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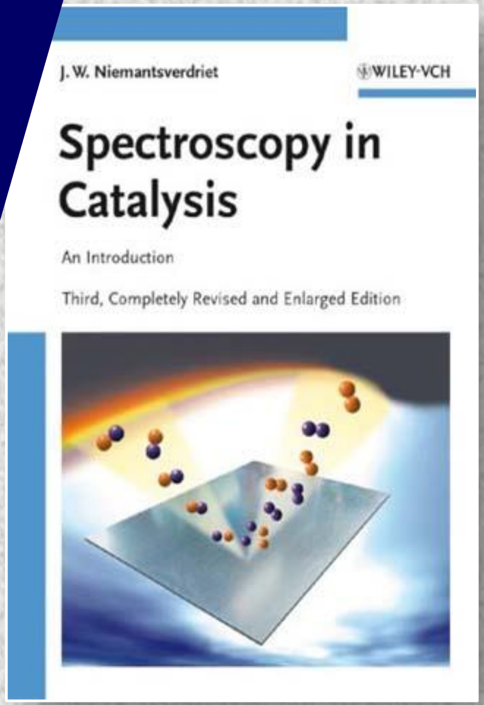
Characterization of solid catalysts

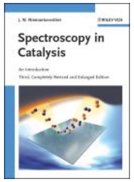
6. X-ray Diffraction

Prof dr J W (Hans) Niemantsverdriet
Schuit Institute of Catalysis

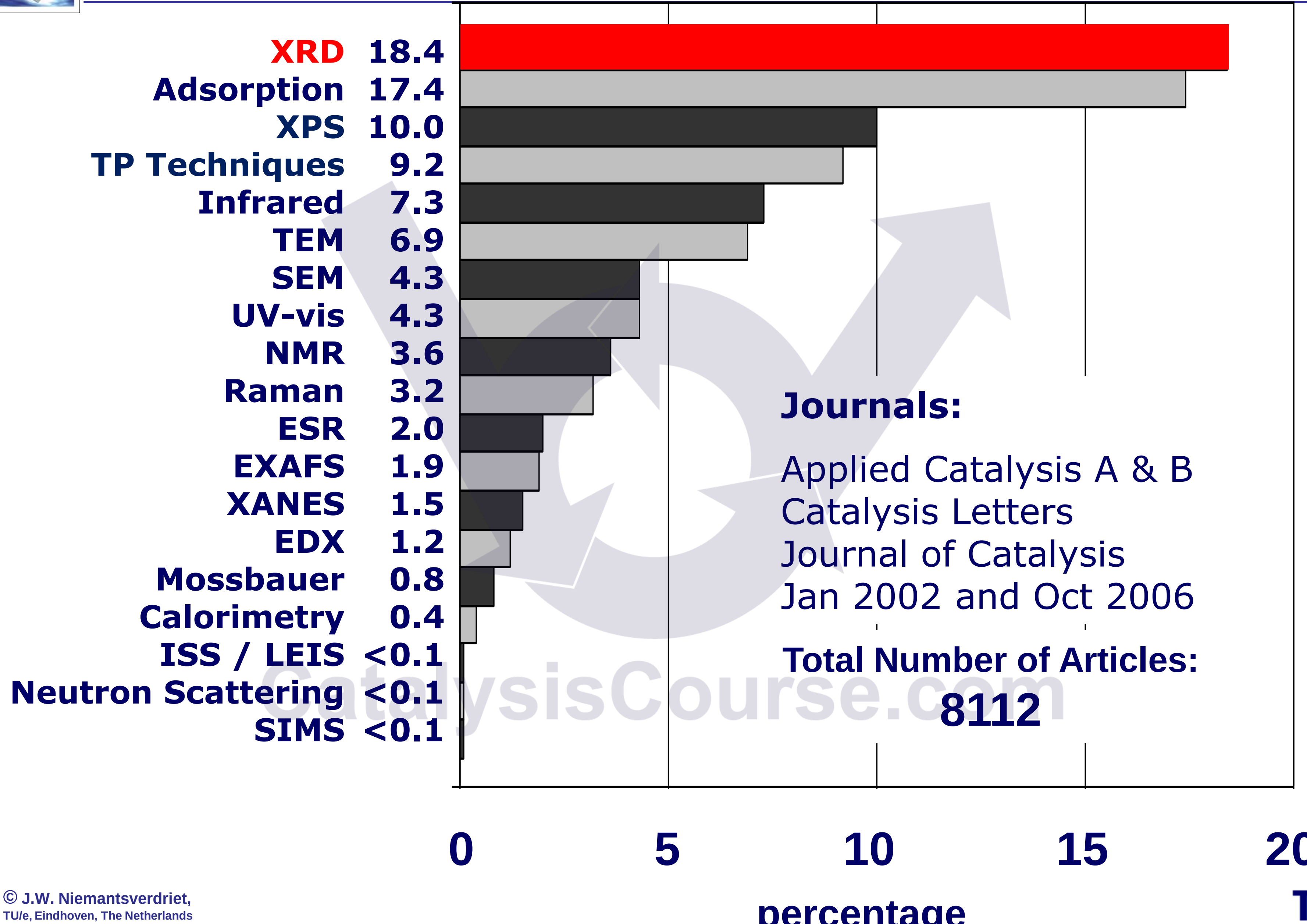


Technische Universiteit Eindhoven University of Technology

Where innovation starts



How often are techniques used



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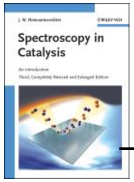
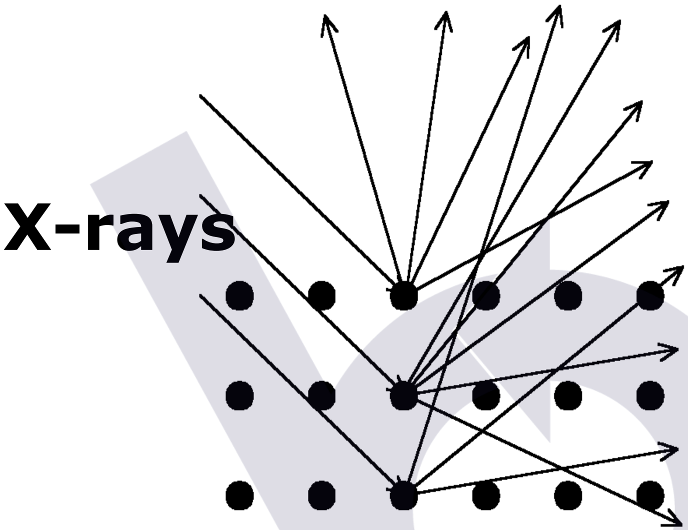
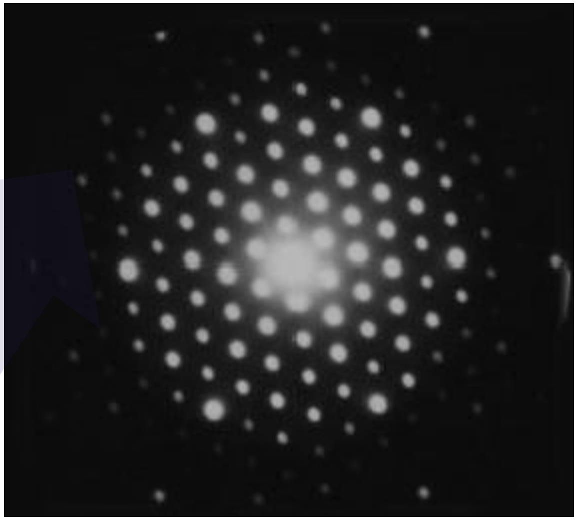
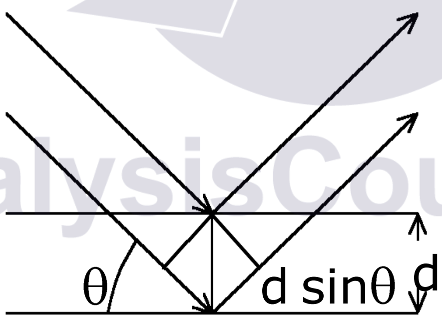


XRD: X-ray Diffraction





Bragg's Law



$$n\lambda = 2\,d\,\sin\theta$$

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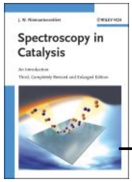
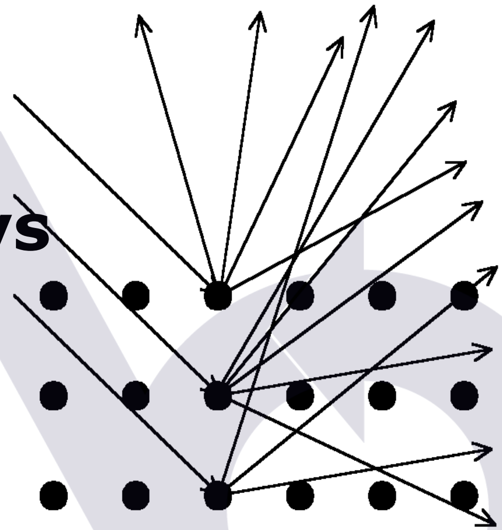
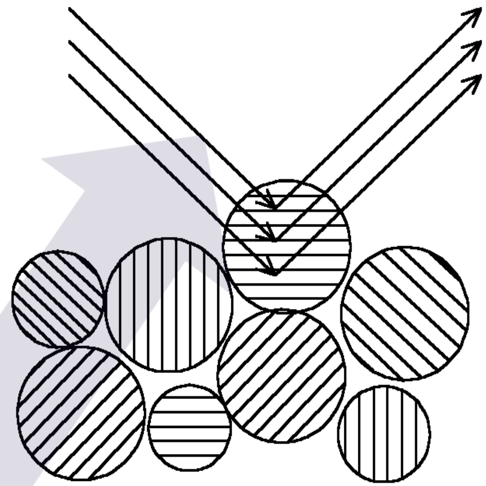
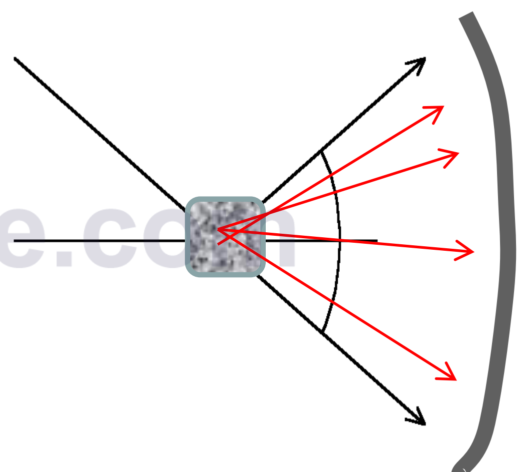
XRD: X-ray Diffraction



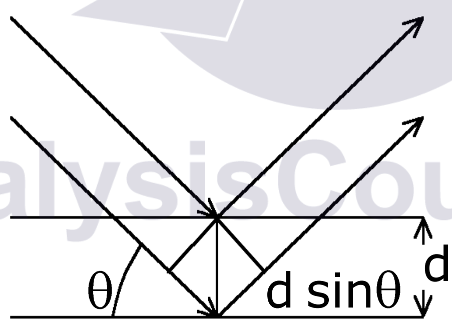




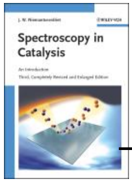
randomly oriented particles



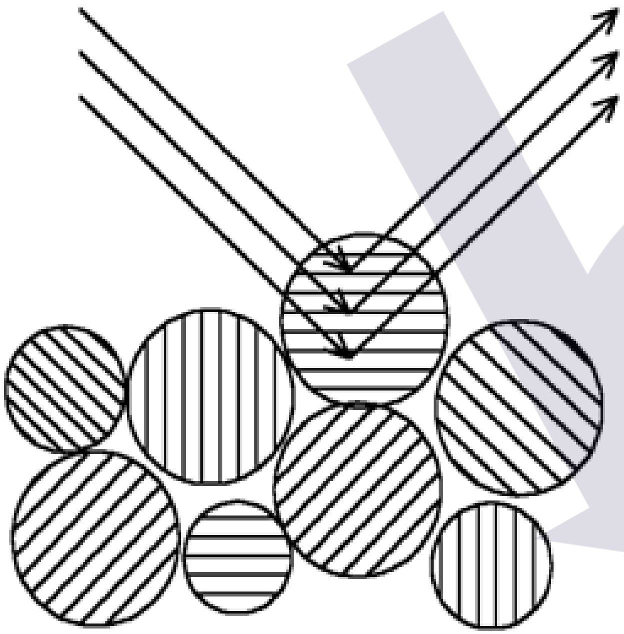
Bragg's Law

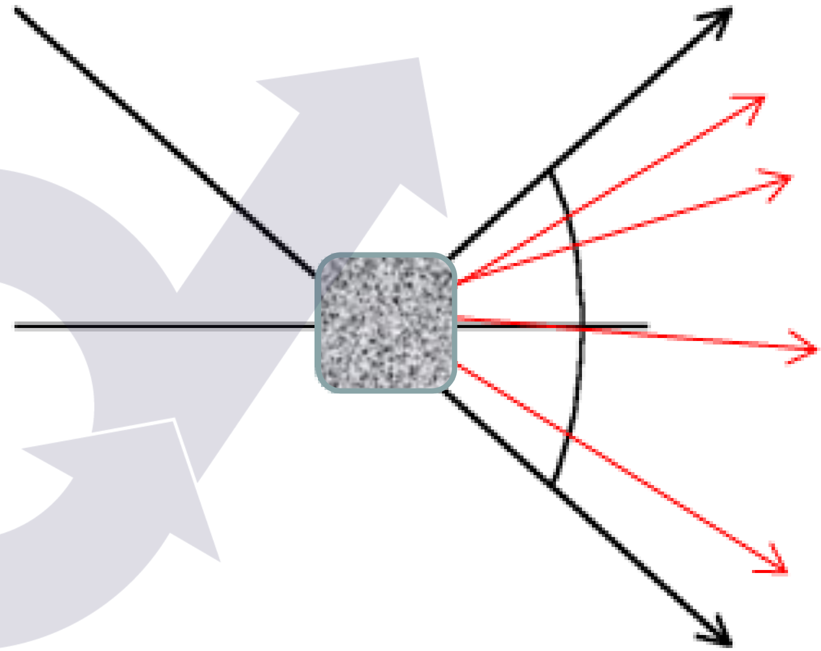


$$n\lambda = 2\,d\,\sin\theta$$

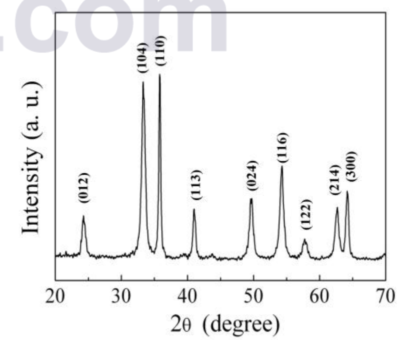


XRD of polycrystalline particles





randomly oriented particles



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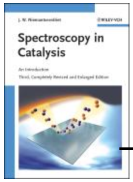
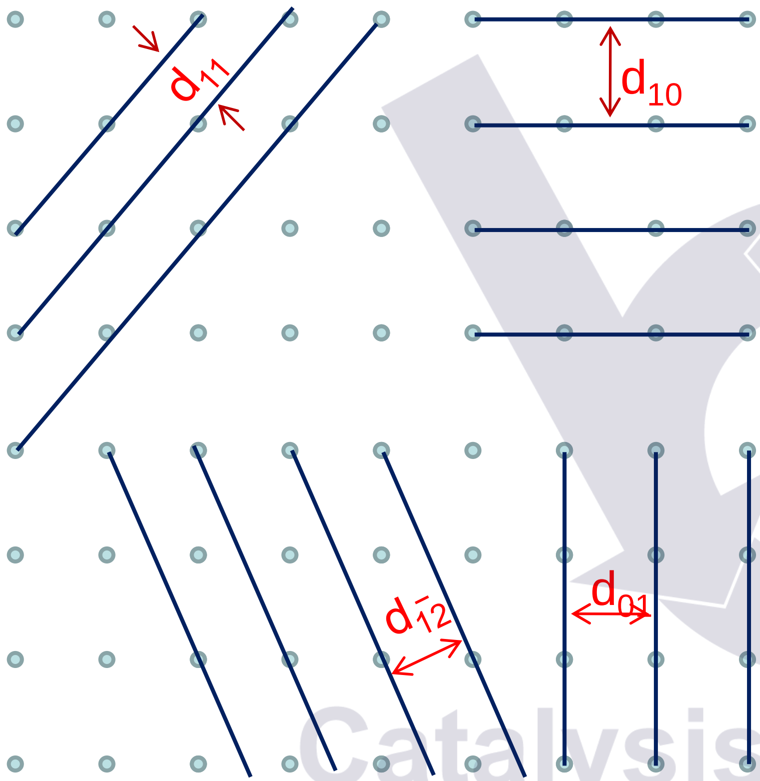
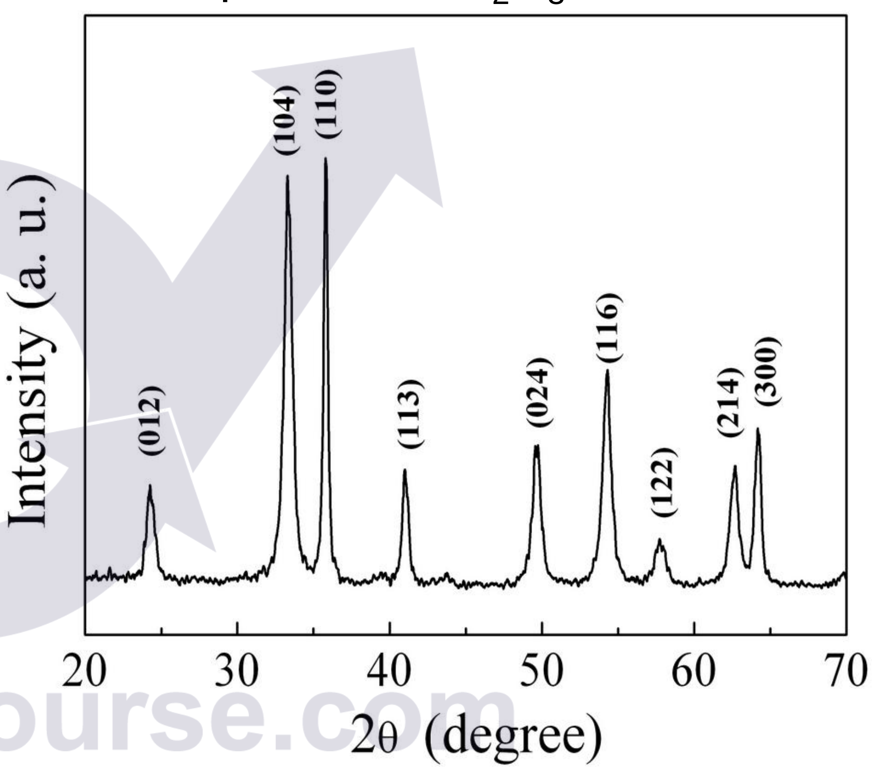
One phase, many lattice spacings

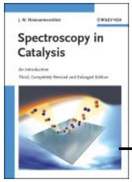


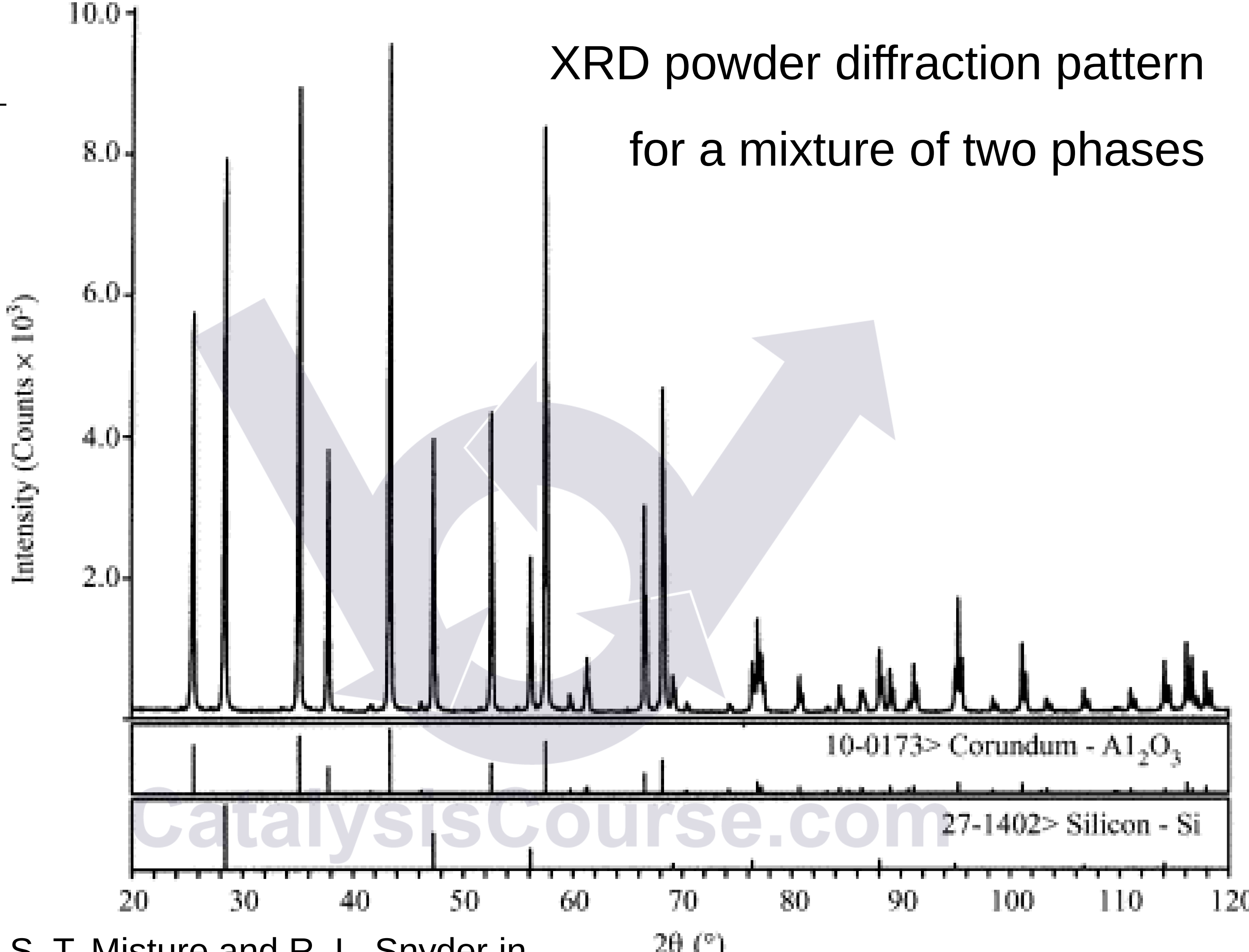


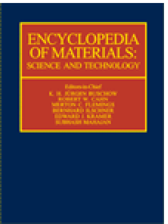
XRD pattern of Fe_2O_3



XRD powder diffraction pattern for a mixture of two phases







S. T. Misture and R. L. Snyder in
Encyclopedia of Materials: Science and Technology
K. H. Jürgen Buschow, et al. (Eds) Elsevier 2007

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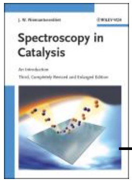
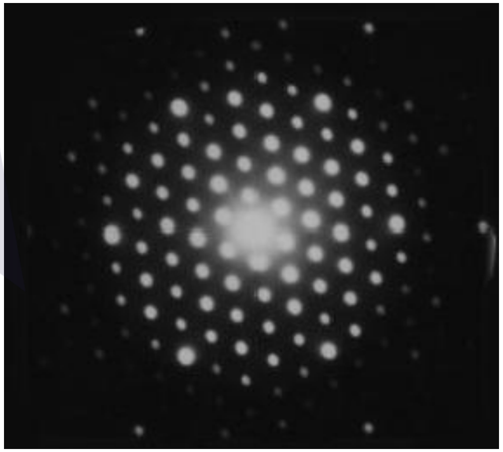
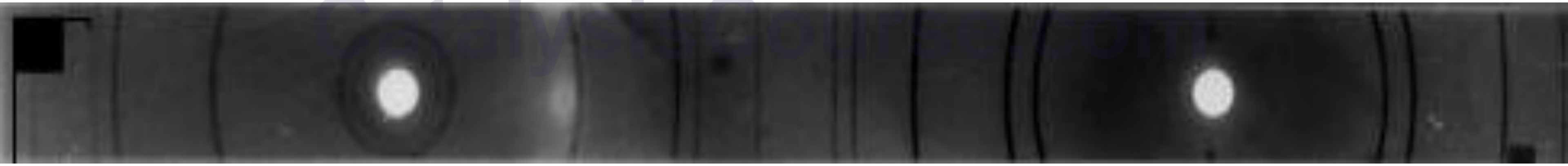


What do we learn from XRD?

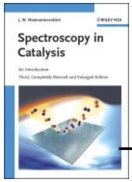
From diffraction patterns we can:



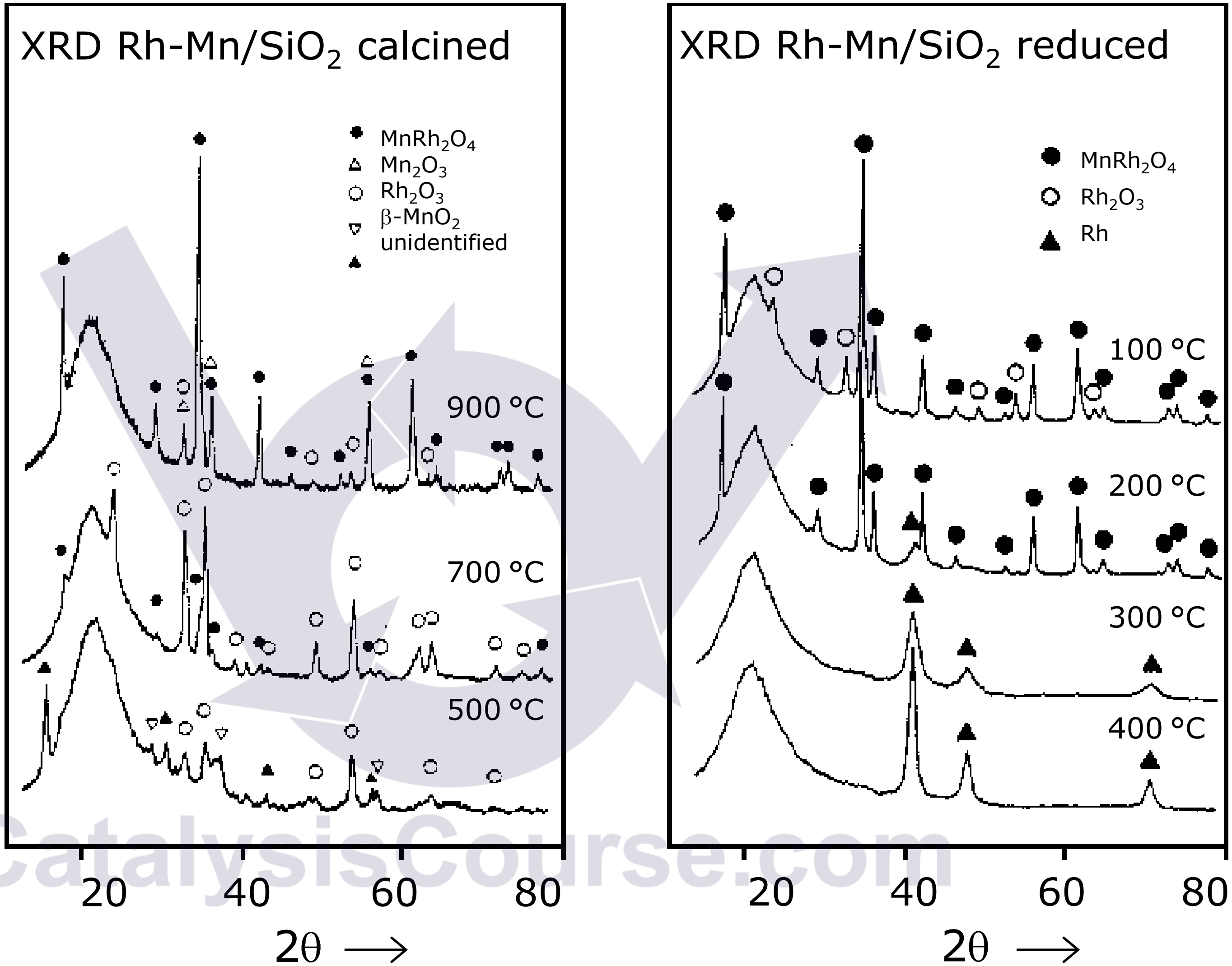
- measure the spacings between layers of atoms, and thus identify phases
- determine the orientation of a single crystal or grain
- find the crystal structure of an unknown material
- measure the size, shape and internal stress of small crystalline regions



from: www.matter.org.uk/diffraction

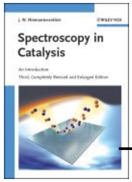


XRD: Identification of Phases in Rhodium Catalysts



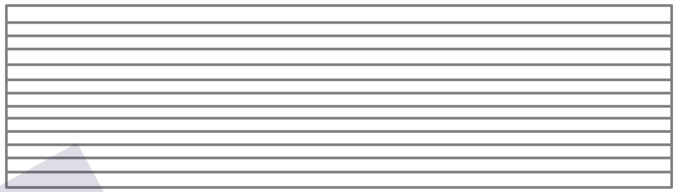
by comparing to standard diffraction data (ASTM)

K. Kunimori, T. Wakasugi, Z. Hu, H. Oyanagi, M. Imal, H. Asano and T. Uchijima, Catal. Lett. 7 (1990) 337.

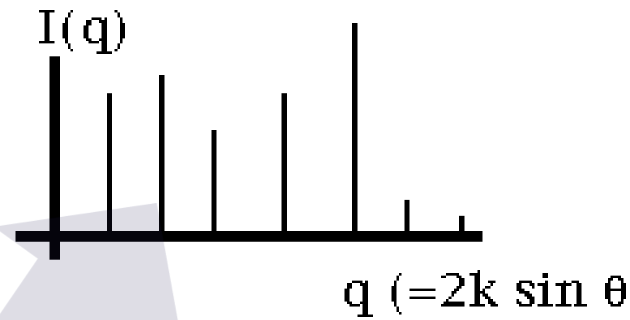


XRD: linewidth and 'coherence length'

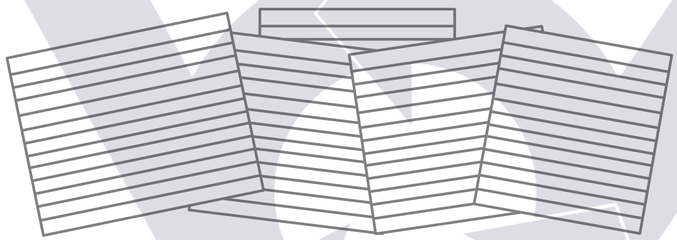
single crystal, large crystalline particles



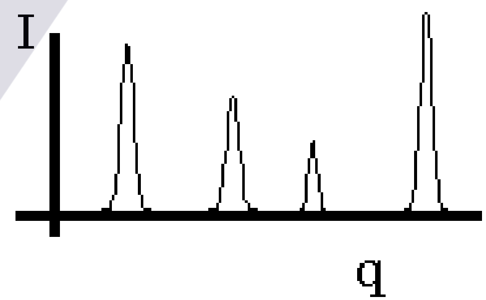
perfect long-range order



imperfect crystals, nano particles

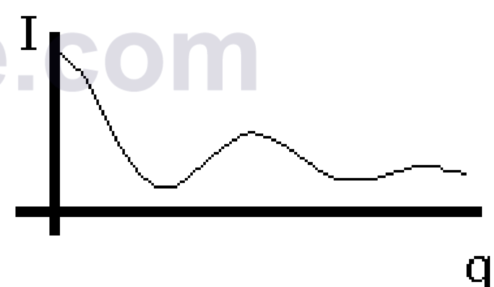


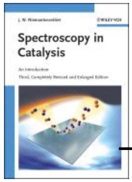
domains of medium-range order



amorphous compounds glasses, liquids

short-range order only





XRD: X-ray Diffraction

Features of Diffraction (Electron, X-ray, or Neutron)

- For a known structure, pattern can be calculated exactly.
- Symmetry of the diffraction pattern given by symmetry of the lattice.
- Intensities of spots determined by basis of atoms at each lattice point.
- Sharpness and shape of spots determined by perfection of crystal.
- Liquids, glasses, and other disordered materials produce broad fuzzy

  rings instead of sharp spots.
- Defects and disorder in crystals also result in diffuse scattering.

Paul A. Heiney
Physics Department
University of Pennsylvania
www.physics.upenn.edu

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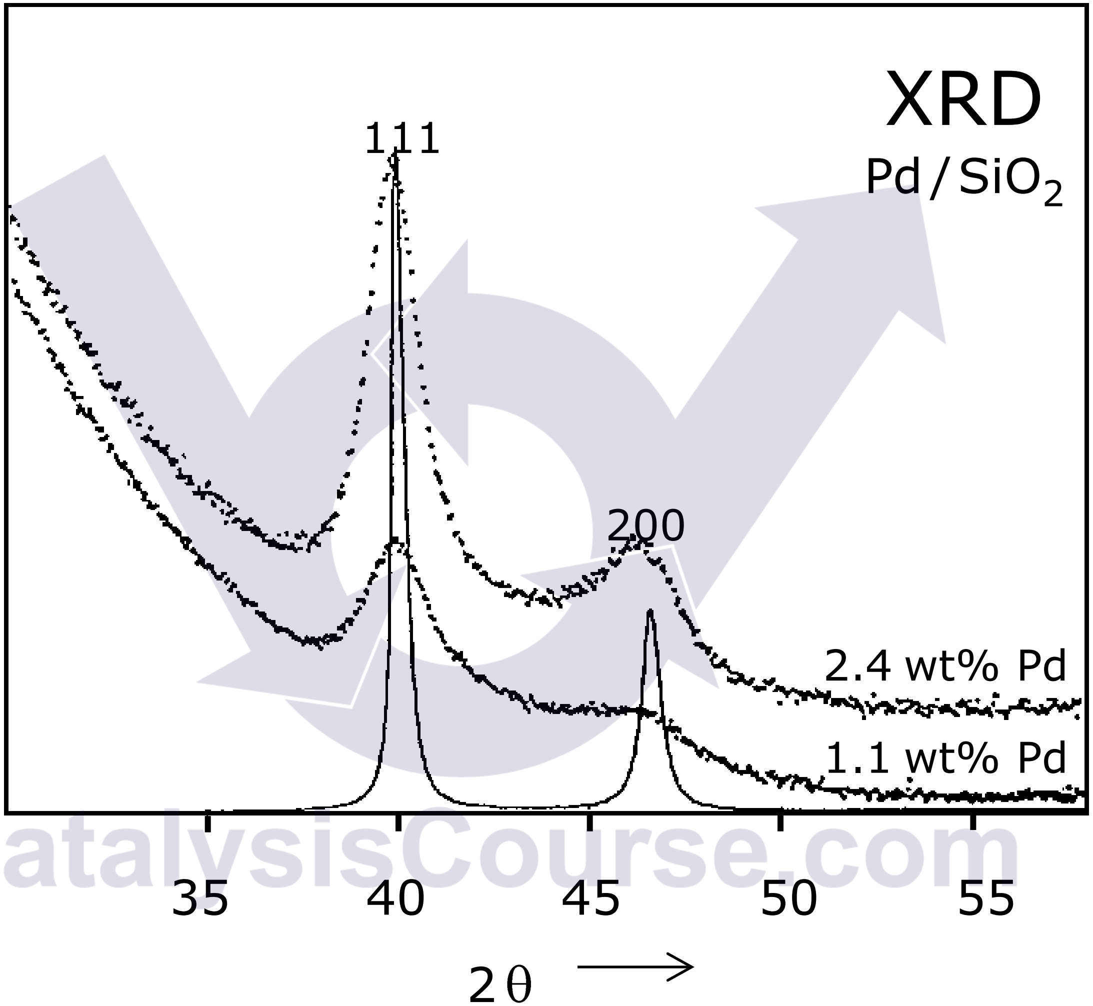
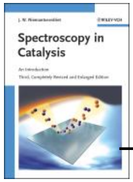
XRD Line-broadening



Particle size estimate possible

G. Fagherazzi, A. Benedetti, A. Martorana, S. Giuliano, D. Duca and G. Deganello, Catal. Lett. 6 (1990) 263.



Particle size from XRD line broadening

Paul Scherrer
1890-1969

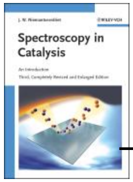
The Scherrer formula relates crystal size to line width:

$$<L> = \frac{K\,\lambda}{\beta\,\cos\theta}$$

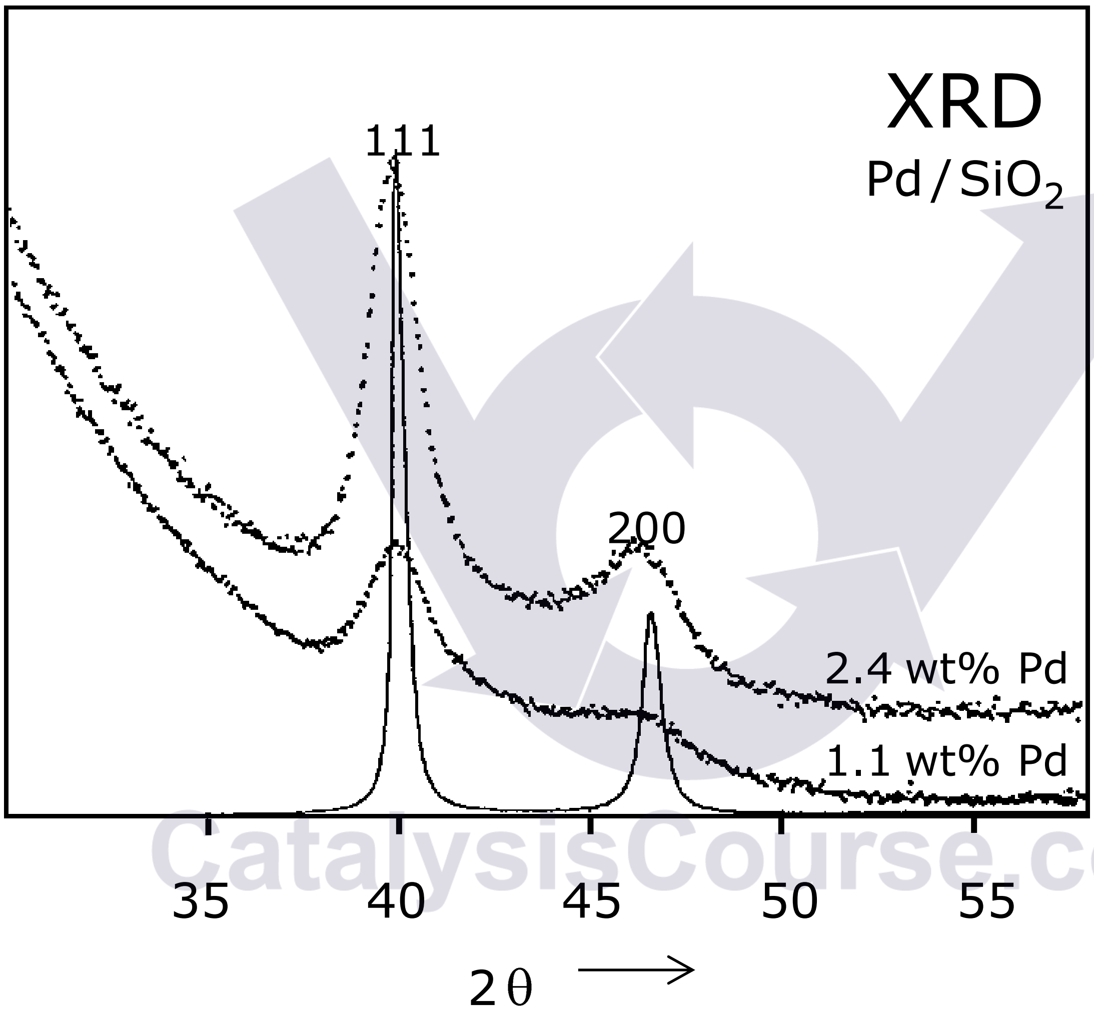
in which

<L>	is a measure for the dimension of the particle in the direction perpendicular to the reflecting plane
λ	is the X-ray wavelength
β	is the peak width
θ	is the angle between the beam and the normal on the reflecting plane
K	is a constant (often taken as 1).

Broadening becomes smaller for smaller wavelength;
Mo Kα (17.44 keV; 0.07 nm) versus Cu Kα (8.04 keV; 0.15 nm)



XRD Line-broadening

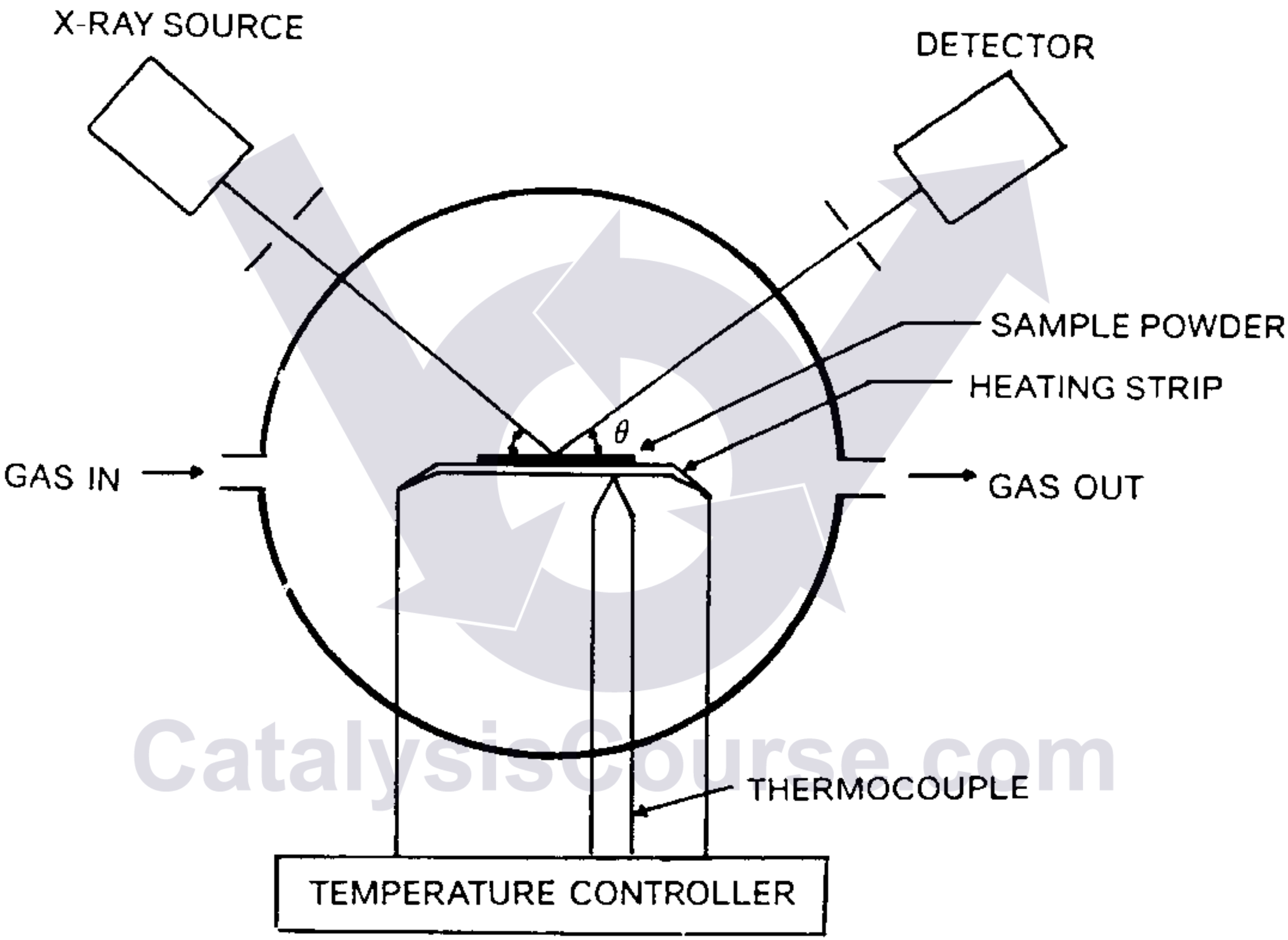


Scherrer equation:

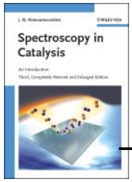
~4.2 nm
~2.5 nm

G. Fagherazzi, A. Benedetti, A. Martorana, S. Giuliano, D. Duca and G. Deganello, Catal. Lett. 6 (1990) 263.

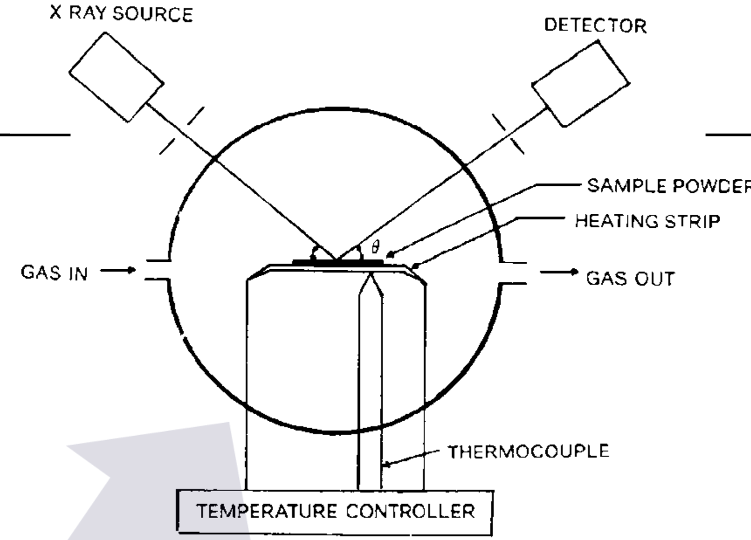
in situ XRD

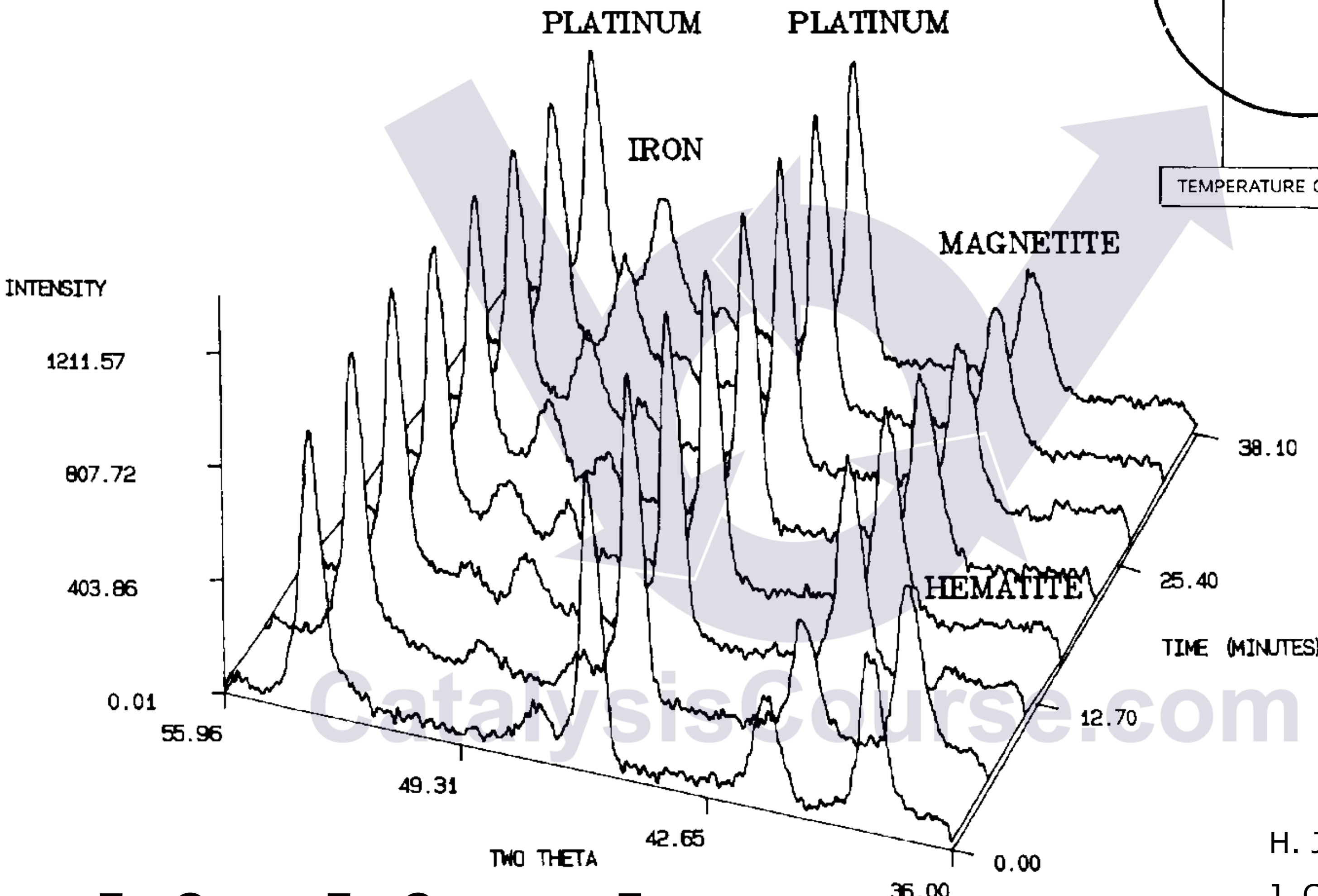


H. Jung and W.J. Thomson, J. Catal. 128 (1991) 218



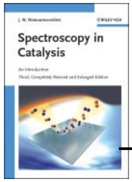
in situ XRD



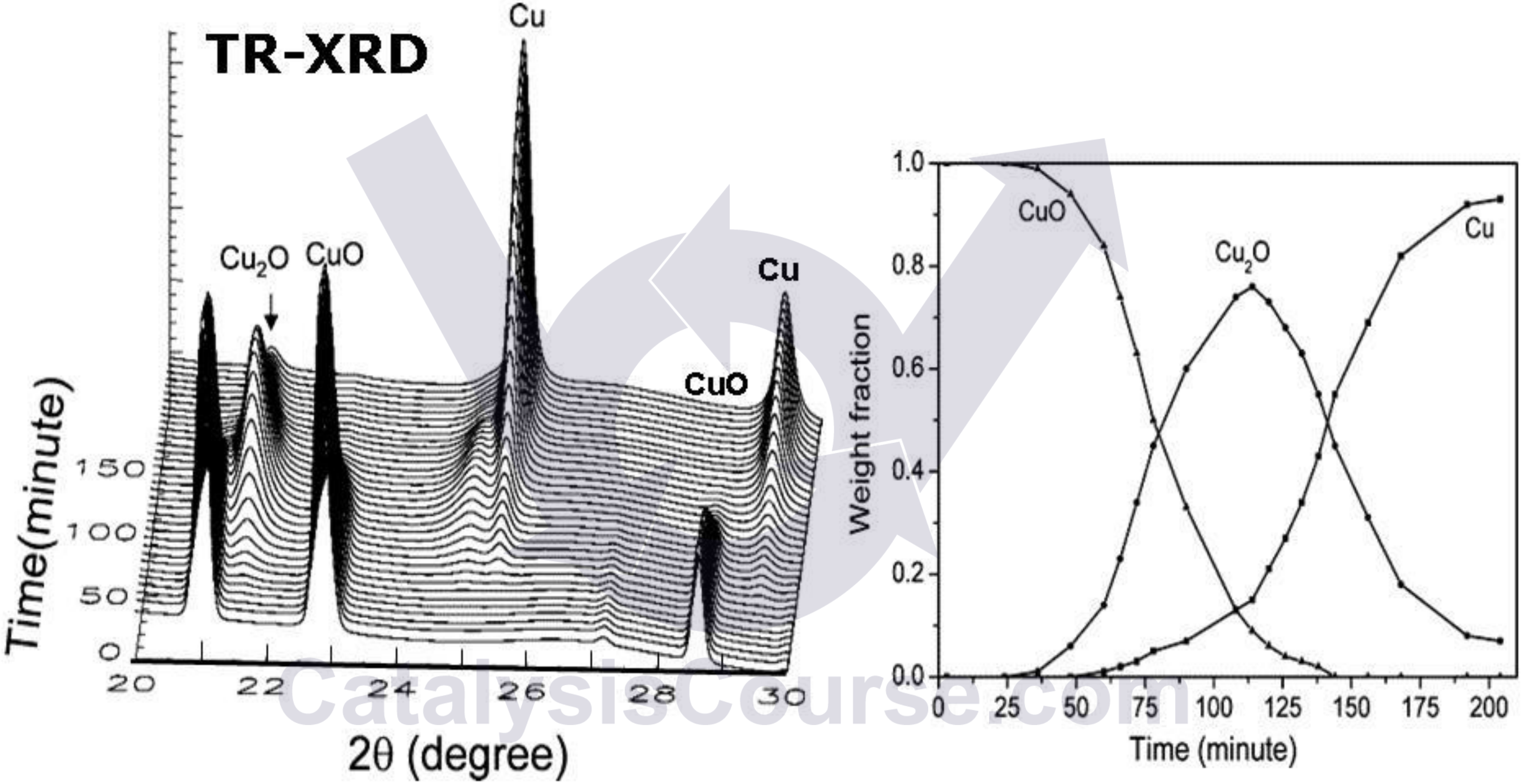


$Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow \alpha\text{-}Fe$

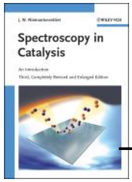
H. Jung and W.J. Thomson,
J. Catal. 128 (1991) 218



XRD: Reduction of CuO by CO



X. Wang, J.C. Hanson, A.I. Frenkel, J.-Y. Kim, and J.A. Rodriguez, *J. Phys. Chem. B,* 108 (2004), 13667



Conclusion

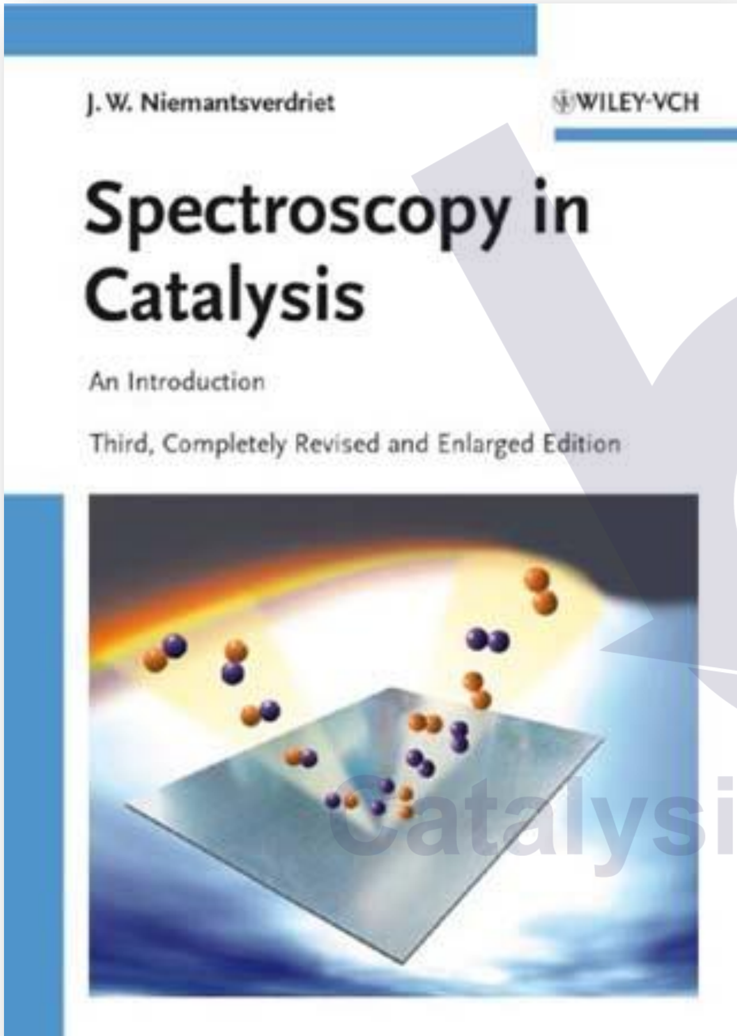
XRD:

- Phase identification
- Particle size estimate from line broadening
- In situ studies
- Careful:
  - only crystalline phases are detected
  - surface region is invisible

recommended: www.matter.org.uk/diffraction

Download the handout for this lecture from

www.catalysiscourse.com



Read more about X-ray diffraction

in Chapter 6 of

Spectroscopy in Catalysis: An Introduction, Third Edition

J. W. Niemantsverdriet

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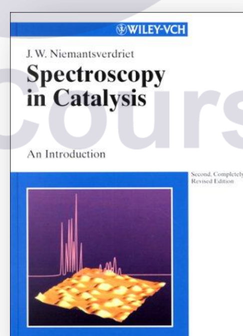
ISBN: 978-3-527-31651-9



Version 2000

gives many examples and references to the literature

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