Neutrons for Catalysis: A Workshop on Neutron Scattering Techniques for Studies in Catalysis
September 16-17, Oak Ridge National Laboratory

Practical Applications in the Chemical Industry:

Proton Dynamics of Technical Catalysts and Materials from Operating Large Scale Plants, Hydrogen on Fuel Cell Catalysts

Peter W. Albers
AQura GmbH

Who is AQura?

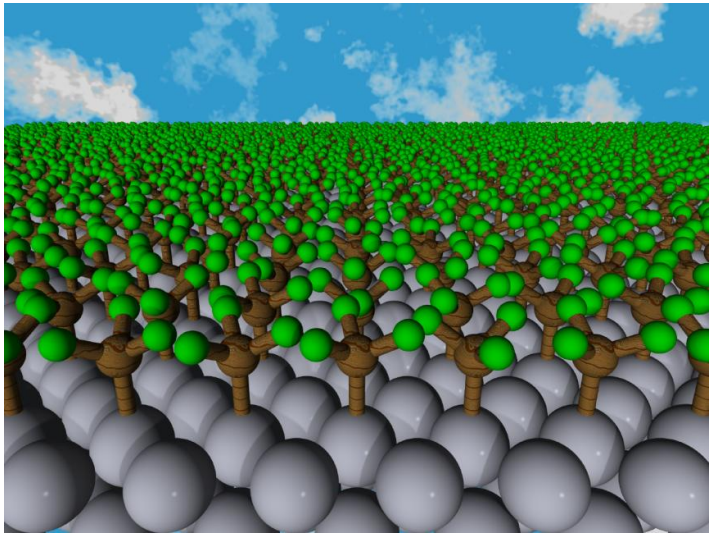
Central Analytical Services of Evonik Industries formed by the physical chemistry-, polymer-, organic- and inorganic-analytical laboratories of the former Degussa AG and Chemische Werke Hüls GmbH, Hanau and Marl, Germany

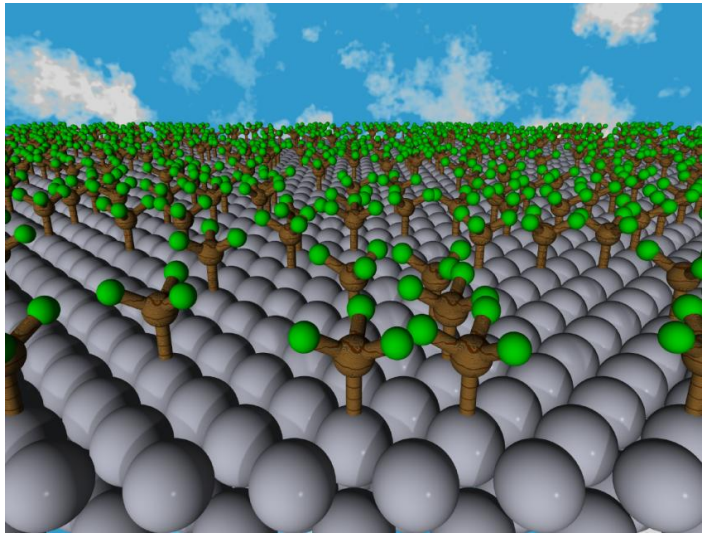
Physical chemistry methods include:

Inelastic, Incoherent Neutron Scattering

We Also Use Neutron Scattering for Solving Analytical Problems in Applied Catalysis and Materials Research; Example:

Catalyst Poisoning by Methyl Groups





Catalyst poisoning by methyl groups

Phenomenon: Irregular behaviour of a Pd-based hydrogenation catalyst in a large scale plant over several months (application: hydrogenation of C=O groups to C-OH)

Results from a broad variety of on-line and off-line characterization methods:

- **No poisoning by CO, S, metallic elements etc.**
- **No unusual loss of surface area by sintering etc.**

→ Plant Manager concludes: Something has blocked considerable amounts of active surface area; must be traces of an unknown chemical species, not accessible by our in-house-analytics:

What is it ???

Clarification? Analytical Results Obtained by Using State of the Art Equipment:

Infrared : no

Raman : no

NMR : no

Sorption Analysis: no

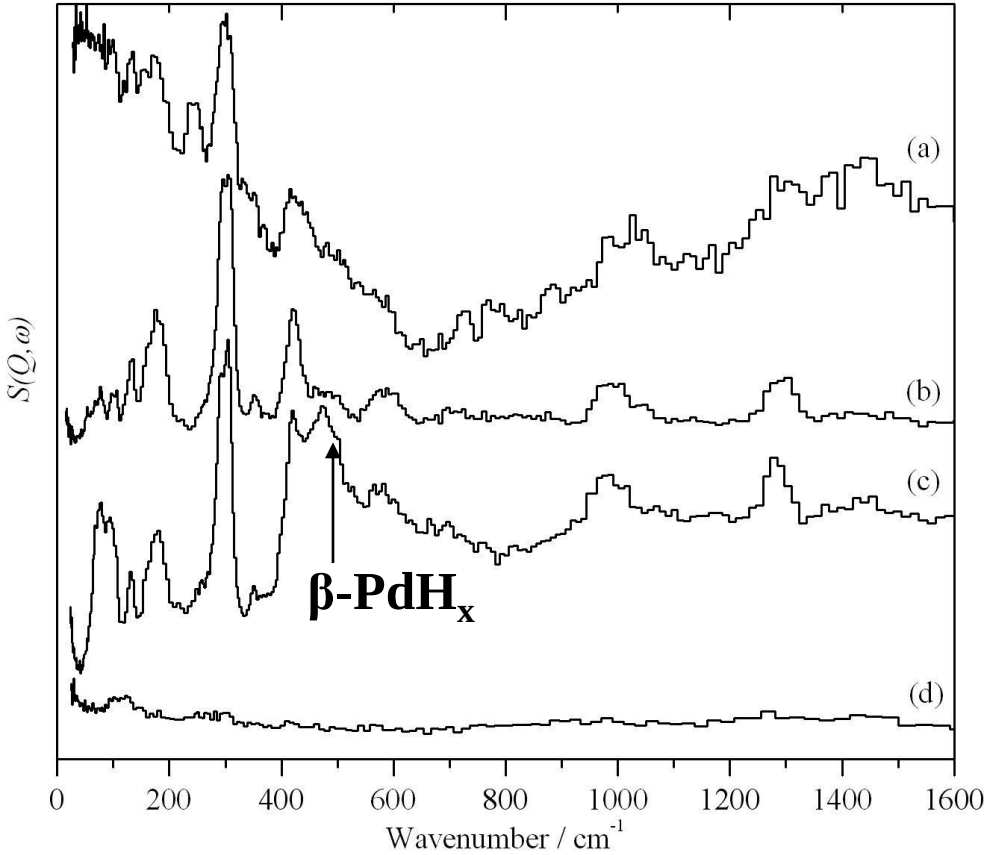
Microscopies: no

Elution/Chromatographies/Mass Spectrometries: no

Elemental Analysis / Inorganic Analyses: no

Cooperation Partners, Application Laboratories…: sorry, no chance..

IINS of Pd-catalyst as taken directly from the operating plant and the operating sister plant



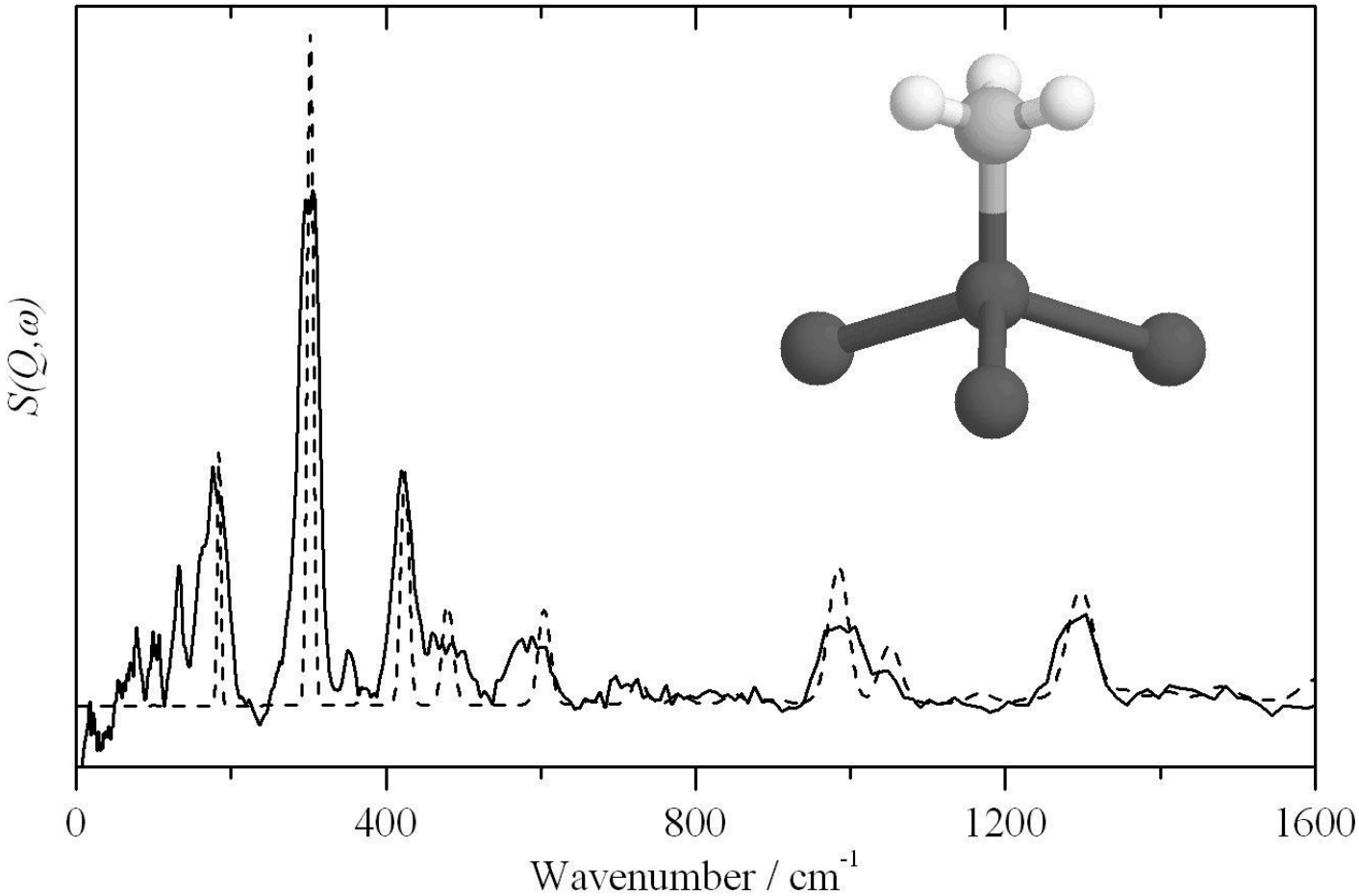
a) **Deactivated, pyrophoric, organic-wet, sealed under Argon**

b) **Extracted**

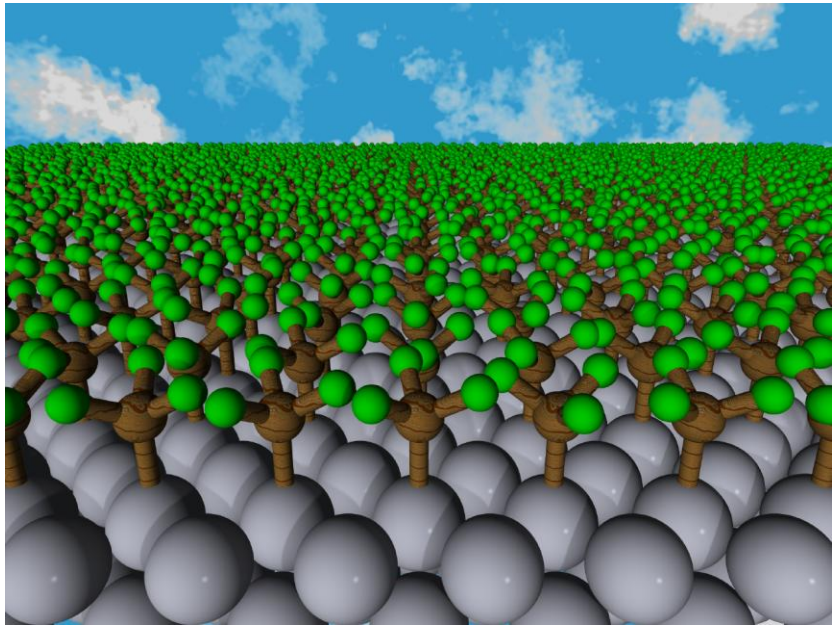
c) **Hydrogenated**

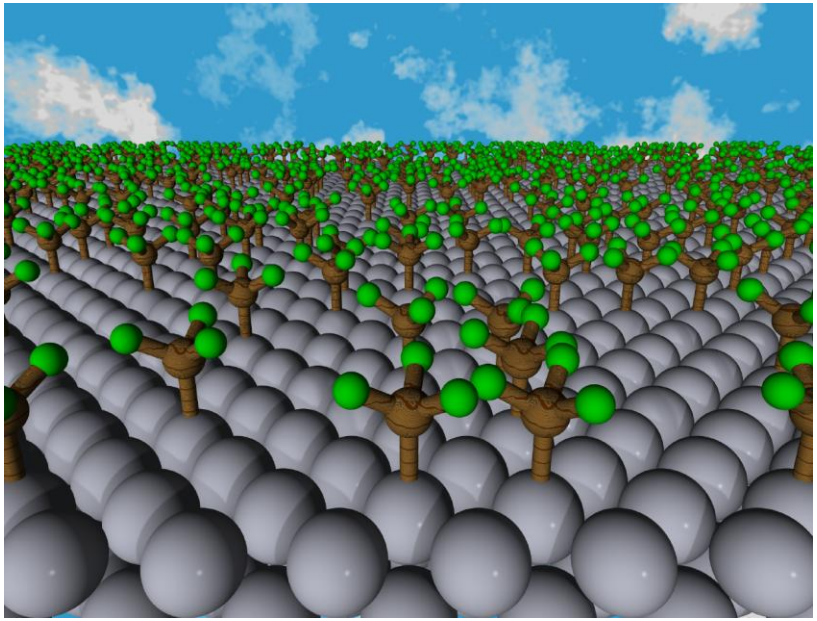
d) **Active catalyst reference from sister plant, extracted**

Result of spectra simulations and conclusion after measuring all the important pure and mixed components involved in the process:
Pd-CH_3 on top Pd(111), C_{3v} , CH_3-torsion 302 cm^{-1}



Disturbed adsorption of larger sp^2 type molecules by stable sp^3-type molecular surface species





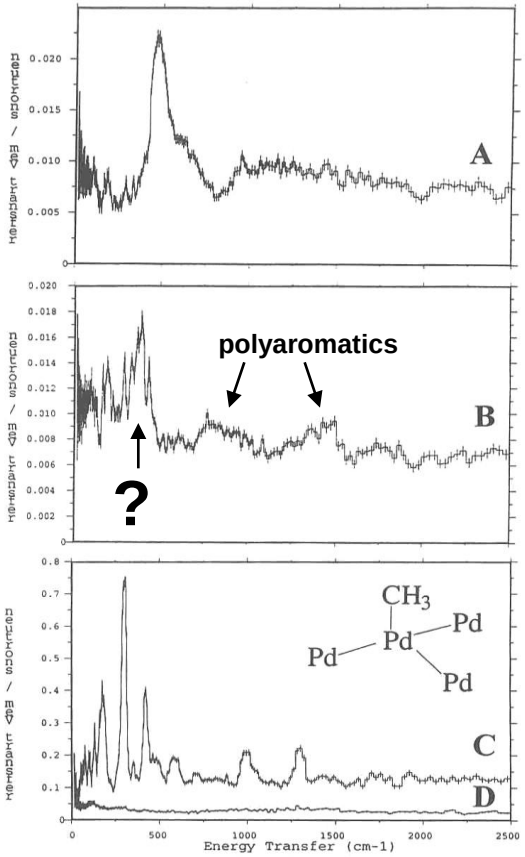
nm

↓

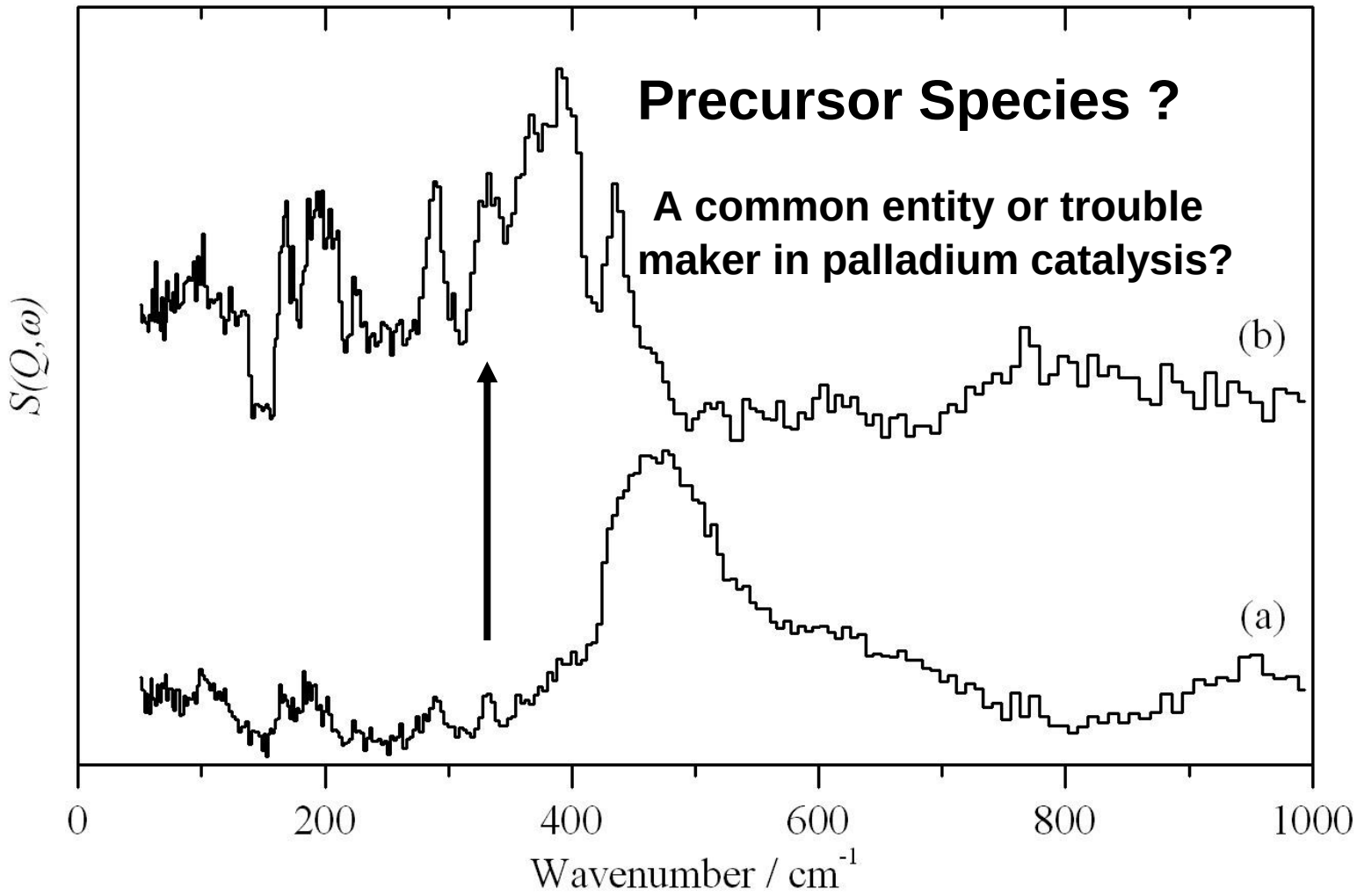
m^3

CH_3 – Pd at different degree of surface coverage: IINS spectra on samples taken over time: perfect agreement between plant performance and normalized, integrated spectral intensity in IINS

Biography of a catalyst deactivation process occuring in a large scale chemical reactor: *Problem in the technical hydrogenation process is not an absorption- but an adsorption-problem*



2 m³ !


Precursor Species ?
A common entity or trouble maker in palladium catalysis?
(b)
(a)
S(Q,ω)
0
200
400
600
800
1000
Wavenumber / cm-1

Stability of the Pd-CH_3 entities

1) the methyls were stable in air under ambient conditions for months

2) there was fast removal of the surface methyls by heating in air to 435 K,

3) immediate removal of the methyls by liquid phase oxidation at 300 K

4) there was slow displacement by CO dosing for competitive adsorption at 300 K with increasing CO pressure

Fischer Tropsch Catalysis on Fe- or Co-catalysts, „CTL“ Coal to Liquids – ‚a rough (?) analogy‘

The observations on the stability of the methyl species are in line with conclusions on the frustration of methane formation in Fischer-Tropsch catalysis and also on the slow step in CO methanation being the reaction between methyl and hydrogen.

→ Syngas (CO/H2) → liquid hydrocarbons

(Ruhrchemie, SASOL)

→ Diesel from Biomass

Carbonaceous Deposits on Catalysts

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IINS on Coked Catalysts from Industrial Plants

High-temperature and low-temperature cokes deposited on catalysts during operation:

$CH_4 + NH_3 \rightarrow HCN + 3\ H_2$ / T ca. 1400 K, Pt/Al_2O_3

→ BMA: HCN for amino acids, PMMA

$C_2H_2 + H_2 \rightarrow C_2H_4$ / T < ca. 473 K, Pd/SiO_2

→ selective catalytic hydrogenation of acetylene to ethylene, purification of HCl recycle gas stream in the vinyl chloride process

Selective catalytic hydrogenation of acetylene to ethylene in the Vinyl chloride process (Pd/SiO_2-catalyst for VCM-plants)

1. Ethylene-Chlorination:

$$H_2C=CH_2 + Cl_2 \longrightarrow ClH_2C-CH_2Cl \qquad \Delta H_R^\circ = -180\ kJ/mol$$

2. Oxichlorination:

$$H_2C=CH_2 + 2\,HCl + 1/2\,O_2 \xrightarrow{CuCl_2\text{-Cat.}} H_2ClC-CH_2Cl + H_2O \qquad \Delta H_R^\circ = -239\ kJ/mol$$

3. EDC-Pyrolysis:

$$ClH_2C-CH_2Cl \xrightarrow{500-600°C} H_2C=CHCl + HCl \qquad \Delta H_R^\circ = +71\ kJ/mol$$

4. Side Reaction:

$$H_2C=CHCl \longrightarrow HC\equiv CH + HCl \qquad \Delta H_R^\circ = +99\ kJ/mol$$

Fig. 2 Reaction scheme of the VC-manufacturing process.

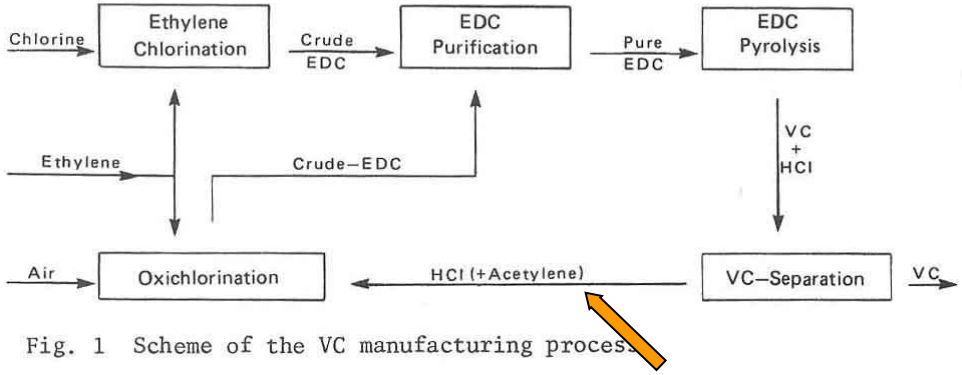
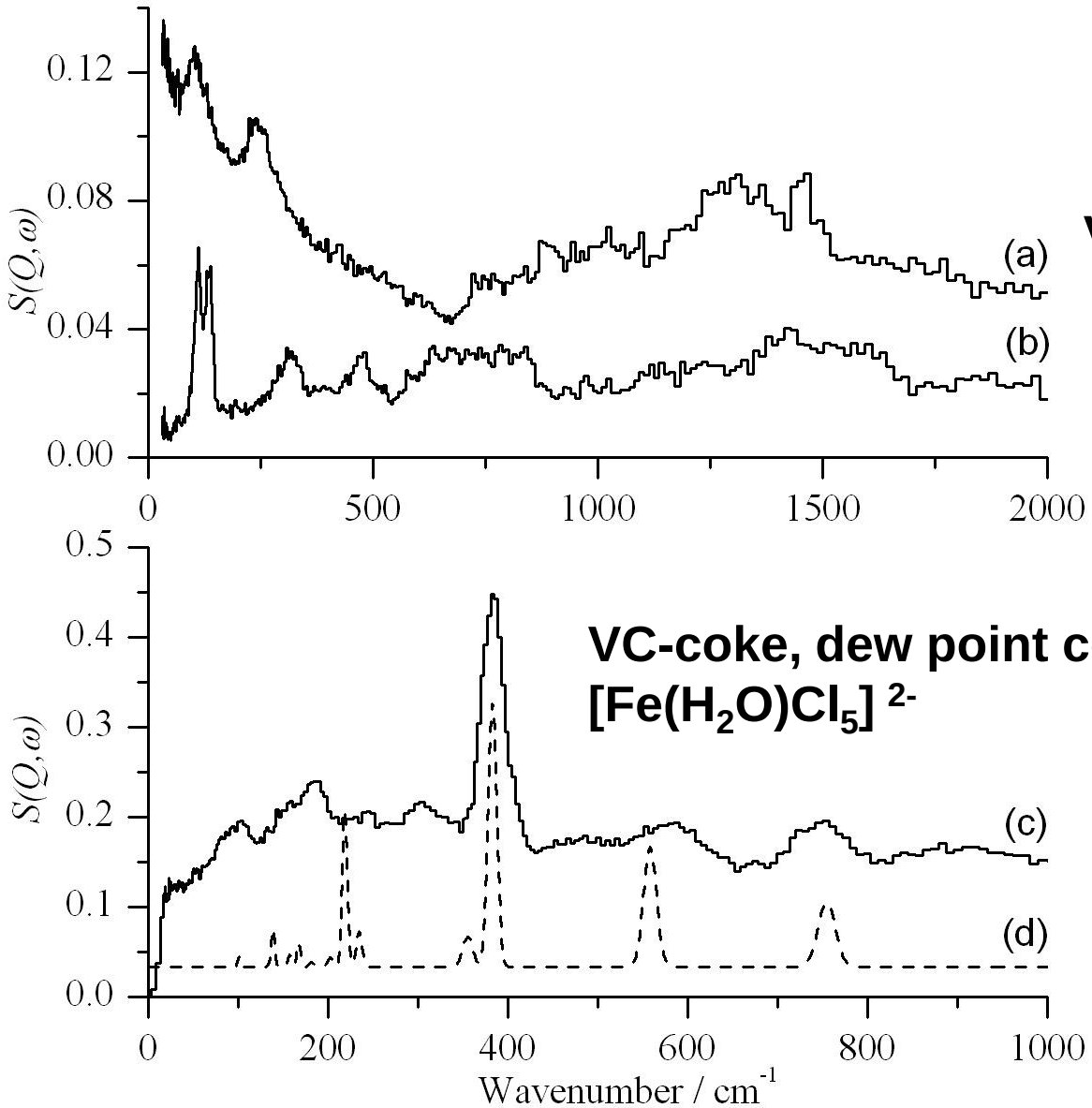


Fig. 1 Scheme of the VC manufacturing process

Problem:
traces of acetylene in the HCl-recycle-gas stream

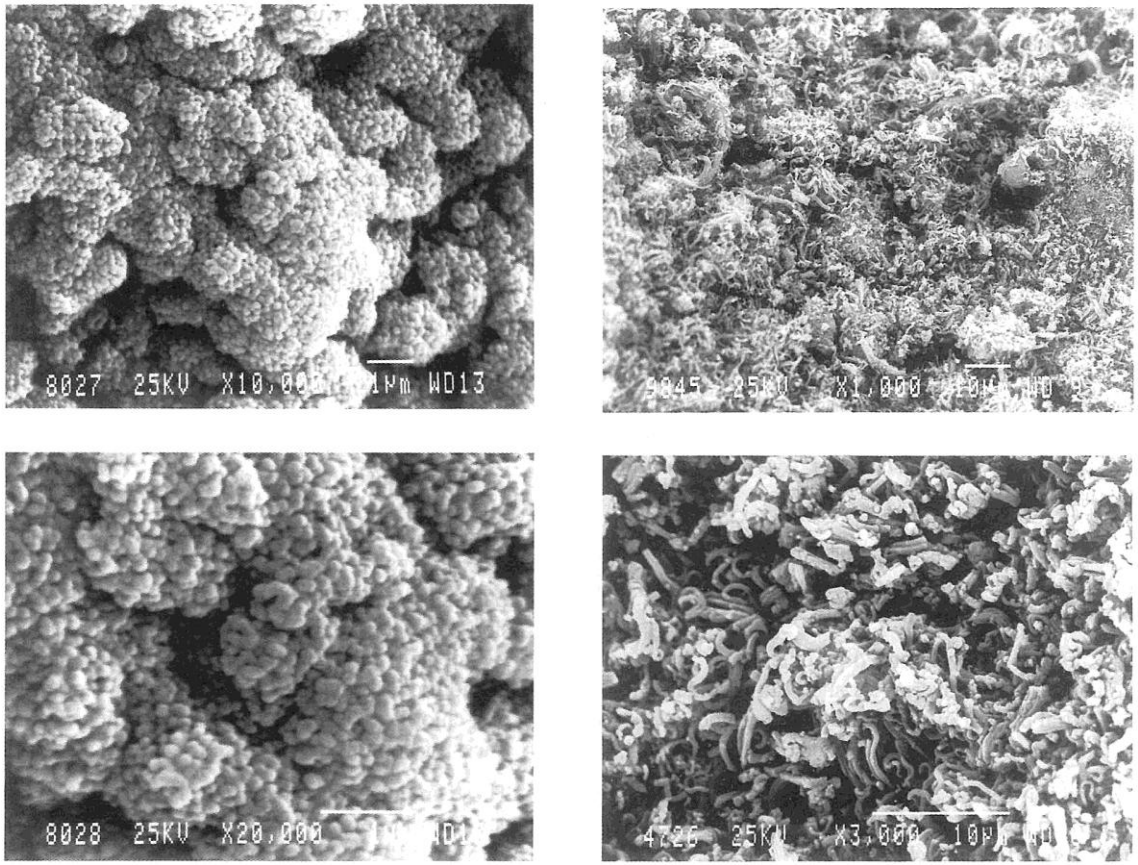


VC-coke: CVD

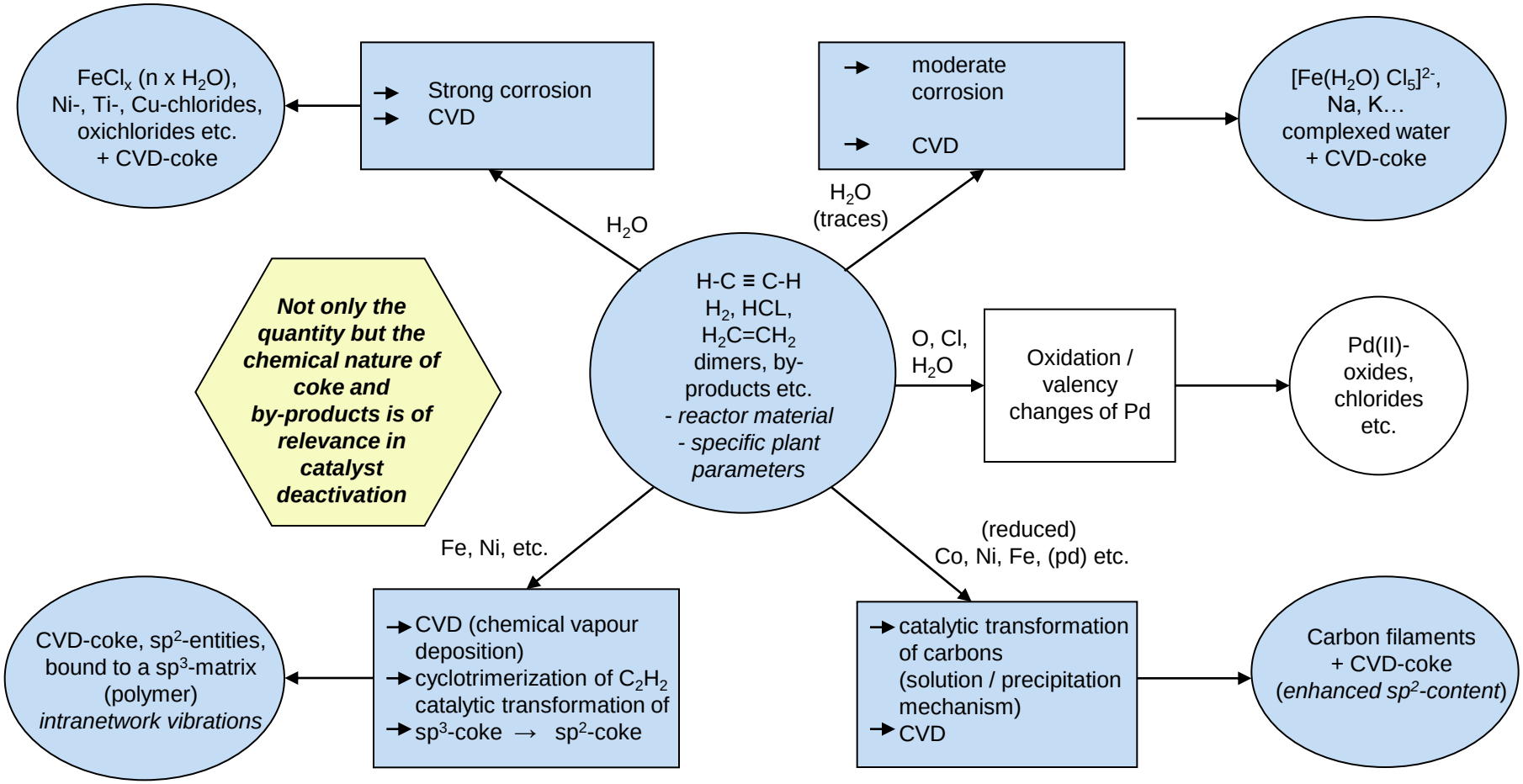
CH_4-coke: graphite

VC-coke, dew point corrosion: $[Fe(H_2O)Cl_5]^{2-}$

Selective Catalytic Hydrogenation of Acetylene to Ethylene, Carbonaceous Deposits at Catalyst Surface



Pd/SiO_2-catalyst: „Road Map of Deactivation“



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Platinum on Carbon Black:

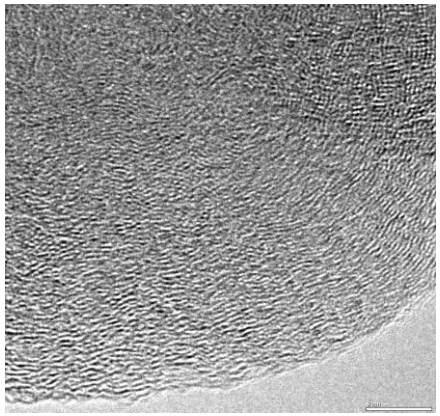
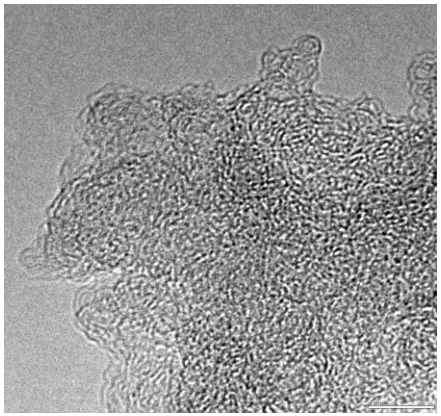
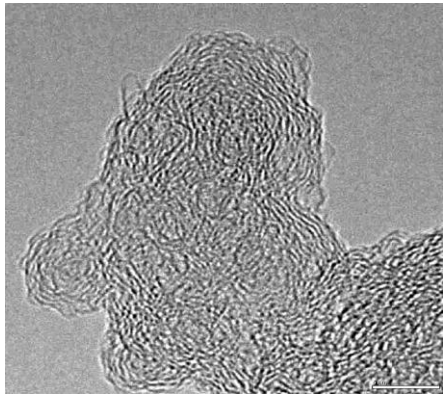
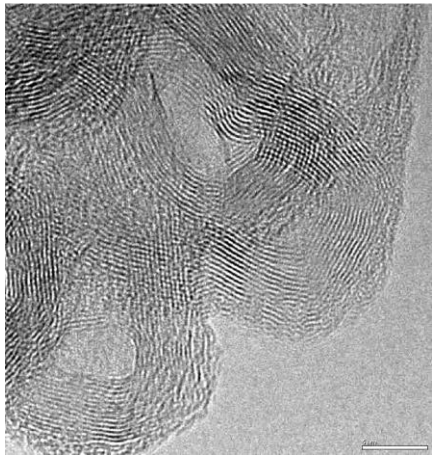
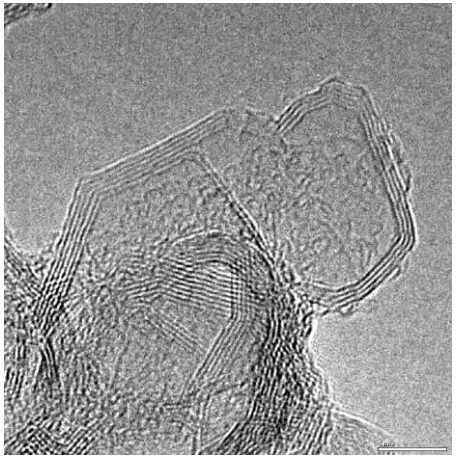
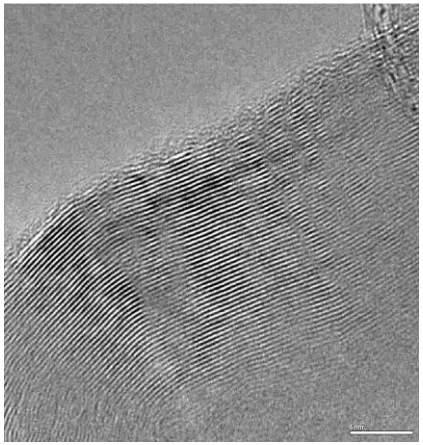
Fuel Cell Catalysts (PEM)

- C-Terminating Protons

- Titration of surface sites on nanosized, supported Pt-particles with atomic hydrogen

- In search for the sites relevant for performance → catalyst optimization

How should the surface of a good carbonaceous catalyst support for fuel cell applications look like?

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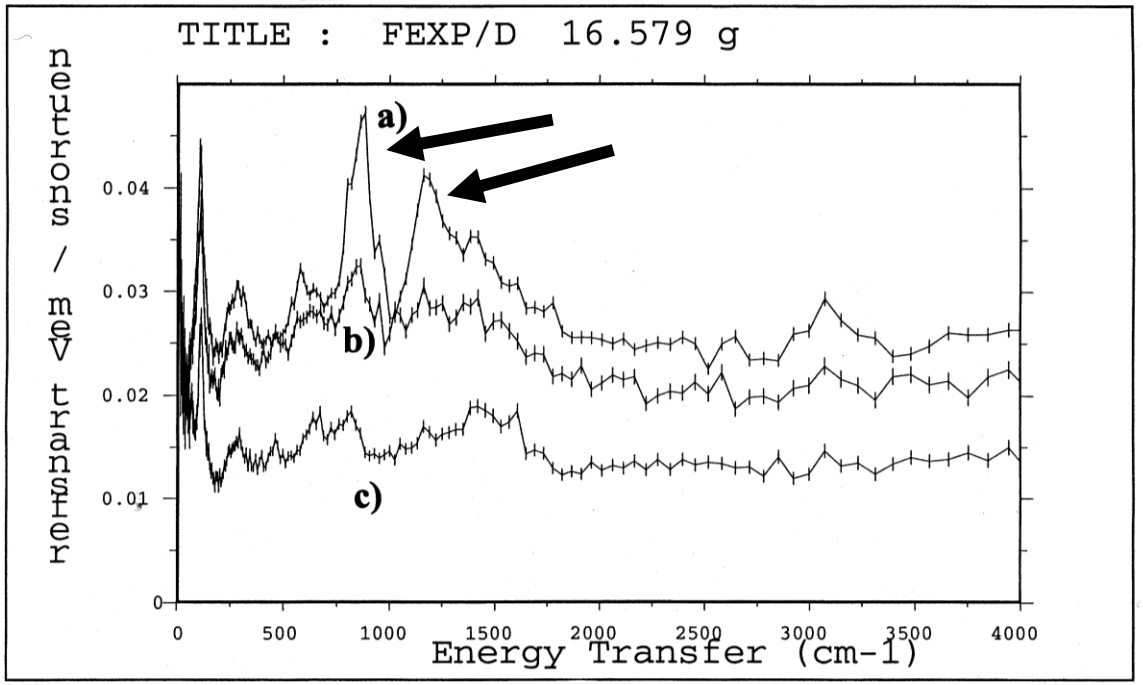
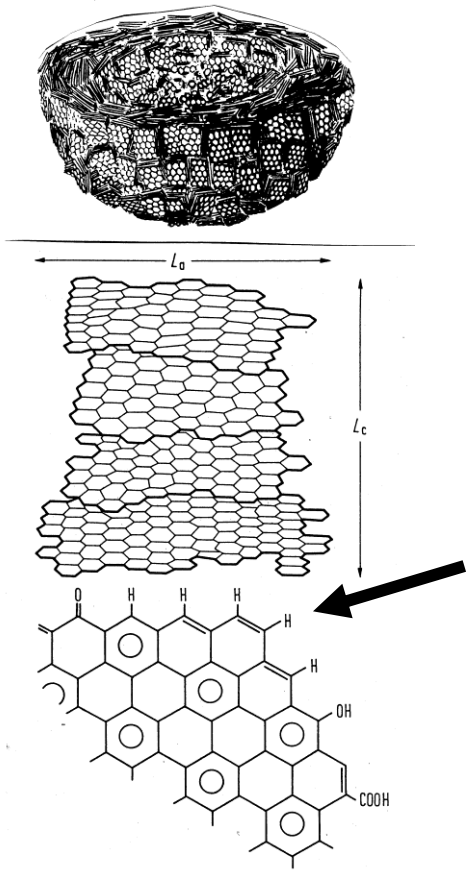
smooth, rugged/sp^2-disorder, graphitic….?

IINS-Spectra of Carbon Black Supports: spectroscopy at 200 - 4000 µg/g H content

IINS spectra of different carbon black supports

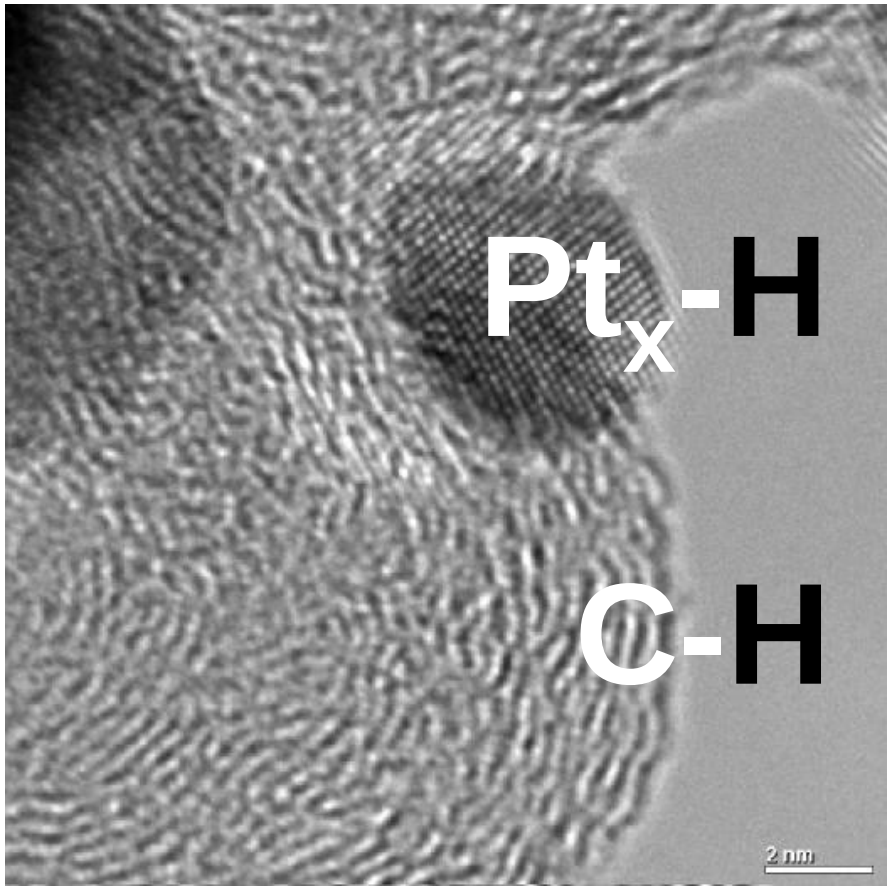
a. Furnace black
b. XC72
c. Acetylene black





Terminating Protons

Pt/C Fuel Cell Catalyst (PEM): Formation of Atomic H, Site Occupation Pt_x-H ? Ideal or real cubooctahedra ?



Pt-H Distance by ND:

0.188 nm

Chem. Comm. 2010

Scale Bar: 2 nm

WANTED: ALIVE (!)

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

H_2 ?

H_2O ?

Pt-OH ?

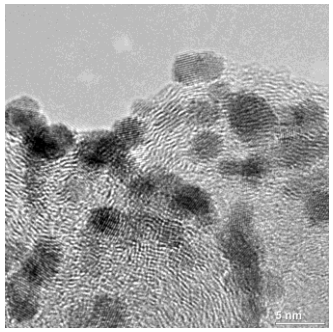
Pt/Ru-OH ?

Atomic H: Pt_x-H ? → IINS

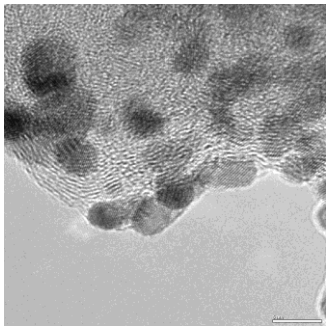
Changes of the relative contributions of (100) and (111) faces on platinum-nanoparticles with increasing particle size (2, 4, 6 ,8 nm), detection of Pt_x–H and Pt-OH. IINS → HREELS on single crystal surfaces; Cs-corrected TEM …

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

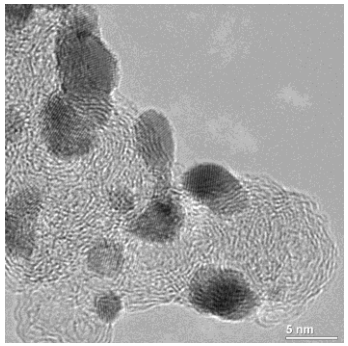
(a) 2 nm



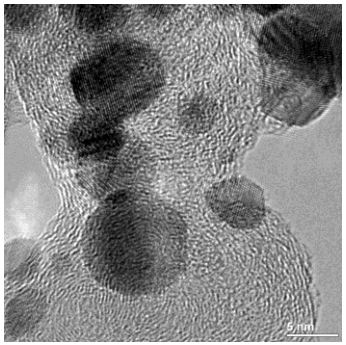
(b) 4 nm

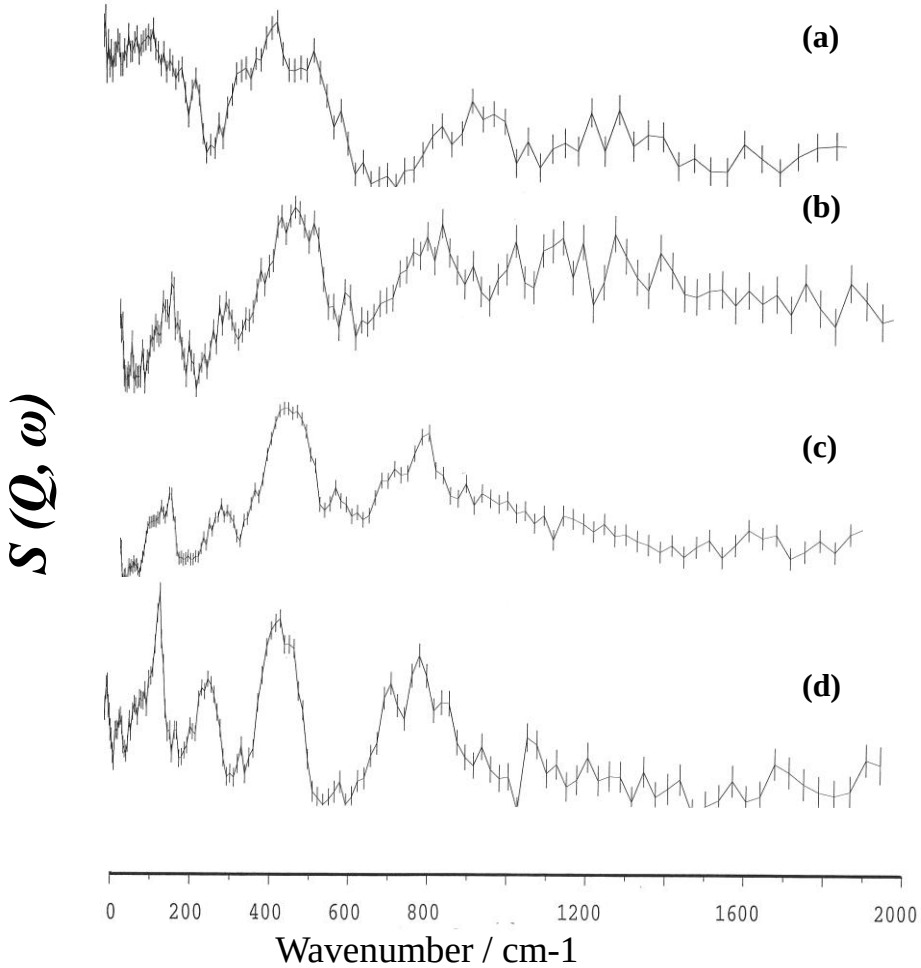


(c) 6 nm



(d) 8 nm





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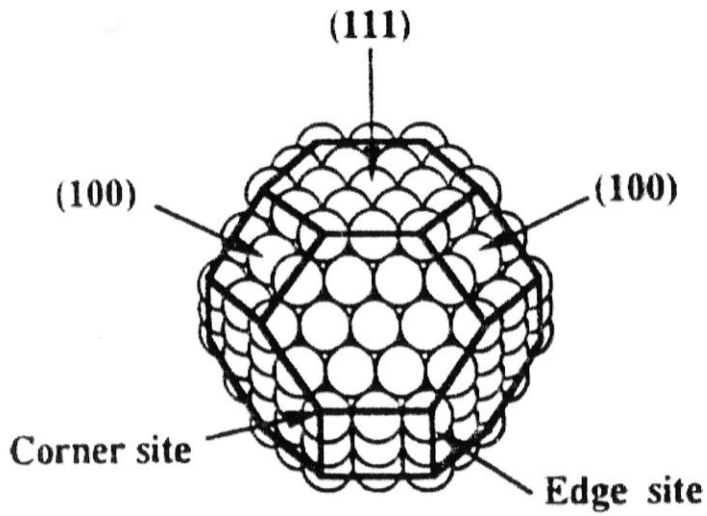
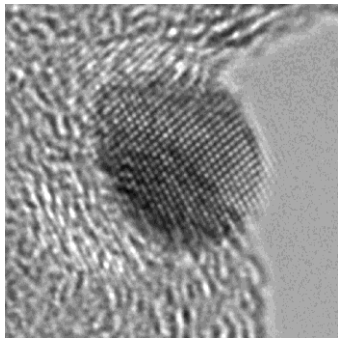
Ideal / real morphology of supported nanoparticles ?

Cubo-octahedral structure of an ideal platinum crystallite



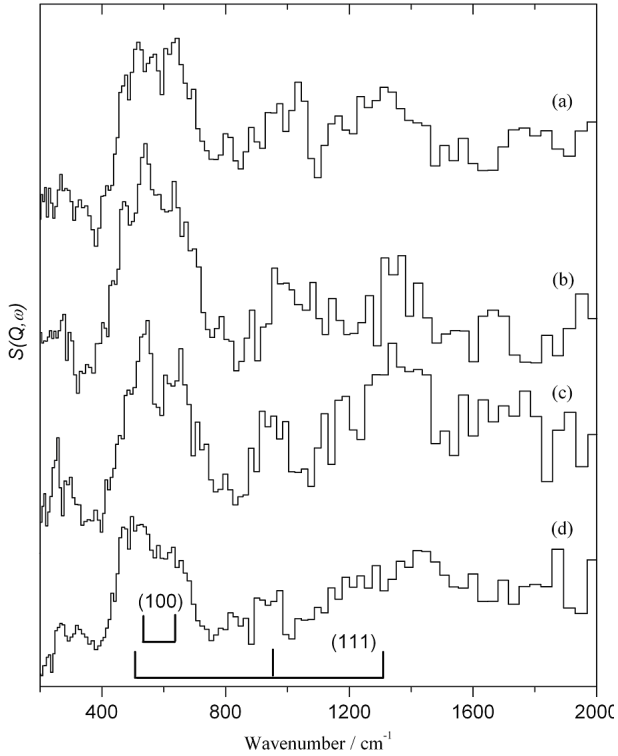
K. Kinoshita, J. Electrochem. Soc. 137 (3) (1990) 845

How to detect the introduction of certain disorder/sites relevant for adequate catalyst performance?



→ **G.A. Somorjai: heterogeneous solid surfaces with different surface sites, different no. of next neighbours**

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



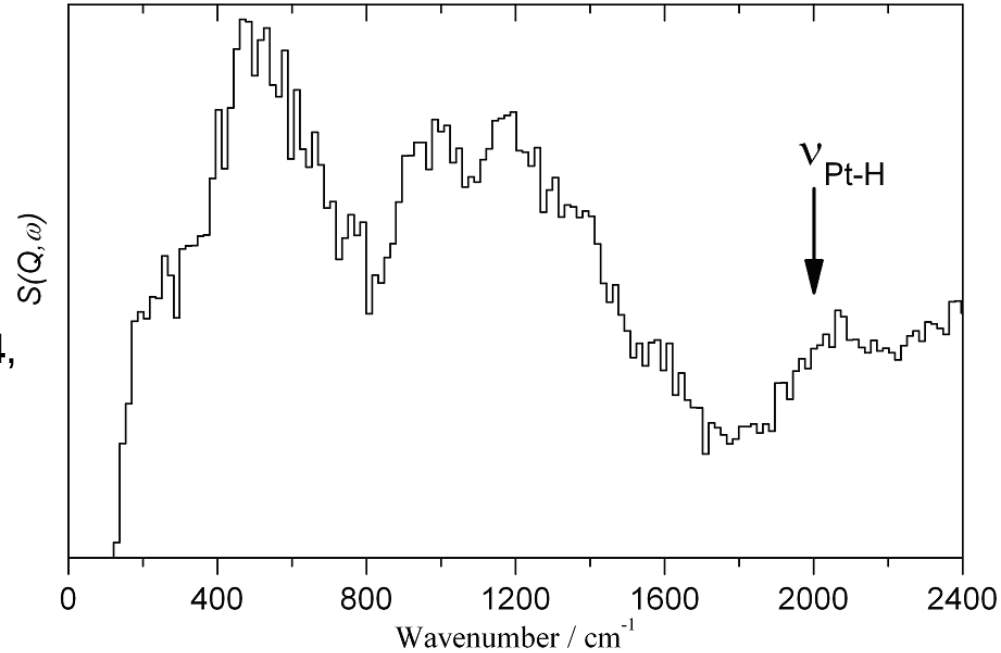
Catal. Today **114**, 418 (2006)

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

→ **Surface Titration with atomic hydrogen**

In-situ IINS of a Fuel Cell Catalyst under 1 bar Hydrogen On-top Pt-H Valence Vibration at 2020 cm-1 Focus: 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 ???

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IINS of fuel cell catalysts

IINS-Information from Pt/H-vibrations + HR-TEM…

- **Different size and morphology of the precious metal particles → different relative contributions of H on lower and higher coordinated sites**
- **To be studied by proton dynamics/ site titration with H: Introduction of disorder/defects in real nanoparticles supported on high surface area supports; Input for future catalyst syntheses**

→ Active centers / „spectator“ sites…..

AQura analytical solutions

Preferential adsorption of an isomer on a Pd/C catalyst

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

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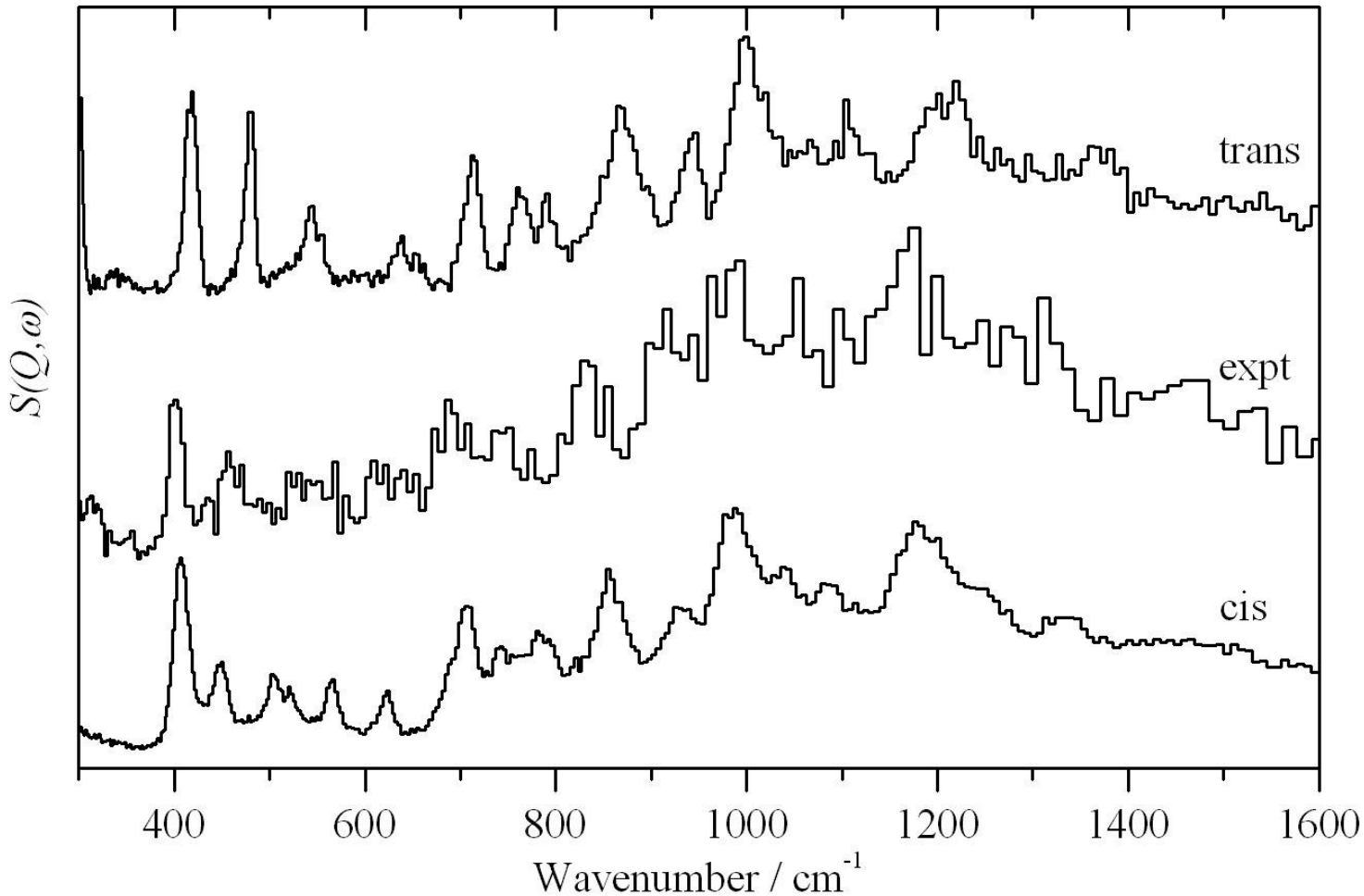
IINS: Mirror image to the organic phase. What is present at the catalyst surface after the organic phase is removed?



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Heck reaction: Bromobenzene and Styrene to Stilbene Supervison of Liquid Phase: Yield 90% of trans-Product IINS: cis-Stilbene enriched on Catalyst Surface

1) ***cis*-Stilbene was accumulated at the surface of a Pd/C catalyst during re-deposition of the palladium particles from the organic reaction mixture. Stronger adsorption or complexation between this isomer and the colloidal or complexed palladium in the solution may play some role in the solution/leaching process of the palladium during the reaction.**

2) ***cis*-Stilbene was retained from the liquid reaction phase and accumulated at the solid surface due to stronger interactions between the edges of the sp2 type basic structural units of the activated carbon support and the *cis*-stilbene than between *trans*-stilbene and the support. This conclusion is in line with the comparatively low hydrogen content of the activated carbon support used in the study (5600 ppm) and, therefore, the enhanced graphiticity of this material.**

IINS: mirror images at the solid catalyst surface to the liquid reaction medium; cis/trans

Such findings are valuable to help understand the phenomena during leaching and re-deposition of the precious metal in-process.
→ heterogenization of homogeneous catalytic processes

Usually it is assumed that educts and products are adsorbed to a similar degree. This was not the case in the present example.

Preferential adsorption is also of relevance for catalytic hydrogenation reactions

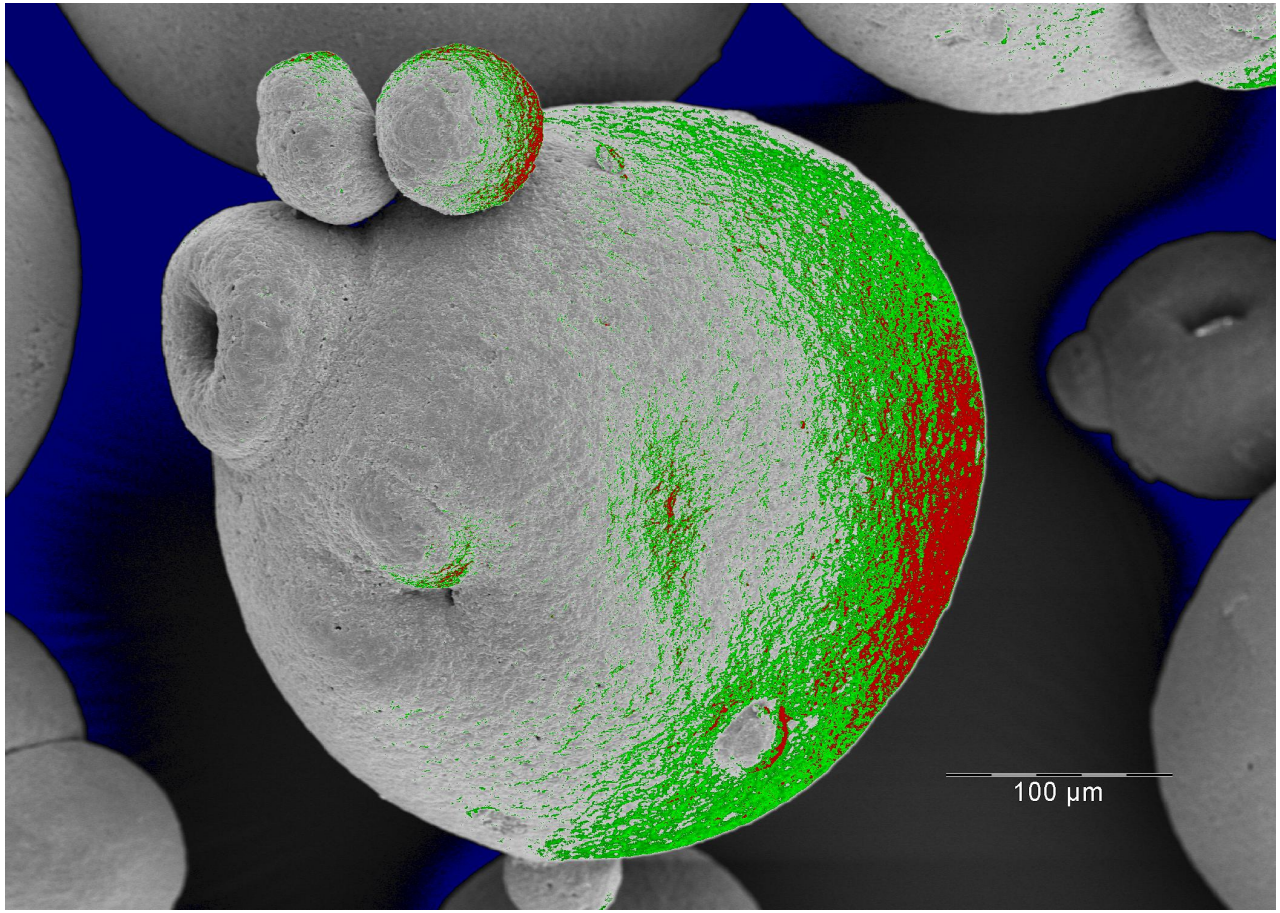
Conclusions

- **Inelastic incoherent neutron scattering is a very helpful and versatile technique for the solution of problems in (*e.g.*) industrial R&D, materials research, applied catalysis and many other areas, especially if all other analytical methods fail**
- **The unique potential of neutron spectroscopies for industrial applications is still not recognized sufficiently**
- **There are serious limits in the accessability of *high flux sources* and *adequate spectrometers* suitable to tackle the practical demands of technologists!**

Many thanks for cooperation in applying neutrons during the last 30 years

- D.K. Ross (Birmingham, Salford)
- C. Windsor, R. Sinclair, D. Cummins (AERE Harwell)
- S.F. Parker, J. Tomkinson, A.J. Ramirez-Cuesta (ISIS)
- J. Penfold, R. Heenan, S. King (ISIS)
- M. Benham (Birmingham, Manchester)
- R. Hempelmann (Münster, Saarbrücken)
- A. Kollmar (ILL)
- M. Sharp (GKSS, SNS)
- F. Fillaux (LASIR)

Looking forward to the future of neutron experiments under improved conditions !



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Our focus of IINS in Industry: Surface Science and Bulk Method

Surface and bulk characterization of carbon blacks for large scale applications in the rubber and printing industry.

Hydrogen bonding of water molecules in confined geometries (activated carbons).

Investigations on activated carbons (improvement of technical catalyst supports).

Hydrogen spillover and hydrogasification effects on Pd/C catalysts for technical hydrogenation reactions.

Heck reaction; heterogenization of homogeneous catalysts.

Impact of exhaust after-treatment catalysts on the surface properties of Diesel soots.

In-situ identification of atomic and molecular hydrogen species on supported precious metal nanoparticles used in fuel cell catalysis.

Surface and bulk properties of technical cokes from high speed and low speed catalyst deactivation processes (observed in large scale chemical reactors and in different production technologies).

Surface and bulk spectroscopy on active and deactivated palladium-based hydrogenation catalysts and on the ternary system Pd/H/C.

Catalyst poisoning by methyl groups.

Hydrogen storage materials……