In situ determination of hydrogen inside a catalytic reactor using Prompt Gamma Activation Analysis

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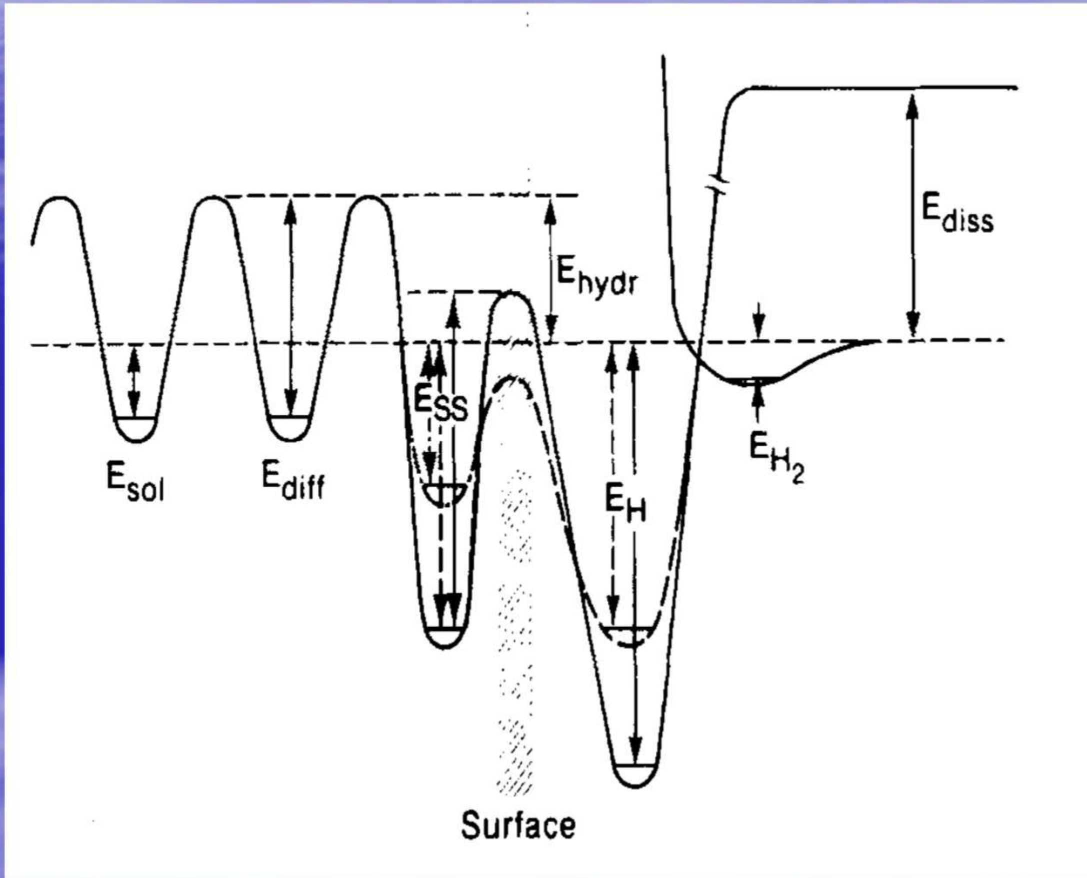
Hydrogen: a problem child



R. J. Behm et al., *J. Chem.Phys.* **1983**, *78*, 7486.

Surface H equilibrates with subsurface and bulk

Hydrogenation (X, S) vs. p(H_2)

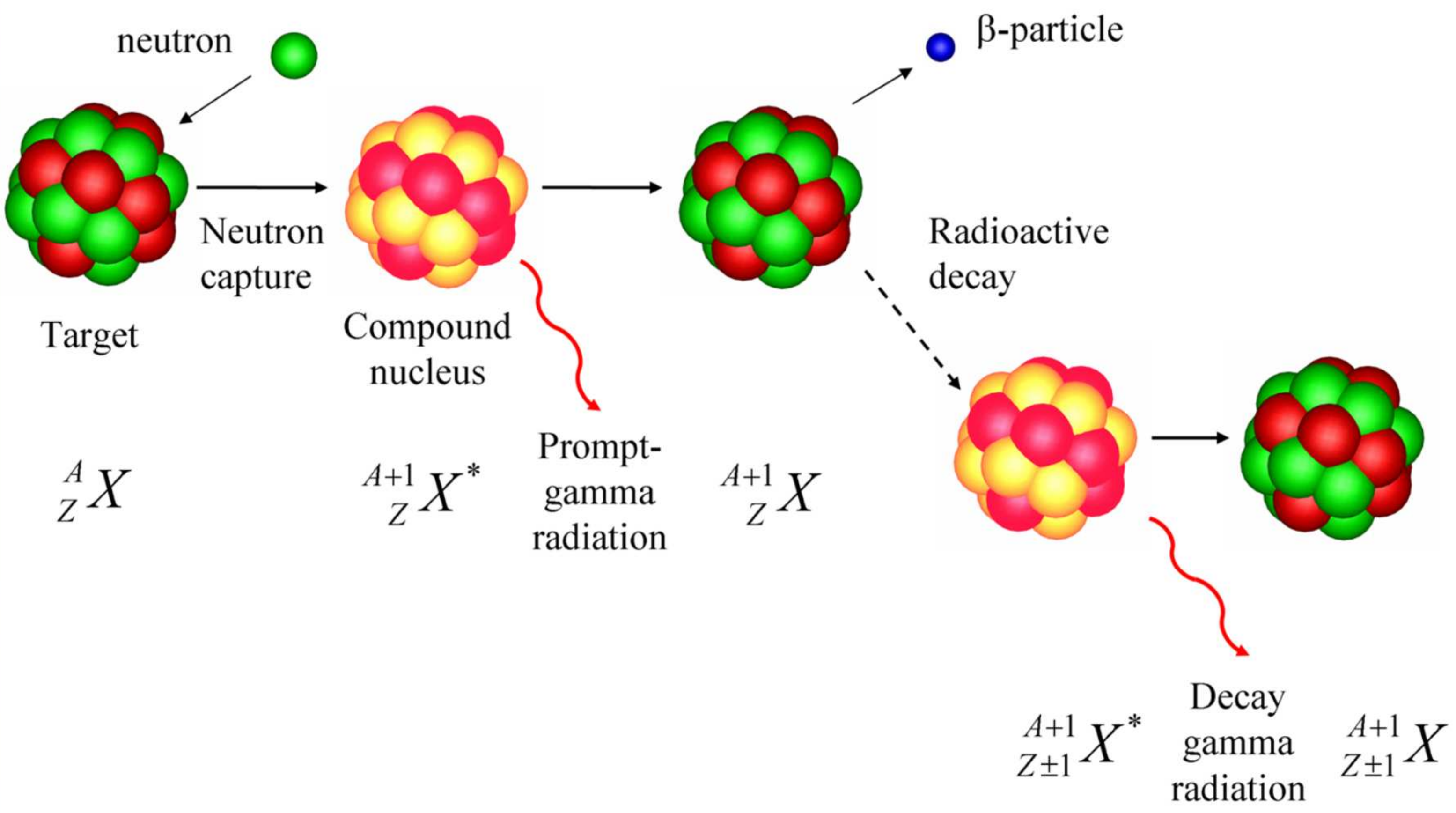
H difficult to catch & quantify by spectroscopy (in situ)

PGAA

In situ Prompt Gamma Activation Analysis

What is PGAA?

Basics



neutron
β-particle
Neutron capture
Radioactive decay
Target
Compound nucleus
Prompt-gamma radiation
$^{A}_{Z}X$
$^{A+1}_{Z}X^{*}$
$^{A+1}_{Z}X$
Decay gamma radiation
$^{A+1}_{Z\pm1}X^{*}$
$^{A+1}_{Z\pm1}X$

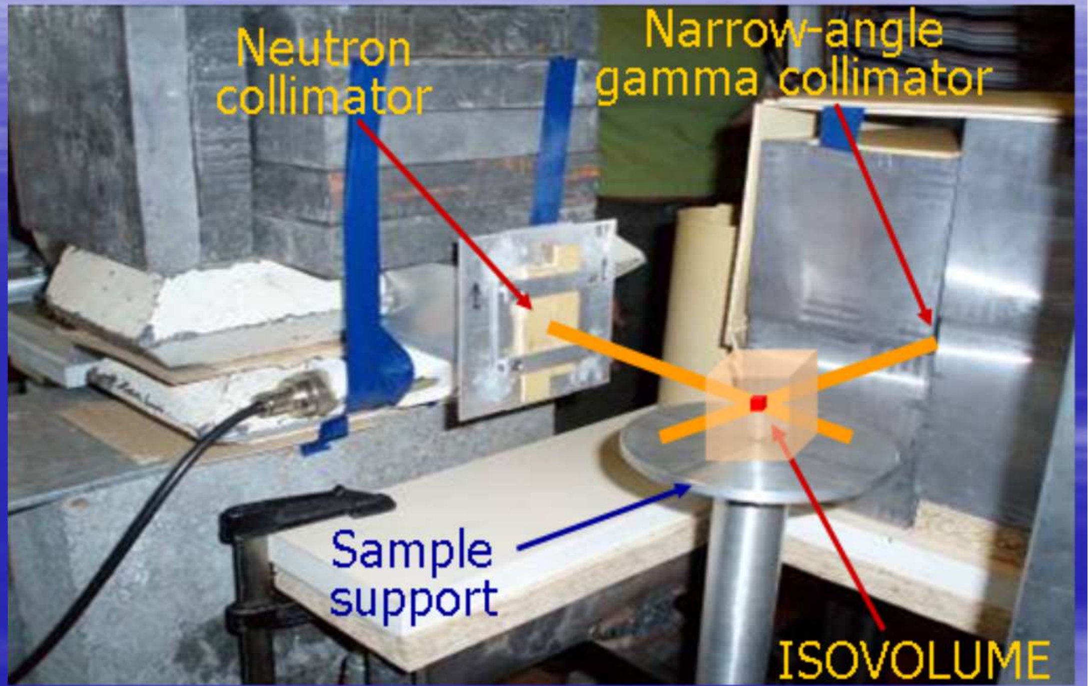
Prompt Gamma Activation Analysis

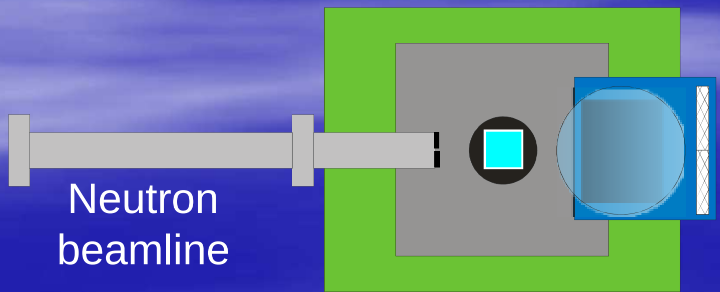
What is PGAA?

- The application of **radiative neutron capture ((n,γ) reaction)** for chemical analysis
- First observed in 1934: $^{1}H(n,\gamma)^{2}H$
  D.E. Lea, Nature, **133** (1934) 24.

Bulk Analysis of Hydrogen

PGAA and neutron tomography





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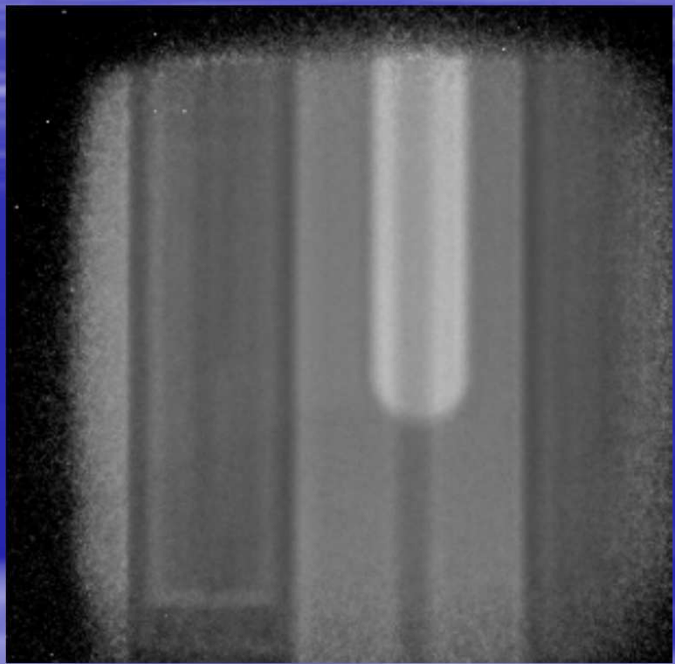
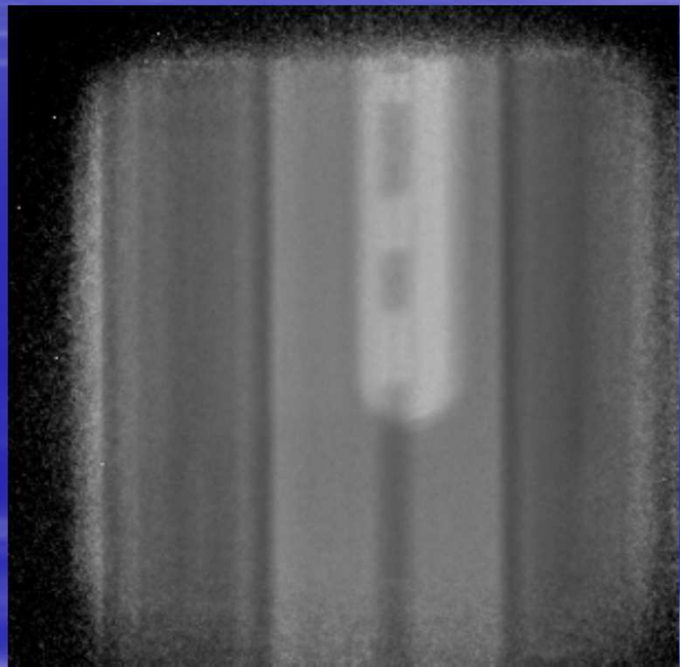
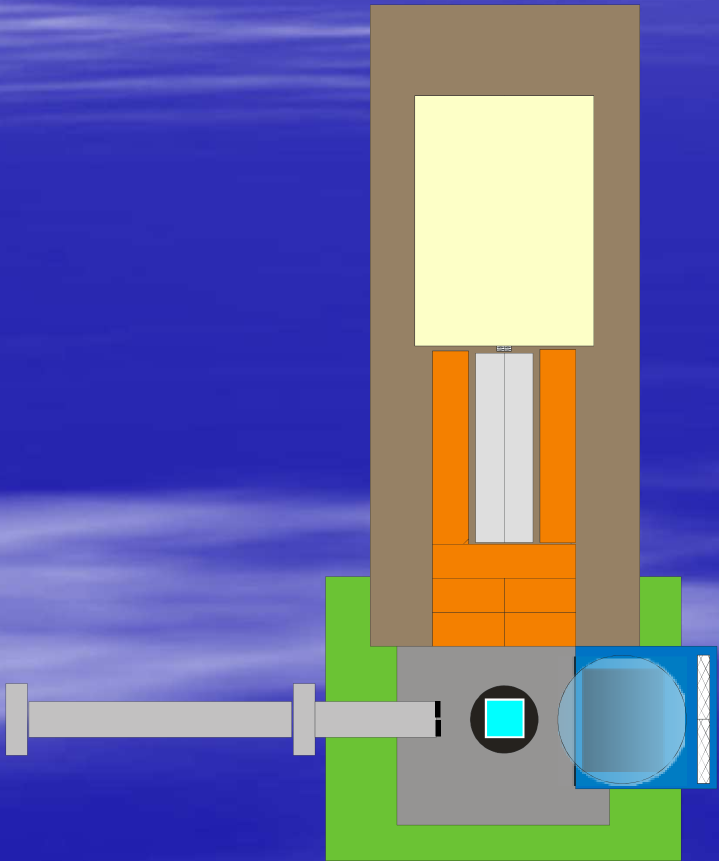
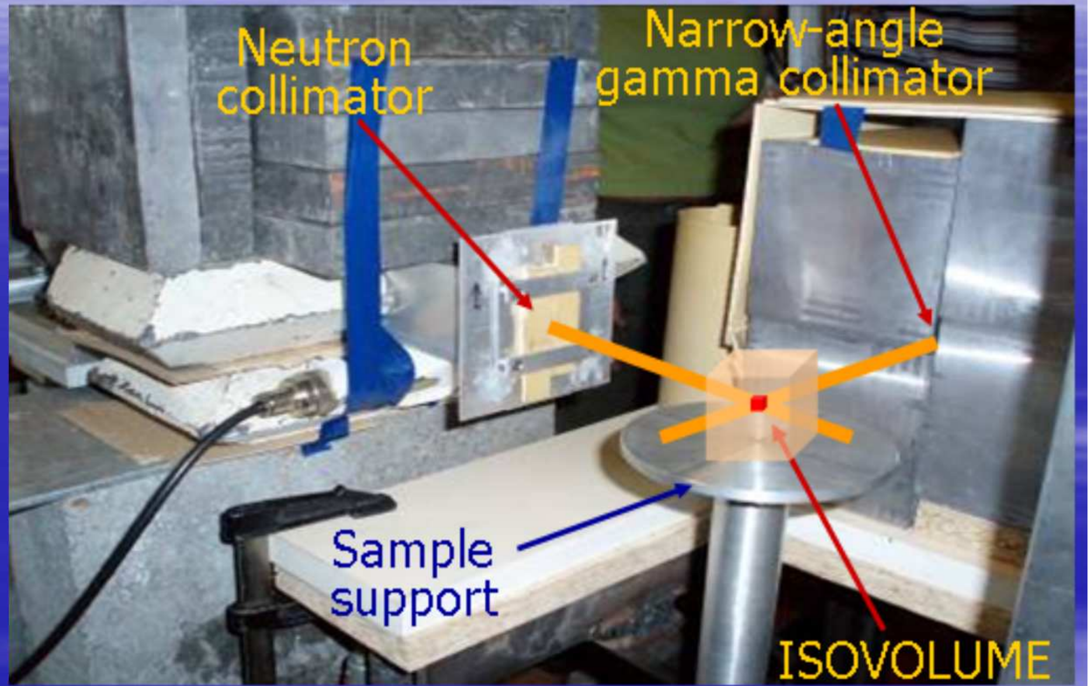
PGAA and tomography





PGAA and neutron tomography





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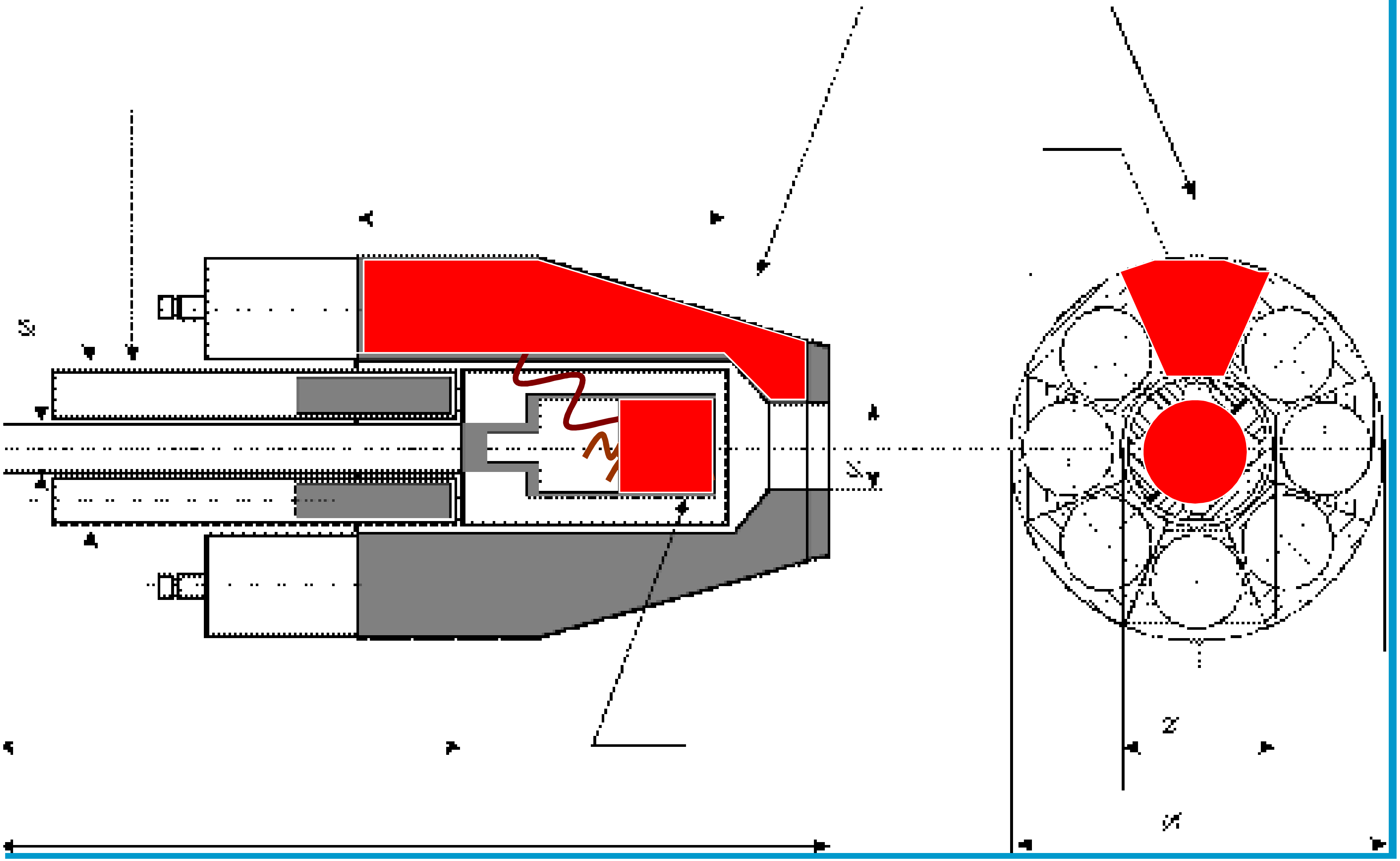
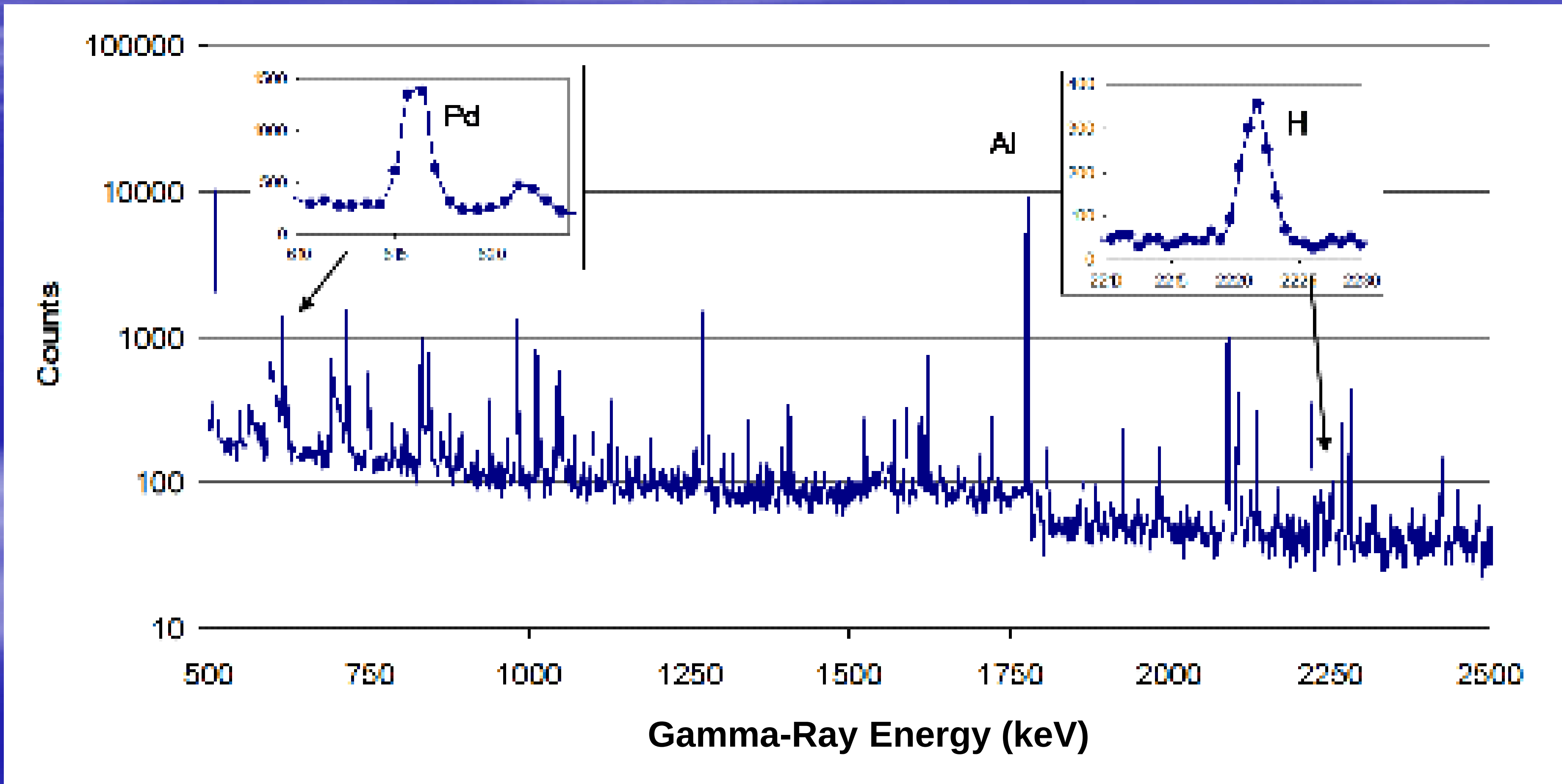
Compton-suppressed HPGe detector

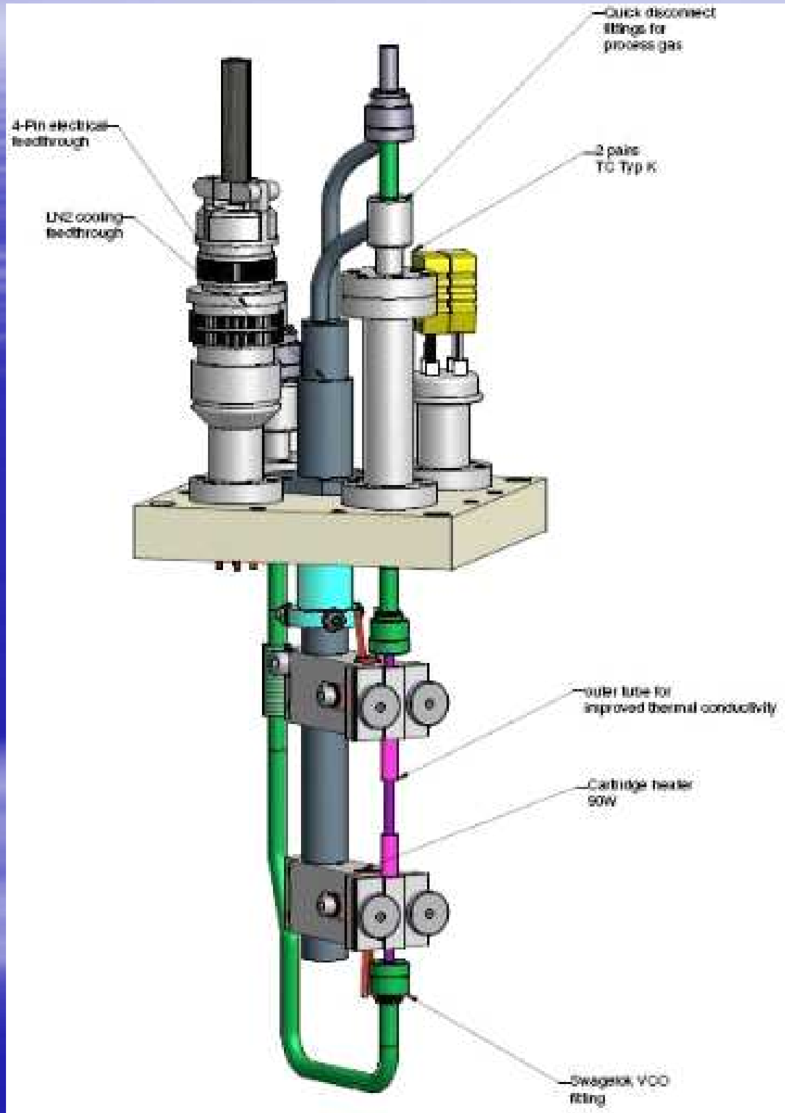


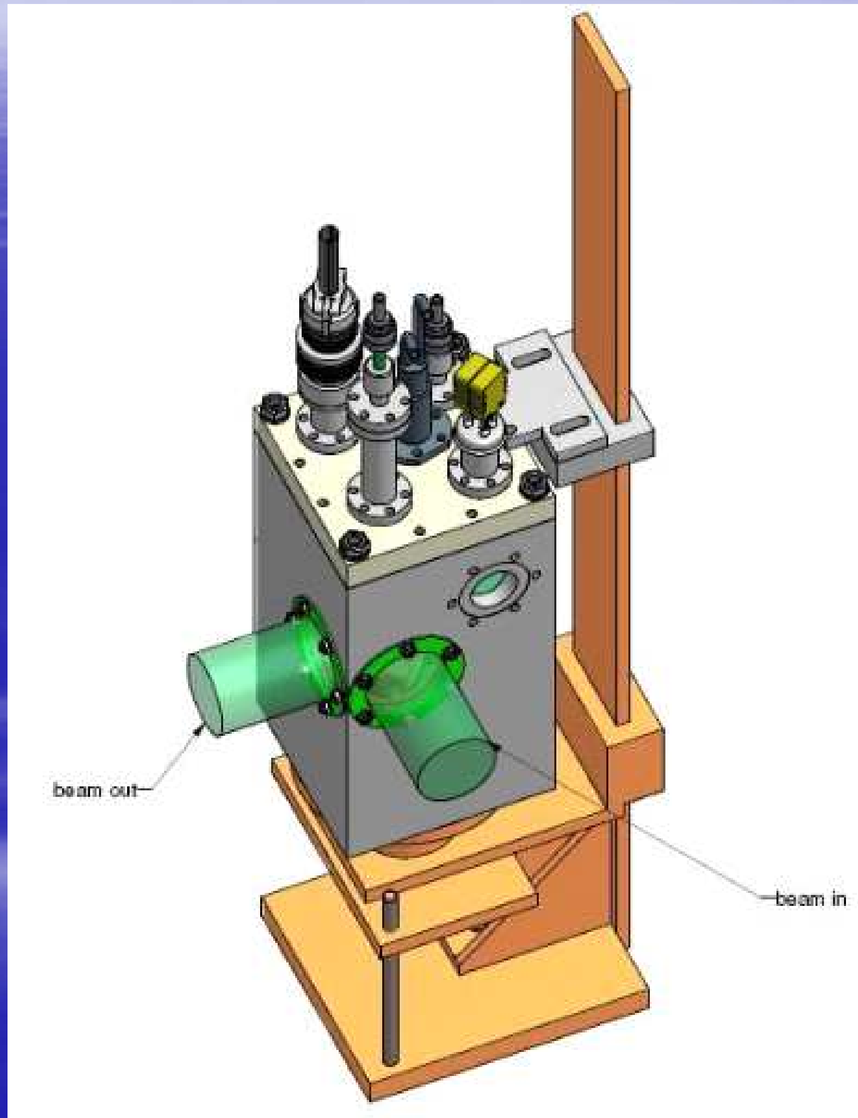
The PGAA spectrum

Energy range: 0-12000 keV
Resolution: 2-3 keV



Reaction cell for PGAA





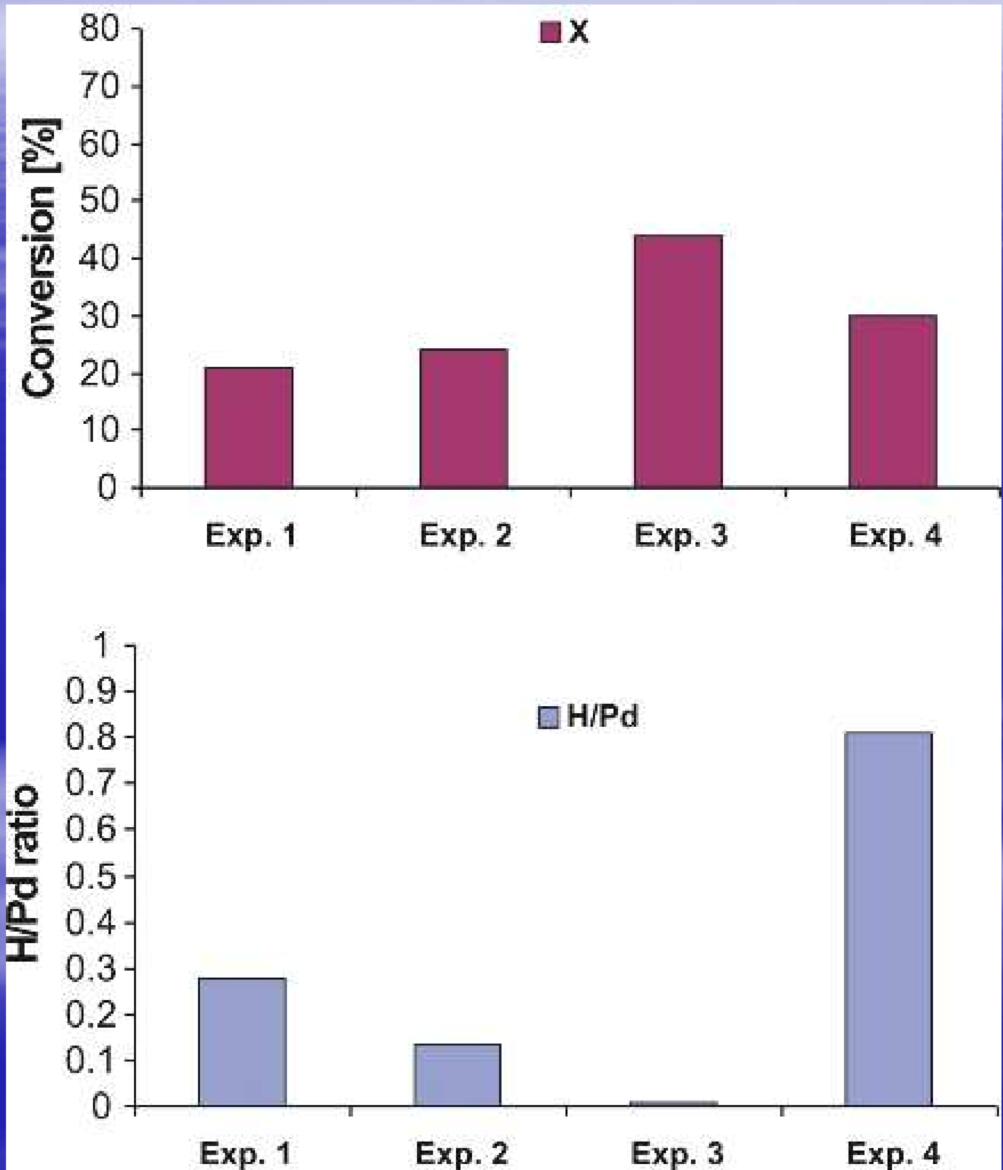
Zs. Révay et al., *Anal. Chem.* **2008**, *80*, 6066.

Methodology

1. Experiment in N_2 (typically @120°C): to measure hydrogen content not related to the sample
2. Experiment in H_2 (typically near RT)
3. Experiments in hydrogenation (e.g. $C_xH_{2x-2}+H_2$; $C_xH_{2x-2}+C_xH_{2x}+H_2$)
4. If needed check [H] in N_2

+ Correction for gas phase H background

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 $cm^3 min^{-1}$
1-pentyne: 1.6 $cm^3 min^{-1}$ in N_2

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

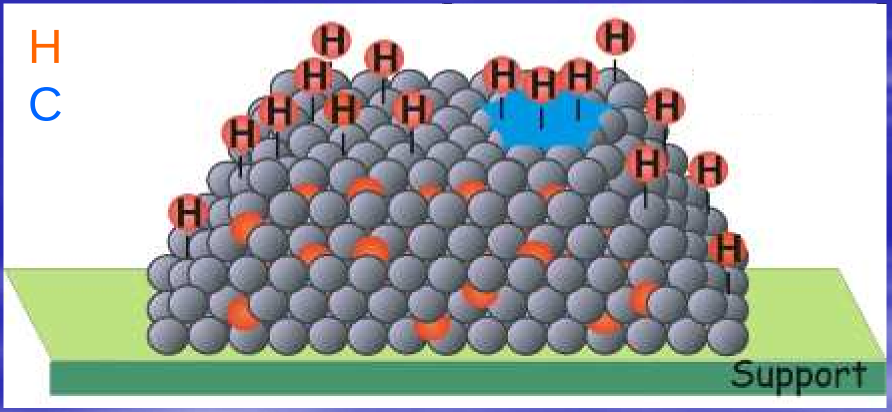
No correlation!

D. Teschner et al., *Science* **2008**, *320*, 86.

PGAA: H/Pd

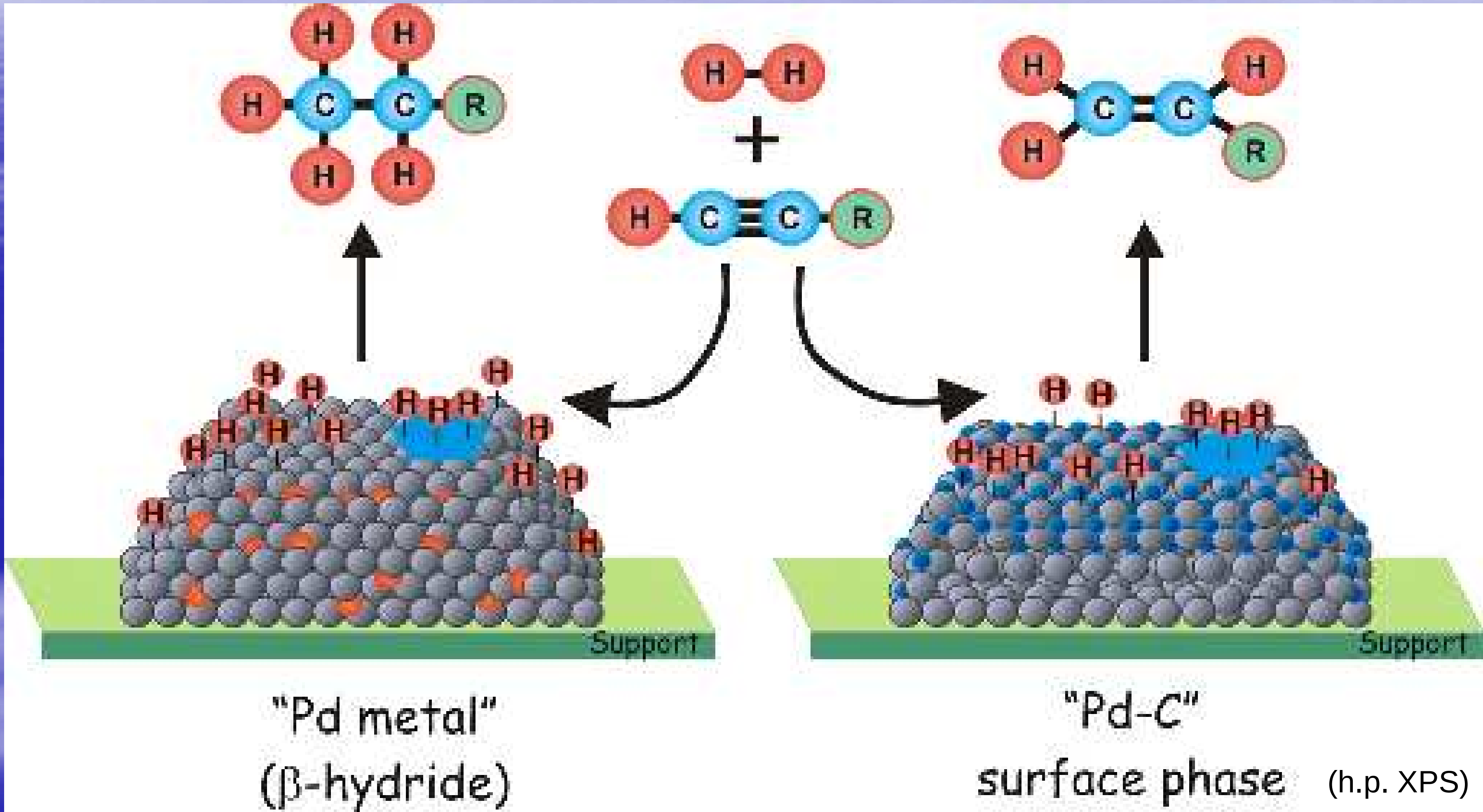
- Alkene → Alkane:
- Alkyne → Alkane:

Hydrogen content always high: 0.8-1 H/Pd



D. Teschner et al., *Science* **2008**, *320*, 86.
D. Teschner et al., *Angewandte Chemie* **2008**, *120*, 9414.

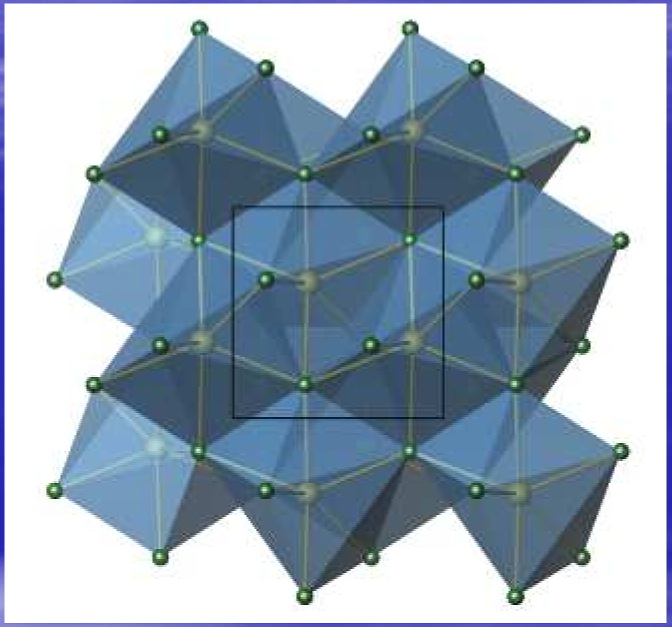
Model: 1-pentyne hydrogenation



(h.p. XPS)

Pd-intermetallic compounds

PdGa



Isolated Pd site

- Covalent bonding
- Modified electronic structure

No H dissolution (PGAA)

Excellent selectivity in acetylene semi-hydrogenation

J. Osswald et al., *J. Catal.*, **2008**, 258, 210.
K. Kovnir et al., *Surf. Sci.*, *in press.*

Pros & Cons; Possibilities

- Bulk characterization (even for H)
- Easy adaptation to “in situ”
- H/D exchange
- Effective detection: H, B, S, Cl, Co

- Time resolution: (min-h) strongly depending on the element sensitivity

- Little sensitivity: C, O, Al, Si, Sn
- Little available: only at cold neutron sources

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