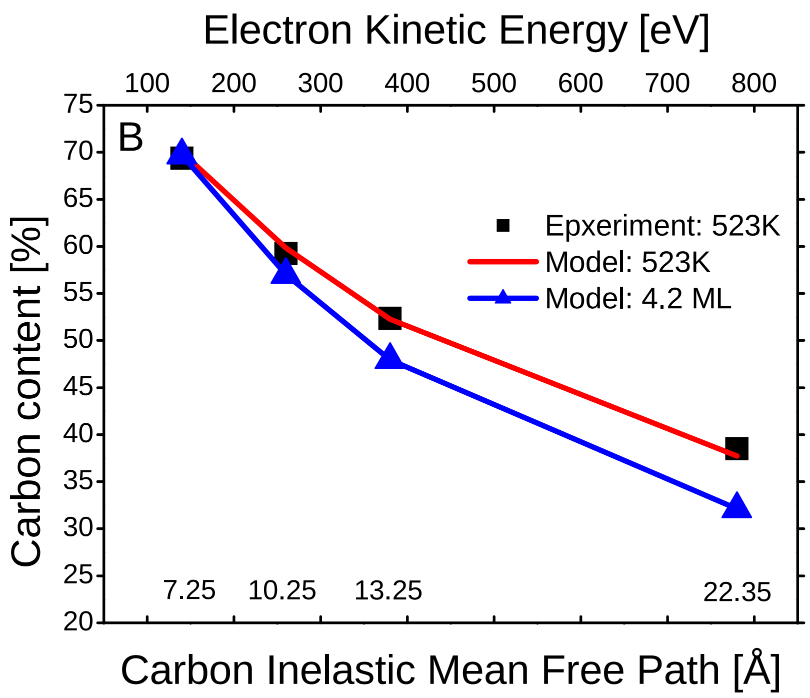
4: reaction; high T

In-situ XPS: Pd vs. C depth profiling

Model







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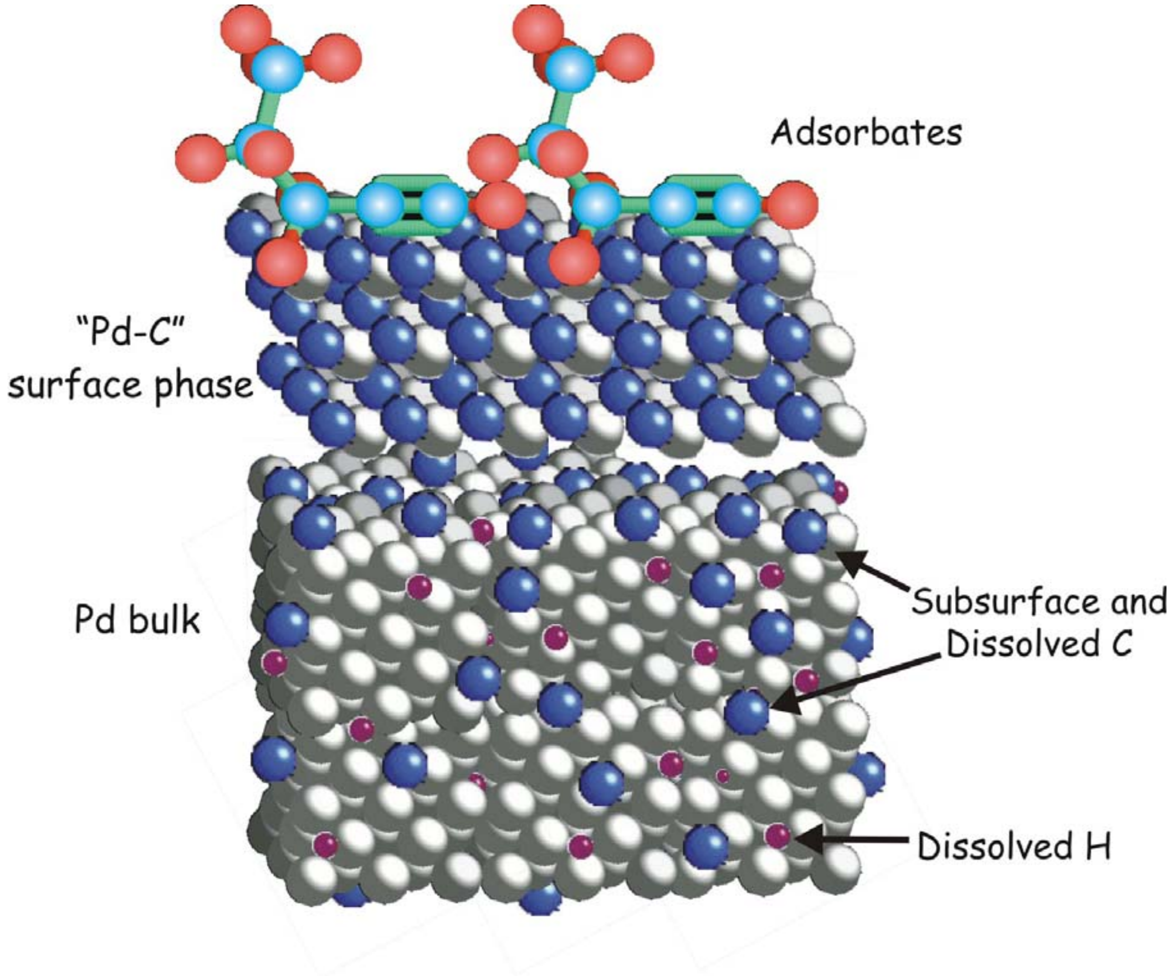
2. *Surface H*: could be selective (spillover)
3. *Different reaction orders* in the different selectivity regimes & Abrupt changes between regimes
4. *C uptake* is considerably more in the selective regime
5. *Pd-C surface phase* forms in the early stage of selective pentyne hydrogenation & there is significant amount of *subsurface C* below of it

Model (during the reaction)



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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

Industry Collaboration of FHI (AC Department) @ BESSY

Sumitomo: Selective Propene Oxidation over Ag Catalysts

BASF: n-Butane Oxidation to Maleic Anhydride over VPO catalysts

Südchemie: VO_x/TiO_2

DaimlerChrysler: surface composition of engine parts

Johnson Matthey: Athena

Outlook: In situ XPS / XAS
The future at BESSY

ISISS:

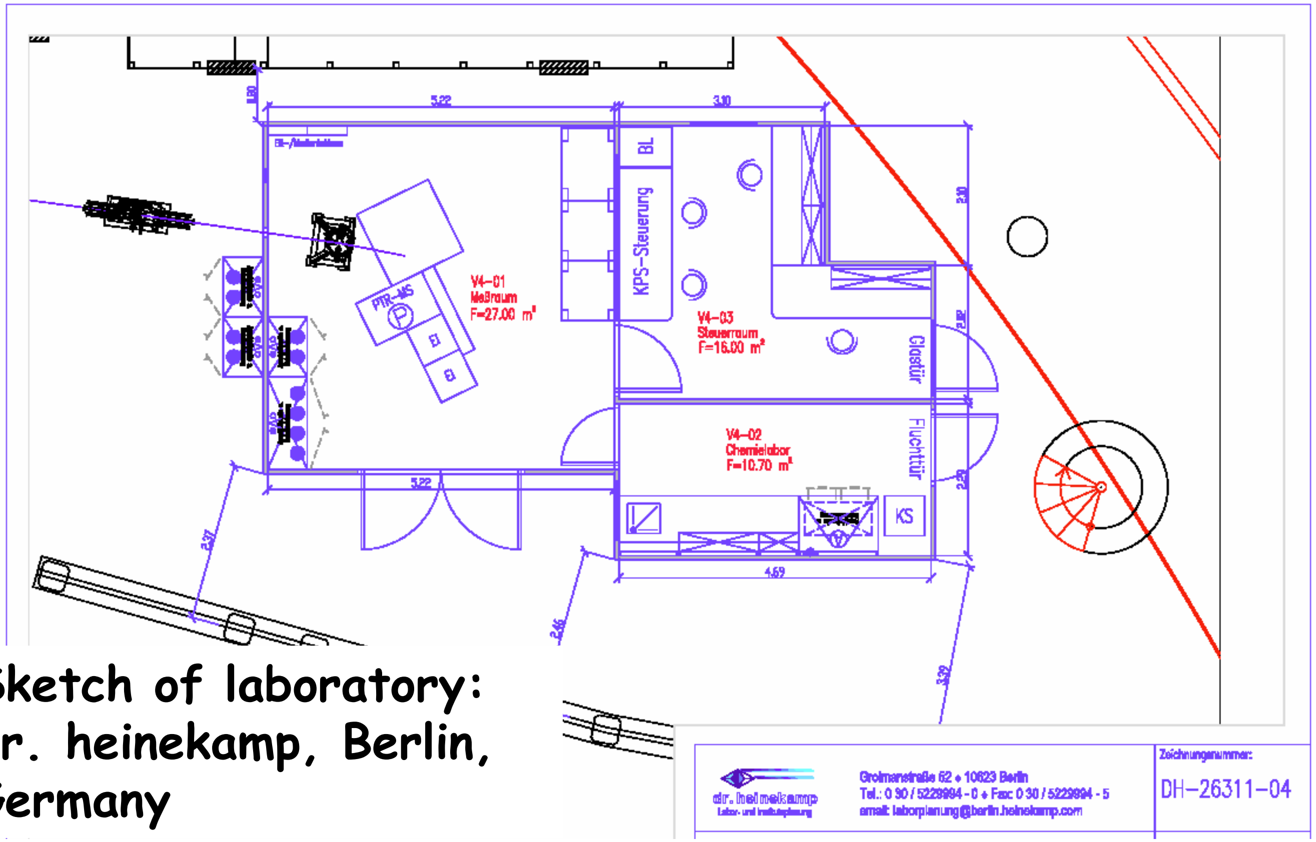
Innovative Station for In Situ Spectroscopy

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