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SCHOOL ON SYNCHROTRON RADIATION AND APPLICATIONS
In memory of J.C. Fuggle & L. Fonda

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Why ASAXS in catalysis ?

A. Benedetti

School on Synchrotron Radiation

Trieste - 7-13 May 2004

Why ASAXS in Catalysis ?

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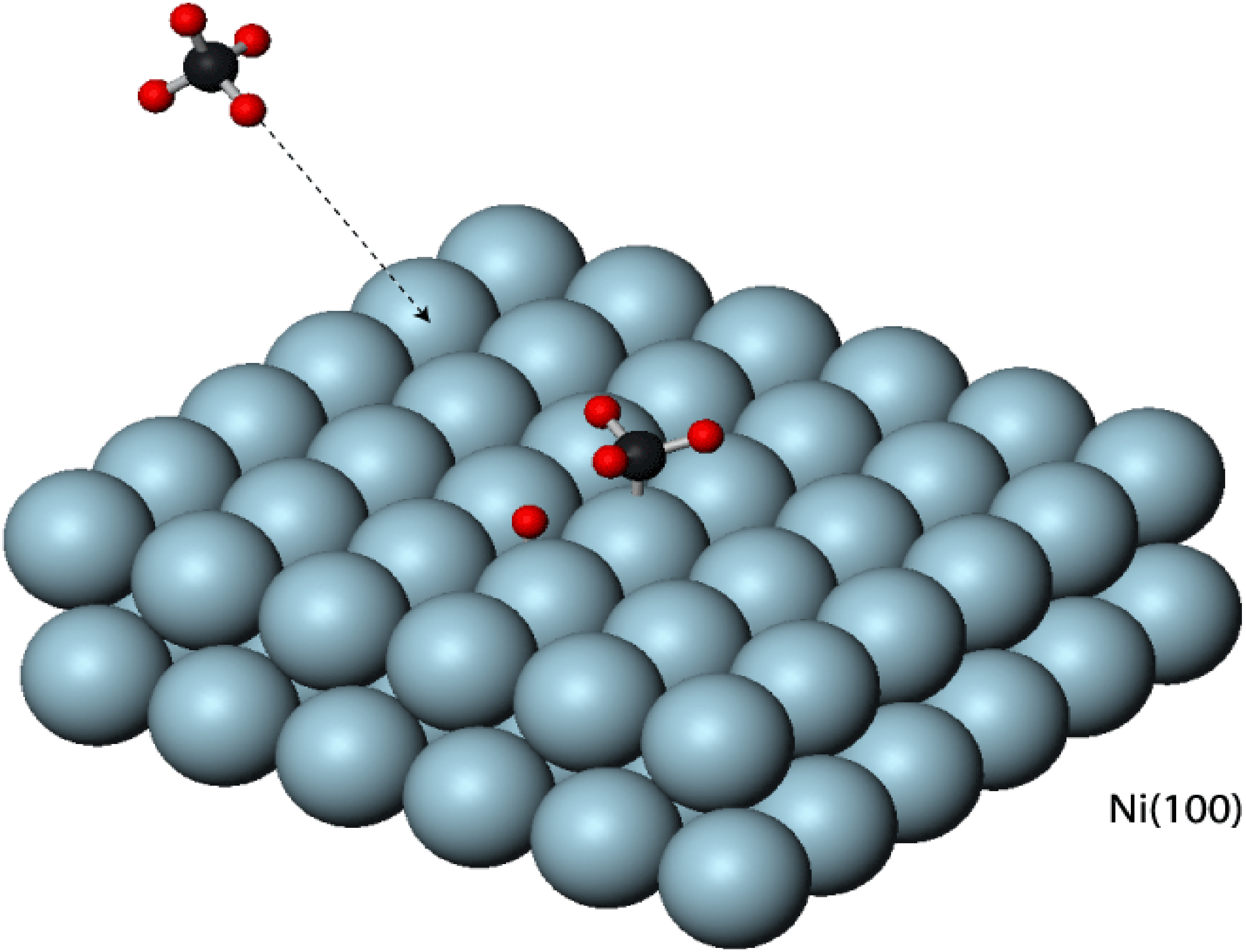
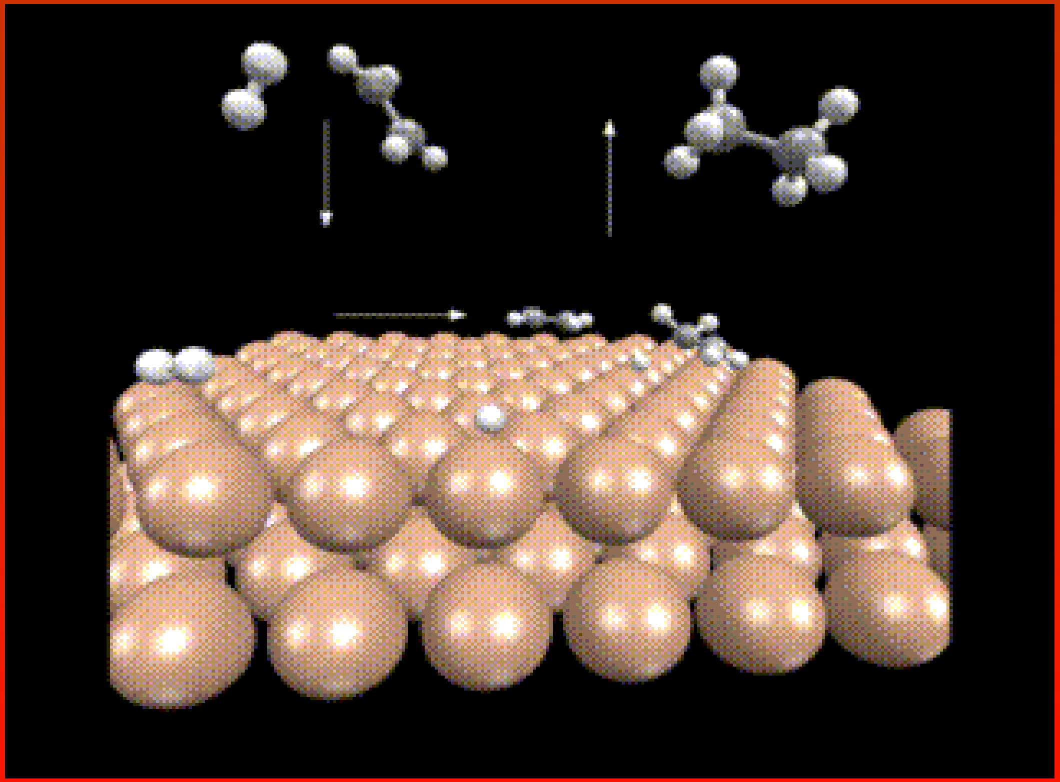
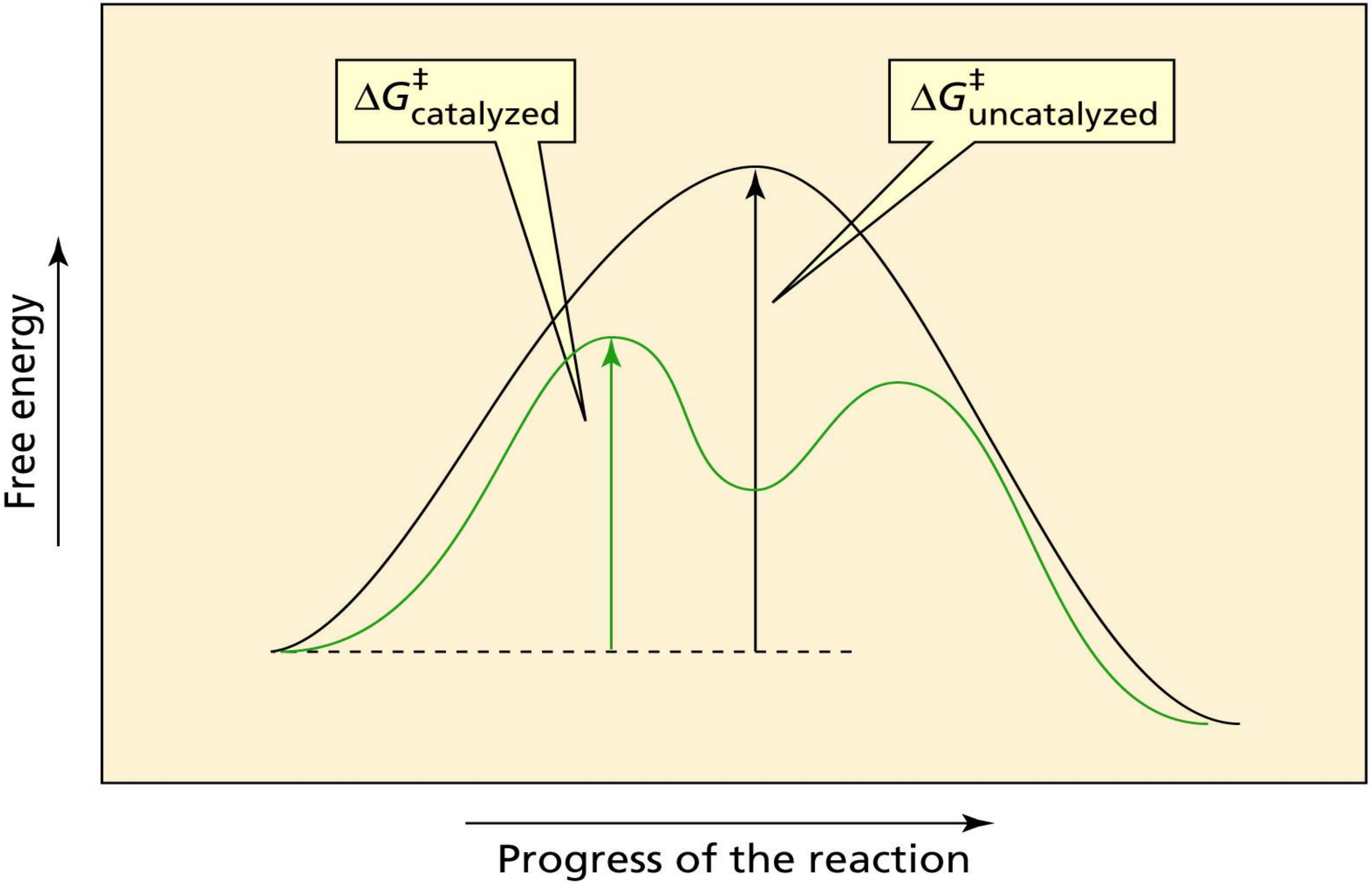
Heterogeneous catalysis deals with the transformation of molecules at the interface between a solid (the catalysts) and the gaseous or liquid phase which carries these molecules.

Consequently quantitative characterization of these systems, concerning both the exposed surface and the bulk structure, is a matter of obvious importance in understanding the mechanisms of the chemical reactions and in developing new catalysts with higher performance.

Moreover, although most practical catalysts are highly complex materials, it has been widely shown that their catalytic activity can be affected by **their nanostructure**.


Ni(100)

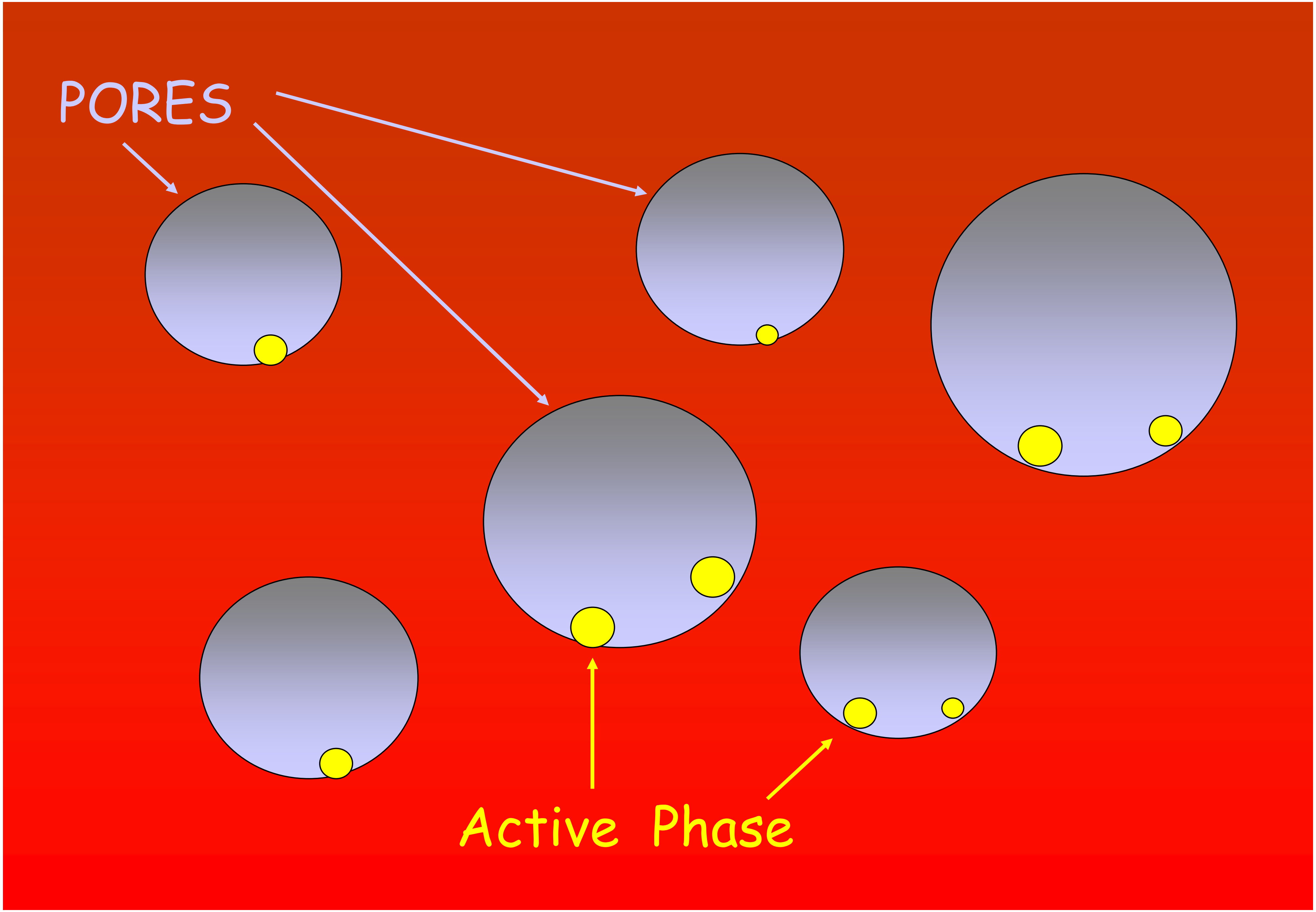



$\Delta G^{\ddagger}_{\text{catalyzed}}$
$\Delta G^{\ddagger}_{\text{uncatalyzed}}$
Free energy
Progress of the reaction

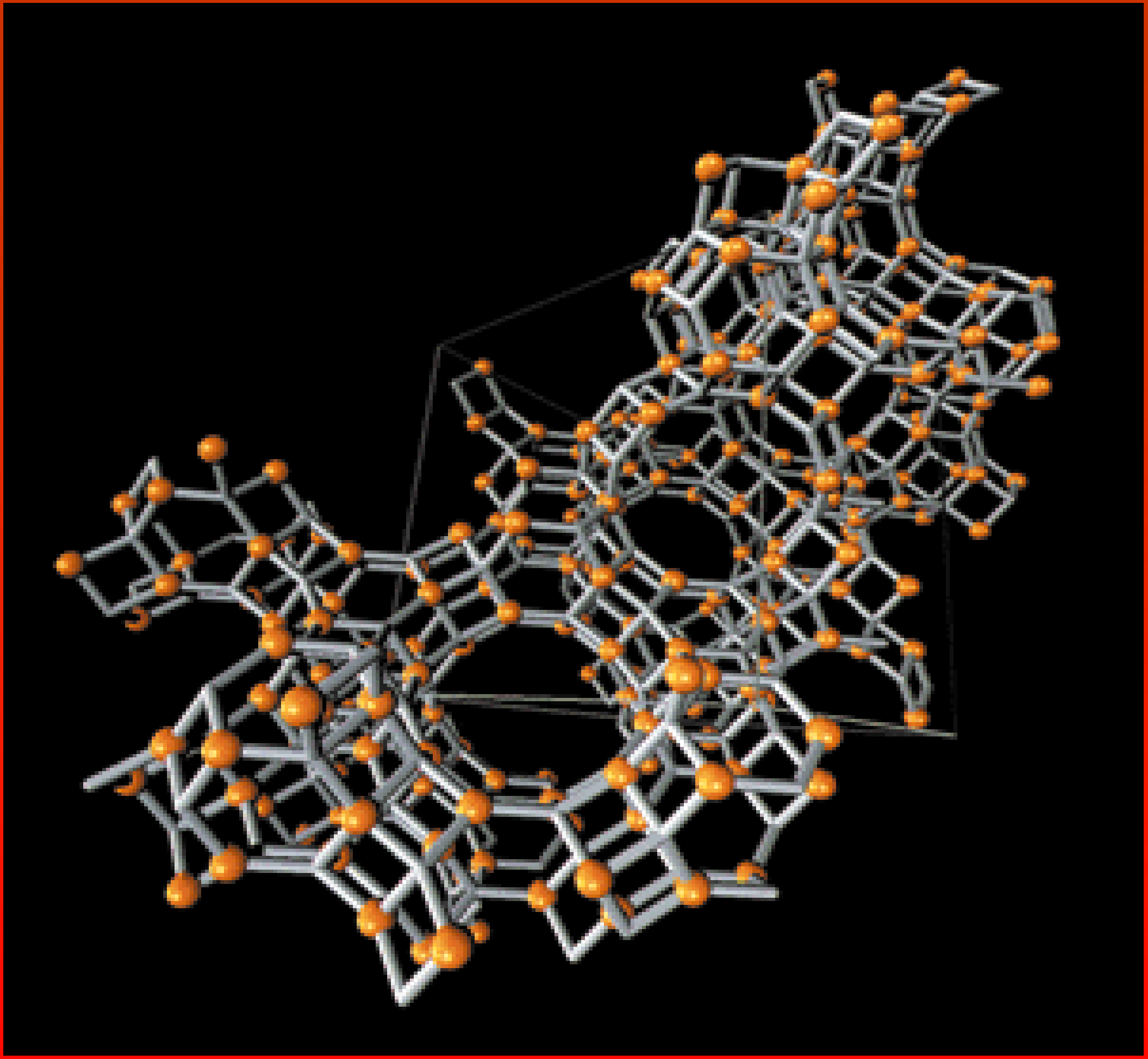
Supported metal catalysts are of particular interest for a variety of reactions involving hydrogen, such as hydrogenation, hydrogenolysis and catalytic reforming.

They are mostly composed of an active phase (metal), responsible for the principal chemical reaction, and a support, or carrier.

Generally, the metal is highly dispersed on the support in aggregates so small that many of the atoms present are on the surface.



PORES
Active Phase



A proper interpretation of heterogeneously catalyzed reaction kinetics requires a precise knowledge of this number of active atoms, exposed on the surface, or, more precisely, of the value of DIPERSION.

The DISPERSION of the active fraction of a catalyst is defined by the ratio between the number of the active atoms exposed at the surface and the total number of active atoms present in the catalyst.

For systems, where the active fraction is present as separate particles, distinguishable from the carrier and characterized by definite shape, simple relationships can be found among the *dispersion*, the *surface area* and the *size of the active particles*.

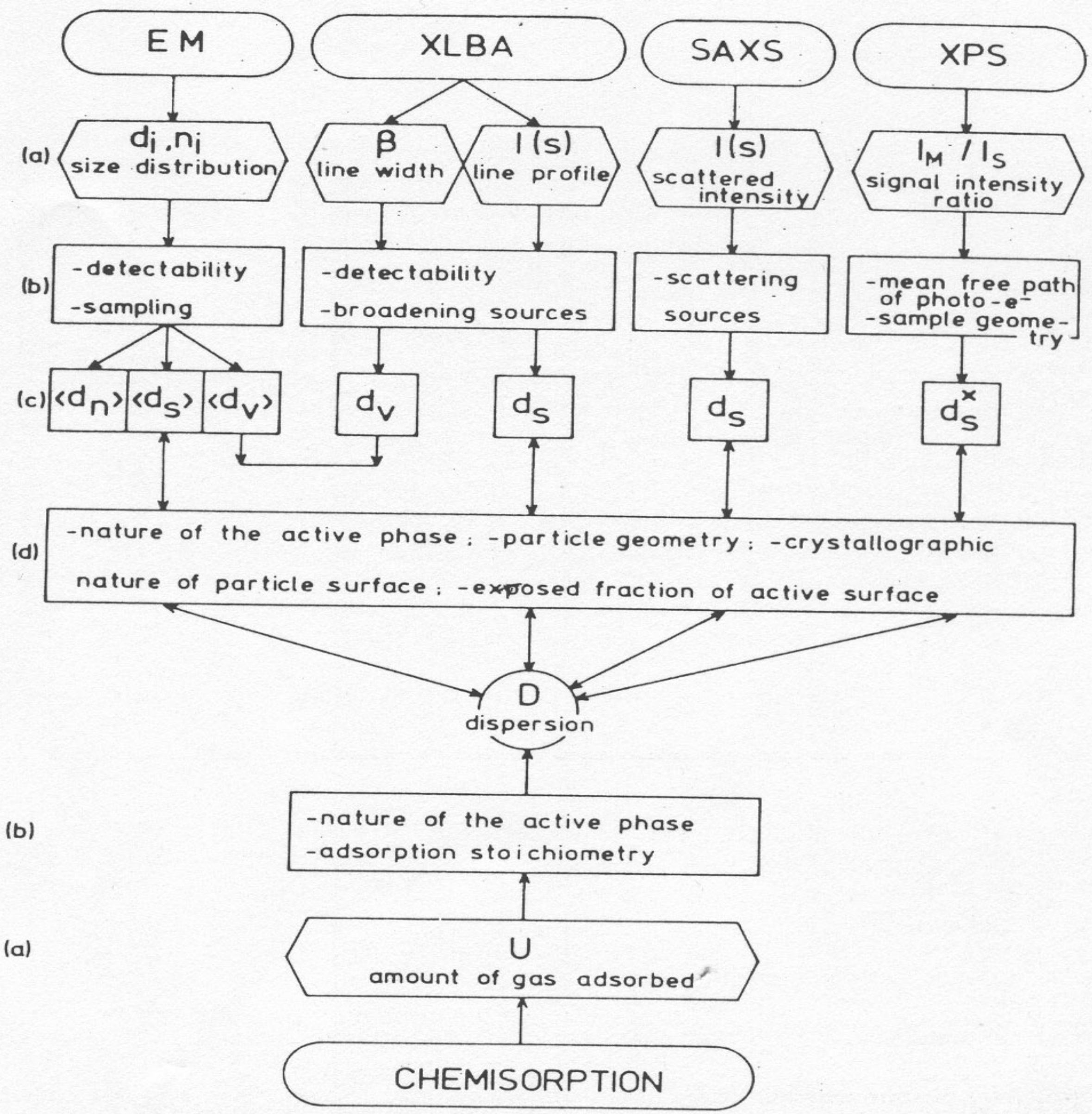
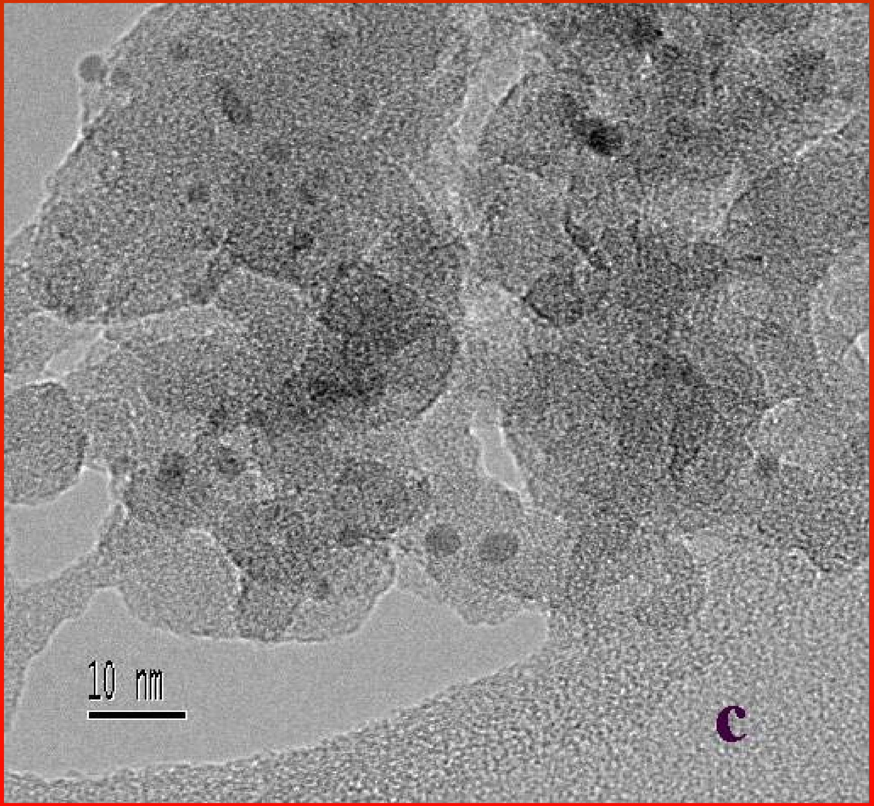


FIG. 11. General scheme of how dispersion D is approached through the various experimental methods.

Nanostructure of Pd/SiO_2 catalysts



Catalysts were prepared by impregnation of SiO_2 (Akzo Chemie F22; surface area 400 m^2 g^{-1}, particle size range 100-150 m) with aqueous solutions of H_2PdCl_4. After drying at 383 K for 18 h, samples were calcined at 773 K for 1 h, then reduced at 623 K for 2 h and passivated (5% O_2 in Ar) before storing exposed to normal room conditions. The Pd content was 2.9 wt.% (sample A) and 5.6 wt.% (sample B), as determined by atomic mass spectroscopy (Perkin Elmer model 500).

Why nanoparticles?

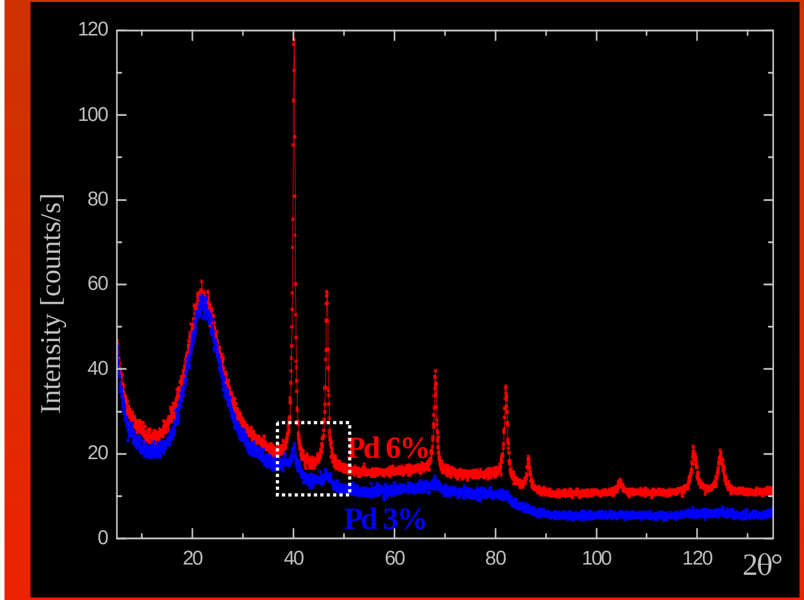
Catalysis is a surface Phenomena

Small Particles→ High surface/volume ratio

Different electronic structure

Increased activity and selectivity

Wide-Angle X-ray Scattering



Hint for very small particles (clusters)

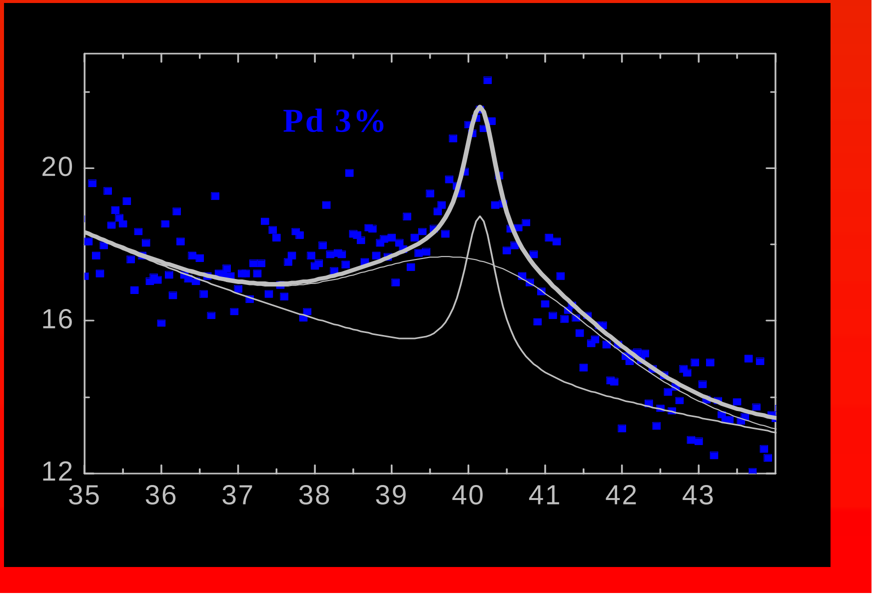
⇑

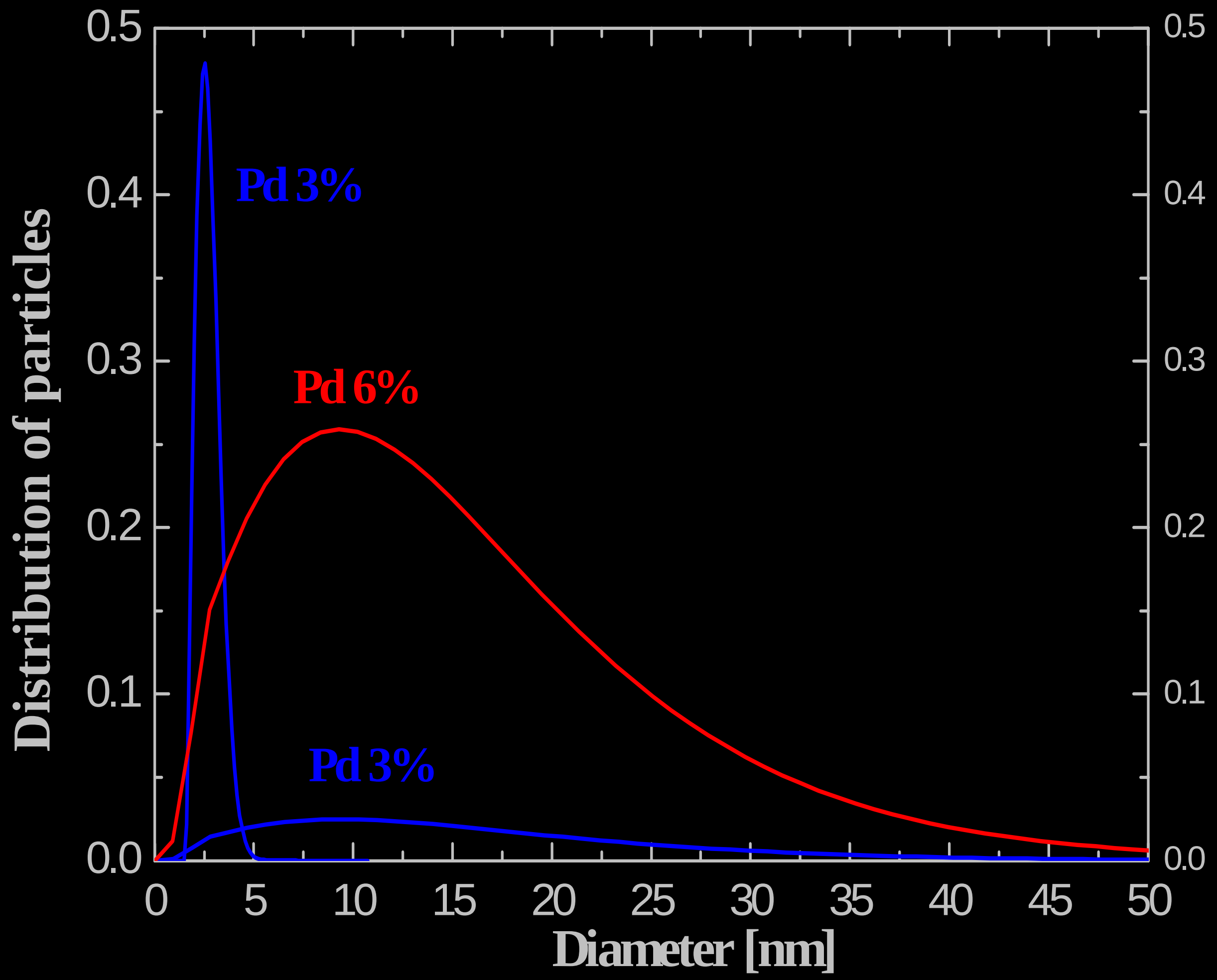
Peak intensities too small compared to those of 6 wt%

Very broad peak with super-lorentzian shape

⇓

Particles smaller than 4-5 nm




Distribution of particles
Diameter [nm]
0.0
0.1
0.2
0.3
0.4
0.5
0
5
10
15
20
25
30
35
40
45
50
Pd 3%
Pd 6%
Pd 3%

In SAXS data, the porous structure of the support produces a scattering which is not easily separated from that due to the metal particles.

The scattering of a blank sample does not match correctly the catalyst scattering; this can be due to modifications of the support along the catalyst preparation when the metal is present and/or to the metal-support cross-scattering.

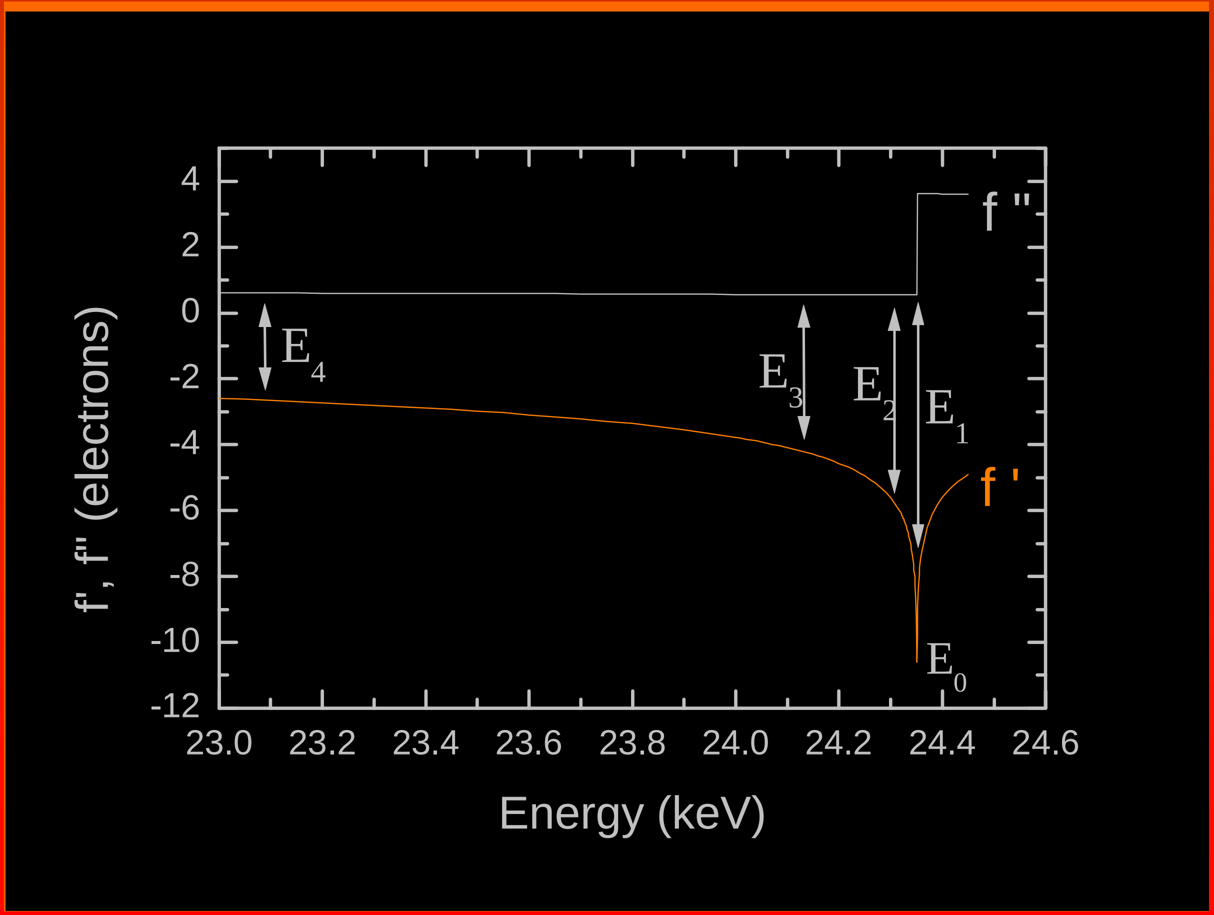
In principle, anomalous scattering is able to subtract the support scattering by exploiting the contrast variations encountered in the neighborhood of an absorption edge.

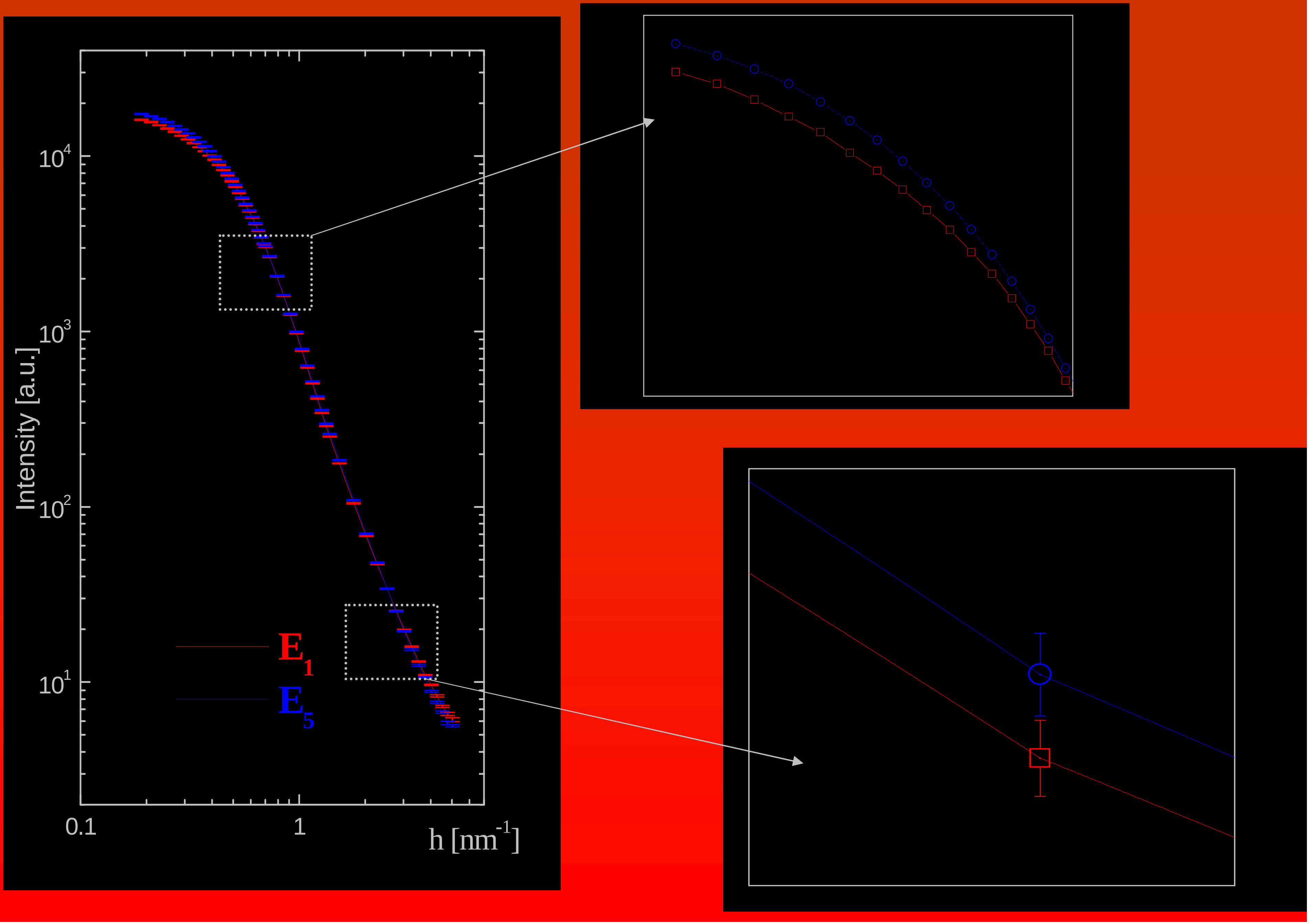
While the scattering factor of the absorbing element varies, all other scattering factors remain unchanged.

Thus, by taking the difference of two measurements close to the absorption edge of the metal, the scattering of the support will be automatically subtracted.

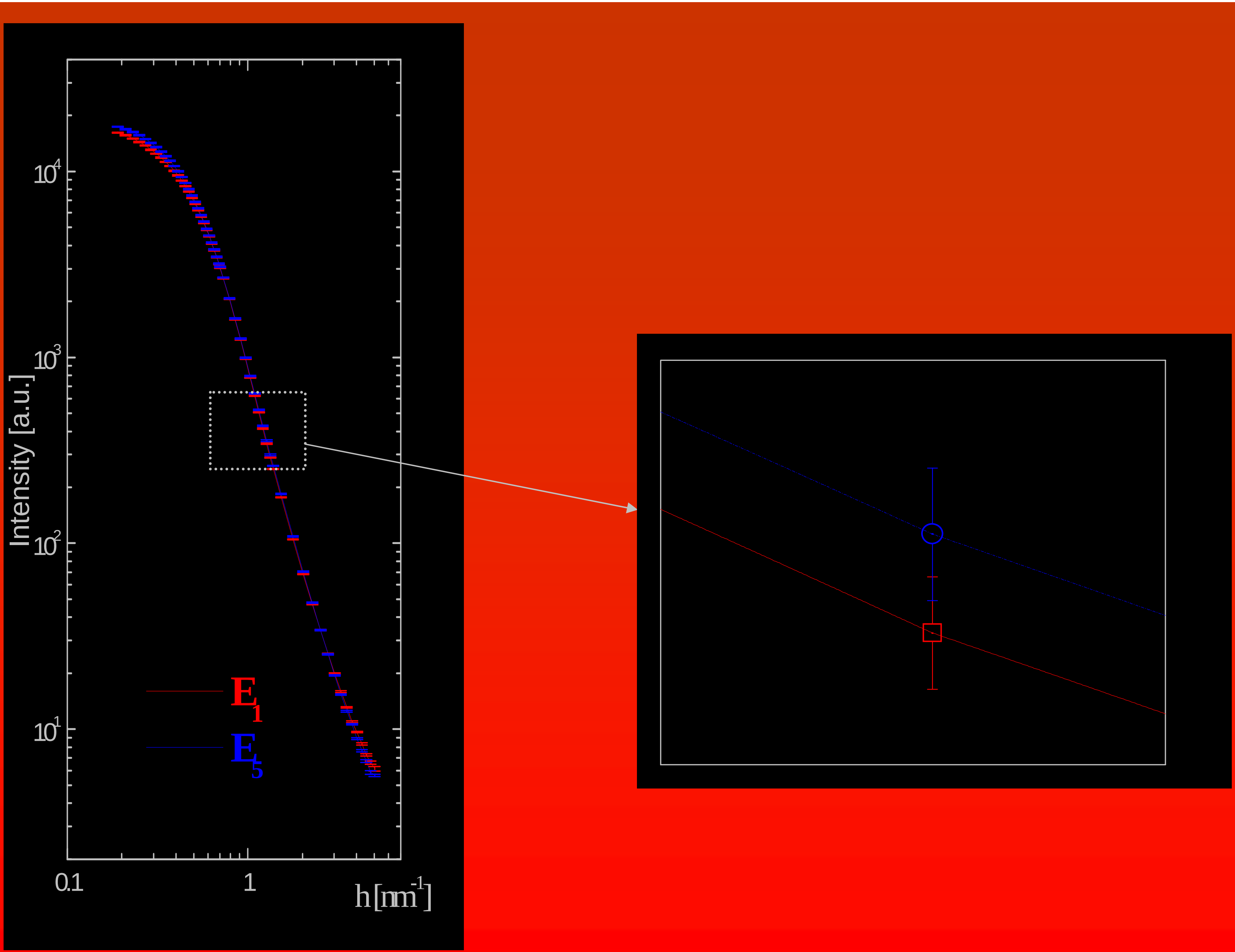
Anomalous Small-Angle X-ray Scattering

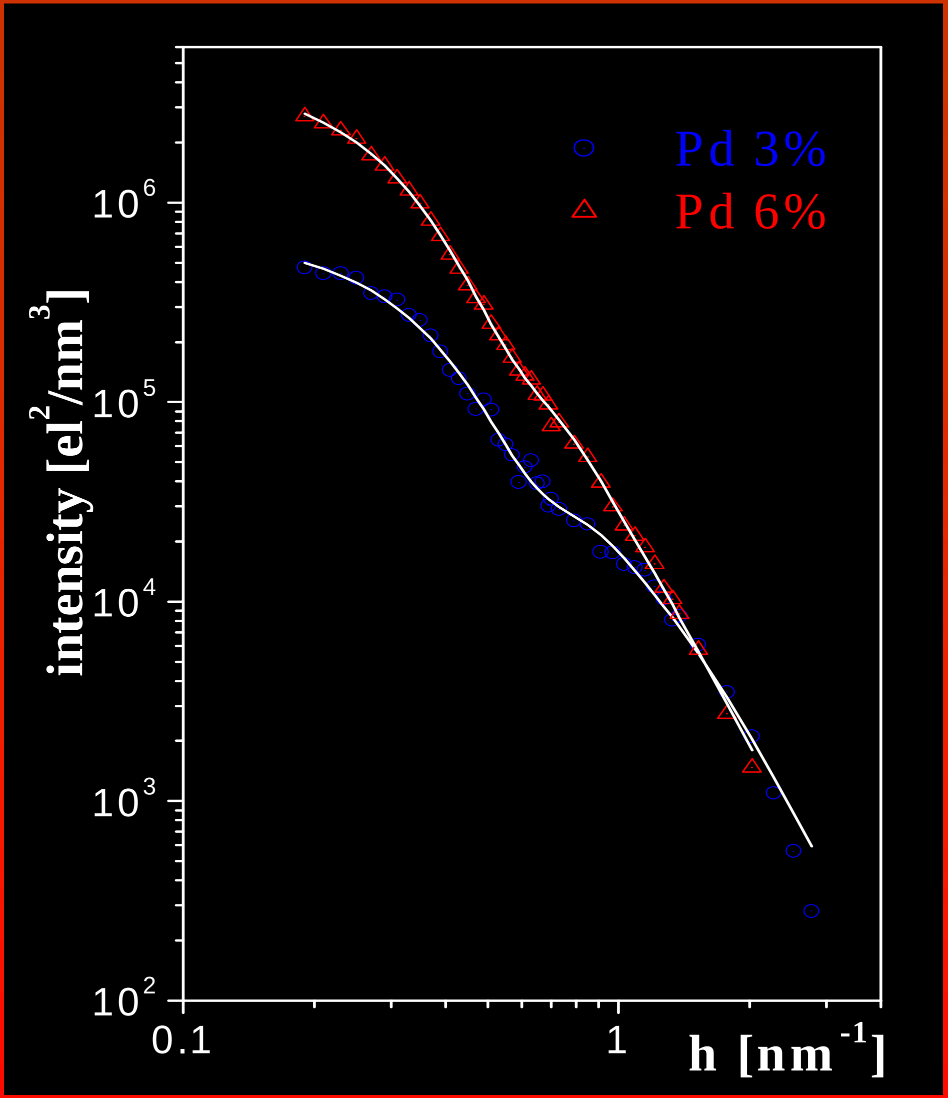
$$f = f_0 + f'(E) + f''(E)$$





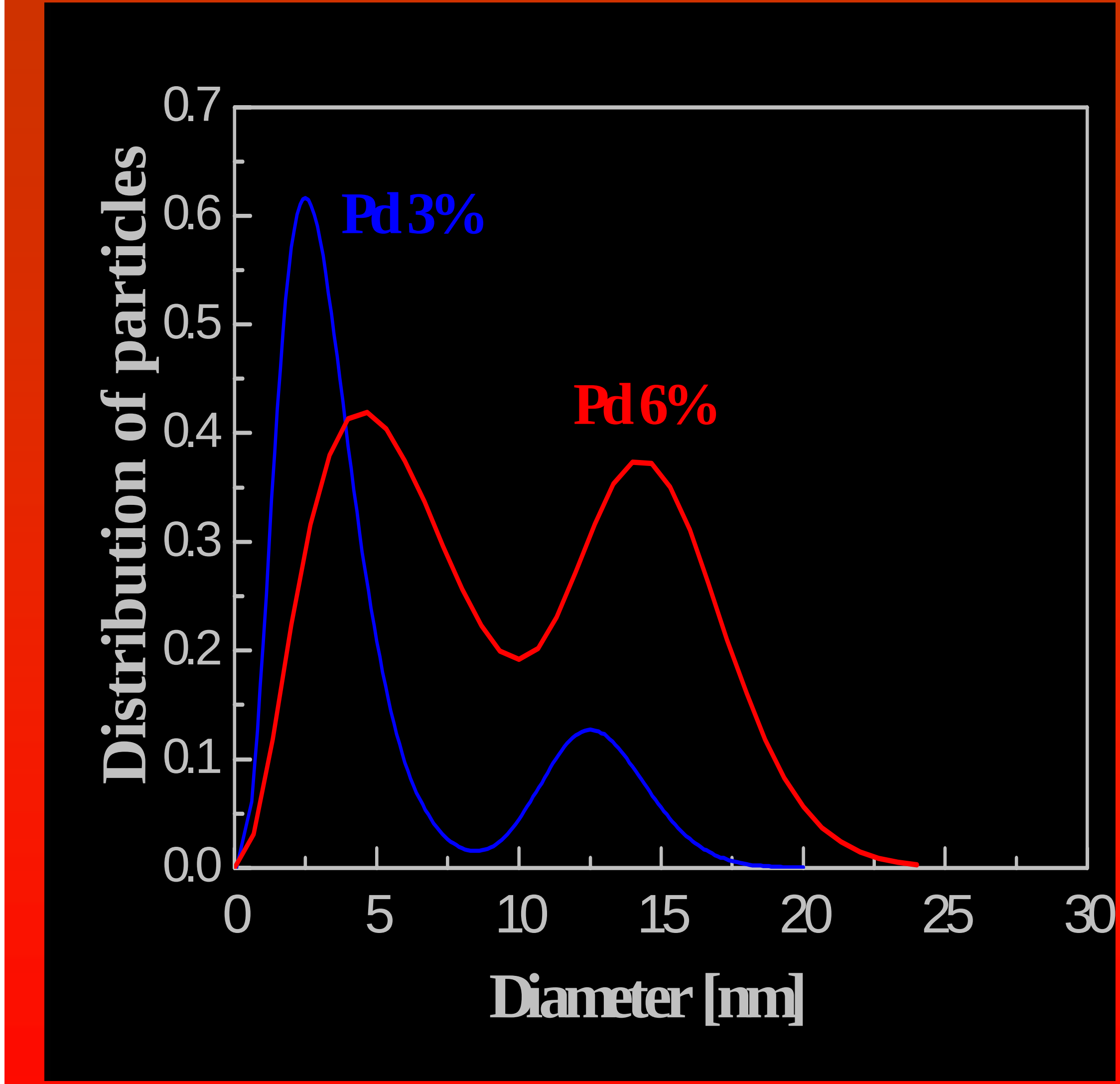
Intensity [a.u.]
10^4
10^3
10^2
10^1
0.1
1
h [nm^{-1}]
E_1
E_5


10^4
10^3
10^2
10^1
Intensity [a.u.]
0.1
1
h [nm^-1]
E1
E5



Both the samples show the presence of a bimodal distributions of particle sizes

The total surface is the same for both the samples



The small particles are

80% in the sample 3 wt%

56% in the sample6 wt%

The cluster size increases with the metal content

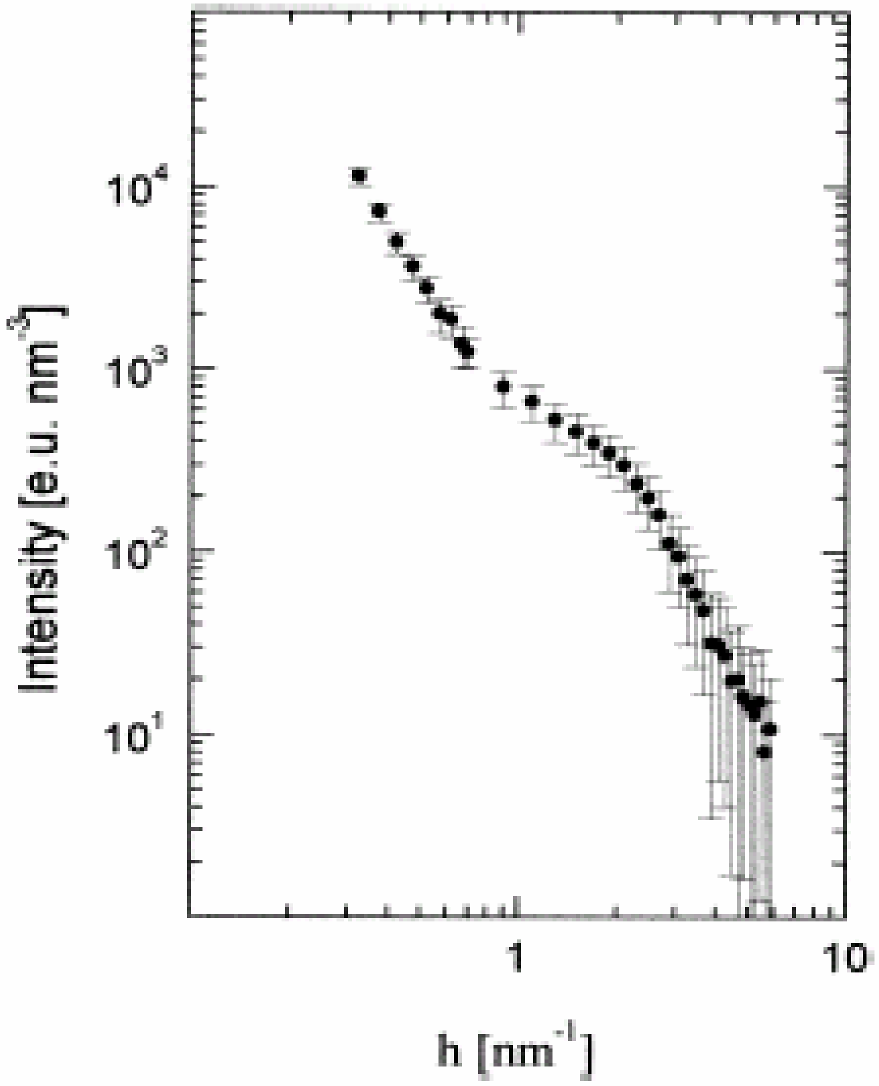


Fig. 1. ASAXS data of sample I A (Au(0.20 wt.%)/C) (●).

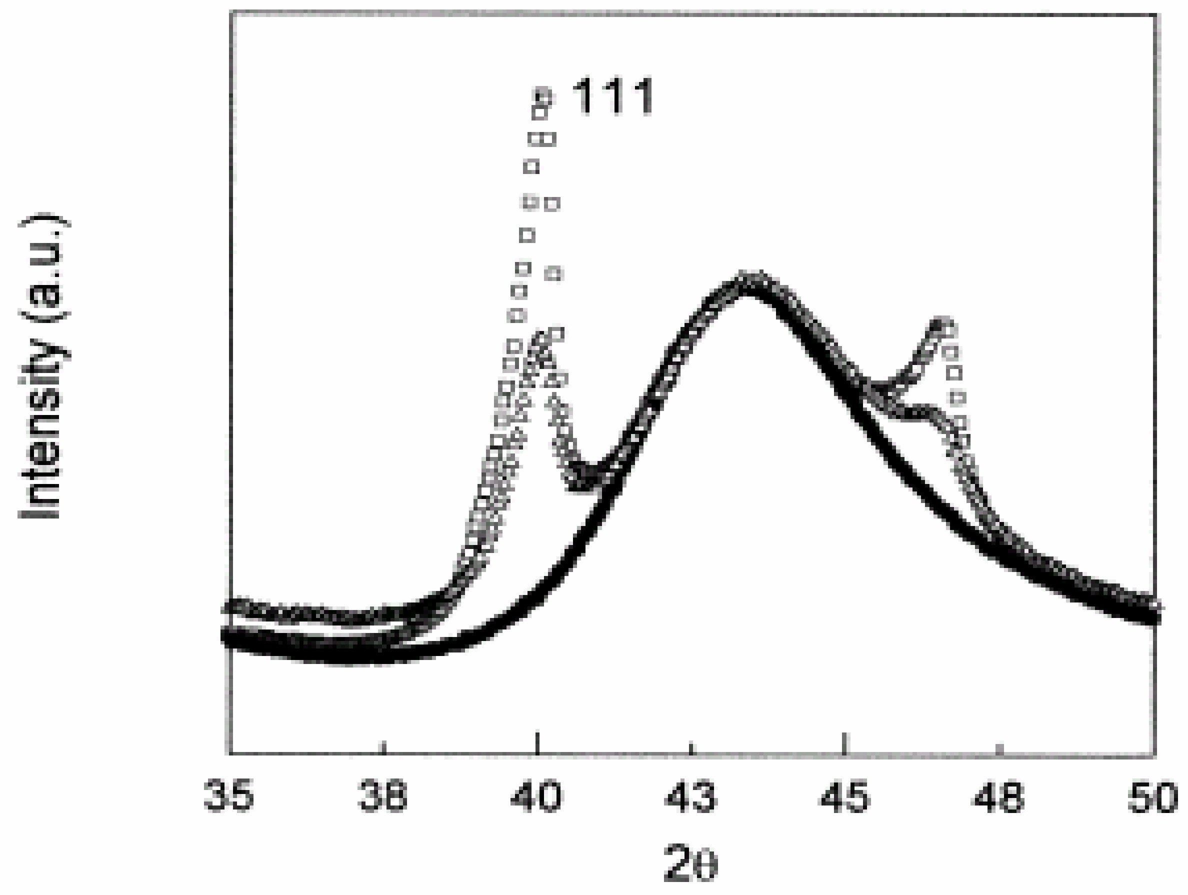


Fig. 3. WAXS data of sample II (Pd(0.72 wt.%)/C) before (Δ) and after thermal treatment (□), together with the scattering of the carbon support (●).The peak at $2\theta = \sim 47^\circ$ corresponds to the 2 0 0 Pd reflection.

<D>ar=13nm

<D>tt=10nm

References

- Benedetti et al. *J.Catal.* **171**, 345 (1997).
- S Polizzi et al. *P.C.C.P.* **3**, 4614 (2001).
- S.Polizzi et al. *J. Synchrotron Rad.* **9**, 65 (2002).