AQura
analytical solutions

materials valley

Workshop 19. April 2012
Neueste Methoden der Analytik und deren industriell nutzbares Anwendungspotential

Struktur und Zusammensetzung von Nanopartikeln

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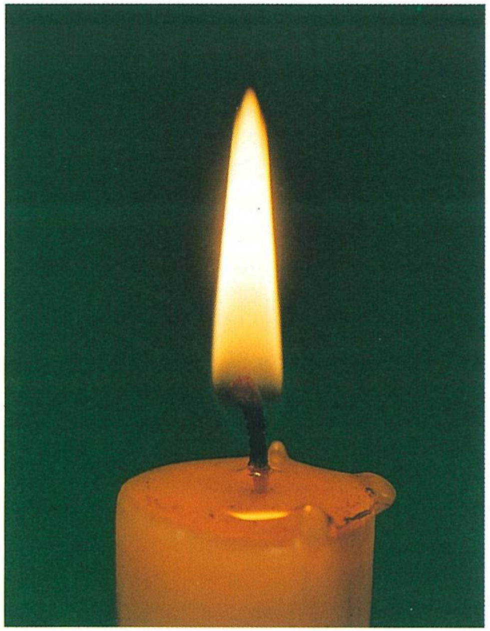
Struktur und Zusammensetzung von Nanopartikeln

1. Industrieruße: Verstärkerfüllstoffe für Polymersysteme
2. Edelmetalle auf Ruß: Brennstoffzellenkatalyse (PEM)
3. Palladium auf Aktivkohle: Heck Reaktion
4. Hydrierkatalysatoren: der Lindlar Katalysator und Pd/C
5. Para-Wasserstoff als Oberflächensonde
6. Zusammenfassung

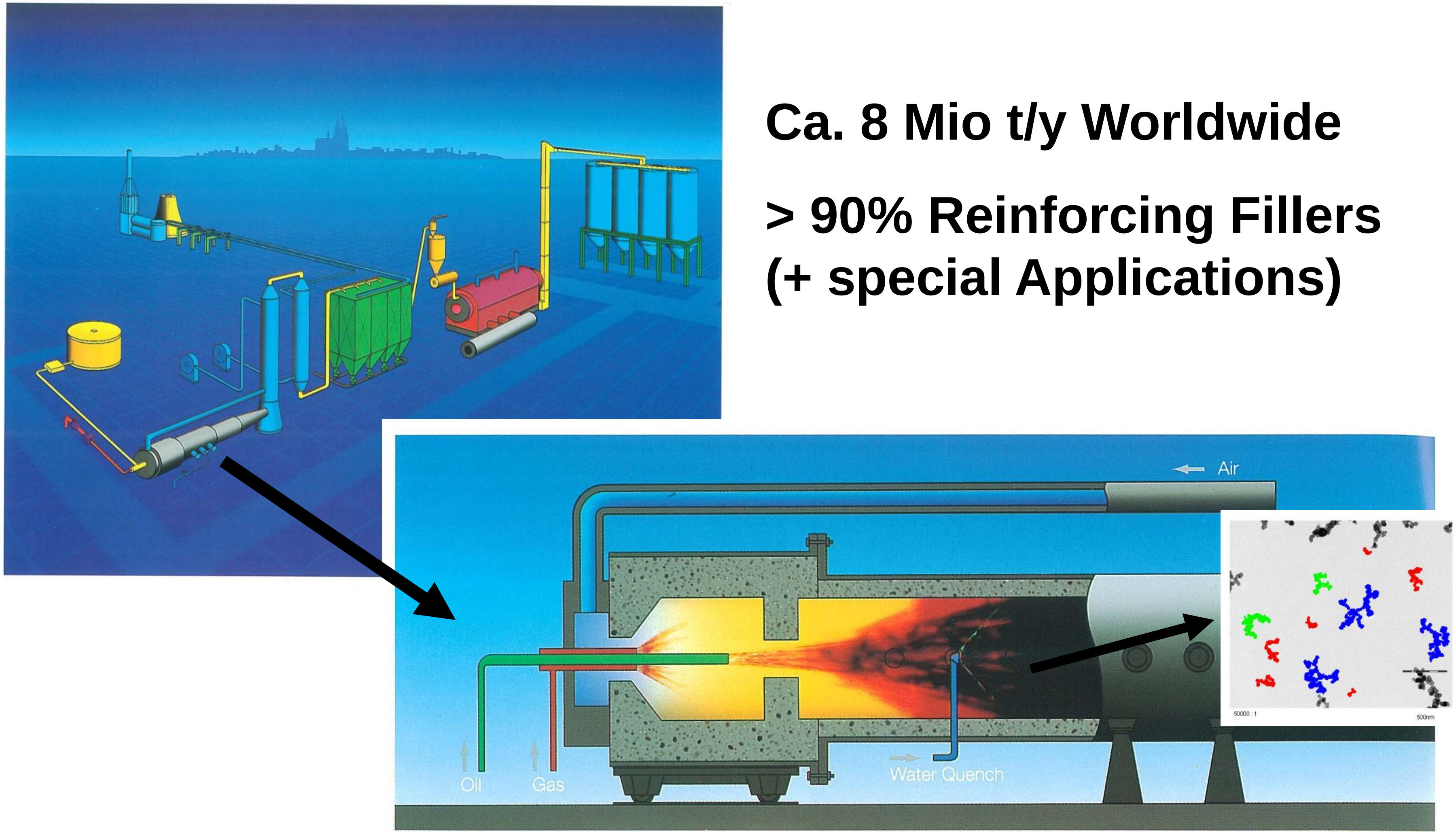
1. Industrieruße: Verstärkerfüllstoffe für Polymersysteme

Soot

Carbon Blacks



Production Plant of Industrial Carbon Blacks: „Gas, Oil, Air minus Hydrogen“ → Tailored Particles



Ca. 8 Mio t/y Worldwide

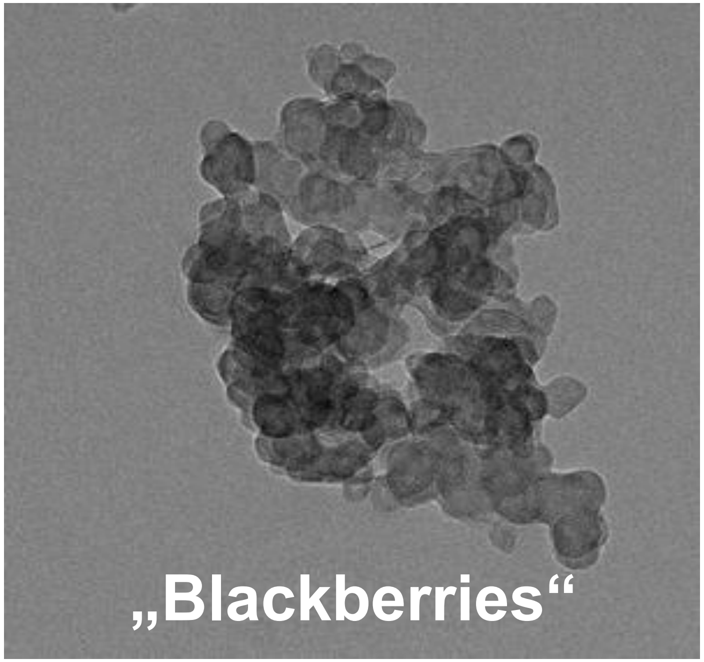
> 90% Reinforcing Fillers (+ special Applications)

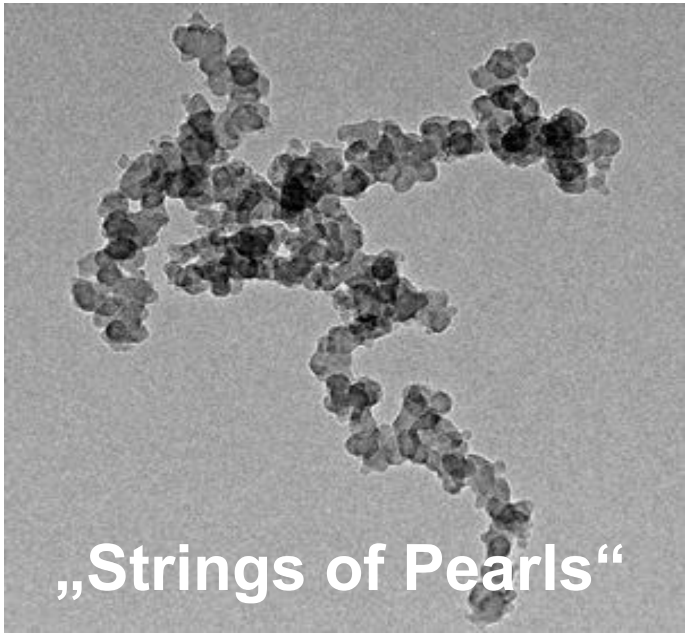
Production of Carbon Black: Abstraction of Hydrogen from Feedstocks; Supervision of Morphological Parameters by Transmission Electron Microscopy (TEM)

$$C_mH_n + yO_2 \rightarrow 2yCO + n/2\ H_2 + (m - 2y)O_2$$

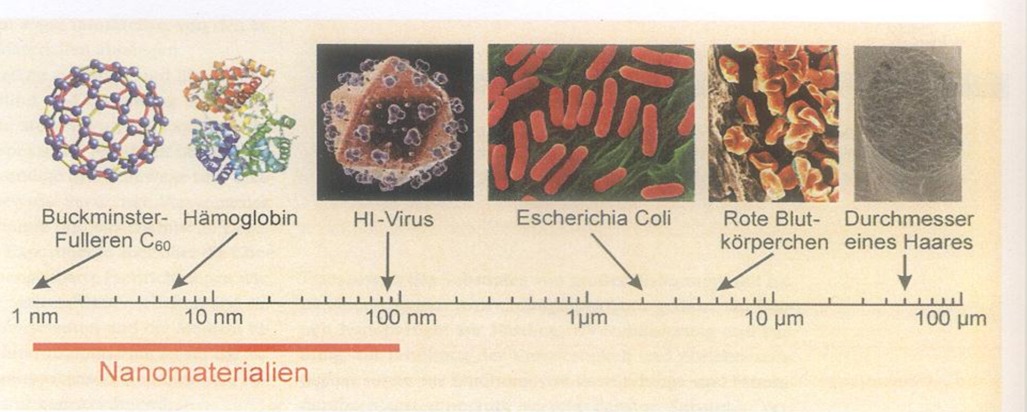
$m > 2y$

$C/O > 1$

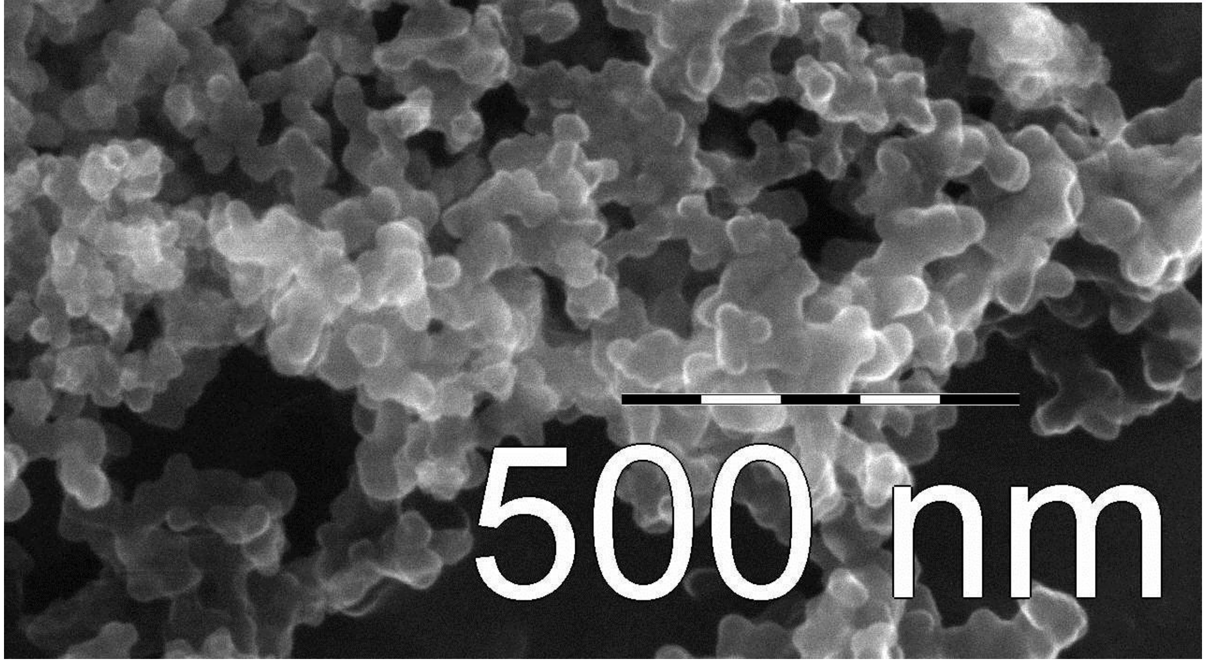




Nanoparticles or nanostructured Particles ?

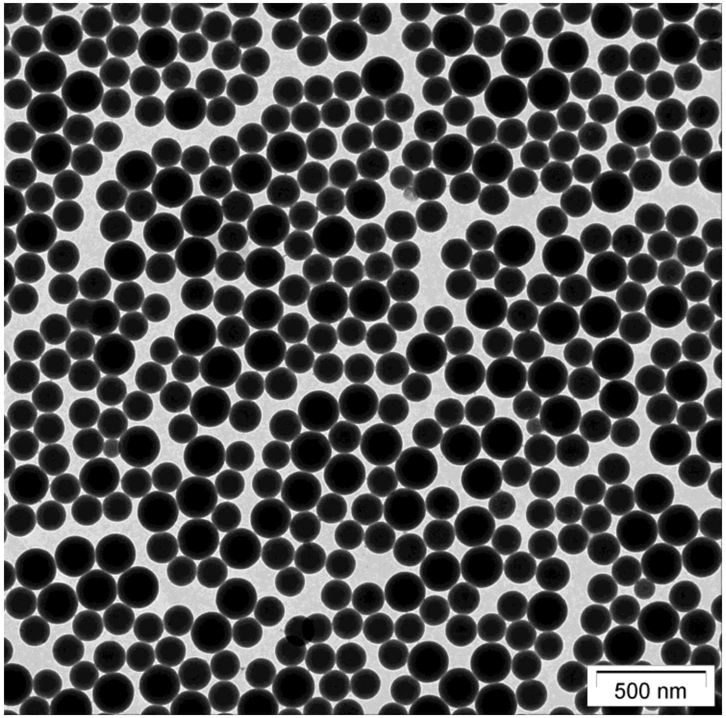


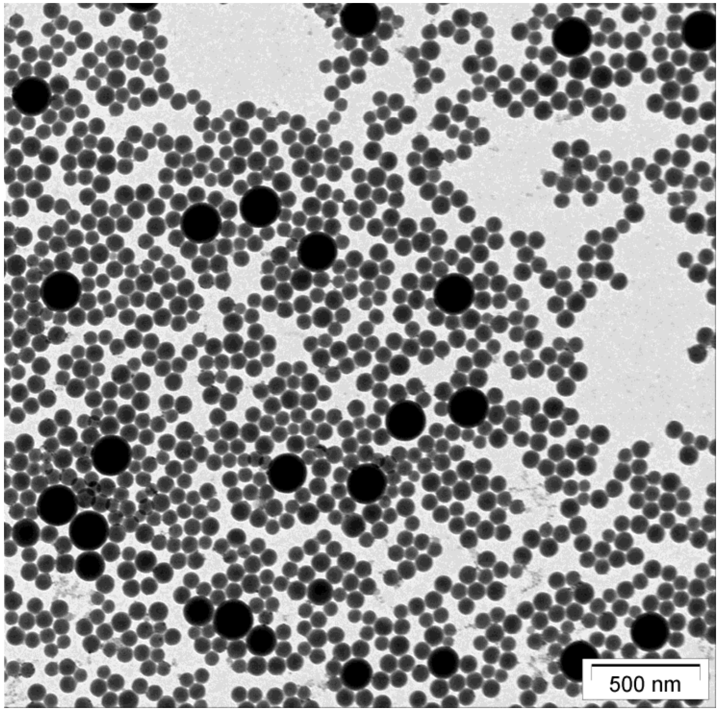
S. Becht, S. Ernst, R, Bappert, C. Feldmann, Chem. in unserer Zeit, 2010, 44, 14.



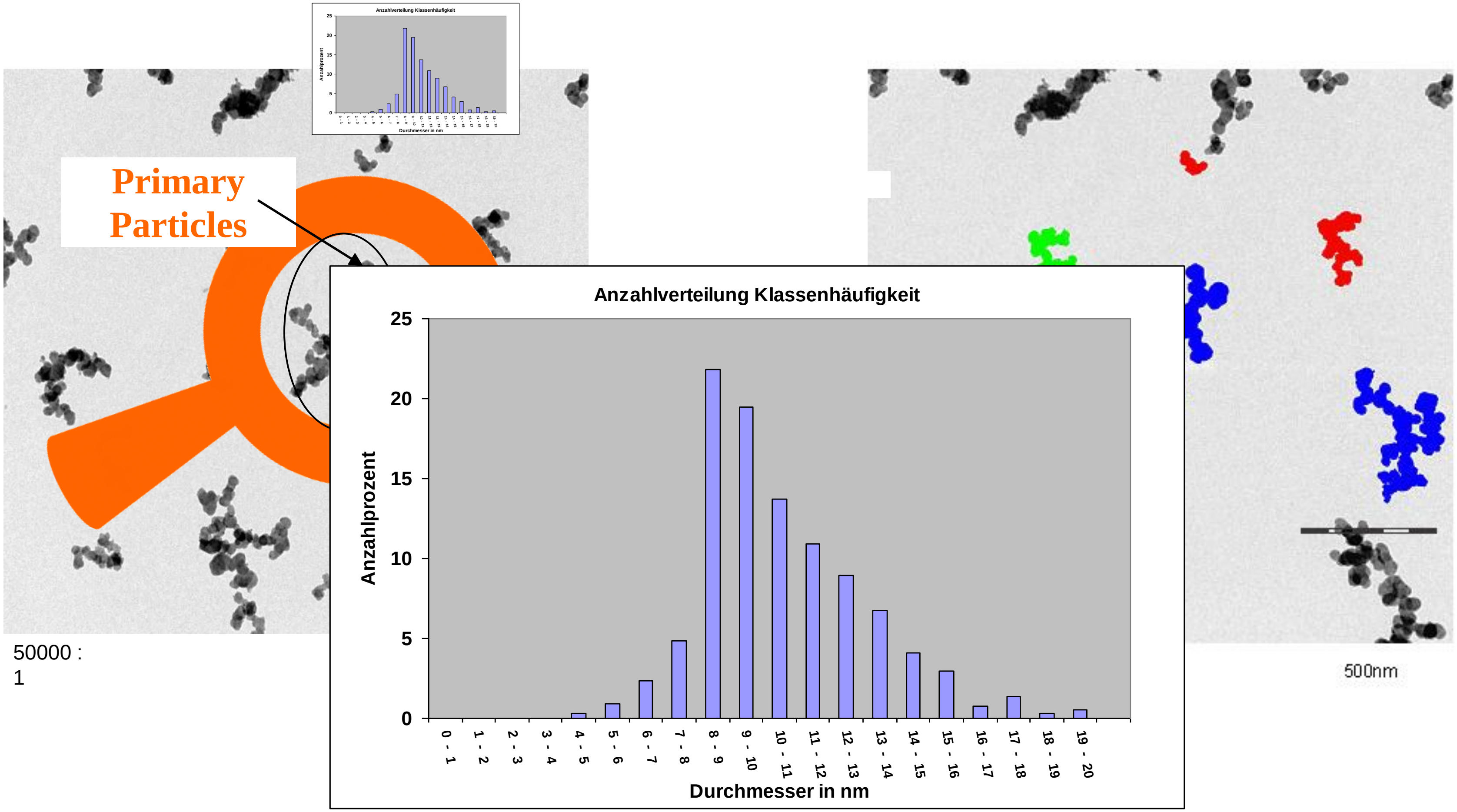
Nano ?

TEM: Particle Size Distribution, Polymer Latices, Bi-Modal Size Distribution, „Easy“-Case

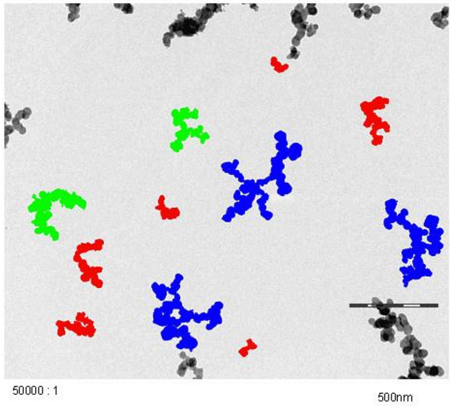




TEM: Characterisation of Primary Particles and Aggregates; Particle Statistics and Classification Analysis; Supervision needed (Carbon Blacks, Silicas, Speciality Oxides….)



On Focus:



Structure / Morphology

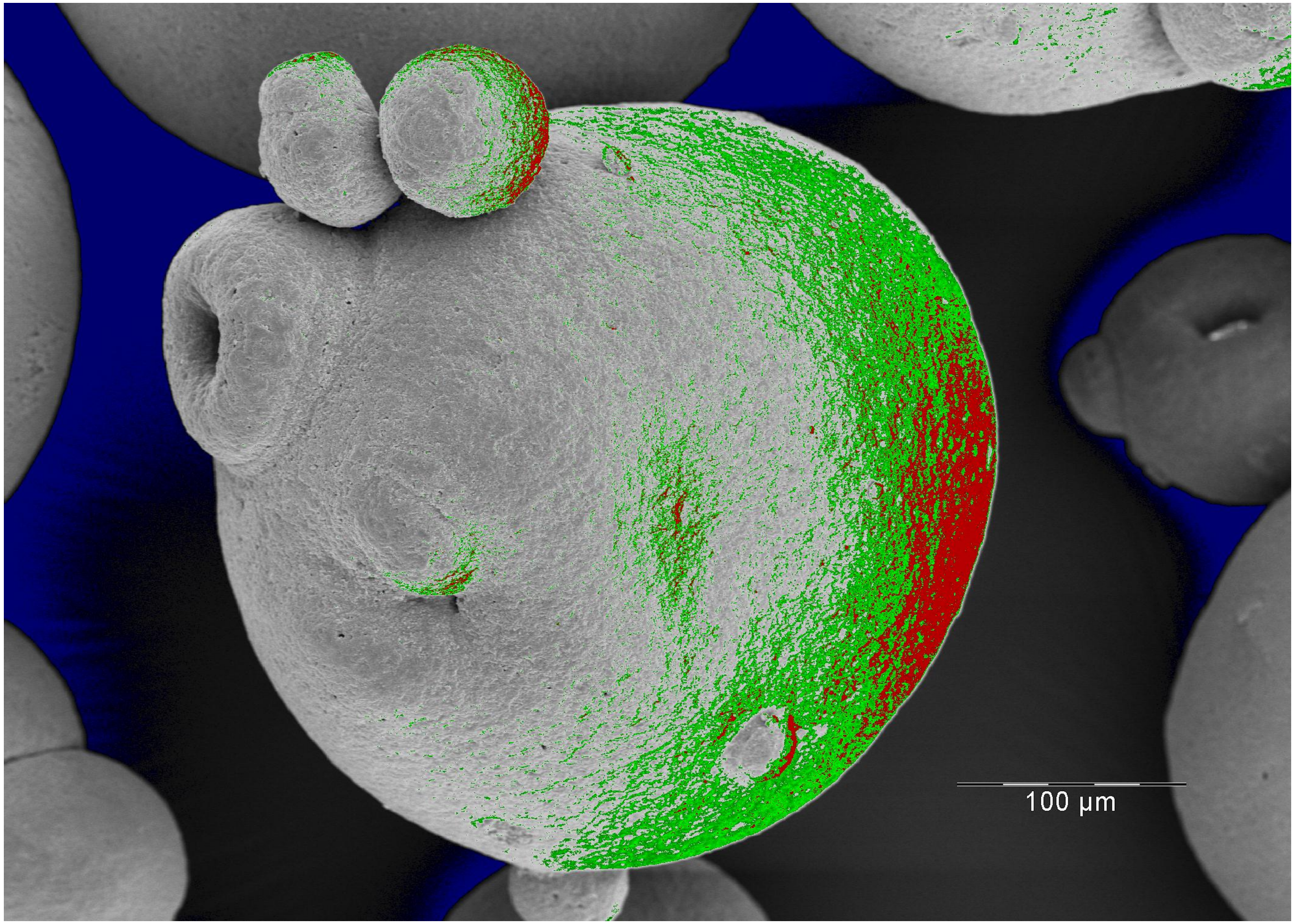
Chemical Composition / Purity

- **Structure Inside of the Primary Particles (Sub-nanometer Range)**
- **Primary Particle Size / Particle Size Distribution**
- **Aggregate Size, Aggregate Shape, Aggregation / Agglomeration**
- **Surface Chemistry and Structure at the Nanoscale (Surface Functional Groups: H, O, N, S…)**

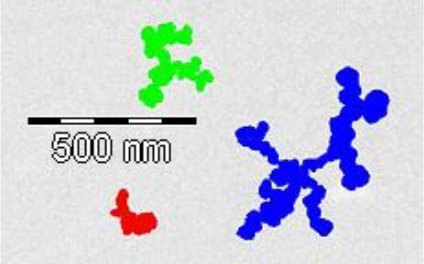
➢ **Rheological Properties (in-rubber)**

➢ **Dispersability in Non-polar or in Polar Media**

Statistical Relevance ???

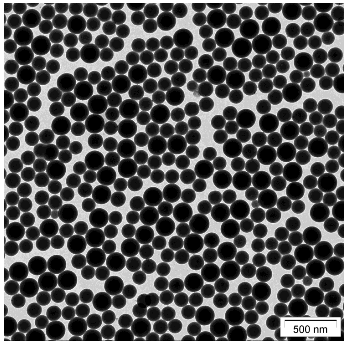


→ Statistically Relevant Data Needed

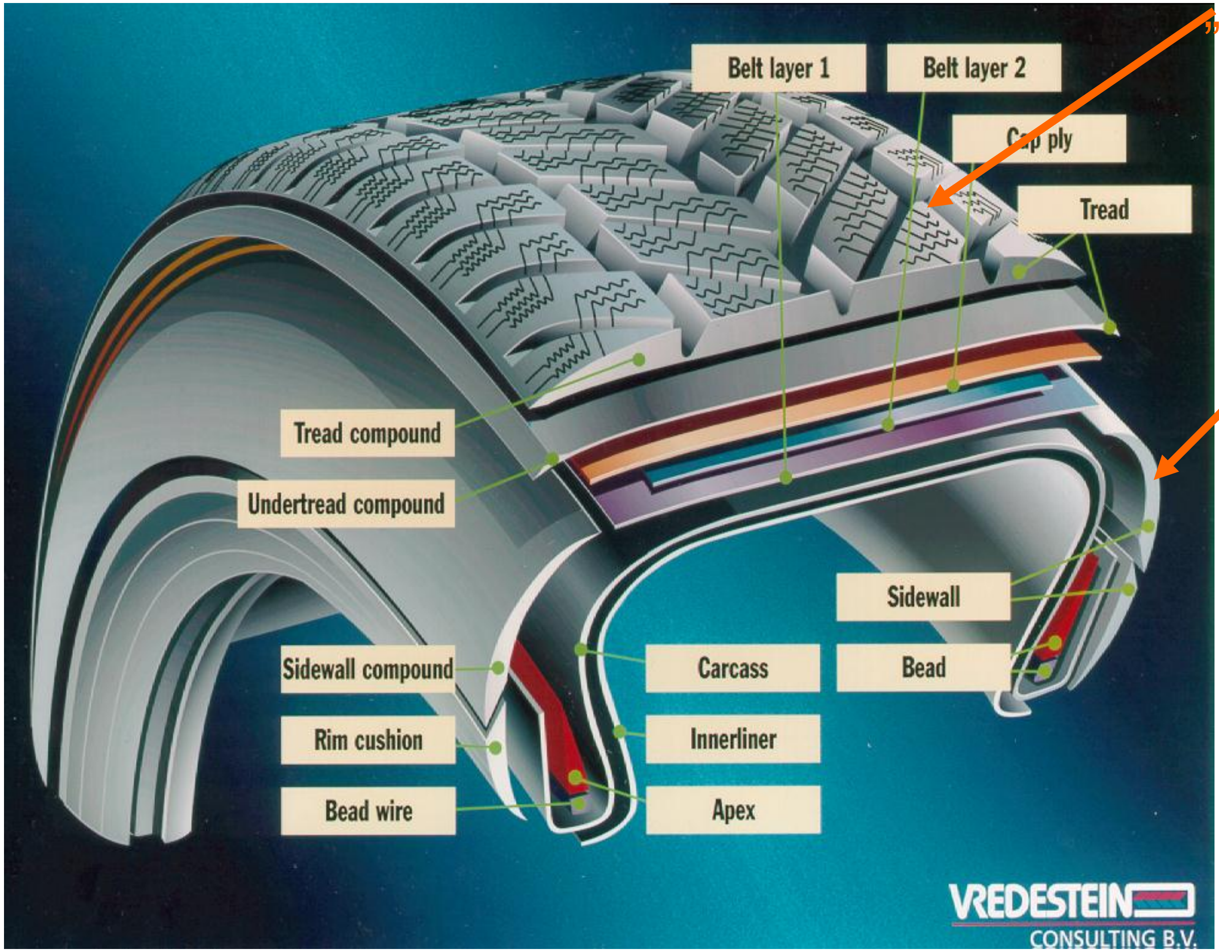


Average Values for 2000-10000 Particles:

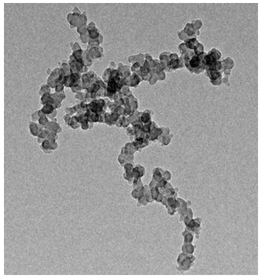
- **Primary Particle Size / Particle Size Distribution / Polydispersity**
- **Projected Area of Aggregates**
- **Circumference / Convex Circumference**
- **Equivalent Circle Diameter (ECD)**
- **Minimum / Maximum Diameter, Feret Min. / Max. Diam.**
- **Shape Factors**
- **Void Volume / „Structure“**
- **Number of Primary Particles/Aggregate …**



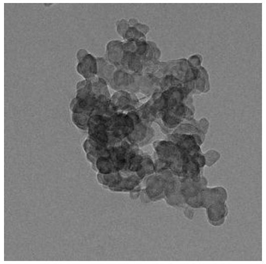
Correlation between Morphology and Surface-Chemistry of Carbon Blacks and their In-Rubber Performance

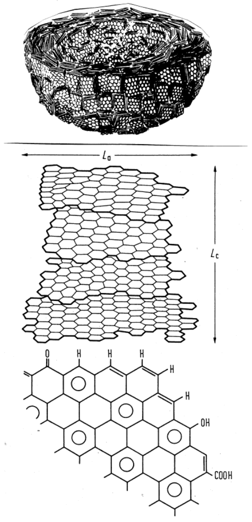


„Strings of Pearls“



„Blackberries“



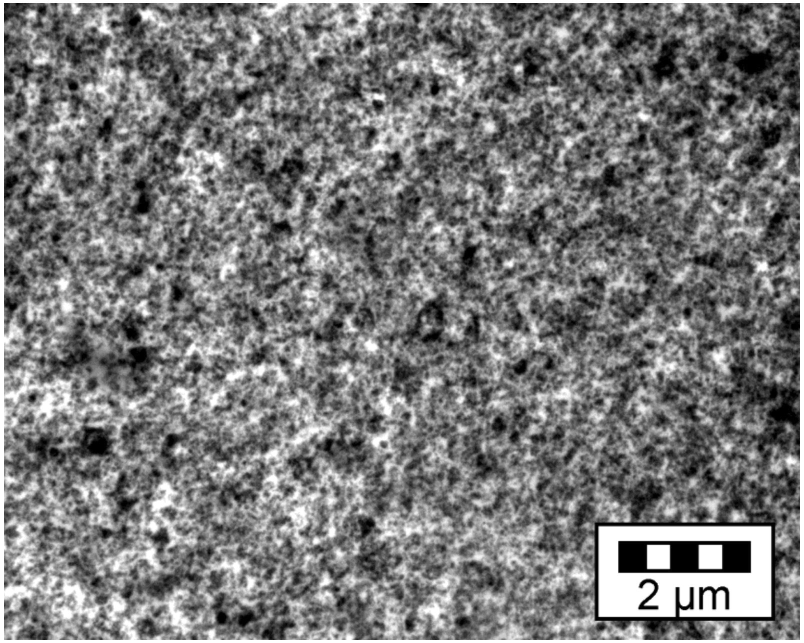


Terminating protons

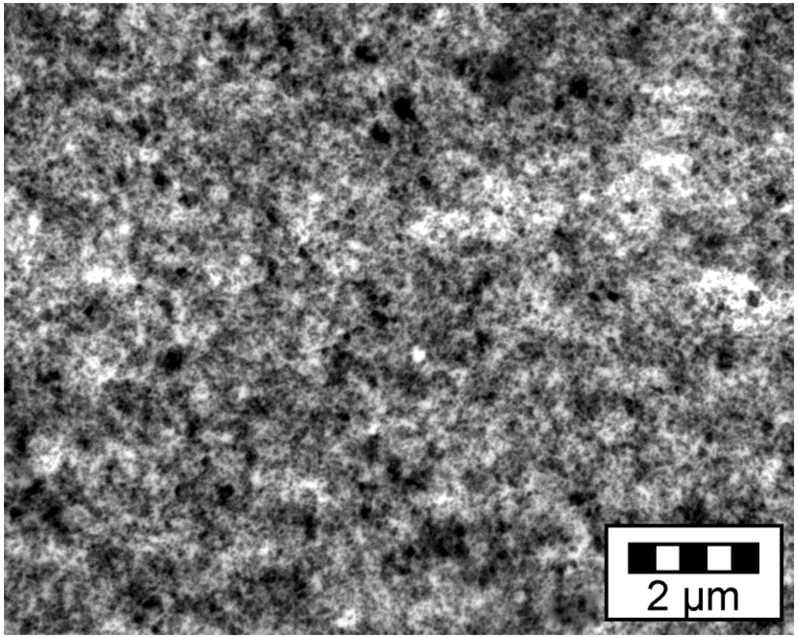
TEM of Cryo-Ultramicrotome Sections of Rubber: Control for Fine-Tuning Product Performance

- Dispersion Techniques
- Dedicated Adjustment of Filler/Matrix-Interactions, Filler/Matrix-Cross-Linking

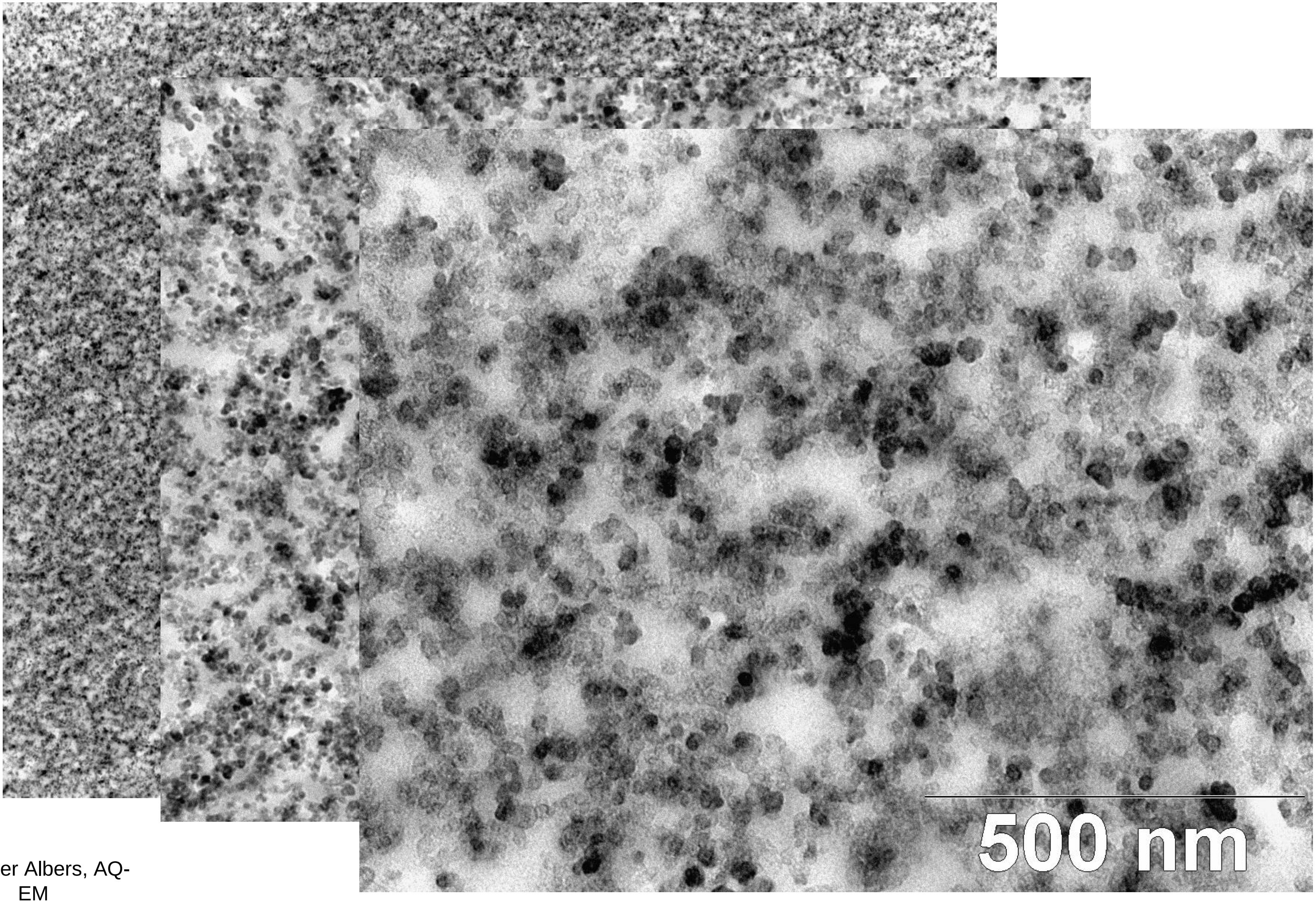
Adequate



To be improved



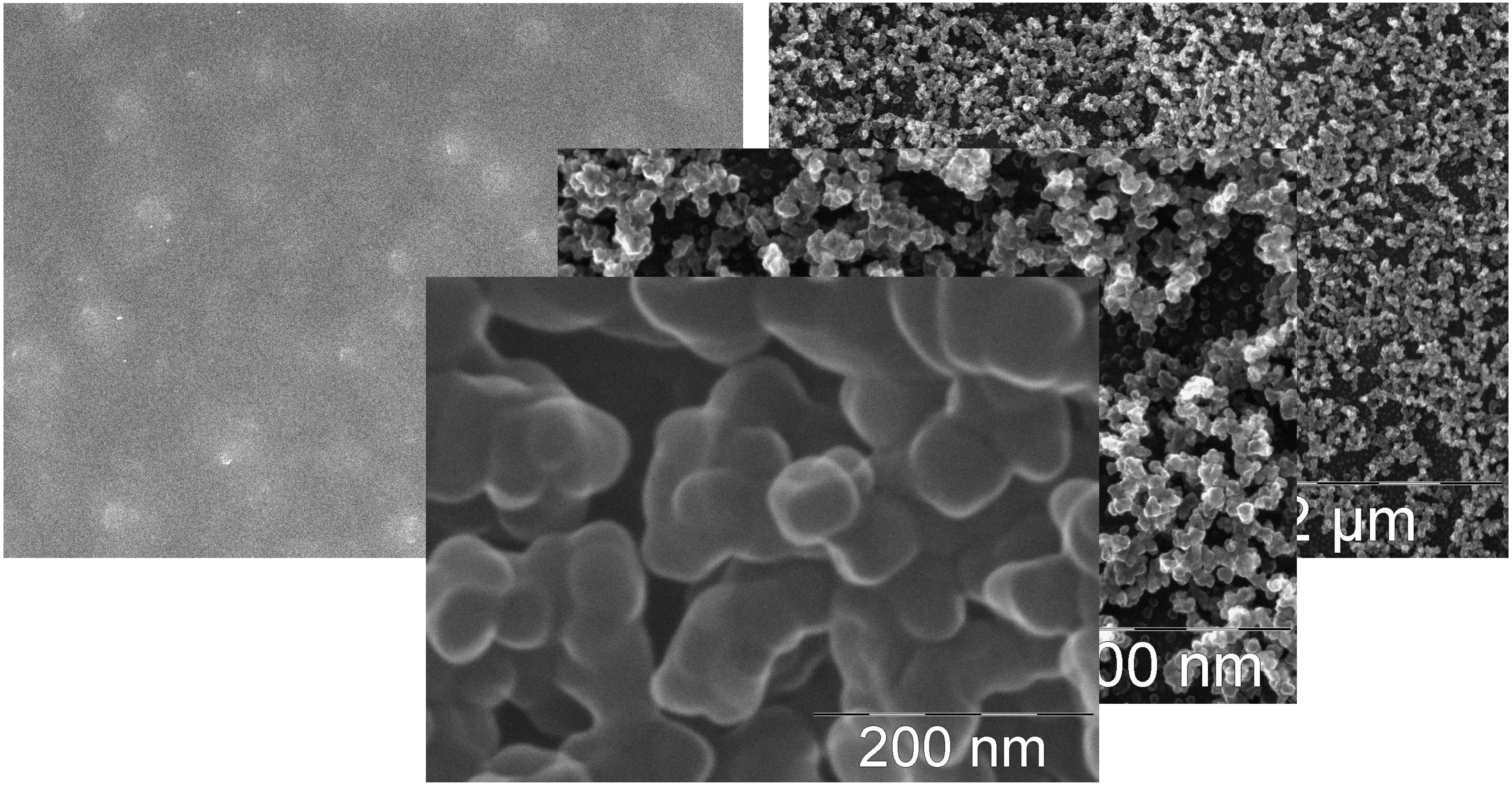
Reinforcing Fillers: Macro-/Micro-Dispersion in the Rubber Matrix; check by TEM of Cryo-Sections



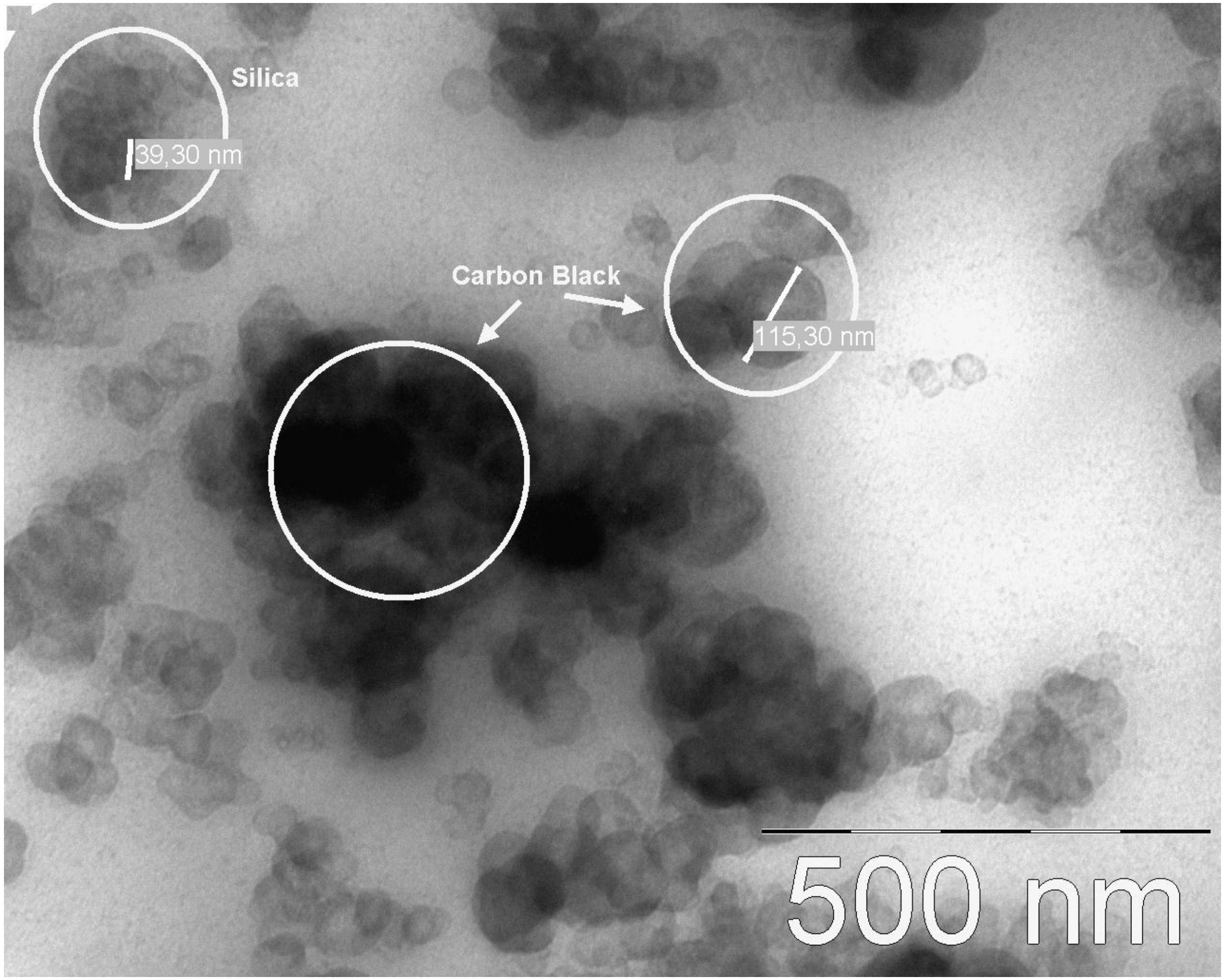
SEM of Tyre Tread before and after Plasma Erosion: Visualisation of the Interpenetrating Network of Aggregates/ Agglomerates of Carbon Blacks (Silicas, ZnO etc.)

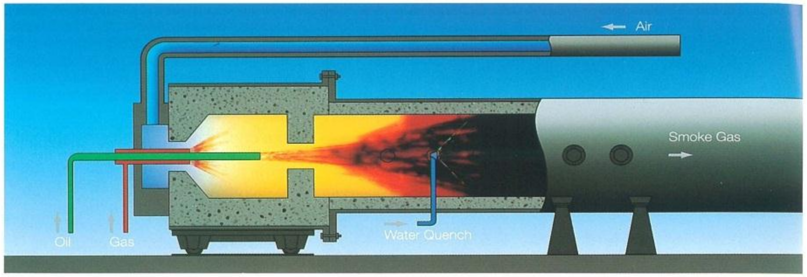
→ Elasticity Module, Energy Storage, Payne-Effect / Temperature- and Frequency-Dependence of Elastic Properties / Enhanced Adsorption Power of CB

→ Lower Dynamic Stress Softening; passenger car / lorry



TEM/EDX: Aggregates consisting of 40 nm silica or 115 nm CB primary particles → local composition





Parameters to be changed:

Gas / Oil / Air ratio

Reactor geometry

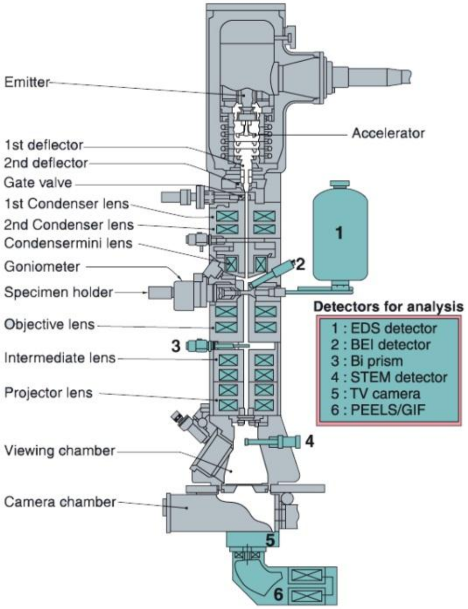
Choke properties

Quench position

→ Fine Structure of the Carbon Black Aggregates

→ Nanostructure at the Surface of the Primary Particles

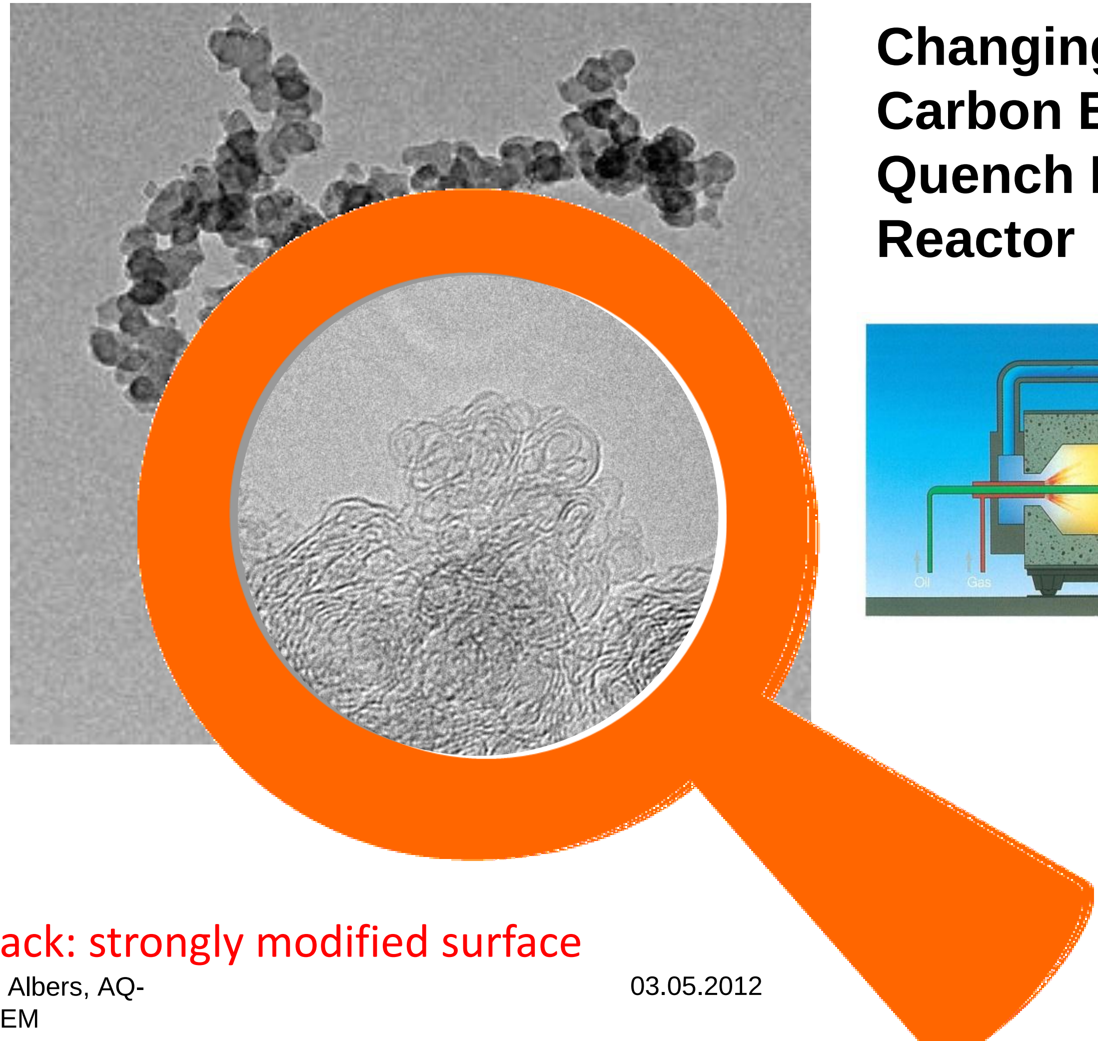
Morphology of CB: High Resolution Transmission Electron Microscopy (HR-TEM), Field Emission Gun



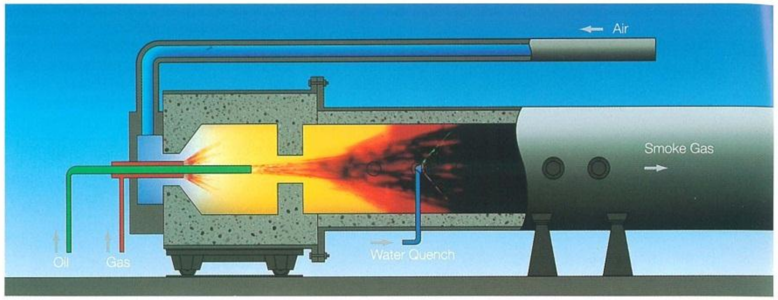
+ Nanoscale-EDX

→ Discrimination between C, ZnO, SiO_2 & others

1) Size, Shape and Structural Complexity of the Aggregates
2) Controlled variation of Surface Structure at the Nanoscale;
size of basic structural units: ca. 1.2 nm → 0.7 nm

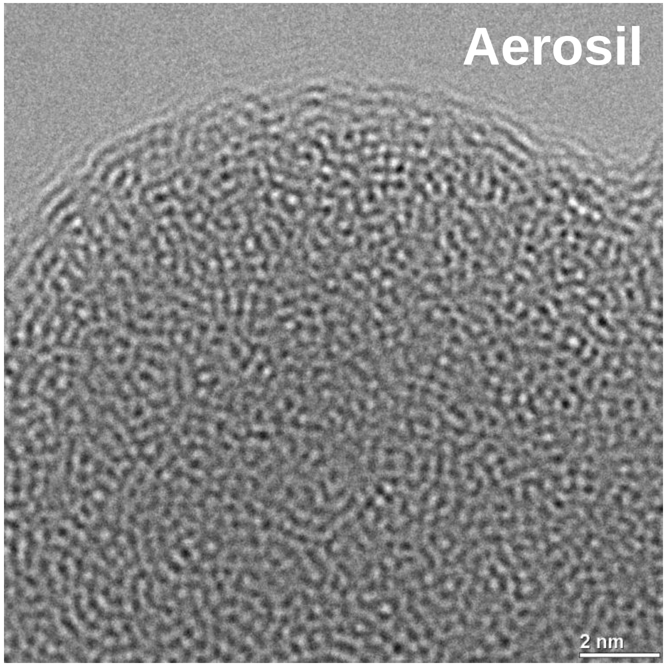


Changing Surface Structure of Carbon Blacks by varying Quench Parameters in the Reactor



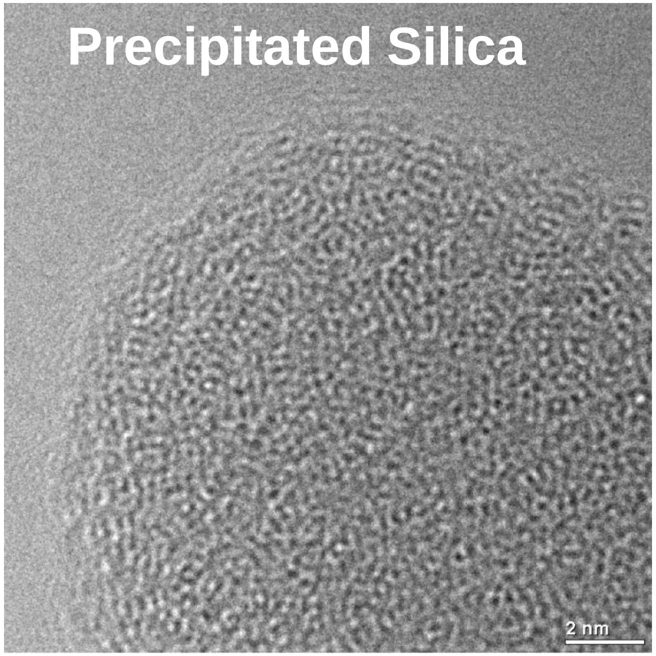
Carbon Black: strongly modified surface

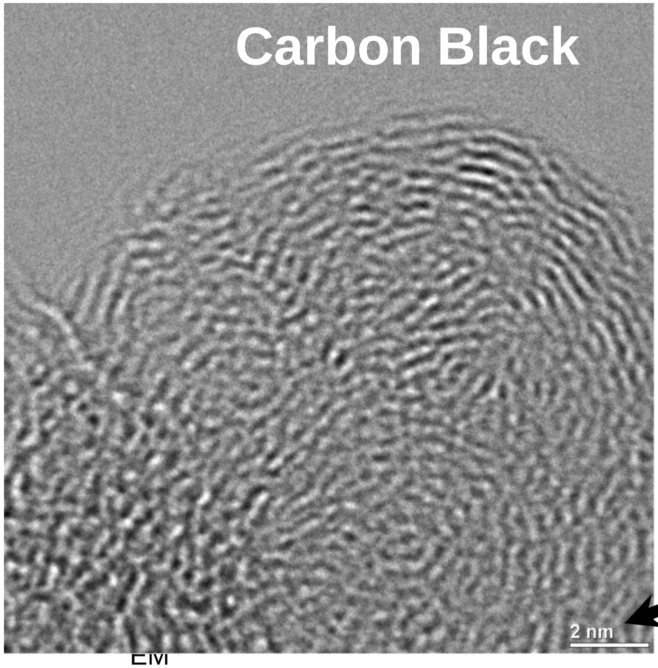
HR-TEM



Amorphous, short-range order

↔

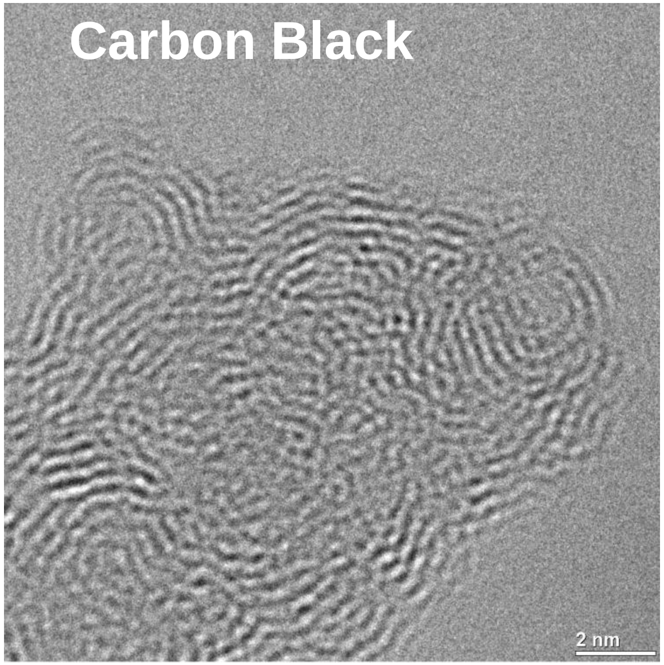




Paracrystalline

↔

Scale bar: 2 nm

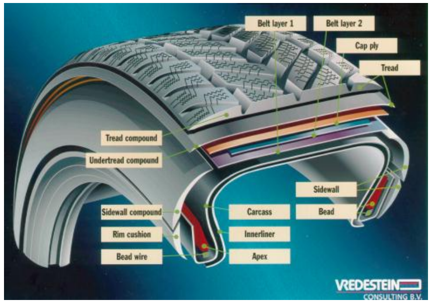


Optimization of the Surface Properties of Carbon Blacks for Tyres: Nanostructure Blacks with enhanced Number of Edges and High-Energic Sites

Lower rolling resistance (EC legal limits) → saves fuel

Improved wet traction, grip → enhanced safety

Reduced abrasion → enhanced time of operation



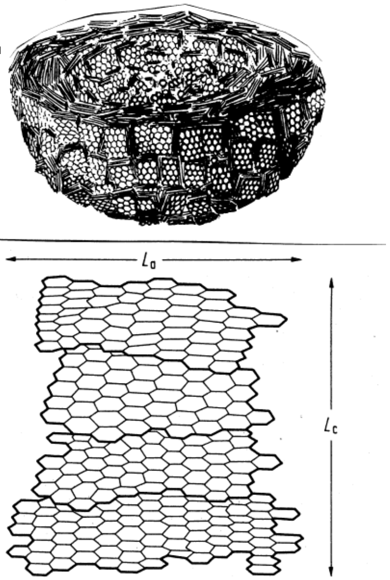
Even a few percent of further improvement of tyre performance by advanced reinforcing carbon blacks and also precipitated silicas and other additives are of high economic relevance and substantially contribute to fuel economy →

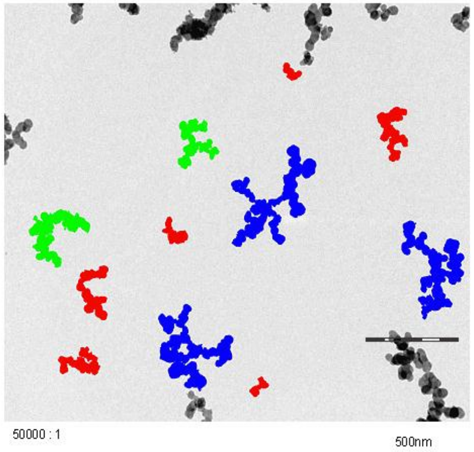
„Green Tyre Mixtures“, ECORAX / Nanostructured Blacks…

- **UN forecast: 2005-2030 No. of passenger cars and heavy trucks worldwide will double**
- **Fuel consumption: largest variable cost factor in operating a fleet on tyres**

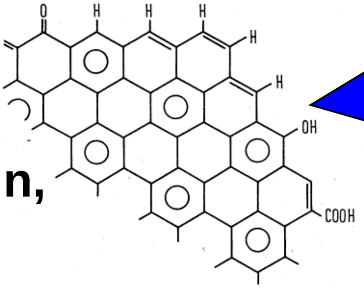
Nanostructure of Carbon Black: Spherical Arrangement of Basic Structural Units (BSU's) in Turbostratic Disorder

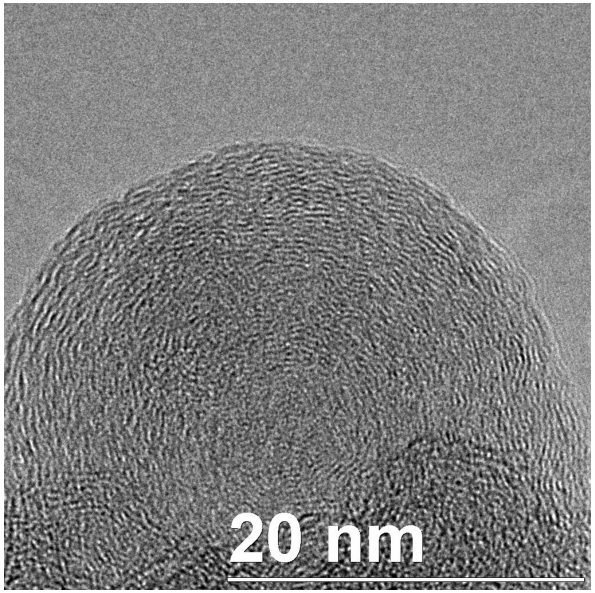
W. Hess et. al.
(TEM) :





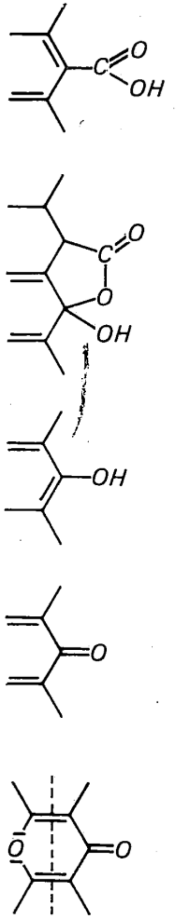
E. Koberstein,
M. Voll :

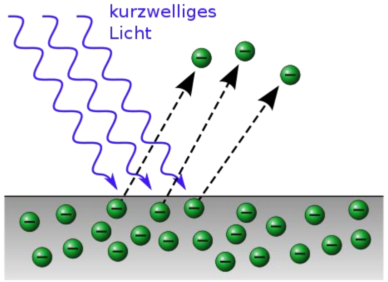




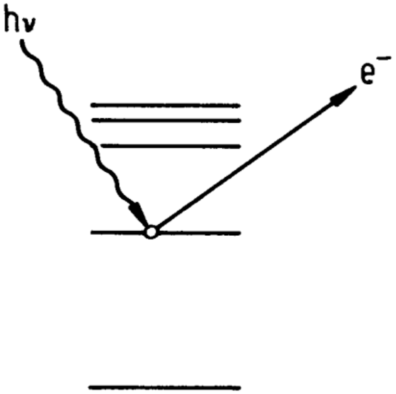
Oxygen-, Nitrogen-, Sulphur-containing Surface Groups and „Terminating Protons"

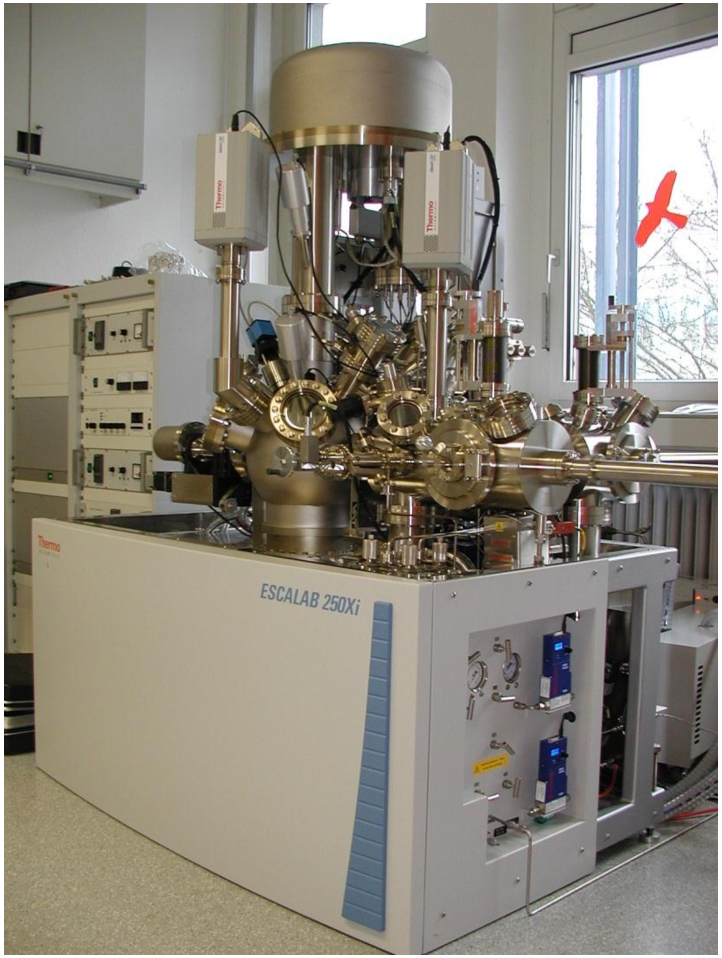
Surface Analysis by XPS and SIMS: Chemical Properties of the Topmost Atomic Layers, the first Nanometers, of Carbon Blacks





XPS





XPS: X-ray Photoelectron Spectroscopy

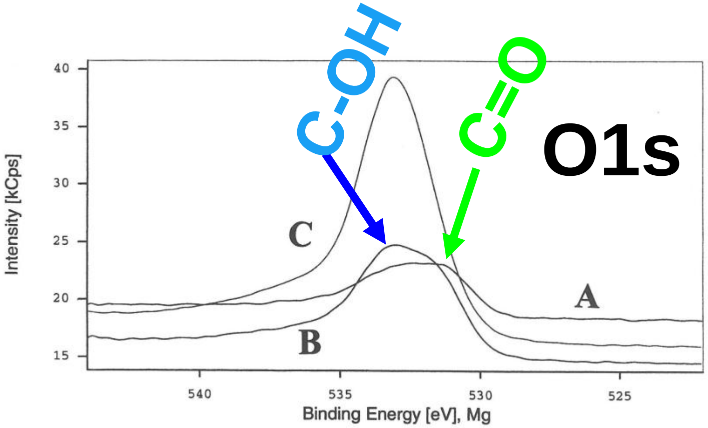
(ESCA: Electron Spectroscopy for Chemical Analysis)

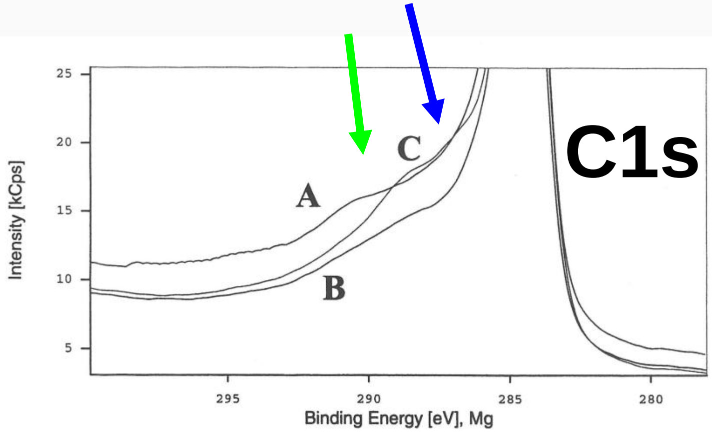
O1s- and C1s-XPS-Signals (+ N1s, S2p) of Carbon Blacks

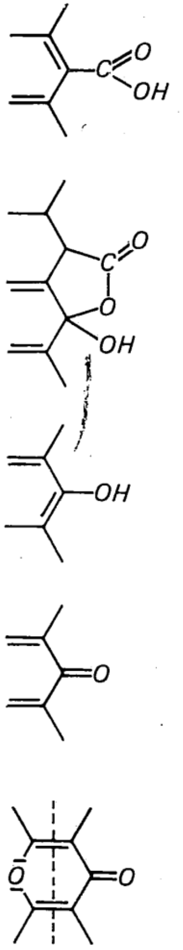
ca. 531 eV C=O groups

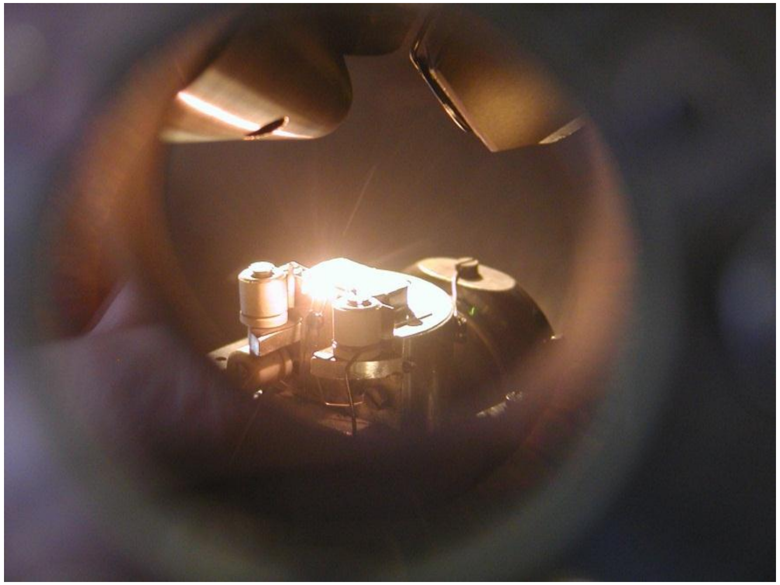
ca. 532-533 eV C-OH groups

ca. 534-535 eV $H_2O_{ads.}$



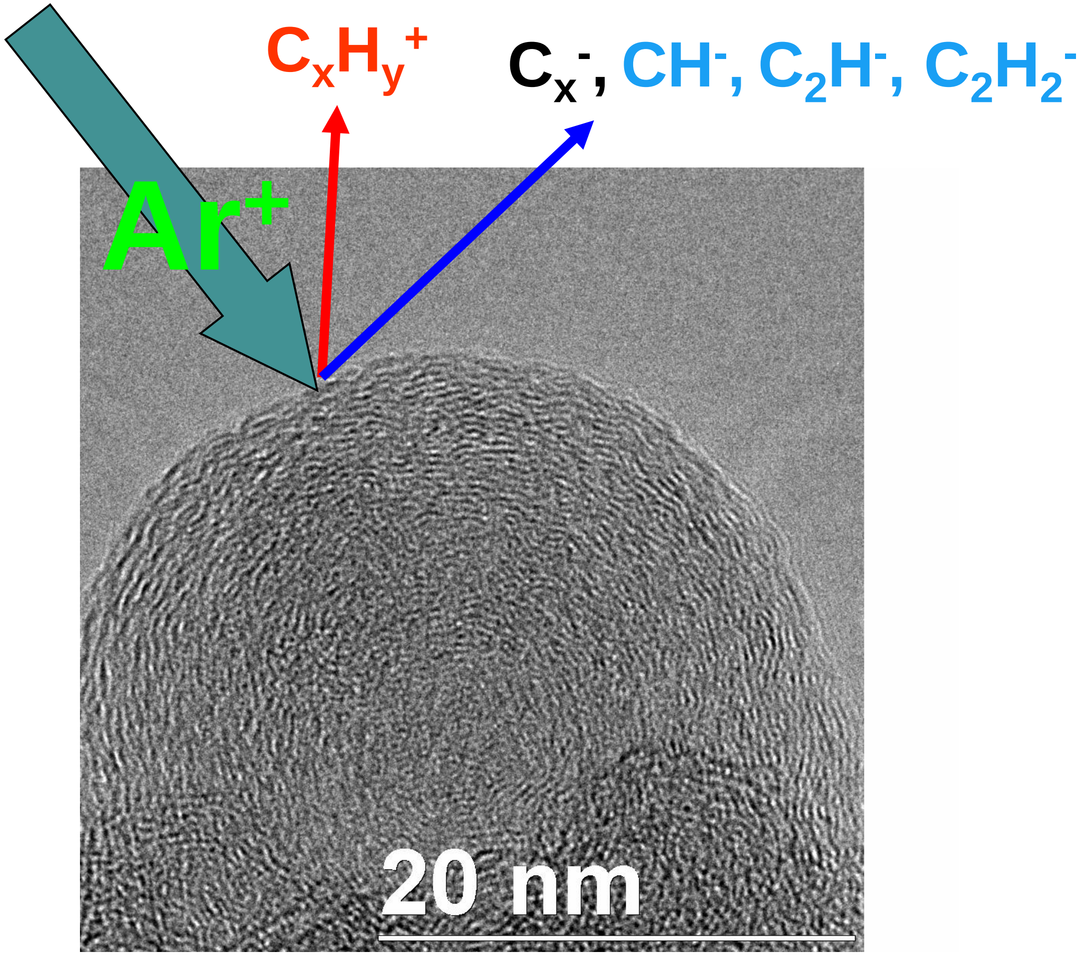


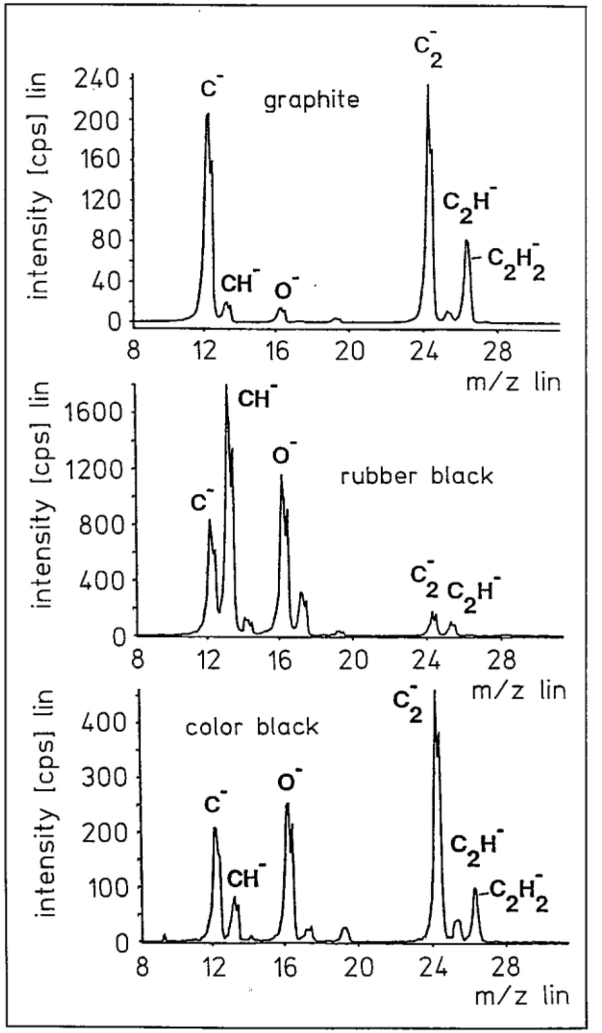




Secondary Ion Mass Spectrometry (SIMS)

static → dynamic mode: ion induced degradation of carbon blacks, measuring aliphatic- and aromatic/graphitic-type fragments – fingerprints for sp^2 /sp^3 character in surface and selvedge regions of CB



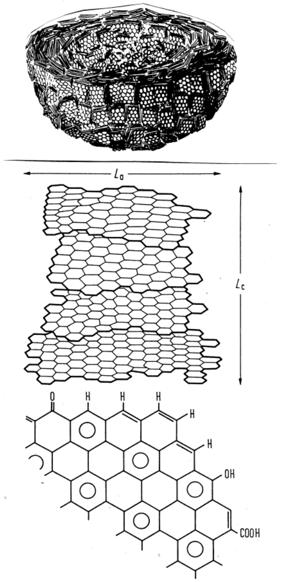


How to further Optimize the Properties of Carbon Black Surfaces? Adjusting the Degree of Filler/Polymer Interaction by controlled Enhancement of sp^2-type Surface-ruggedness. Analytical Proof and Indicator: Terminating Protons

Terminating Protons at the Edges of the BSU‘s are relevant and sensitive indicators for

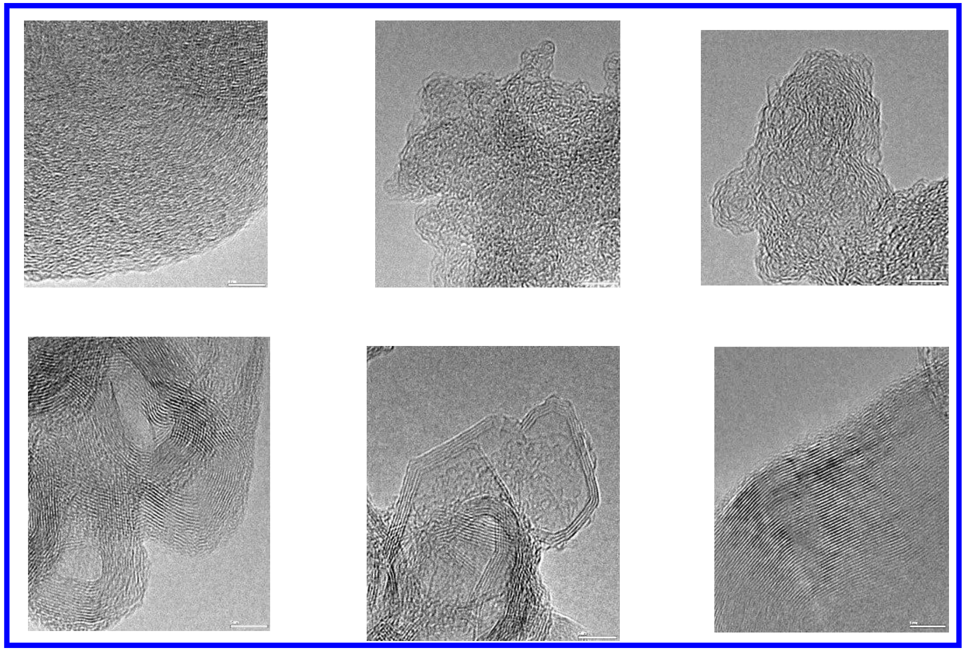
→ Enhanced *Physical* Interaction with the Polymer Chains of the Rubber Mixtures: Surface Roughness/Ruggedness

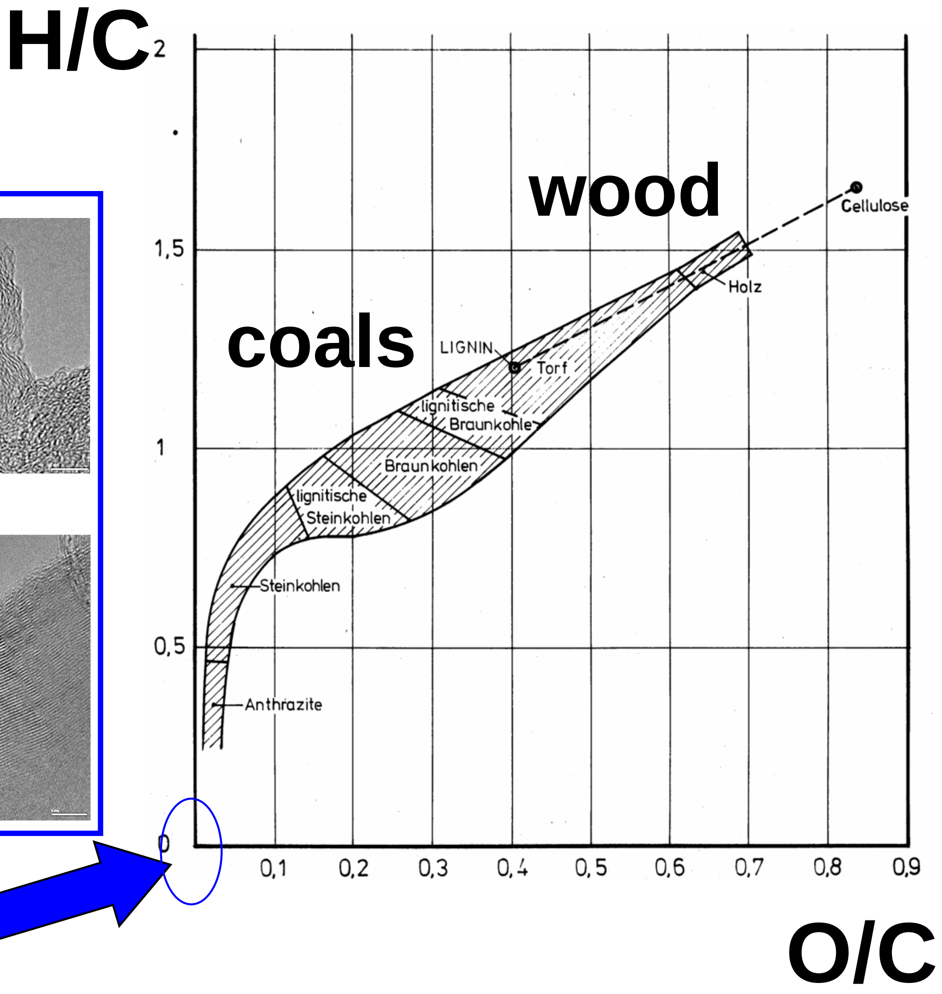
→ Surface Reactivity, *Chemical* Interaction: Conjugated/Non-conjugated Double Bonds, „Bound Rubber Effect“, Vulcanization / Metathesis Reactions….



Challenge: Determination of Proton Dynamics of Carbon Blacks at ca. 4000 µg/g H

(gas blacks, furnace blacks, graphitic matter 6000 → 4000 → 100 µg/g H etc.)





Carbon blacks

- **TEM: imaging at the nanoscale**
- **XPS: C-OH, O=C-OH…**
- **SIMS: C/H-fragmentation characteristics**

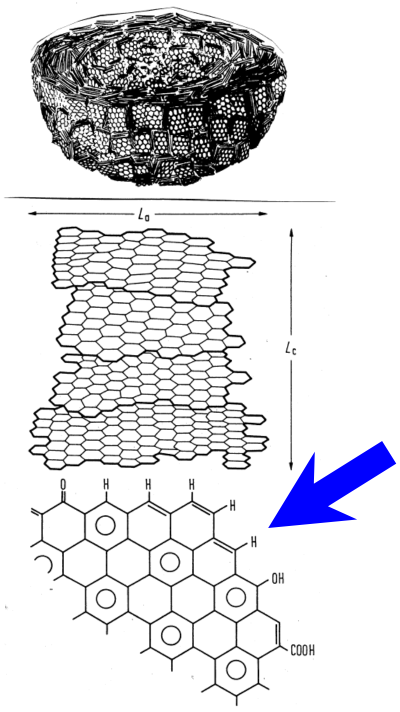
How to Analyze the Hydrogen Bonding on CB?
Spectroscopic techniques?
Terminating Protons ???

Carbon Blacks: Very Finely Divided Materials,
Electrically Conductive Powders :
Infrared-Spectroscopy or NMR may come to Physical Limits: „Carbon Black is Black…“

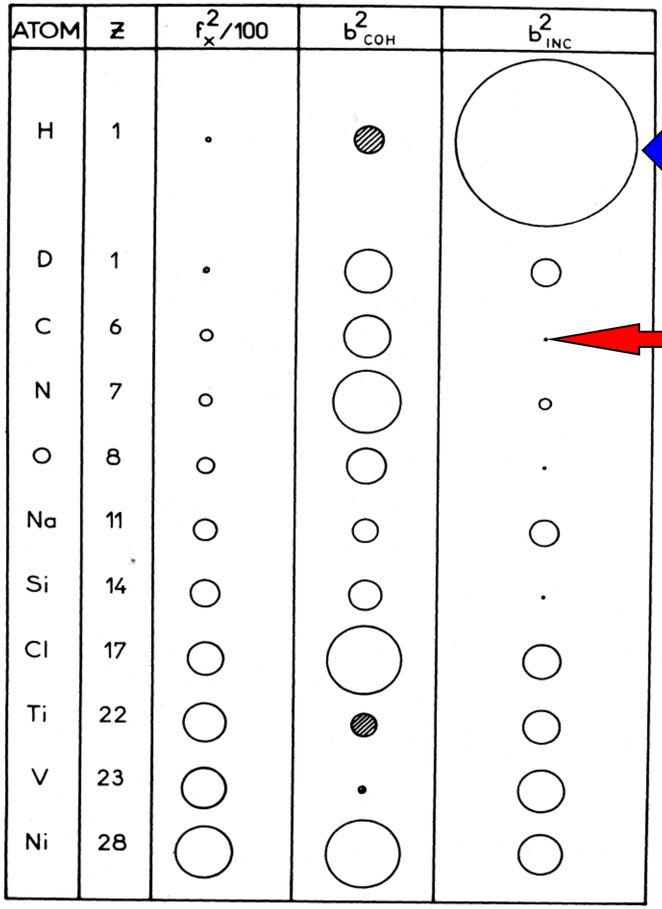
Solution:

IINS Inelastic Incoherent Neutron Scattering

Scattering Cross Sections of Some Elements X-rays: Electron Shell, Neutrons: Atomic Nucleus



Z. Phys. Chem. NF
128, 1; **129**, 29.



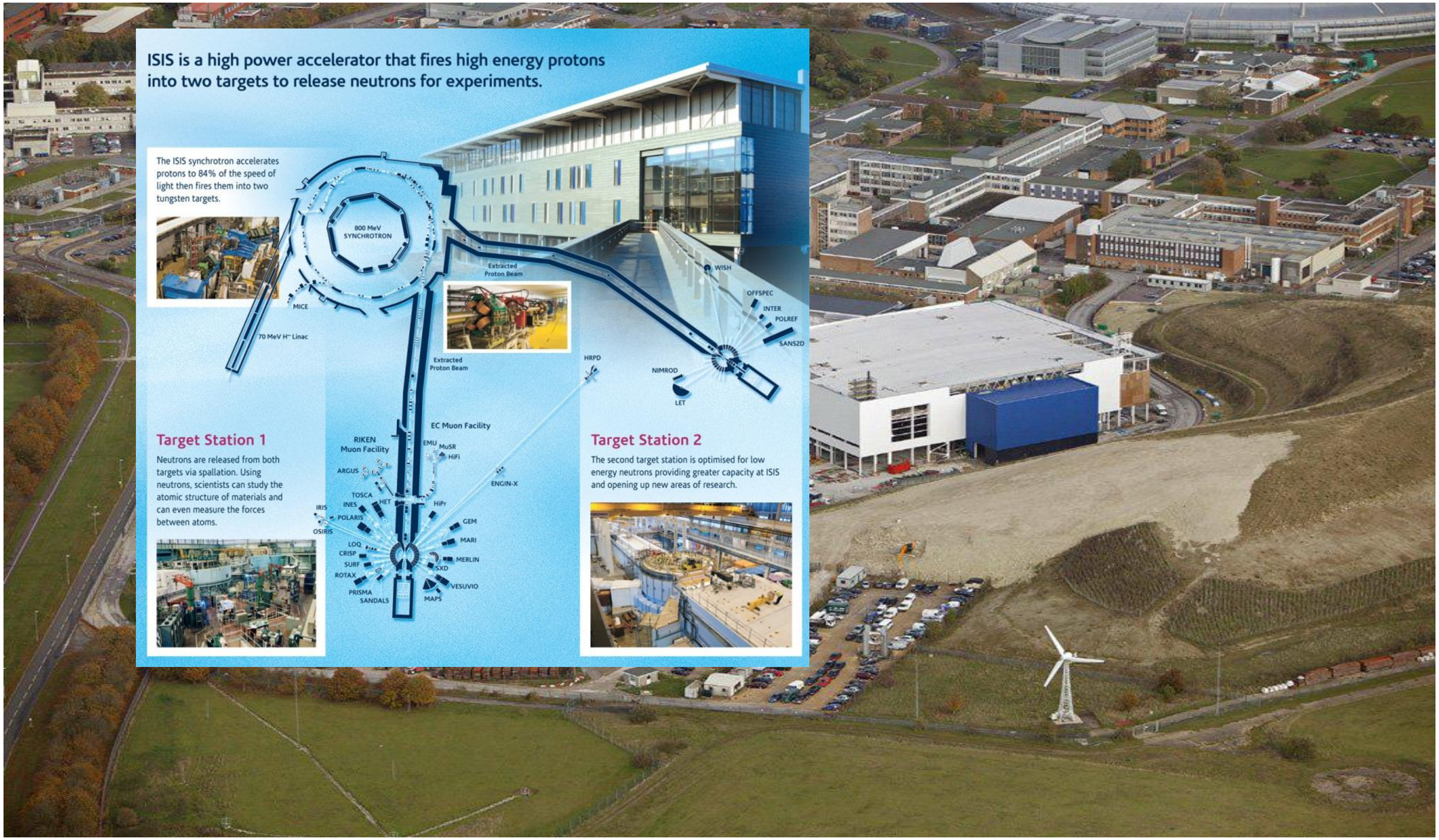
ATOM	Z	$f_x^2/100$	b^2_{COH}	b^2_{INC}
H	1	·	▨	○
D	1	·	○	○
C	6	○	○	·
N	7	○	○	○
O	8	○	○	·
Na	11	○	○	○
Si	14	○	○	·
Cl	17	○	○	○
Ti	22	○	▨	○
V	23	○	●	○
Ni	28	○	○	○

H

C

„Carbon Black is NOT Black“ – for Neutrons

Spallation Neutron Source ISIS, (UK)
Rutherford Appleton Laboratory, Chilton/Oxfordshire



ISIS is a high power accelerator that fires high energy protons into two targets to release neutrons for experiments.

The ISIS synchrotron accelerates protons to 84% of the speed of light then fires them into two tungsten targets.

Target Station 1

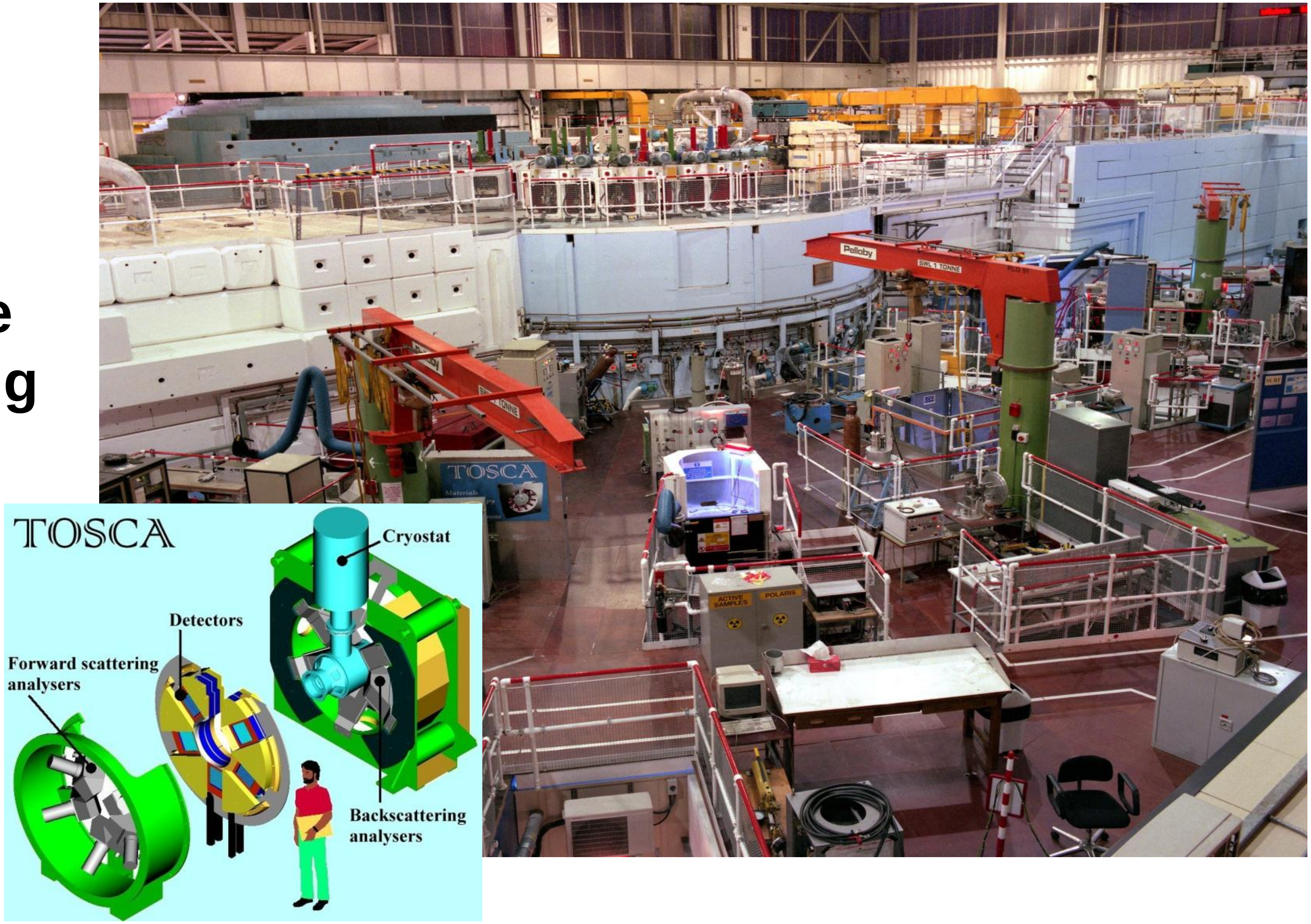
Neutrons are released from both targets via spallation. Using neutrons, scientists can study the atomic structure of materials and can even measure the forces between atoms.

Target Station 2

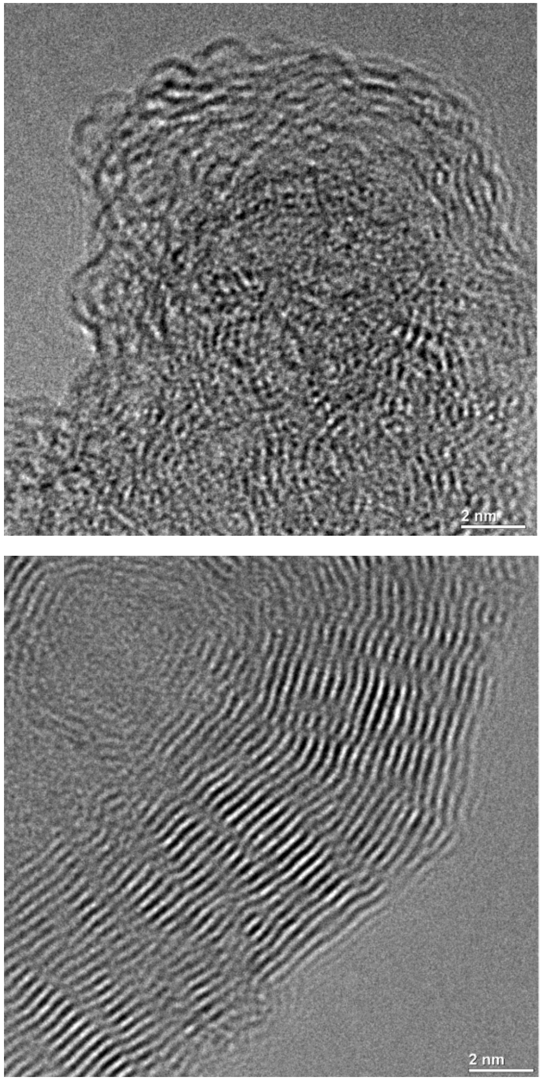
The second target station is optimised for low energy neutrons providing greater capacity at ISIS and opening up new areas of research.

ISIS Target Region and Spectrometer Hall

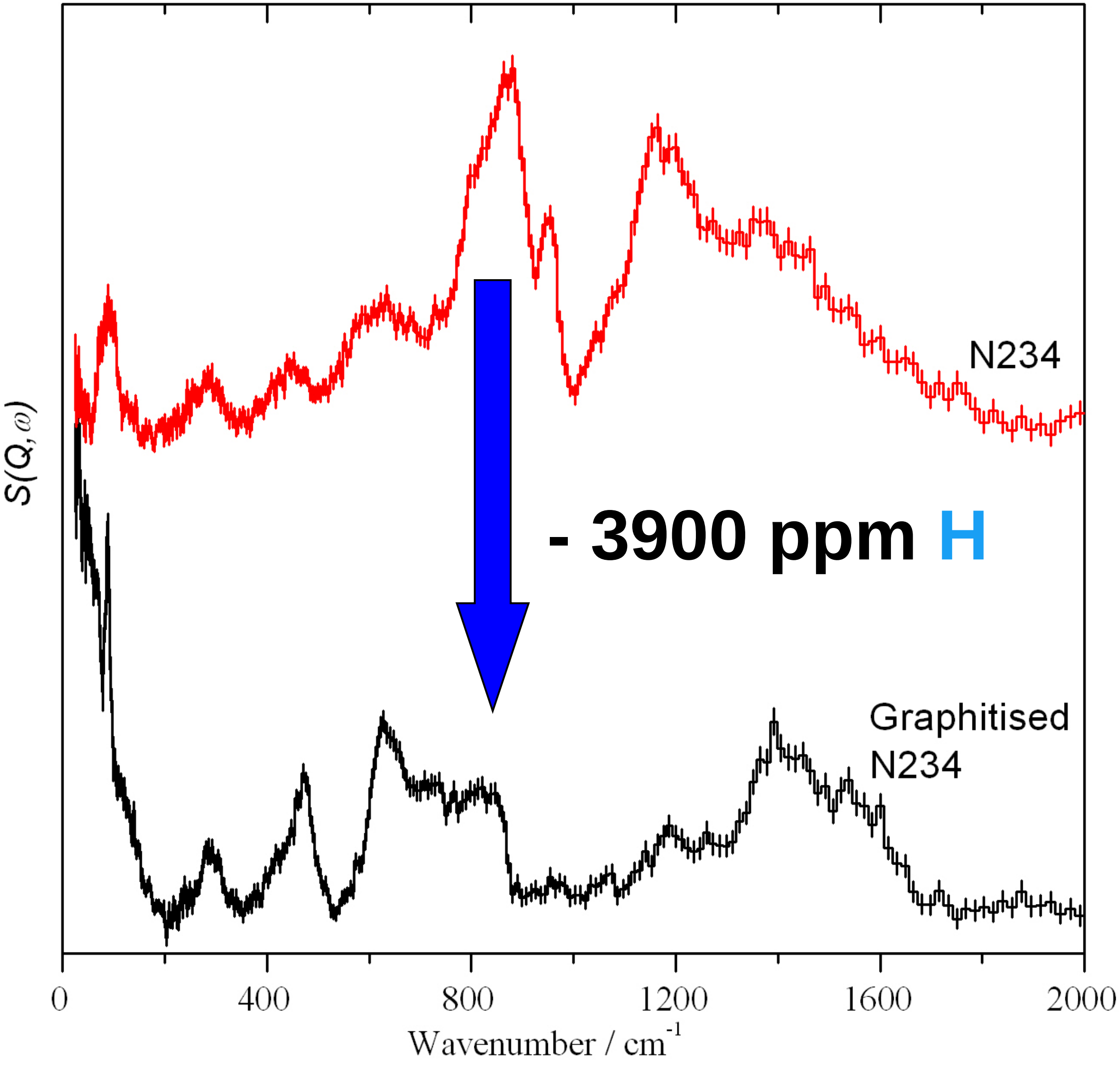
CB Sample
Size 10-20 g



IINS spectra of N234; red: as produced, 4200 μg/g H
black: after graphitisation treatment, 290 μg/g H

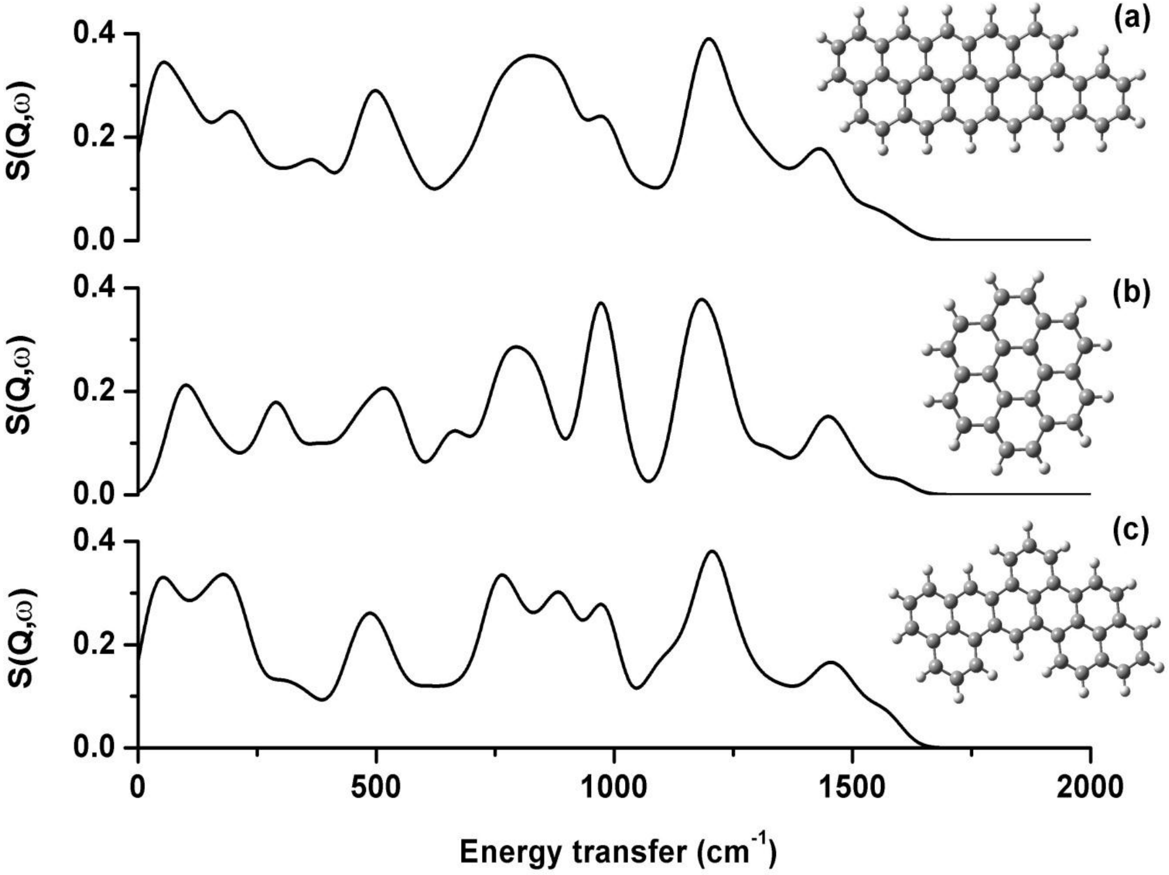


Dr. Peter Albers, AQ-EM



- 3900 ppm H

Spectra Simulations of Structures with Different Amount of Isolated (a), Vicinal (b) and Ternary (c) Neighbouring of Hydrogen Entities



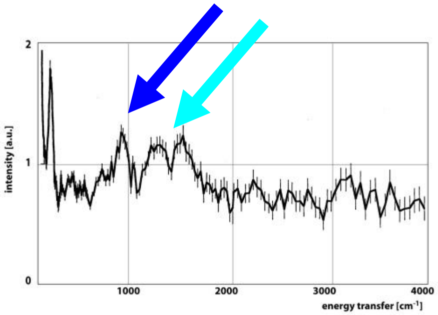
Isolated H

Vicinal H

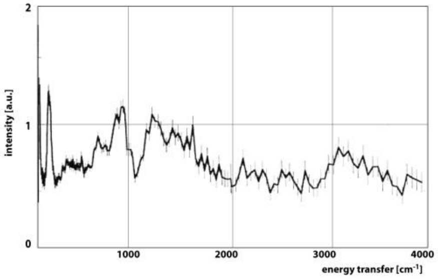
Ternary H

IINS Spectra of Carbon Blacks of Slightly Different Hydrogen Content: Out-of-plane and In-plane C-H Deformational Modes (Aryl C-H wagging) of Basic Structural Units (BSU's)

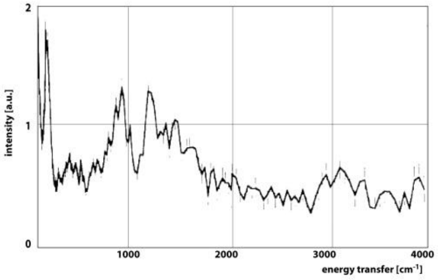
4400 µg/g H

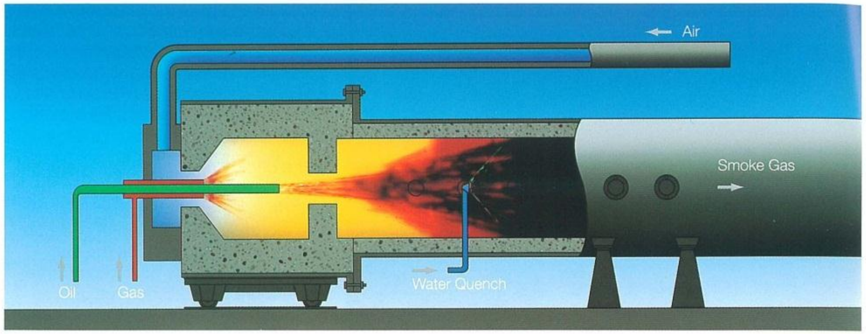


3100 µg/g H



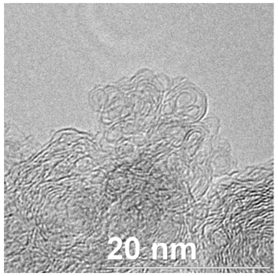
4200 µg/g H

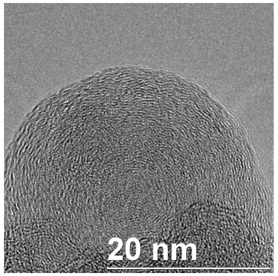


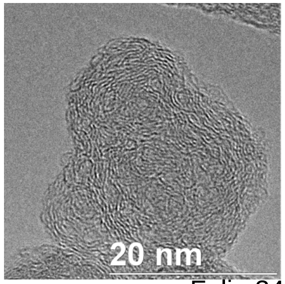


→ **Analytical information for filler/rubber interaction to improve efficiency and product performance:**

Terminating protons

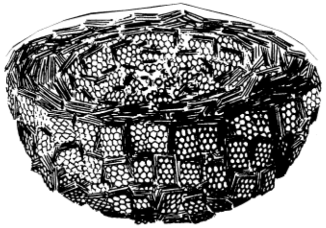


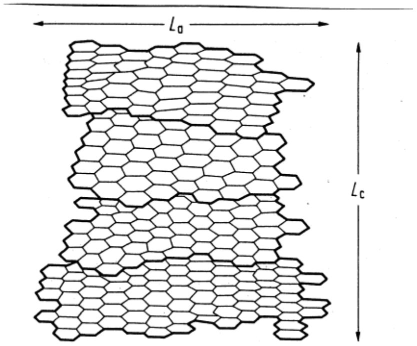


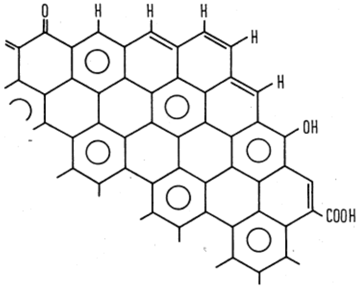


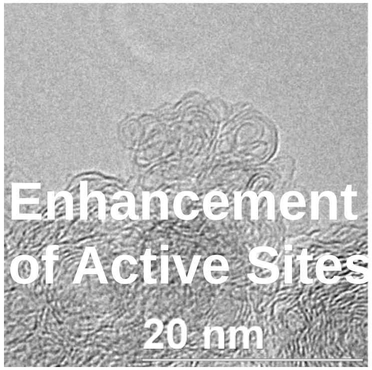
Conclusion: HR-TEM, SEM, XPS, SIMS, IINS are needed – complementary - to obtain a complete coherent picture:

Proton Dynamics

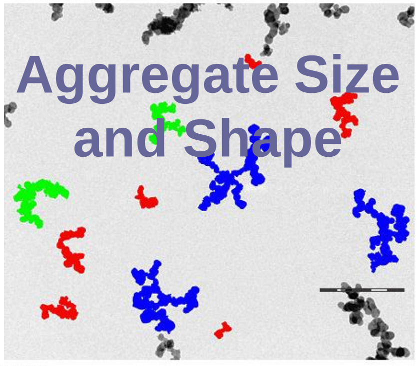




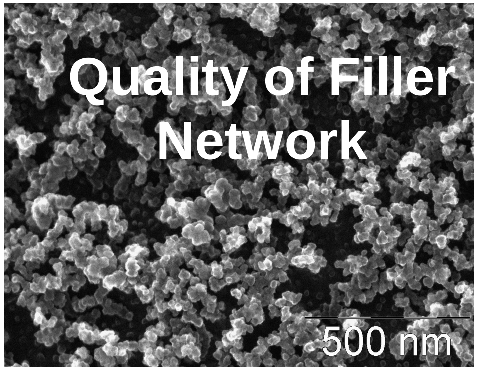




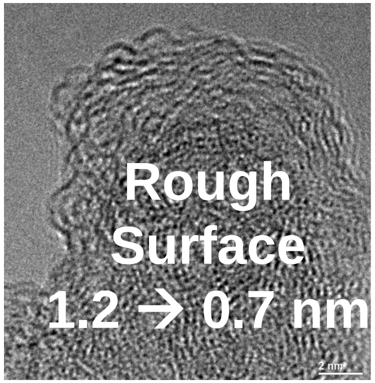
Enhancement of Active Sites



Aggregate Size and Shape

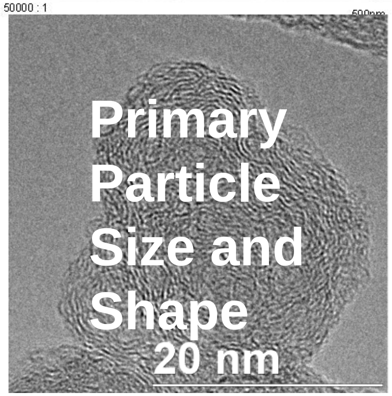


Quality of Filler Network

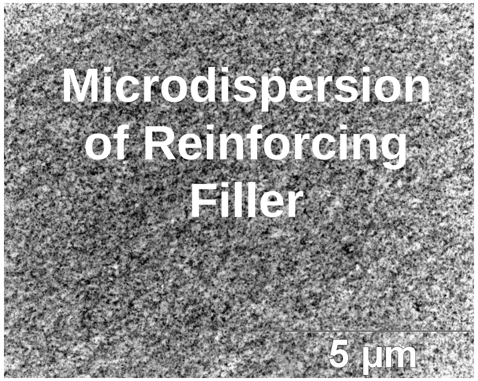


Rough Surface

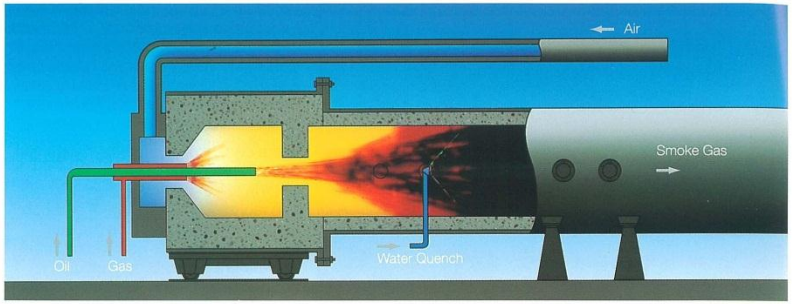
1.2 → 0.7 nm

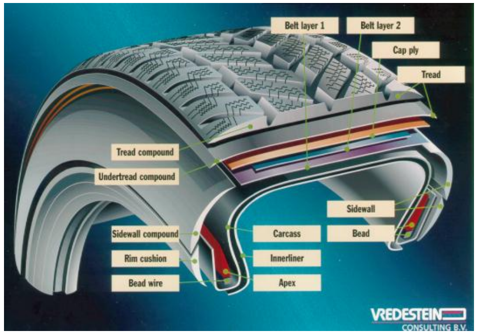


Primary Particle Size and Shape

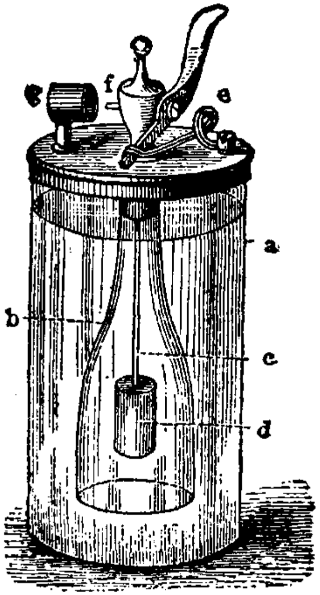


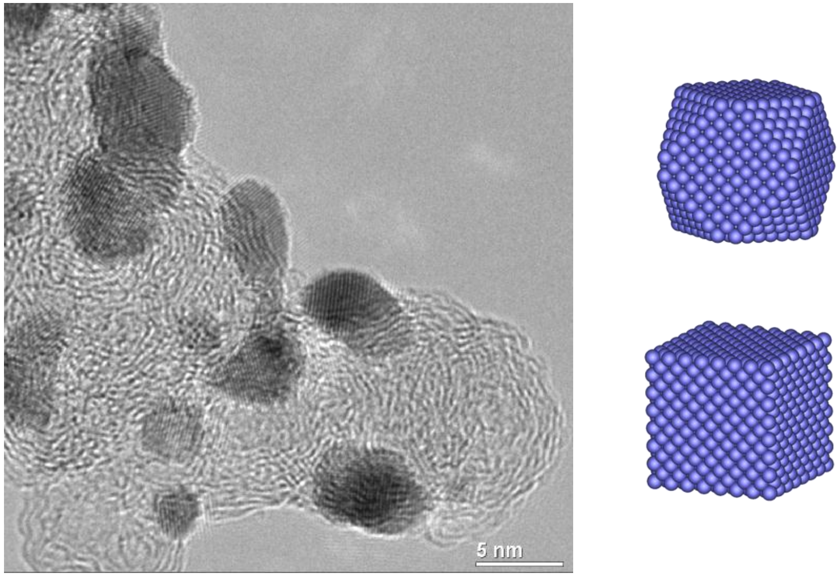
Microdispersion of Reinforcing Filler





2. Edelmetalle auf Ruß: Brennstoffzellenkatalysatoren (PEM)





Platinum sponge
→ Döbereiner Feuerzeug

Platinum and Platinum/Ruthenium on Carbon Black

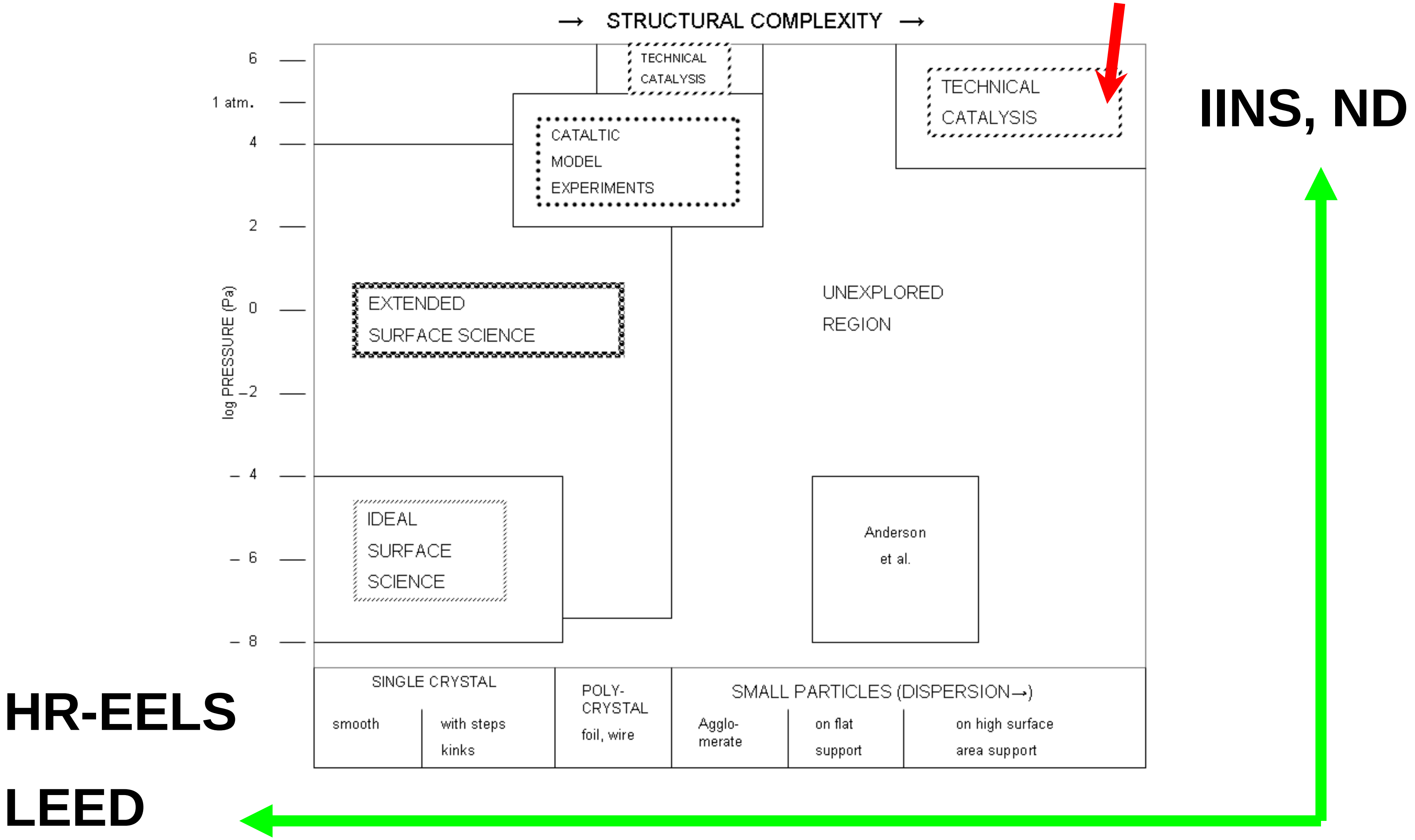
Hydrogen on Metals / Hydrogen in Metals Platinum / Palladium

„Das Verhalten von H_2 und Pt zueinander ist wenig untersucht, obwohl es durchaus von praktischem Interesse ist, z.B. für den Gebrauch von Pt als Elektrodenmaterial in der Elektrochemie.“ E. Raub

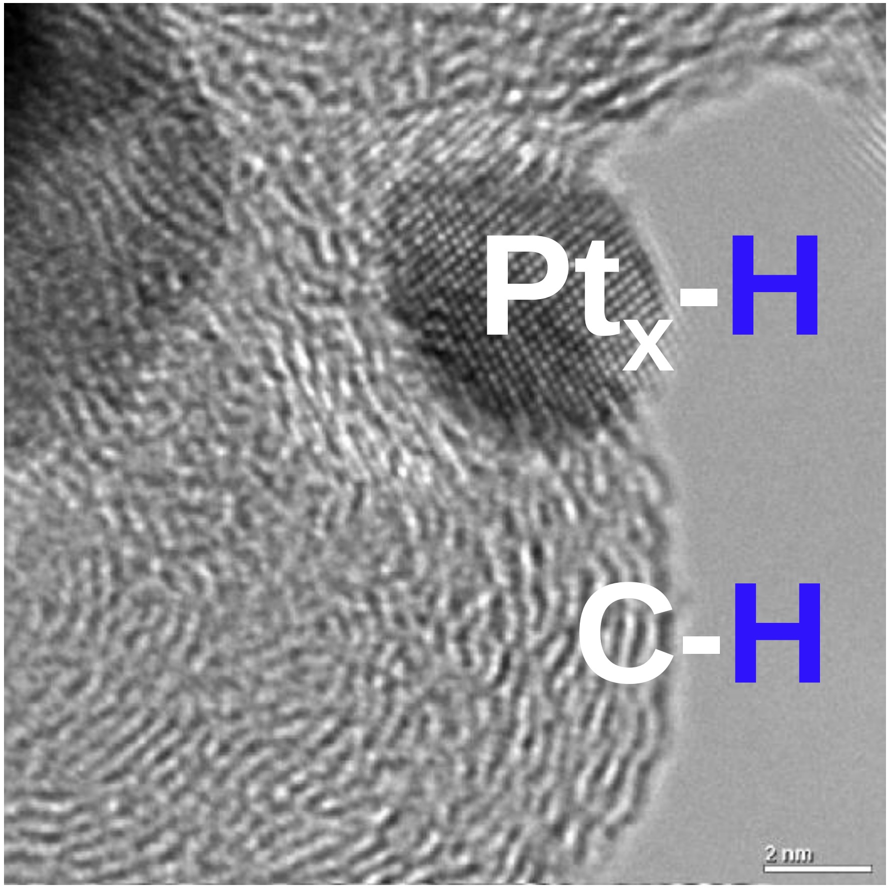
Gase und Kohlenstoff in Metallen
Hrsgb. E. Fromm, E. Gebhardt, Springer Verlag 1976, S. 648
Reine und angewandte Metallkunde in Einzeldarstellungen, Band 26.

Example supported Platinum and Palladium
H.P. Bonzel: ‚Pressure Gap Concept‘,
Surf. Sci. 68 (1977) 236-258.

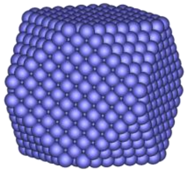
Powder,
800 m2/g,
1 bar H2



Fuel Cell Catalysis: Formation of Atomic H, Site Occupation Pt_x-H ?



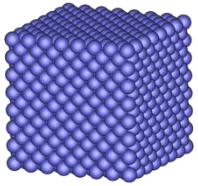
‚ideal‘ / ‚real‘ cubo-octahedra ?



Pt-H Distance by ND:

0.188 nm

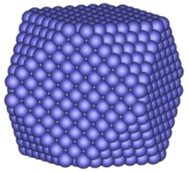
Chem. Commun. 2010



Scale Bar: 2 nm

WANTED: ALIVE (!)

→ In-situ-conditions, Surface Science Measurements under 1 bar Hydrogen Pressure?



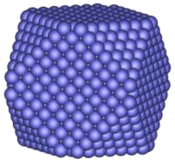
H_2 ?

H_2O ?

Pt-OH ?

Pt/Ru-OH ?

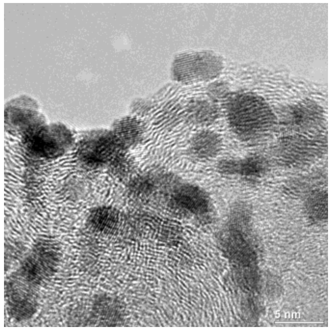
Atomic H: Pt_x-H ? → IINS



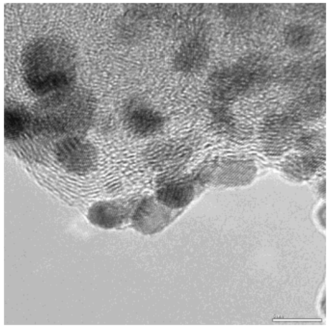
Changes of the relative contributions of (100) and (111) faces on platinum-nanoparticles with increasing particle size (2, 4, 6 ,8 nm), detection of Pt_x–H and Pt-OH. IINS → HREELS on single crystal surfaces; Cs-corrected TEM …

J. Catal. **223**, 44 (2004)

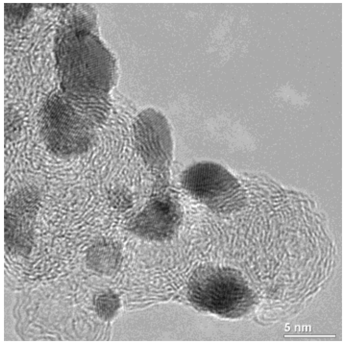
(a) 2 nm



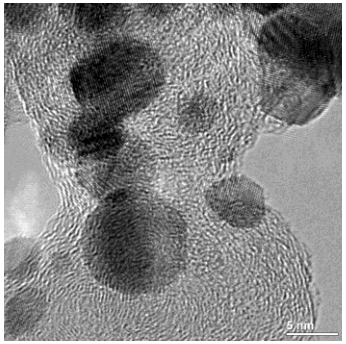
(b) 4 nm

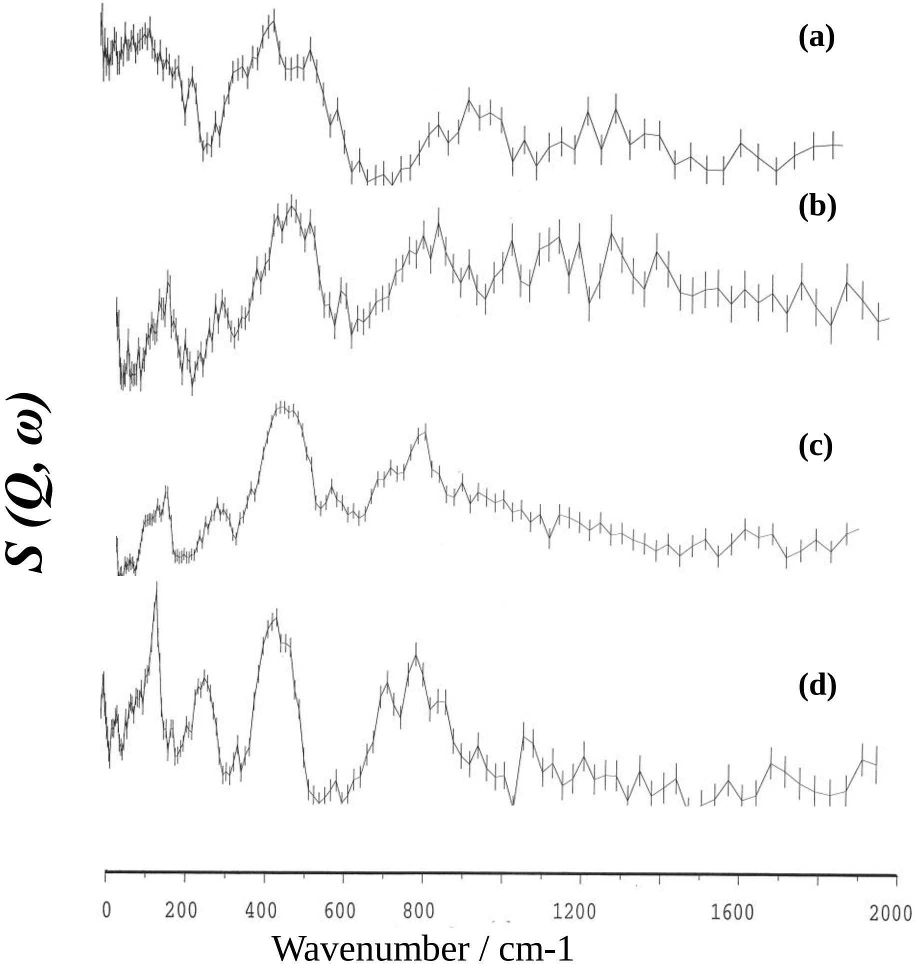


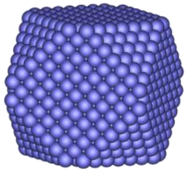
(c) 6 nm



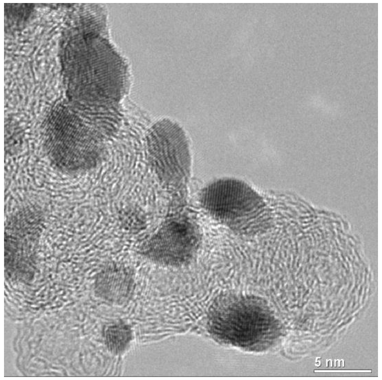
(d) 8 nm



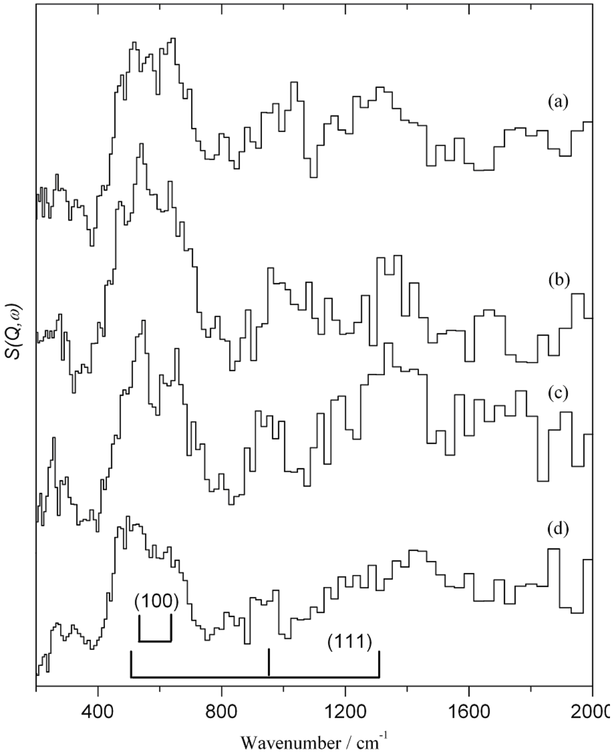




Ptx-H Vibrations on 4 nm Platinum Particles/C Obtained by Different Preparation Techniques

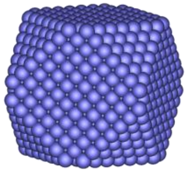


Catal. Today **114**, 418 (2006)



→ **Target of IINS: Fingerprints for certain surface properties of finely divided, supported, non-ideal, real catalyst particles**

→ **G.A. Somorjai: „heterogeneous solid surfaces with different surface sites and different next neighbours“**



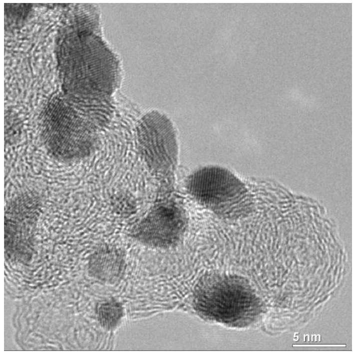
In-situ IINS of a Fuel Cell Catalyst under 1 bar Hydrogen

On-top Pt-H Valence Vibration at 2020 cm-1

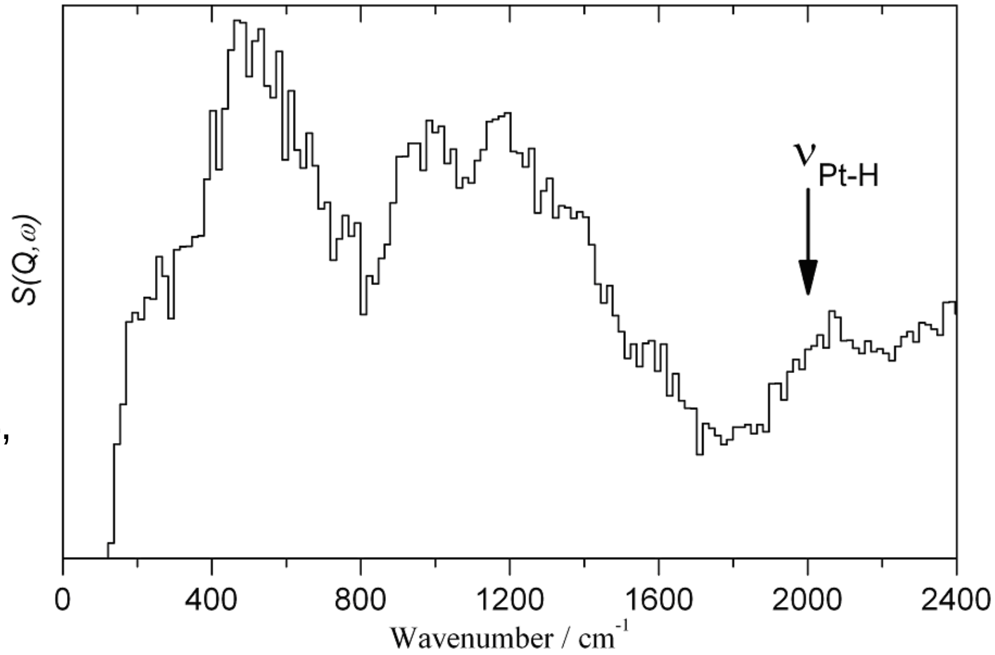
<u>Focus:</u> Catalytically Active Centers ? / „Spectator“ Sites ? Who is who ?

How to improve catalyst properties and save/ spare bound capital?

How to promote the formation of the relevant sites?



Catal. Today **114**, 418 (2006)



1 : 100 ?

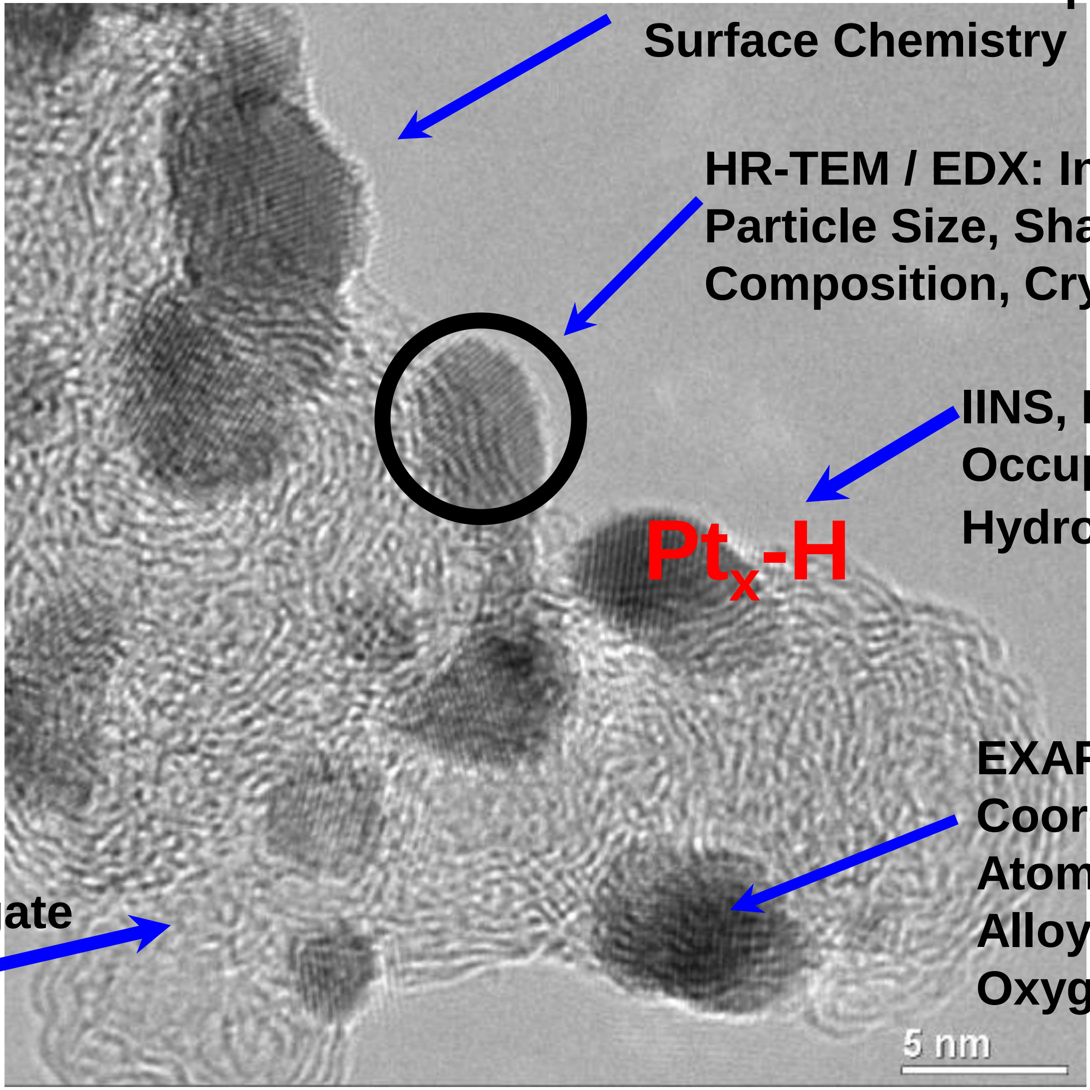
1 : 10000 ?

1 : 1000000 ?

1 : 10^n ???

Supported Nano-Particles: Nano-Analytics!

Lateral Resolution Required !



XPS: Surface Composition, Surface Chemistry

HR-TEM / EDX: Individual Particle Size, Shape, Local Composition, Crystallinity

IINS, ND: Surface Site Occupation by Atomic Hydrogen, Bond Length

EXAFS, XANES: Local Coordination numbers, Atomic Distances, Alloying, Traces of Oxygen

HR-TEM: Aggregate Size, Shape, Paracrystalline Structure

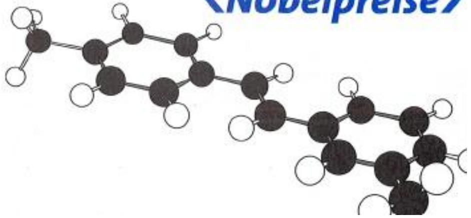
3. Palladium auf Aktivkohle: Heck Reaktion

C-C Coupling by Heck reaction of Bromobenzene and Styrene to Stilbene

- Heterogenization of homogeneous catalysts
- Improved recovery of precious metal inventory
- Checking open questions on catalyst selectivity

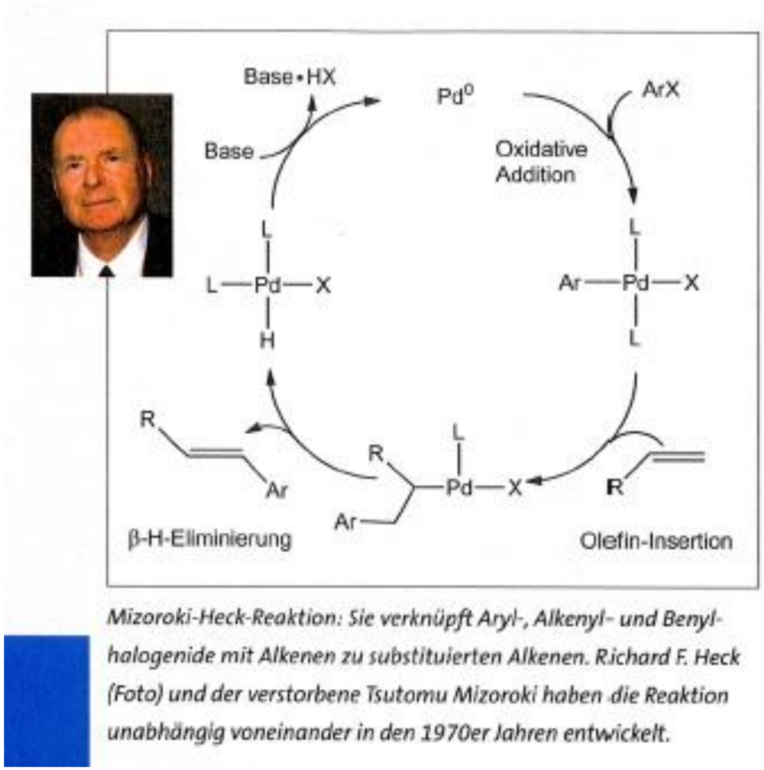
‹Nobelpreise›

Kuppler unter sich



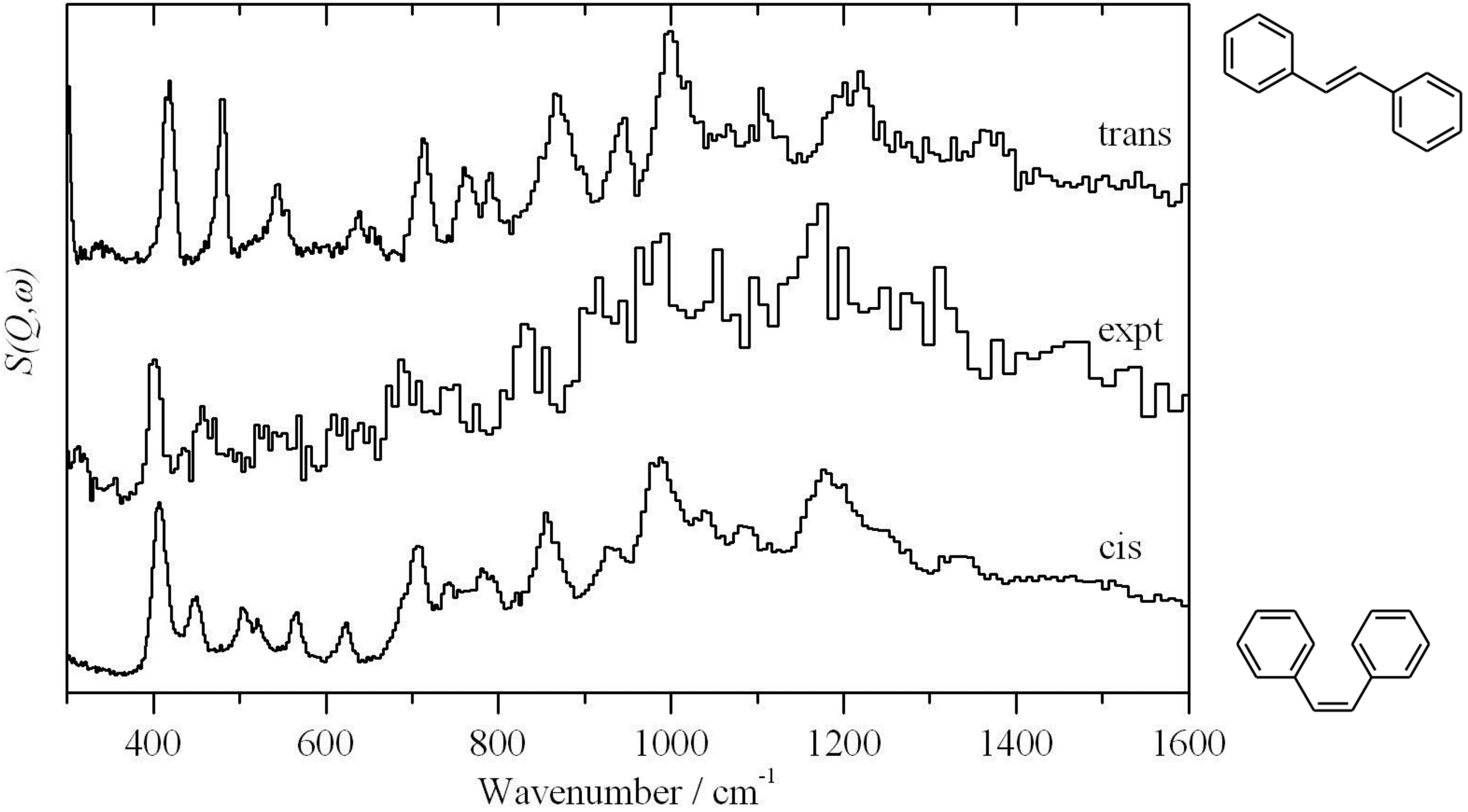
Heck-Reaktion:

Matthias Beller, Nachrichten aus der Chemie, November 2010, S. 1105

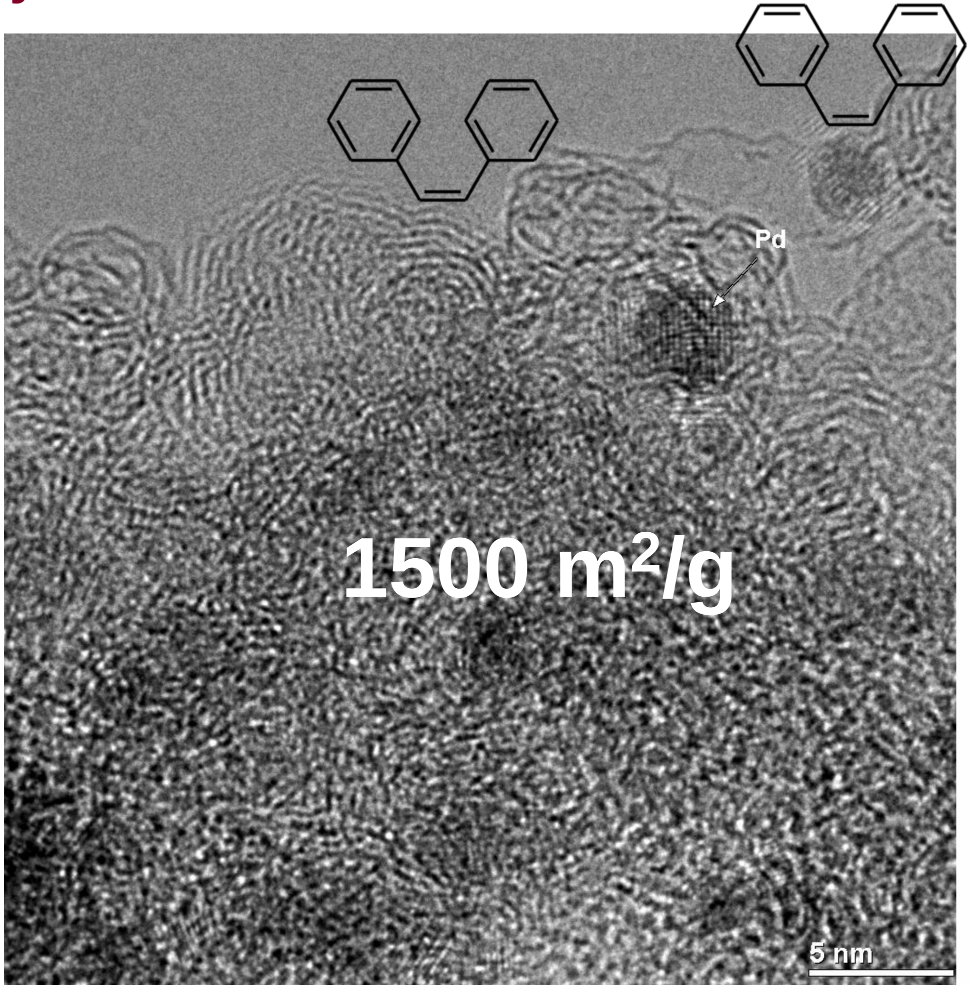


Mizoroki-Heck-Reaktion: Sie verknüpft Aryl-, Alkenyl- und Benyl-halogenide mit Alkenen zu substituierten Alkenen. Richard F. Heck (Foto) und der verstorbene Tsutomu Mizoroki haben die Reaktion unabhängig voneinander in den 1970er Jahren entwickelt.

IINS: Mirror image to organic phase. What is present at the catalyst surface after the organic phase is removed?



Heck reaction: Bromobenzene and Styrene to Stilbene Supervison of liquid phase: Yield 90% of trans-product; IINS: cis-Stilbene isomer enriched on Pd/C catalyst surface

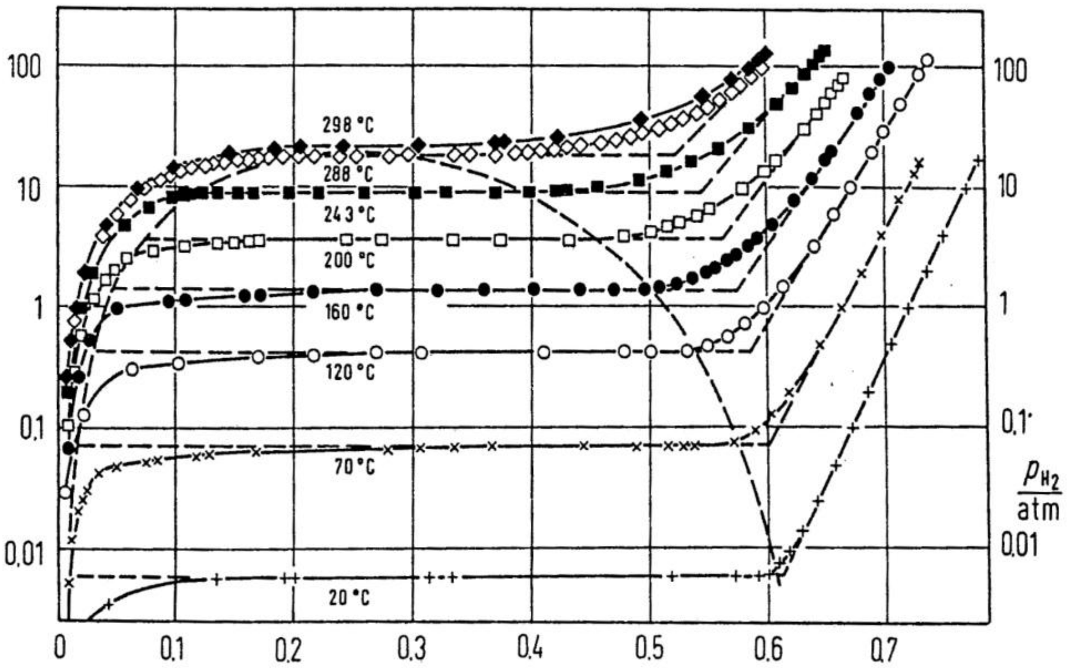


Scale Bar: 5 nm

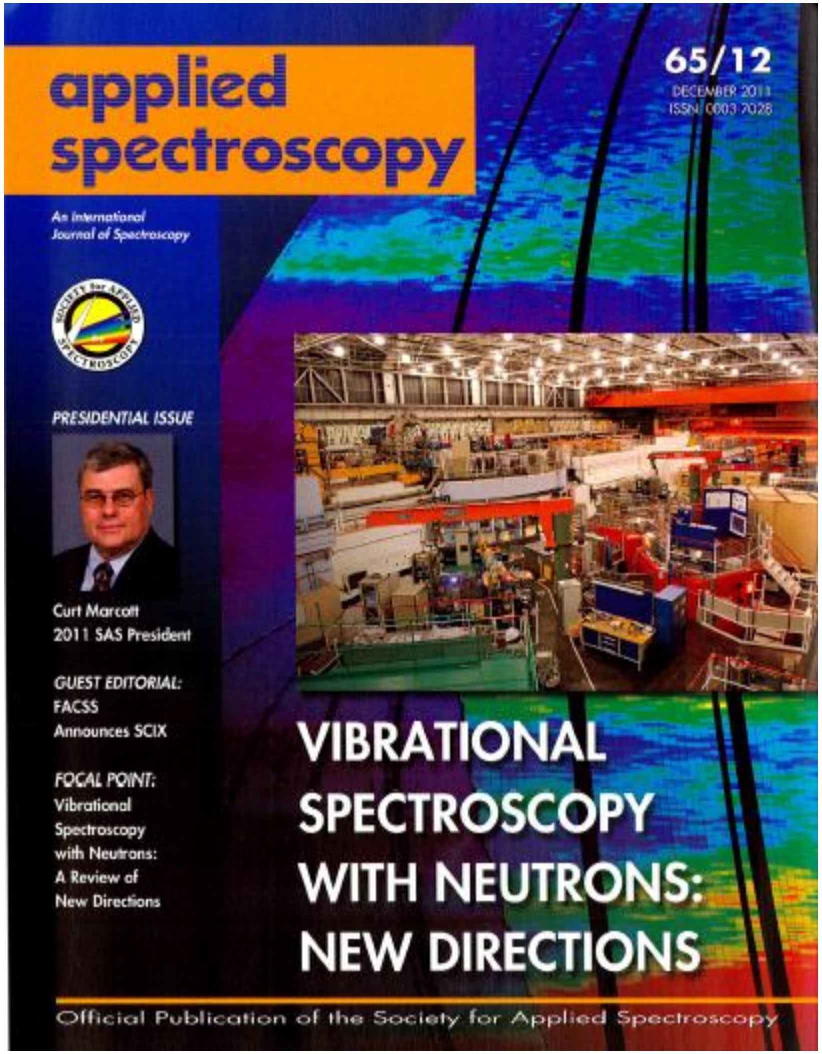
4. Hydrierkatalysatoren: der Lindlar Katalysator und Pd/C

‚Lindlar catalyst‘ (Pd/Pb/CaCO3): used for selective catalytic hydrogenation of triple bonds to double bonds; this catalyst is moderated by addition of lead and quinolines to generate the best selectivity for a given process; Example: Production of Vitamin A

Under the access of hydrogen: Palladium forms α- and β-phase hydride but: very small particles show different hydrogen absorption properties compared to large particles (Kirchheim, Reetz et.al.)



Pd/H phase diagram



applied spectroscopy

65/12
DECEMBER 2011
ISSN 0003 7028

An International Journal of Spectroscopy

PRESIDENTIAL ISSUE

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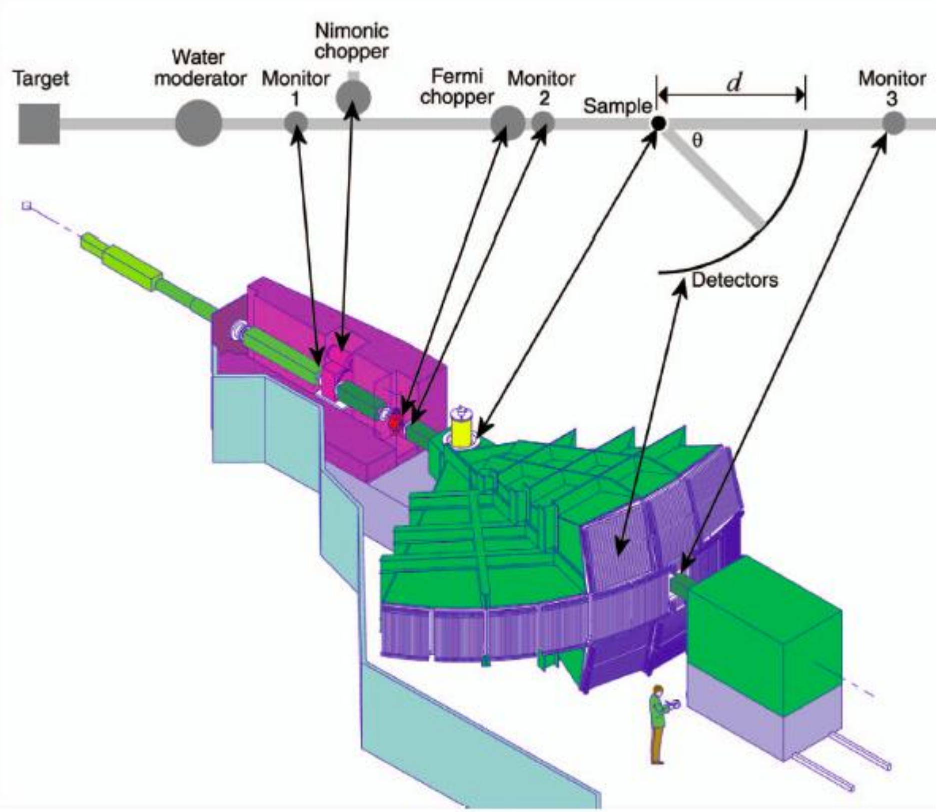
FACSS Announces SCIX

FOCAL POINT:
Vibrational Spectroscopy with Neutrons: A Review of New Directions

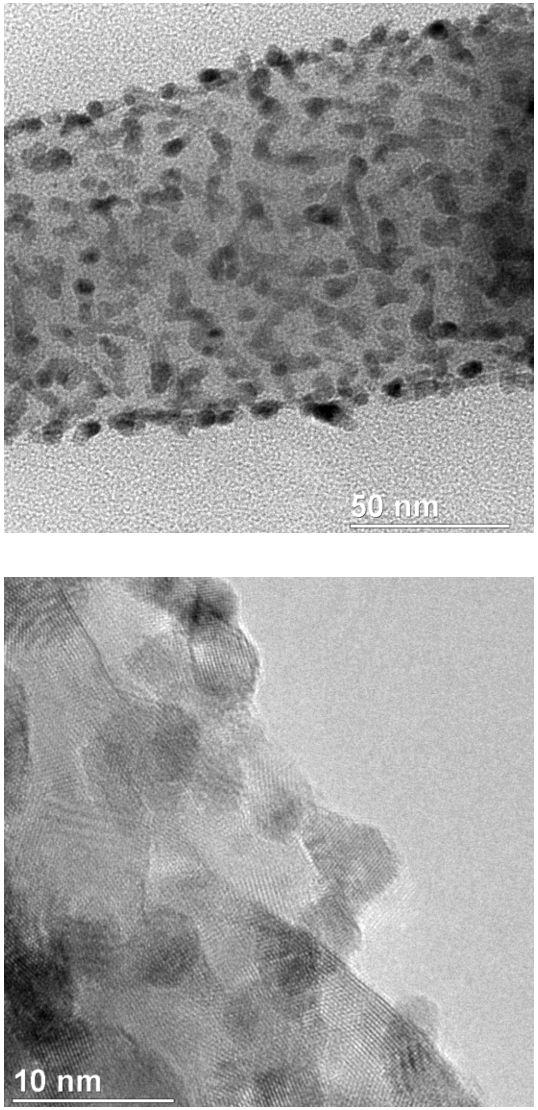
VIBRATIONAL SPECTROSCOPY WITH NEUTRONS: NEW DIRECTIONS

Official Publication of the Society for Applied Spectroscopy

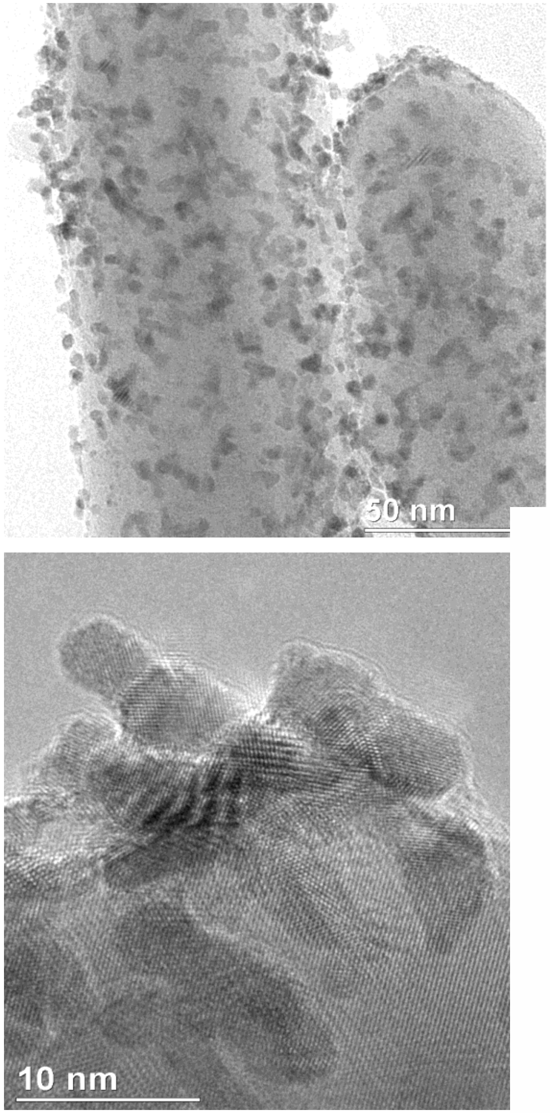
MAPS Spectrometer
→ 1 mol.-% H



Pd-only/CaCO3

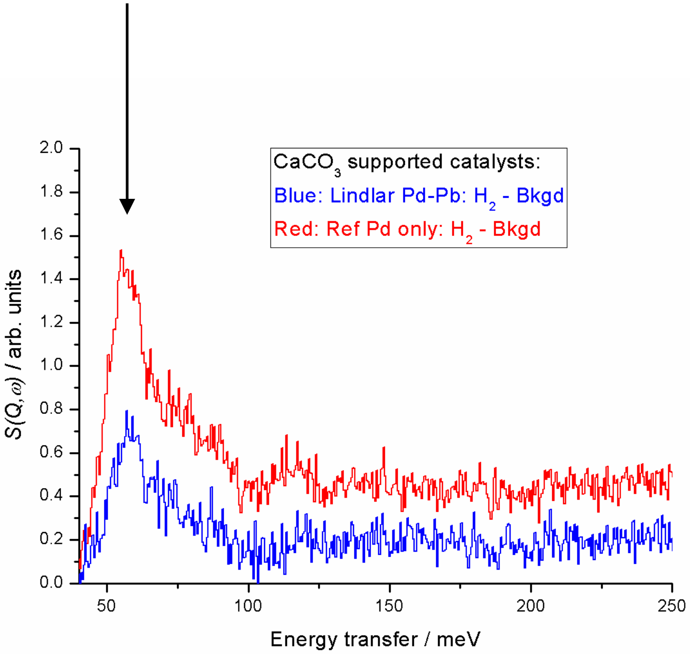


Pd/Pb/CaCO3



Pb reduces the hydrogen storage capability of Pd in the Lindlar catalyst

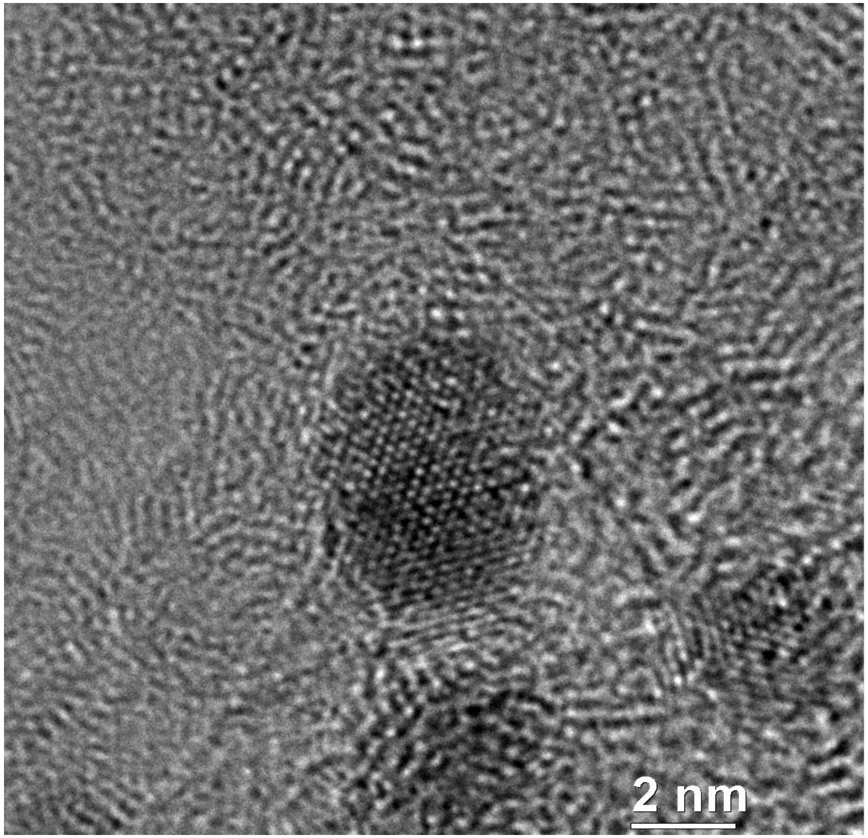
β-palladium hydride

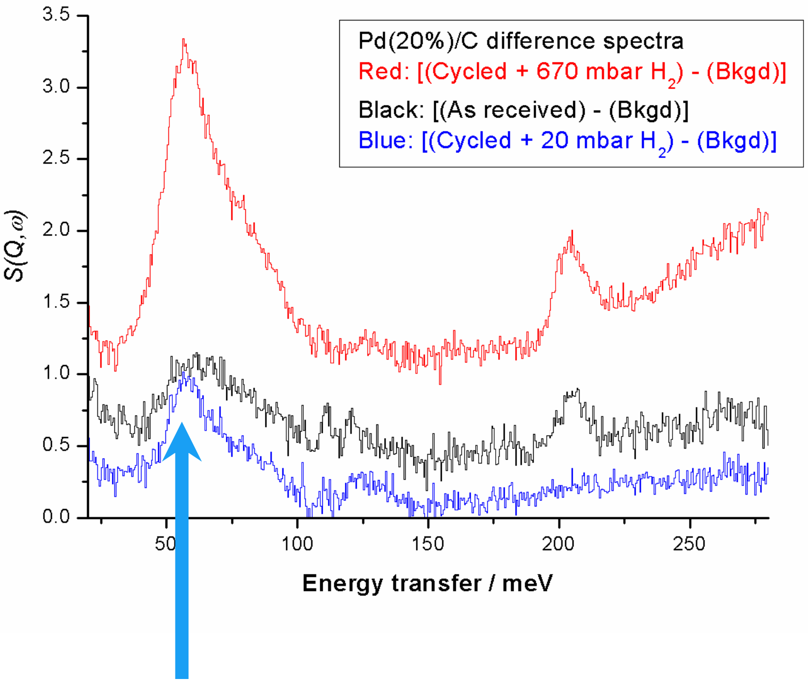


Lindlar Catalyst

- **Moderation of the Lindlar catalyst by lead improves the selectivity by blocking certain surface sites and also by changing the hydrogen storage capacity of the supported Pd/Pb particles**
- **Lower amounts of β-palladium hydride are formed**
- **It is reported that α- and β- phase hydride show different selectivity in catalytic hydrogenations: the α- phase provides selectivity, the β- phase provides activity but low selectivity**
- **Controlled changing the β- phase formation allows to enhance and fine-tune the selectivity in more detail**

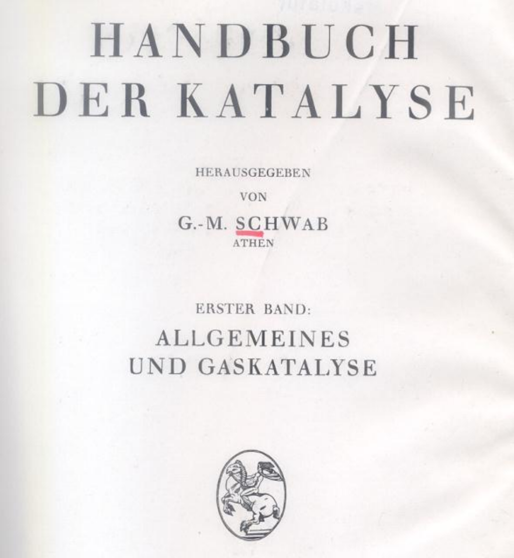
Pd/C – Hydrogenation Catalyst: 3 nm isolated primary particles show 3.5x lower β-phase Pd/H than 10-15 nm Pd aggregates of 3.7 nm particles → lowering long range phase coherence for α/β-phase transition





β-Palladium Hydride

5. Para-Wasserstoff als Oberflächensonde



HANDBUCH
DER KATALYSE

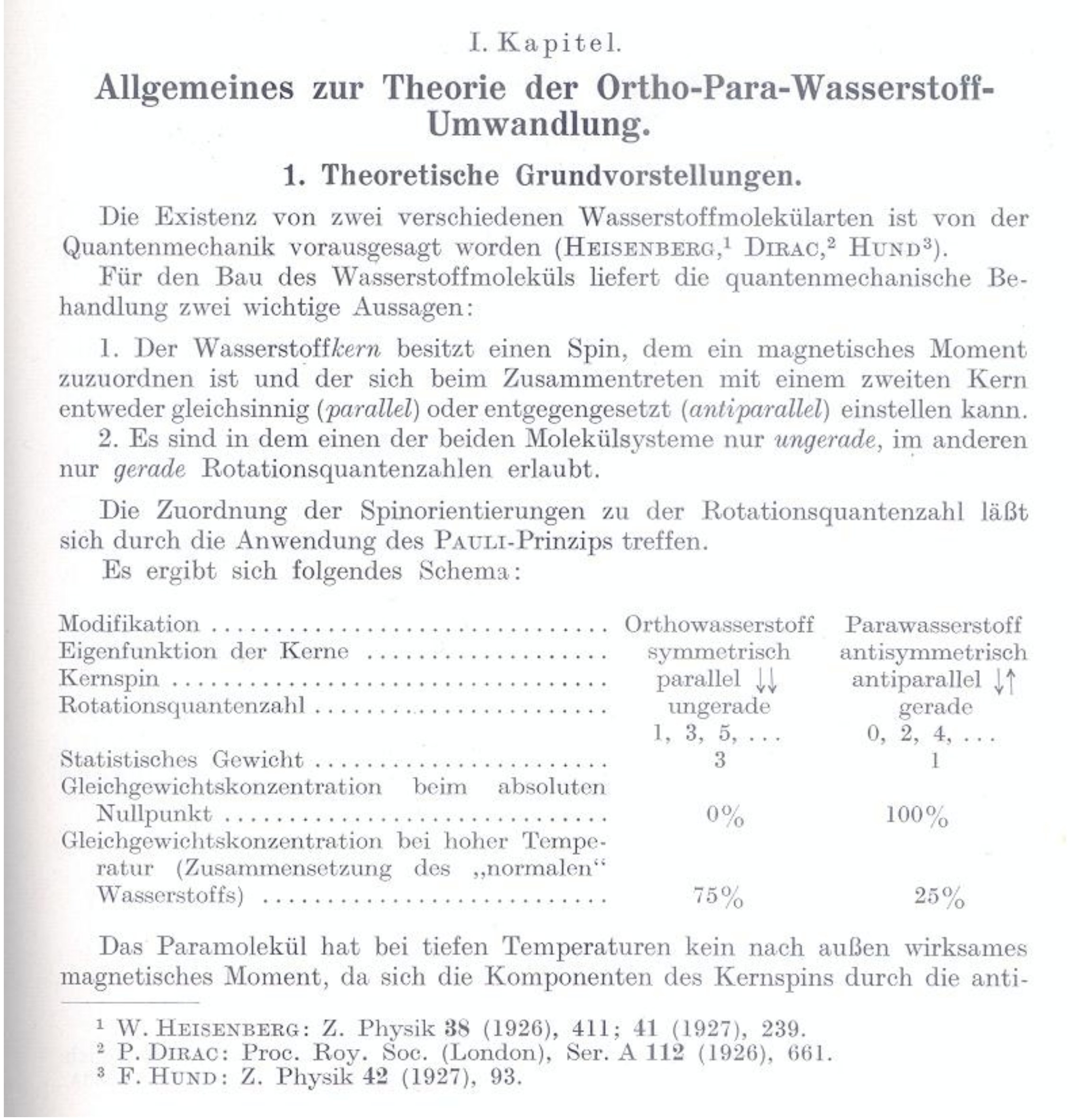
HERAUSGEGEBEN
VON
G.-M. SCHWAB
ATHEN

ERSTER BAND:
ALLGEMEINES
UND GASKATALYSE

Homogene Ortho- und Parawasserstoffkatalyse.

Von
E. Cremer, Berlin-Dahlem.[1]

Eucken; Bonhoeffer, Harteck… :



I. Kapitel.

Allgemeines zur Theorie der Ortho-Para-Wasserstoff-Umwandlung.

1. Theoretische Grundvorstellungen.

Die Existenz von zwei verschiedenen Wasserstoffmolekülarten ist von der Quantenmechanik vorausgesagt worden (Heisenberg,[1] Dirac,[2] Hund[3]).

Für den Bau des Wasserstoffmoleküls liefert die quantenmechanische Behandlung zwei wichtige Aussagen:

1. Der Wasserstoff*kern* besitzt einen Spin, dem ein magnetisches Moment zuzuordnen ist und der sich beim Zusammentreten mit einem zweiten Kern entweder gleichsinnig (*parallel*) oder entgegengesetzt (*antiparallel*) einstellen kann.
2. Es sind in dem einen der beiden Molekülsysteme nur *ungerade*, im anderen nur *gerade* Rotationsquantenzahlen erlaubt.

Die Zuordnung der Spinorientierungen zu der Rotationsquantenzahl läßt sich durch die Anwendung des Pauli-Prinzips treffen.

Es ergibt sich folgendes Schema:

Modifikation	Orthowasserstoff	Parawasserstoff
Eigenfunktion der Kerne	symmetrisch	antisymmetrisch
Kernspin	parallel ↓↓	antiparallel ↓↑
Rotationsquantenzahl	ungerade 1, 3, 5, . . .	gerade 0, 2, 4, . . .
Statistisches Gewicht	3	1
Gleichgewichtskonzentration beim absoluten Nullpunkt	0%	100%
Gleichgewichtskonzentration bei hoher Temperatur (Zusammensetzung des „normalen“ Wasserstoffs)	75%	25%

Das Paramolekül hat bei tiefen Temperaturen kein nach außen wirksames magnetisches Moment, da sich die Komponenten des Kernspins durch die anti-

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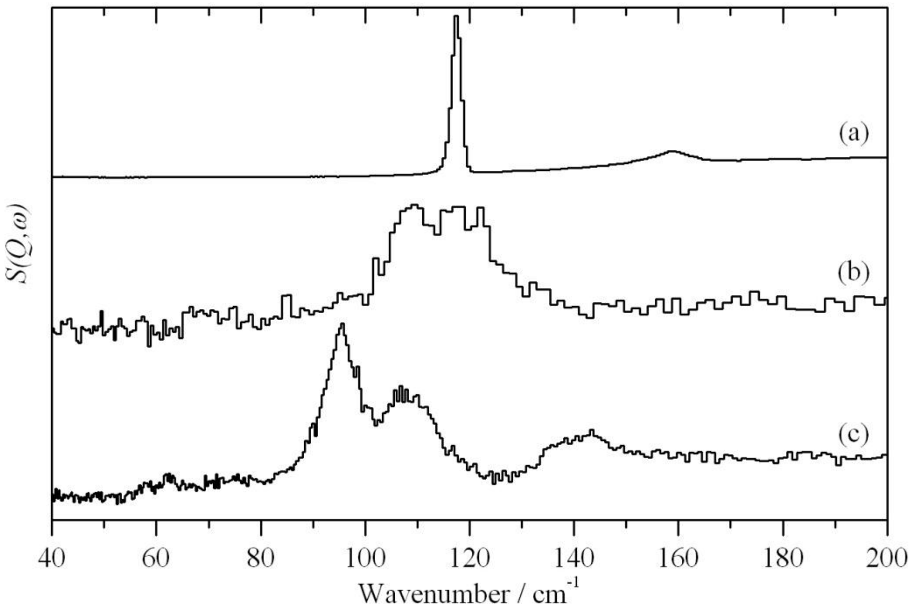
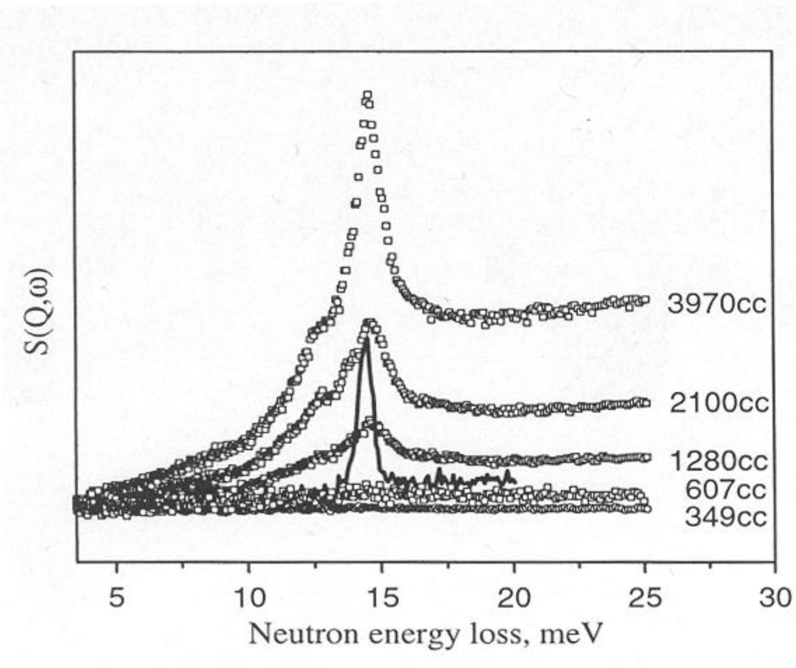
[1] W. Heisenberg: Z. Physik **38** (1926), 411; **41** (1927), 239.
[2] P. Dirac: Proc. Roy. Soc. (London), Ser. A **112** (1926), 661.
[3] F. Hund: Z. Physik **42** (1927), 93.

Molecular hydrogen (p-H_2) as a sensitive surface probe





J=0 → J=1 rotational transition of H2, IINS allowed due to nuclear spin flip in neutron scattering

a) Solid H2 at 13 K b) H2 adsorbed on carbon nano-tubes c) H2 adsorbed on CoAlPO

J. Phys. Condens. Matter 16, L73 (2004)

J. Mol. Catal. A: Chemical 167, 217 (2001)

H2 adsorbed in activated carbon, occupation of ultra-micropores, new aspects for characterizing porous matter (catalyst supports, zeolites..), supplementing gas adsorption techniques (BET..)
13 meV Rotational Splitting in 0.6 nm pores
→ isosteric heat of adsorption
Carbon 44, 2724 (2006)

6. Zusammenfassung

If the Focus is Set on Hydrogen-containing Entities in-situ-IINS is the Method of Choice:

- **Utilization of *Covalently Bound*, of *Atomically Chemisorbed* and of *Physisorbed Molecular Hydrogen and Hydrogen-containing Molecular Species***
- **A Selective, Local Probe for the Adsorption/ Absorption Characteristics of Particles of Varying Size, Morphology and Surface Properties**
- **In-situ Surface Titration of Nanoparticles / Assessment of Catalytically Active Centres**
- **Complements: Microscopies (Aberration-corrected TEM), Surface- and Bulk-Analytical Techniques**

Many thanks for Your Attention !