

PHOTONS AND NEUTRONS:
UNDERSTAND HETEROGENEOUS CATALYTIC
HYDROGENATION CHEMISTRY

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Introduction to Hydrogenation

Adding hydrogen to a molecule

One of the most important basic industrial reactions on:

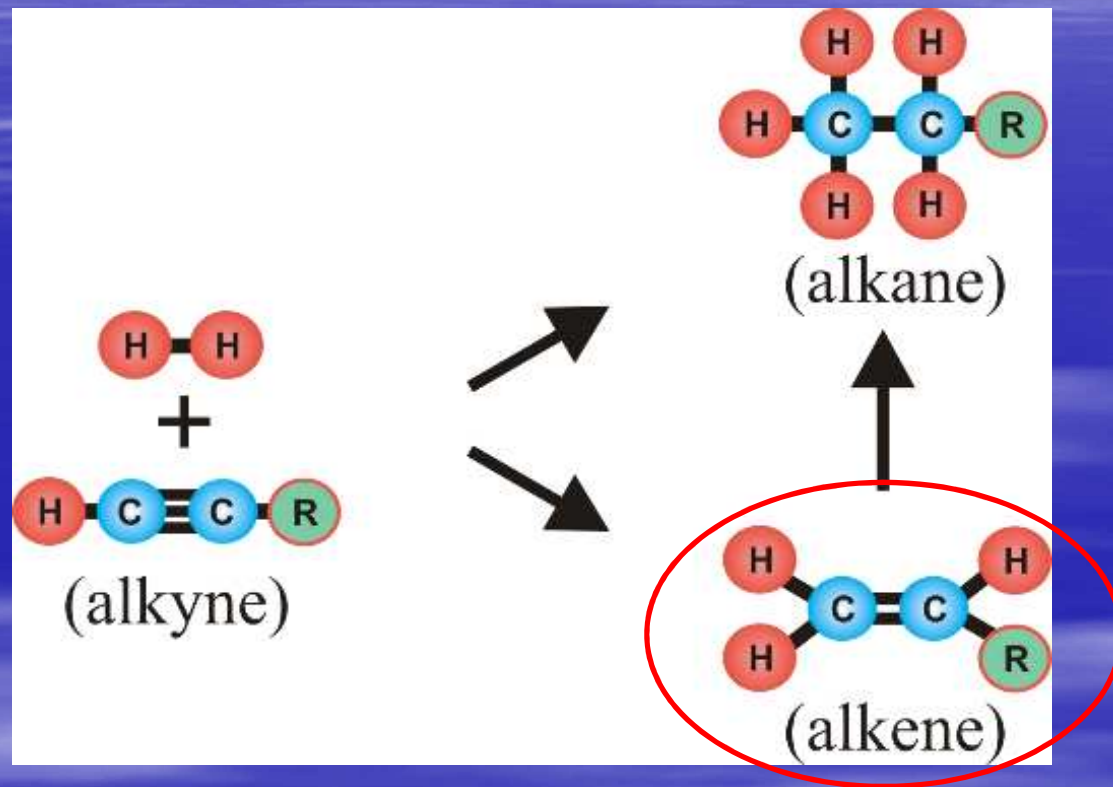
Alkenes, alkadienes, **alkynes**

Aromatics

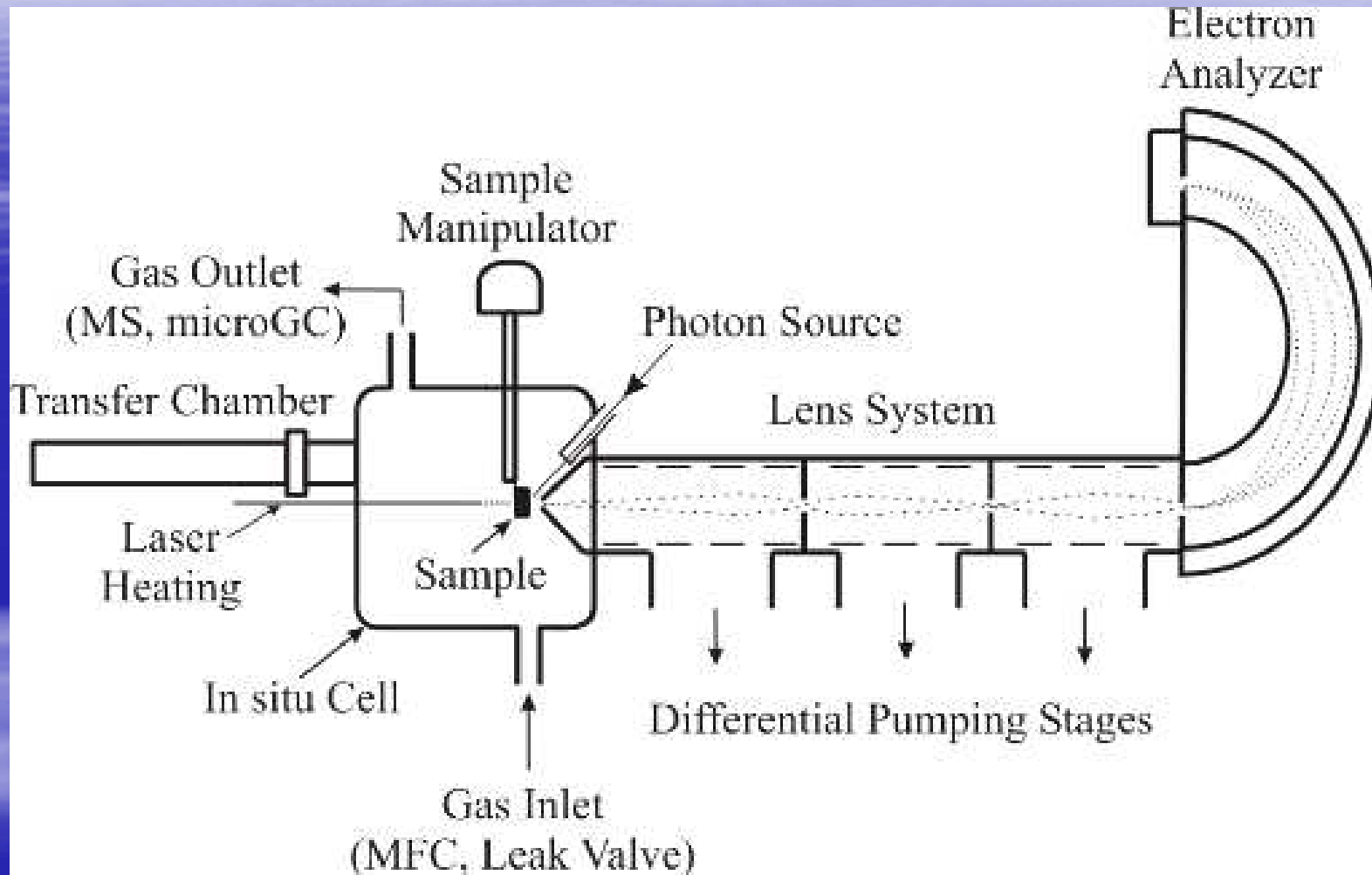
Nitriles

(Edible) oils, fats

Introduction to Hydrogenation

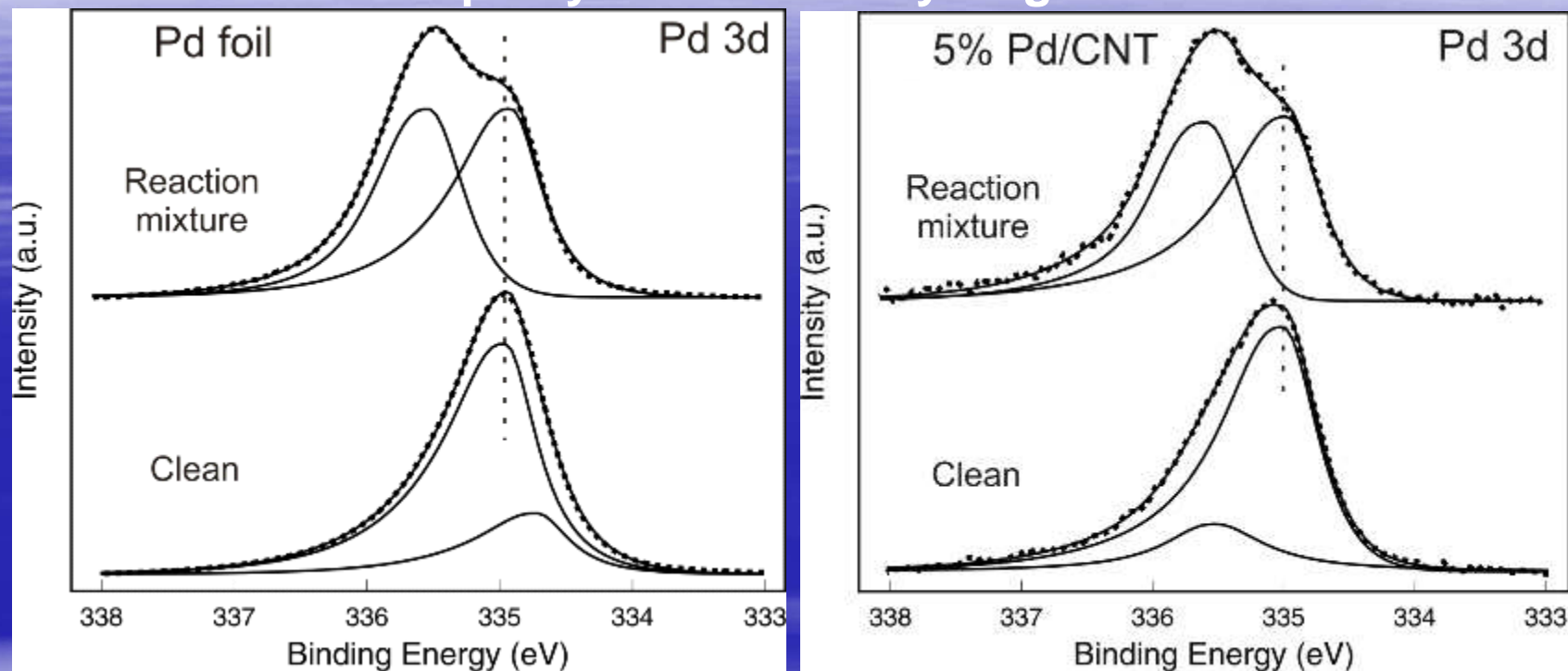


High-pressure XPS



High-pressure XPS

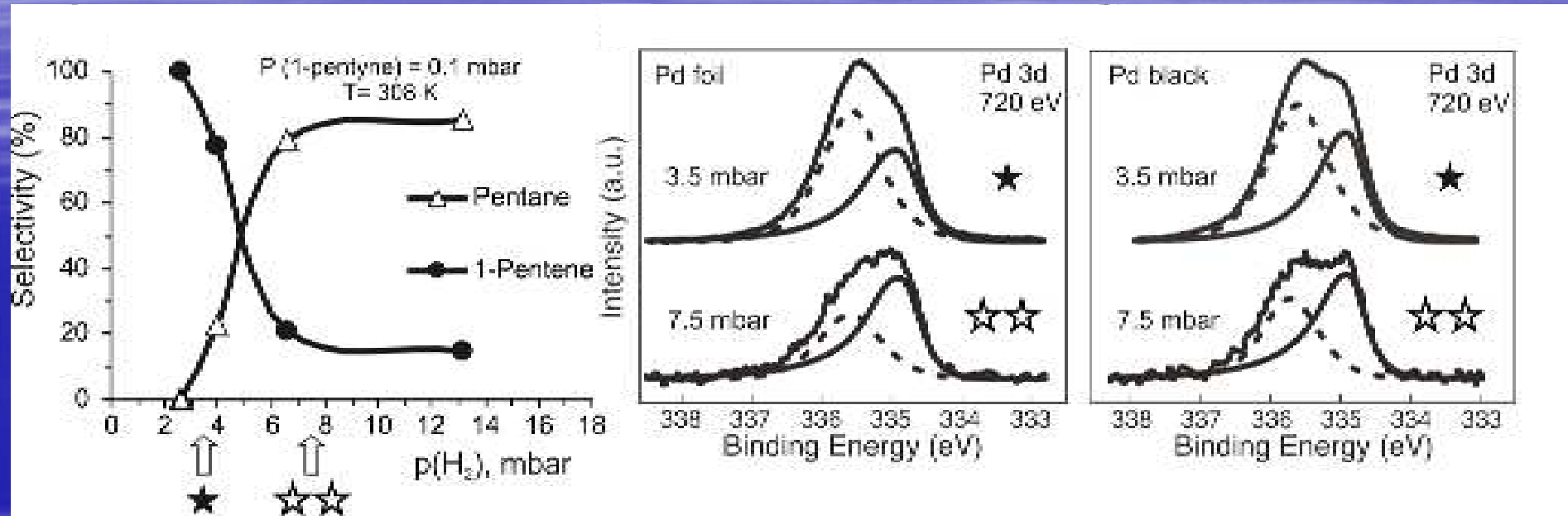
1-pentyne selective hydrogenation



New state evolves under selective hydrogenation condition

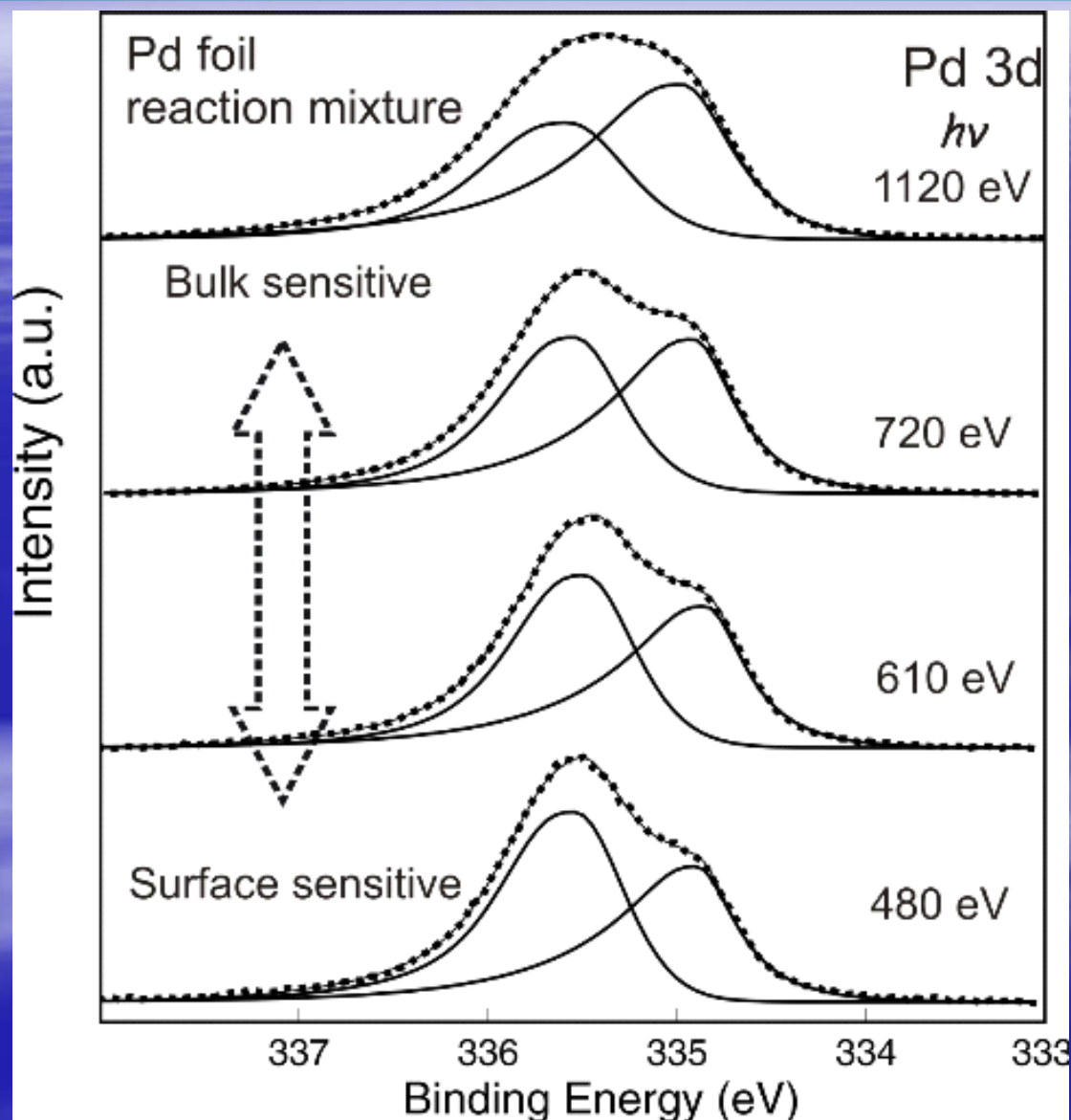
High-pressure XPS

Correlate catalysis with surface state



Selectivity correlates with the „Pd 3d state“

High-pressure XPS



Not only
adsorbate-induced
surface core level
shift!

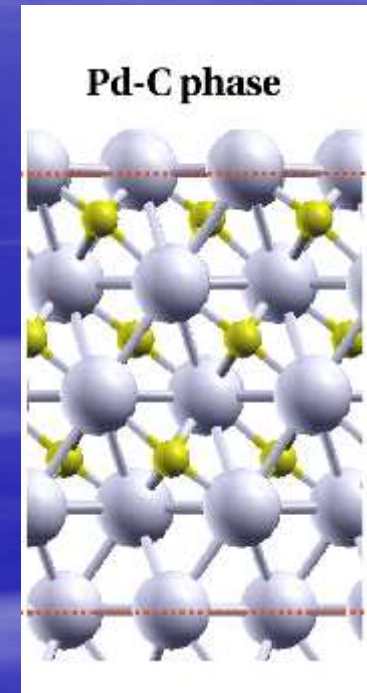
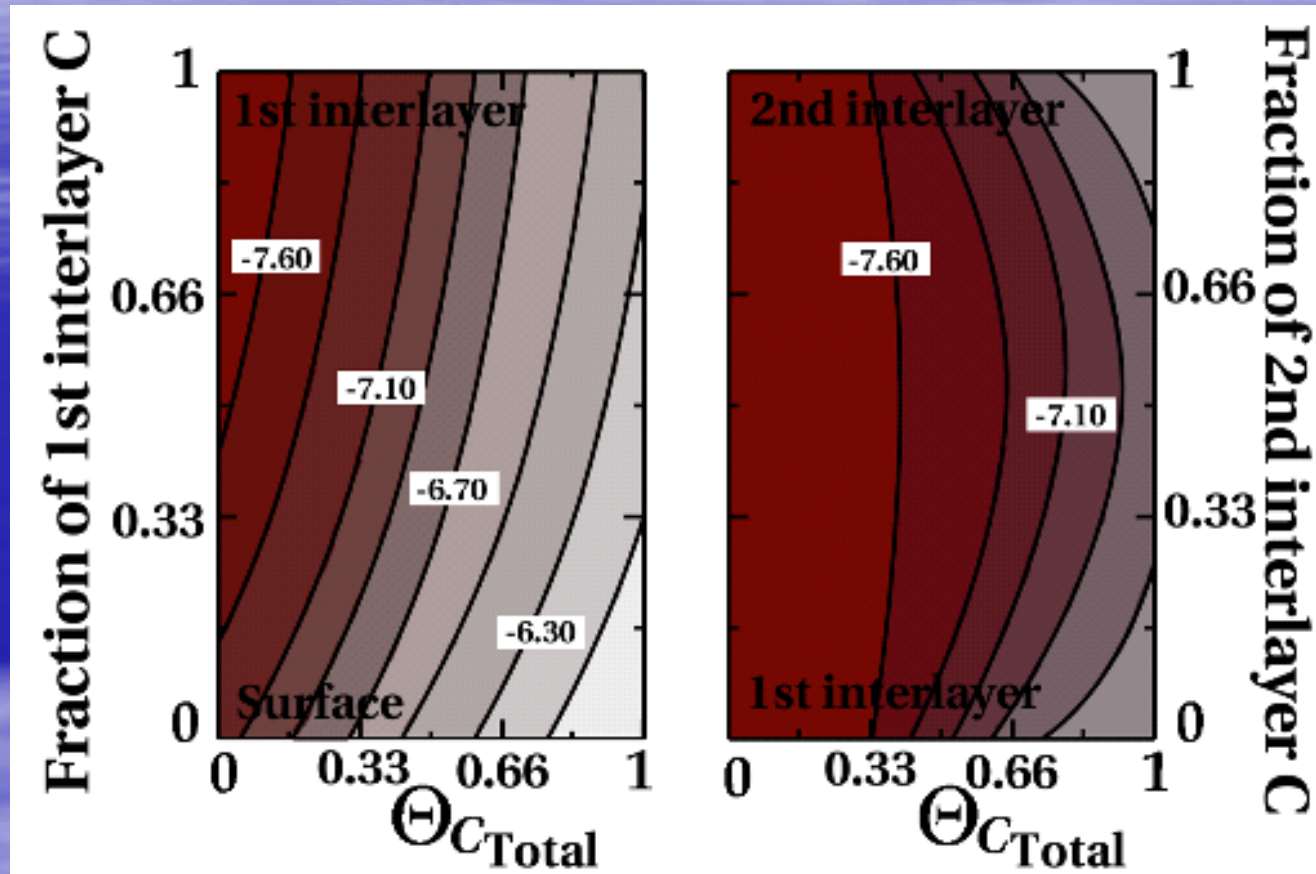
But on-top location!

Carbon dissolves in the
top Pd layers

surface „Pd-C phase“

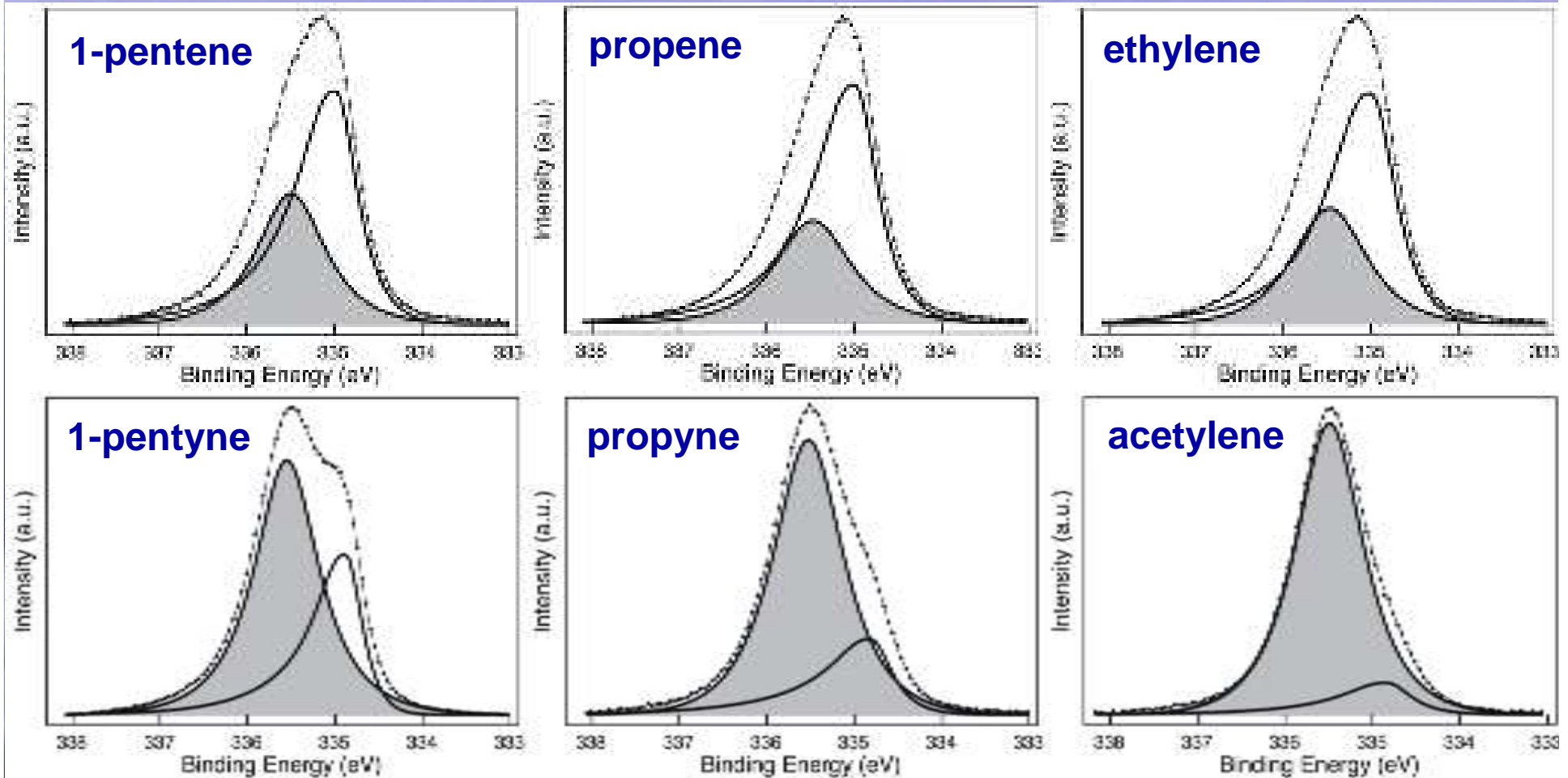
Teschner et al.: J. Catal. 242 (2006) 26.

DFT



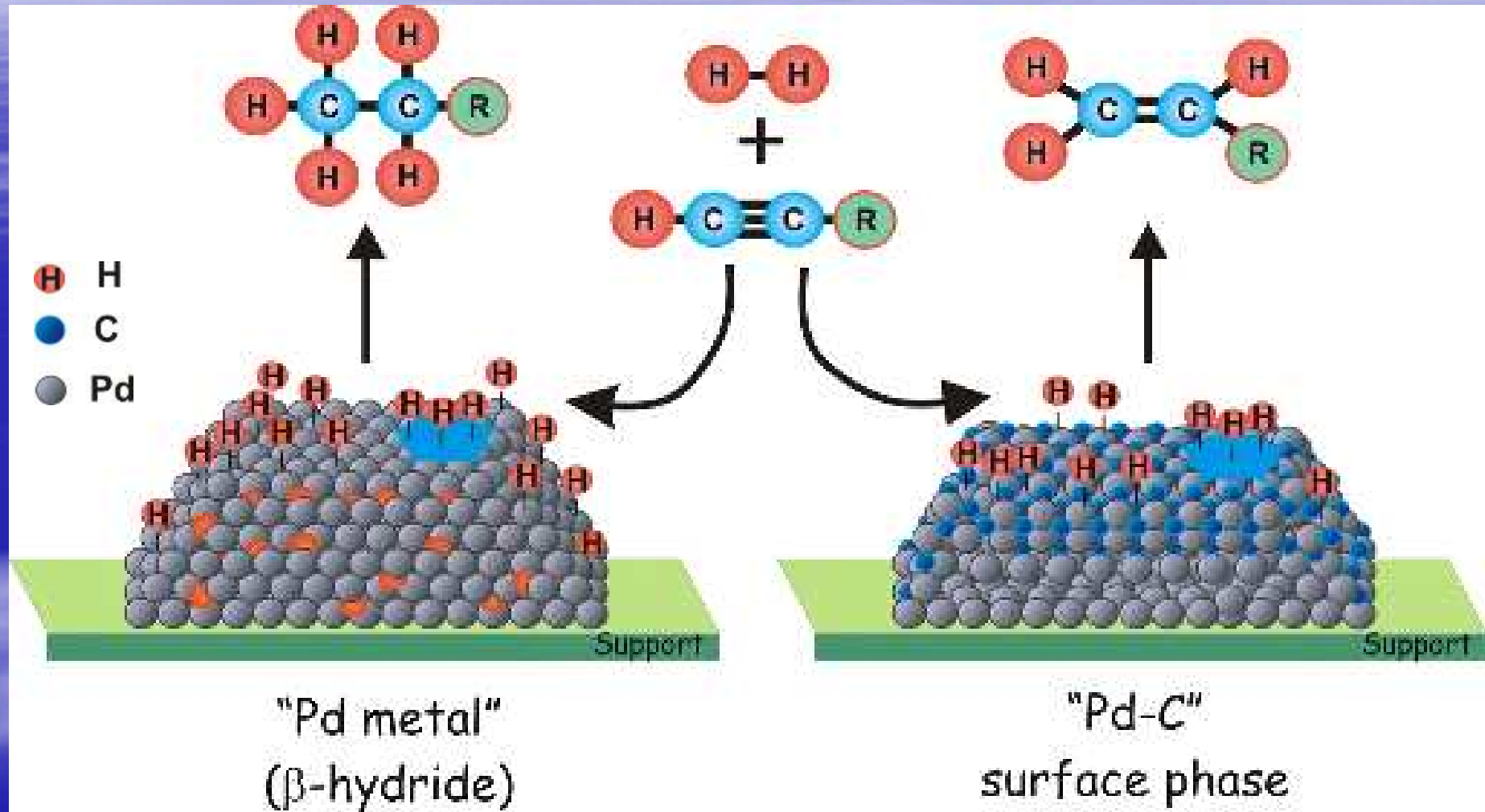
Teschner et al.: Angew. Chem. Int. Ed. 47 (2008) 9274.

High-pressure XPS



Teschner et al.: Angew. Chem. Int. Ed. 47 (2008) 9274.

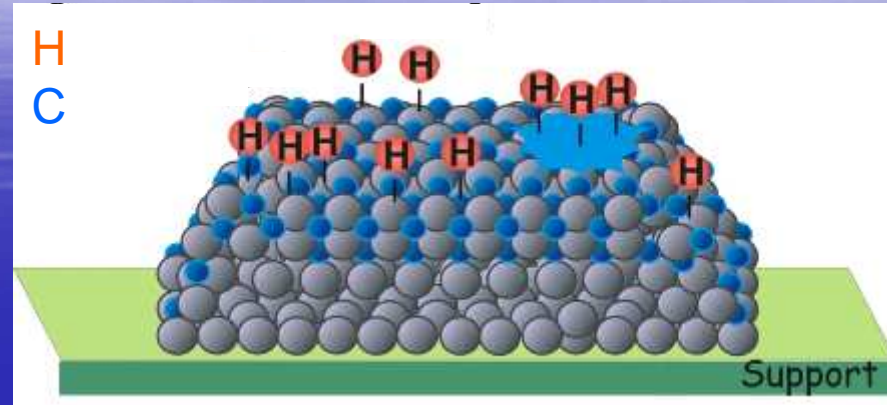
Model



D. Teschner, et.al. Science 320 (2008) 86.

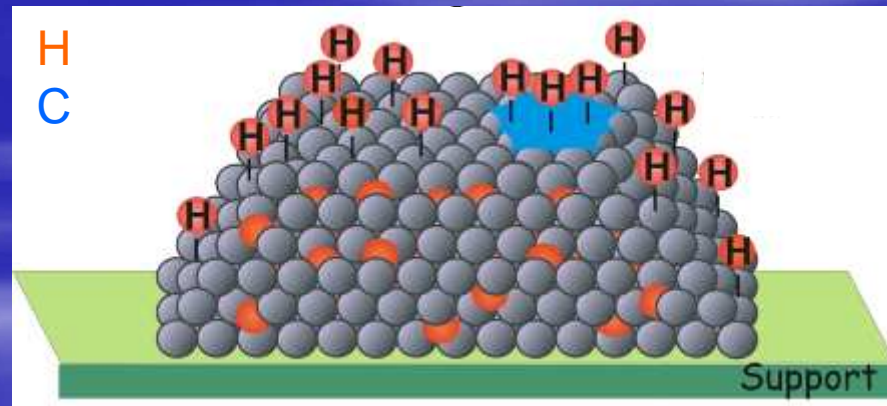
XPS Summary

Alkyne \rightarrow Alkene:

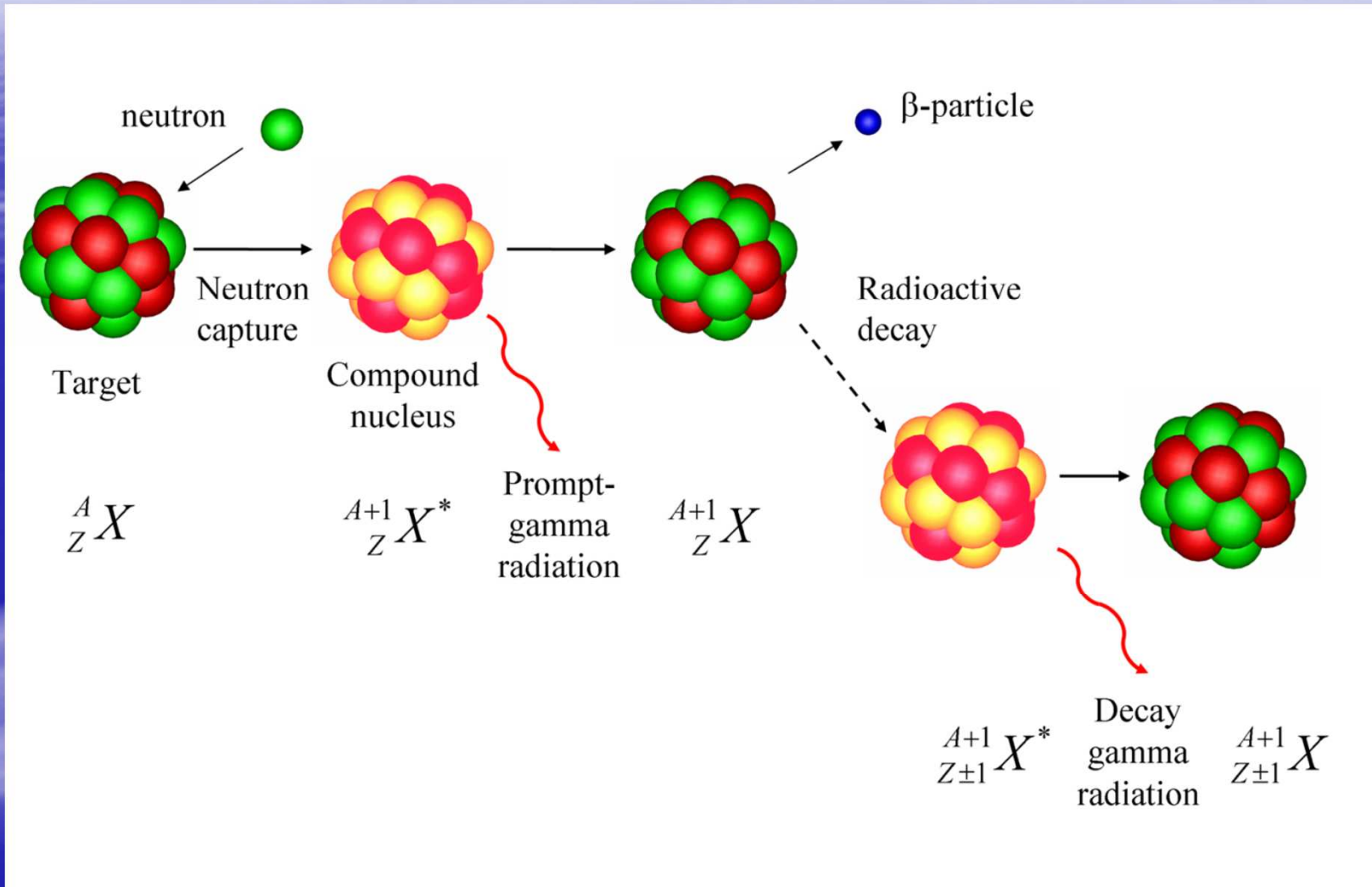


Alkene \rightarrow Alkane:

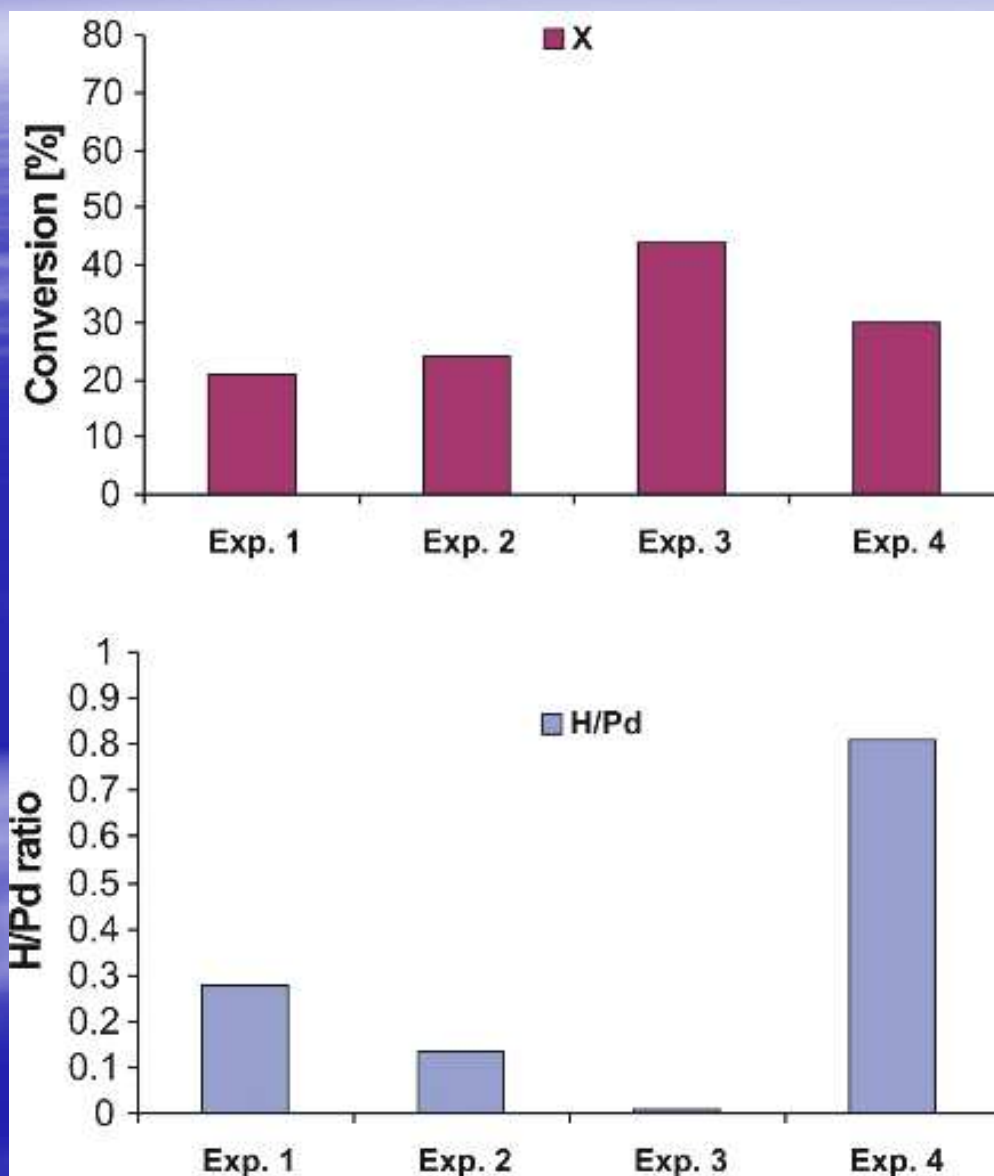
Alkyne \rightarrow Alkane:



PGAA: Basics



1-pentyne conversion and corresponding bulk H/Pd values



Sample: 7 mg Pd black
(200 nm mean p.s.; in SiC)
Temperature: RT
 H_2 : $4 \text{ cm}^3\text{min}^{-1}$
1-pentyne: $1.6 \text{ cm}^3\text{min}^{-1}$ in N_2

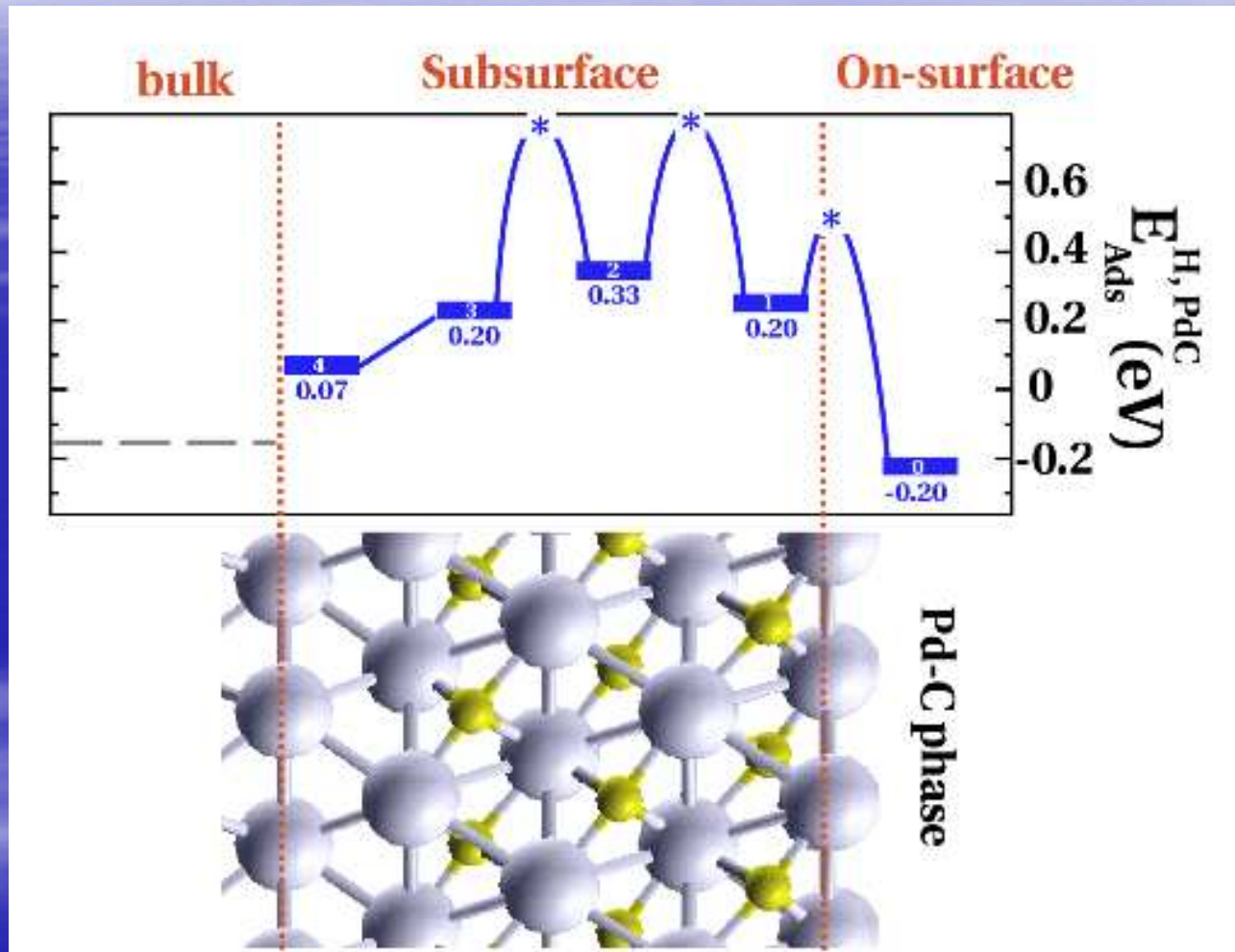
- Always selective hydrogenation to 1-pentene
- wide variation in H/Pd



No correlation!

D. Teschner, et.al. Science 320 (2008) 86.

DFT



D. Teschner, et.al. J. Phys. Chem. C 114 (2010) 2293.

Conclusion

- The chemical potential of the reaction feed and product molecules strongly affects the surface and subsurface state of palladium. Such in situ modification can be nicely explored by in situ XPS preferentially coupled with tunable X-ray source.
- Subsurface carbon decouples bulk properties from the surface events enabling selective hydrogenation over Pd catalysts.
- Neutron techniques, like Prompt Gamma Activation Analysis, have the possibility to be applied as in situ spectroscopic techniques for hydrogen quantification.
- The combination of in situ experimentation and DFT calculation is a powerful tool in the catalytic basic research.

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