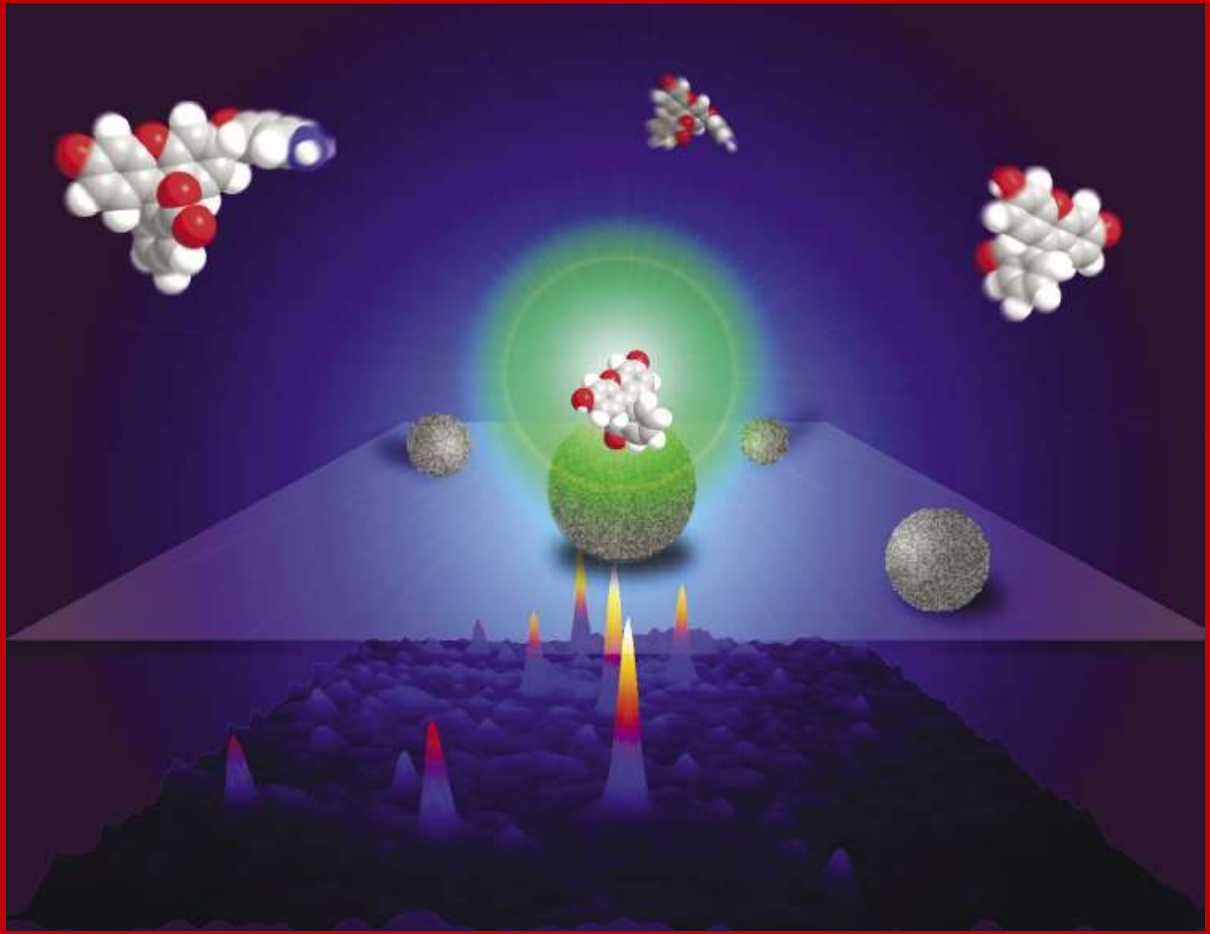
Catalysis
Characterization of Catalysts



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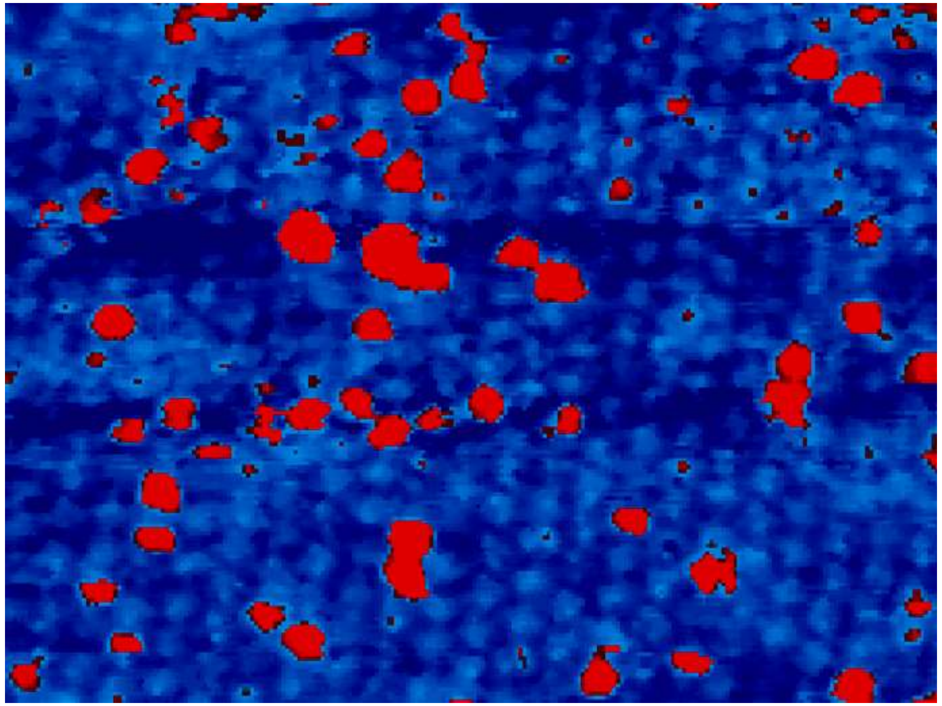
Importance

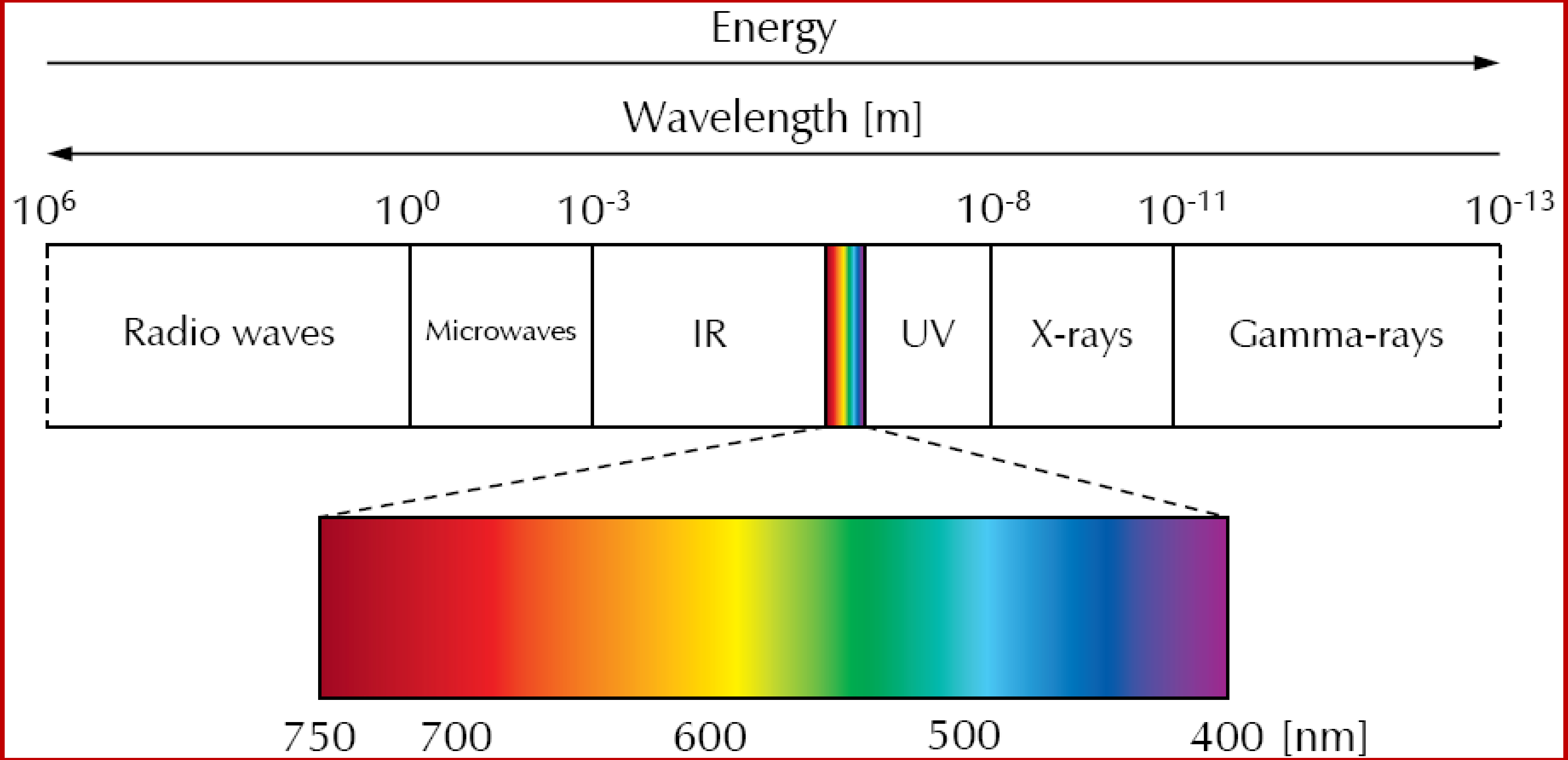
Establish in detail the structure-activity relationships of catalysts

- Stability, (local) activity, selectivity, regenerability
- *In situ*: under reaction conditions at highest detail possible
- *In operando*: at the moment the catalytic reaction is going on

Goals: understand precisely how catalysts work → design & development of better catalysts (→ €€€)



Spectroscopic Characterization



Spectroscopic techniques

Spectroscopic characterization in solution

- Nuclear Magnetic Resonance (NMR)
- Electron Paramagnetic Resonance (EPR)
- UV-vis
- Fluorescence
- Infrared (IR)
- Raman

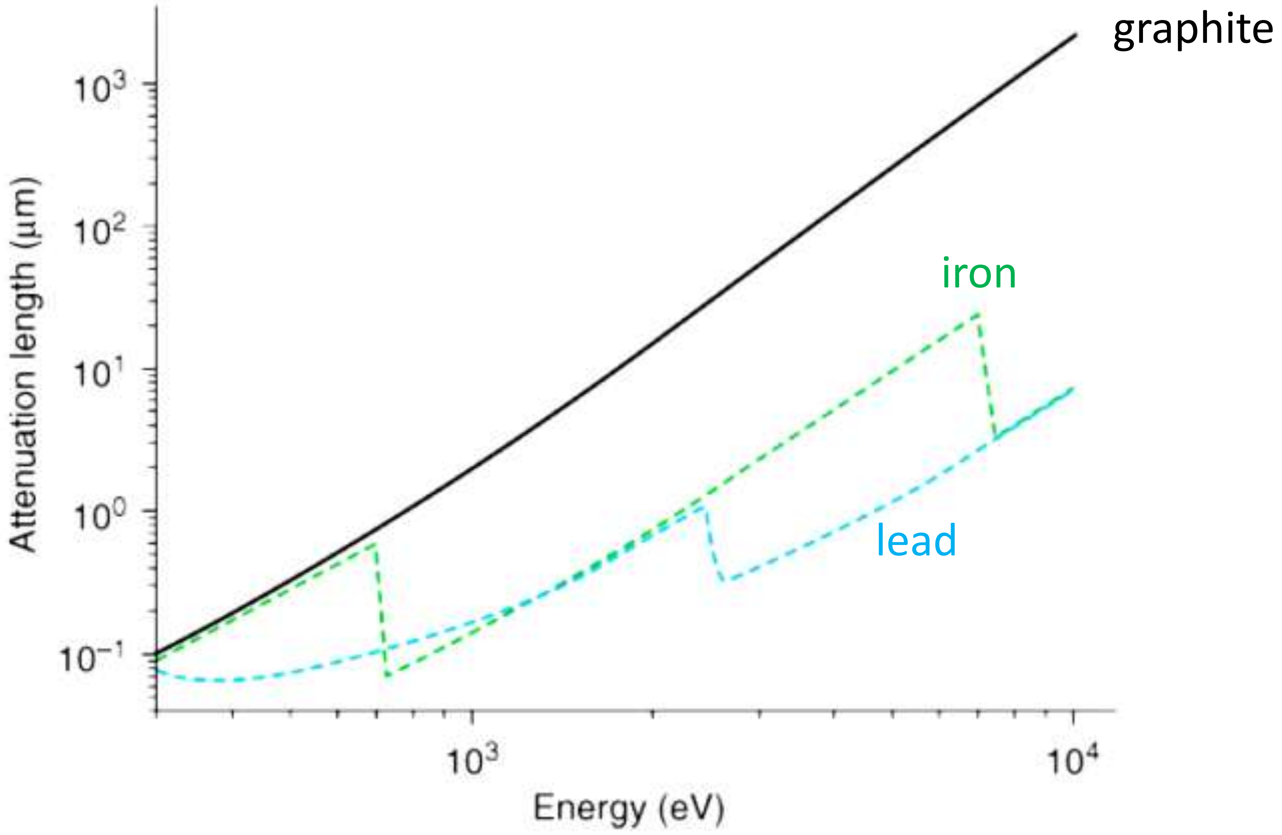
Spectroscopic characterization in solid state / on surfaces

- NMR, EPR, IR, UV-vis
- X-ray Diffraction (XRD)
- X-ray Absorption (XAS)
- X-ray Scattering
- X-ray Photoelectron Spectroscopy (XPS)

X-rays

Electromagnetic radiation with λ < 10 nm (*E* > 100 eV)

- Generated by interaction of high energy electrons with a material
- Soft X-rays: < 2 keV. Prefer vacuum and have low penetrating power
- Hard X-rays: > 5 keV. High penetrating power

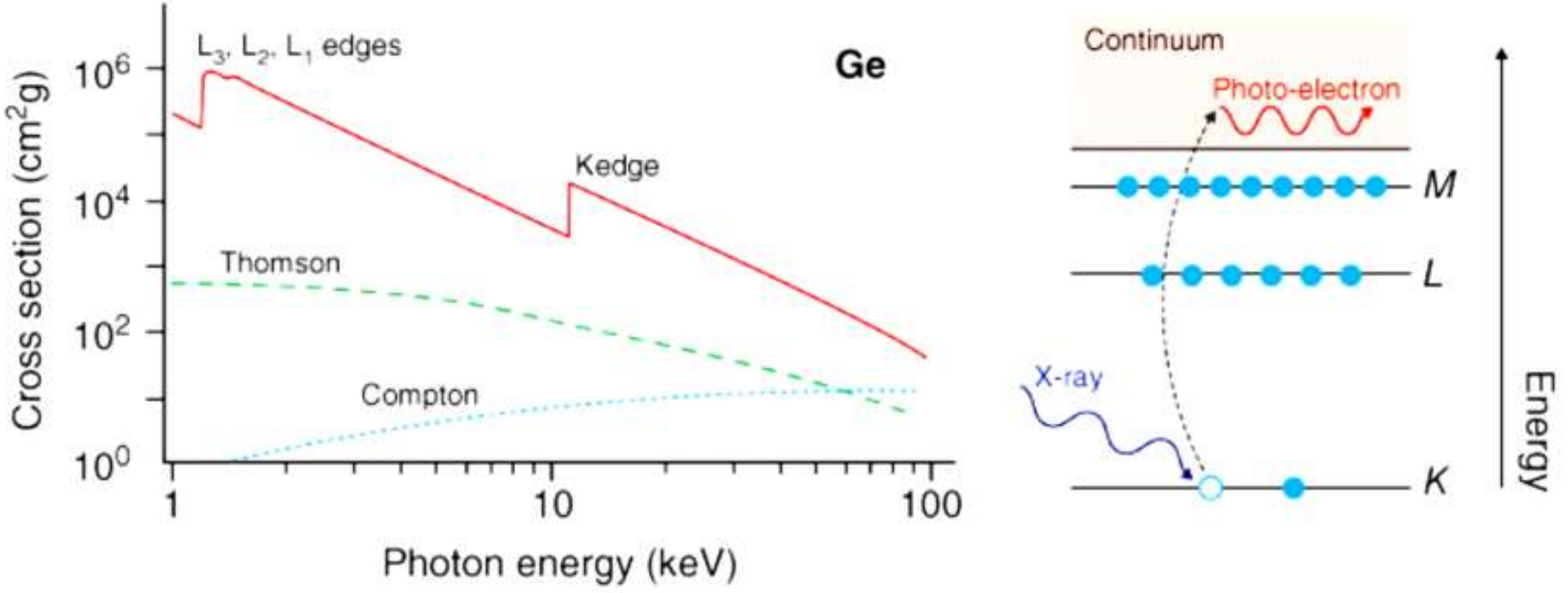


Attenuation length: depth at which energy intensity is reduced by 1/e of the starting value

X-rays

Types of interactions with matter

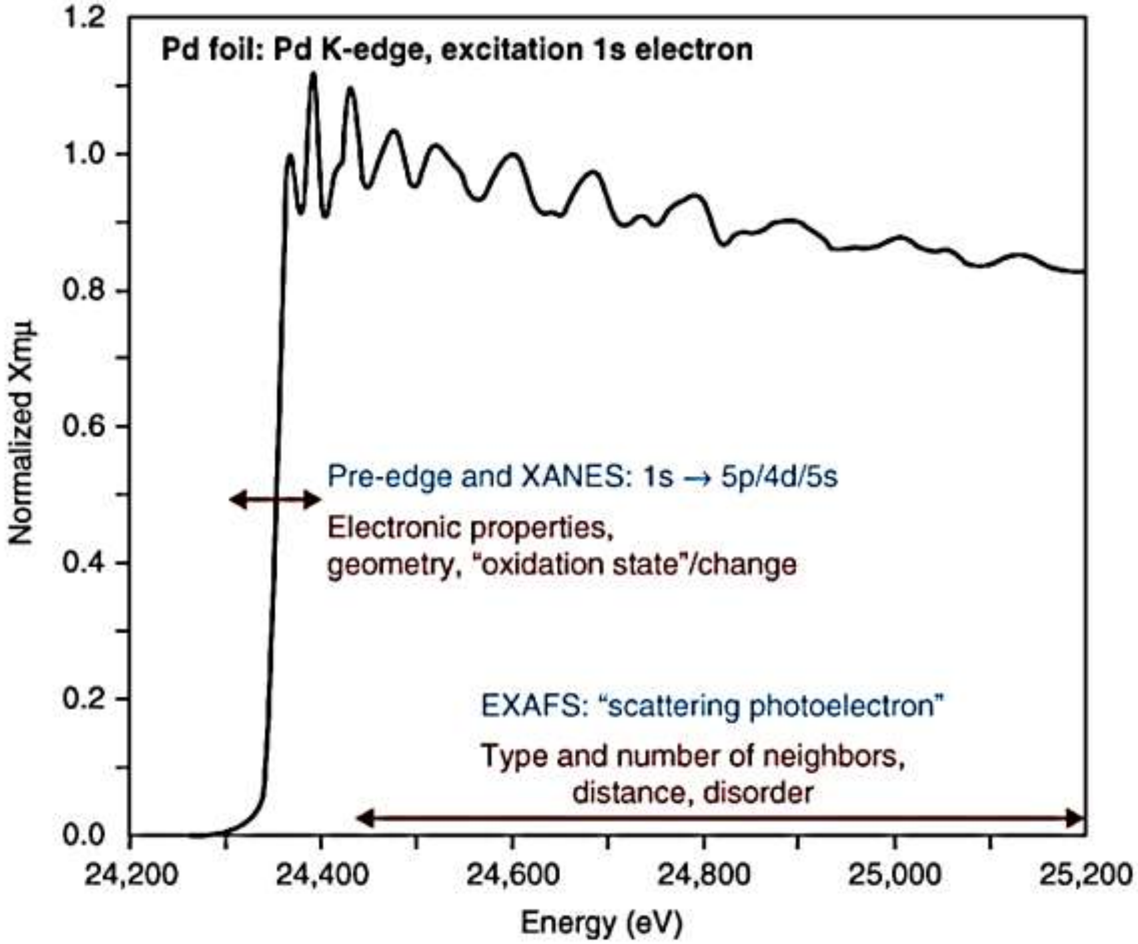
- X-ray photon can be absorbed by exciting an electron of an element to an empty state or to the continuum (photoelectric effect). Probing excitation spectrum as function of X-ray energy: X-ray Absorption Spectroscopy (XAS) and X-ray Photoelectron Spectroscopy (XPS)



- X-ray photon can be elastically scattered by electrons in a material (Thomson scattering). Techniques: X-ray diffraction (XRD), Wide-Angle X-ray Scattering (WAXS) and Small-Angle X-ray Scattering (SAXS)

X-ray absorption spectroscopy (XAS)

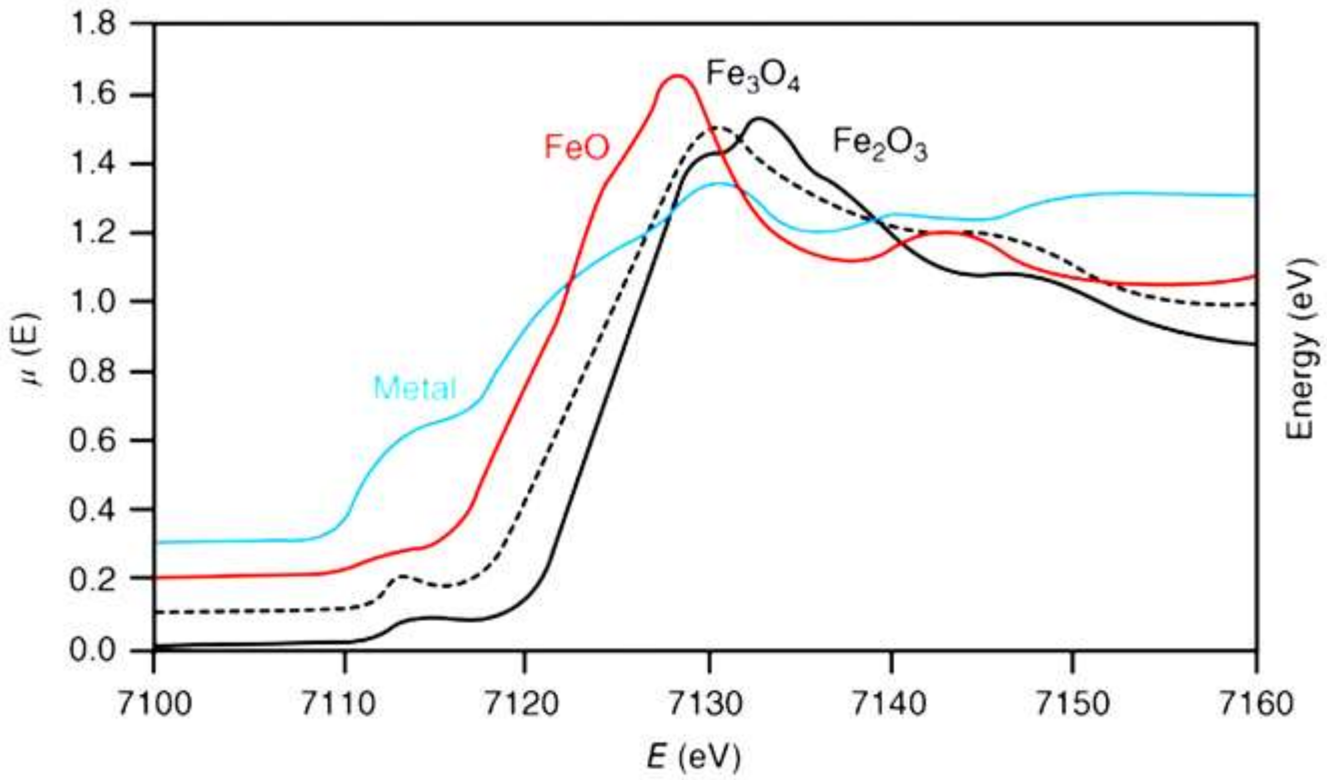
- **XANES**: X-ray Absorption Near Edge Structure. Provides direct information on the energy difference between core and excited state
- **EXAFS**: Extended X-ray Absorption Fine Structure. Provides information about the close environment of the excited electron



XANES

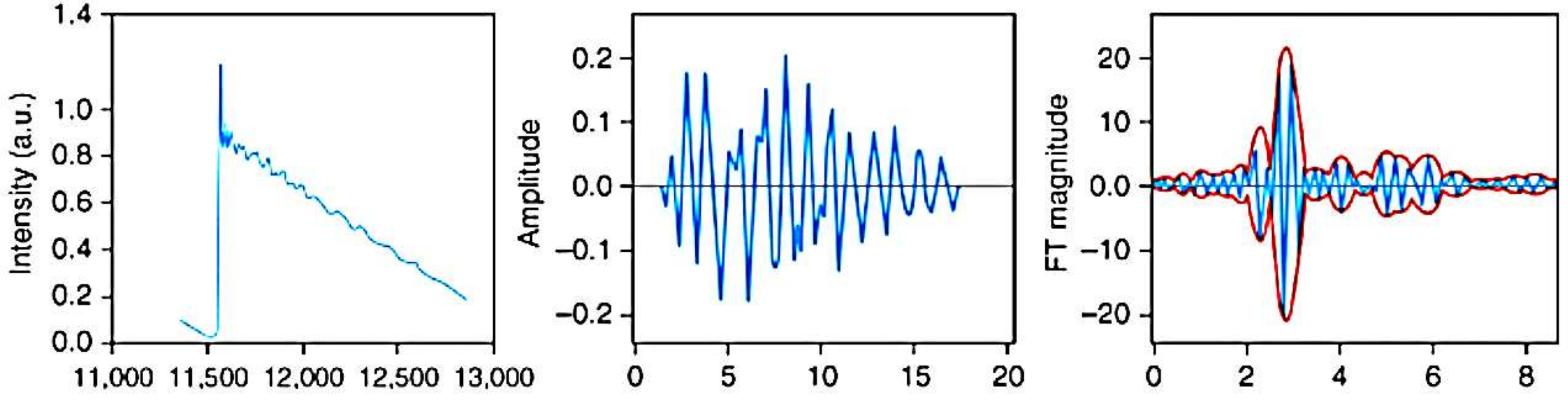
- Information about direct environment of excited electron
- E.g. oxidation state and charge of an element
- Local geometry, e.g. ligands bound to metal

- Quantitative analysis (still) not straightforward; trends may be observed but they become complicated rapidly



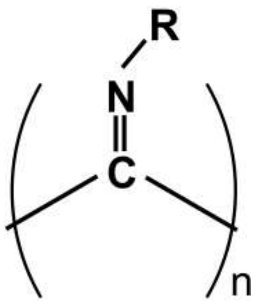
EXAFS

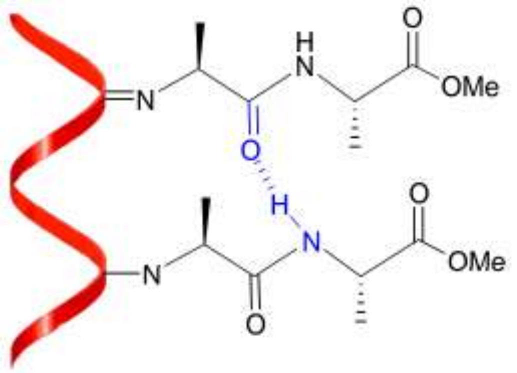
- If energy of outgoing electron > ~50 eV: spherical wave that will be scattered against electron clouds of neighbouring atoms and backscattered to emitting atom
- Interference pattern between outgoing and backscattered waves produces specific EXAFS pattern → Information about wider environment of excited electron
- Information about number and type of neighbours, and their position (distance)

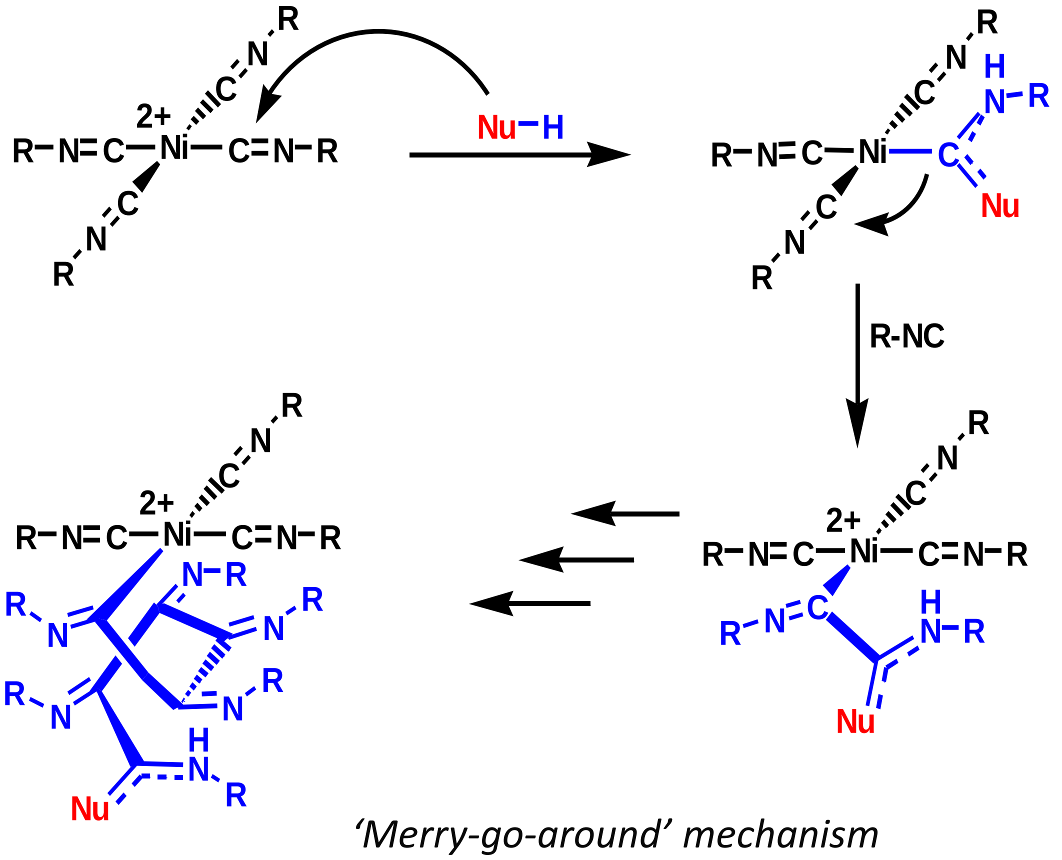


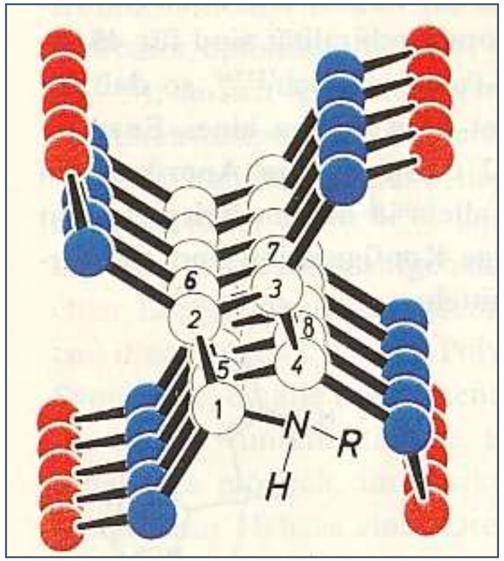
Example of EXAFS

Polymerization of isocyanides



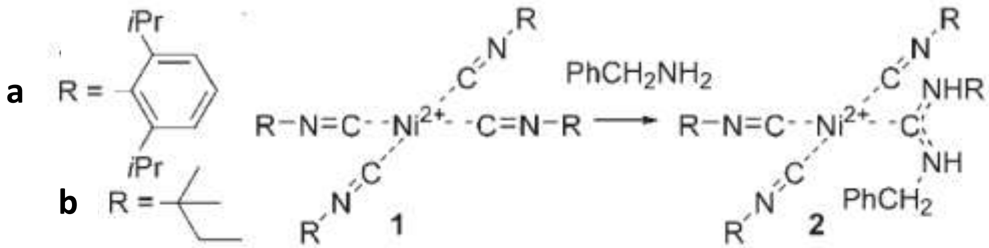


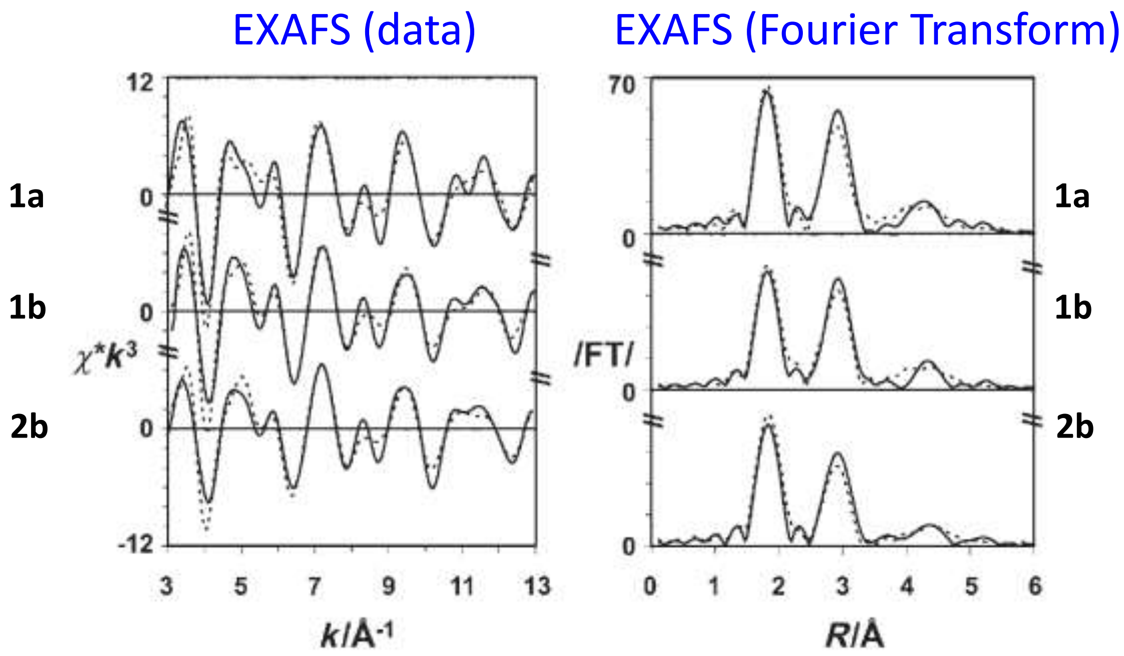


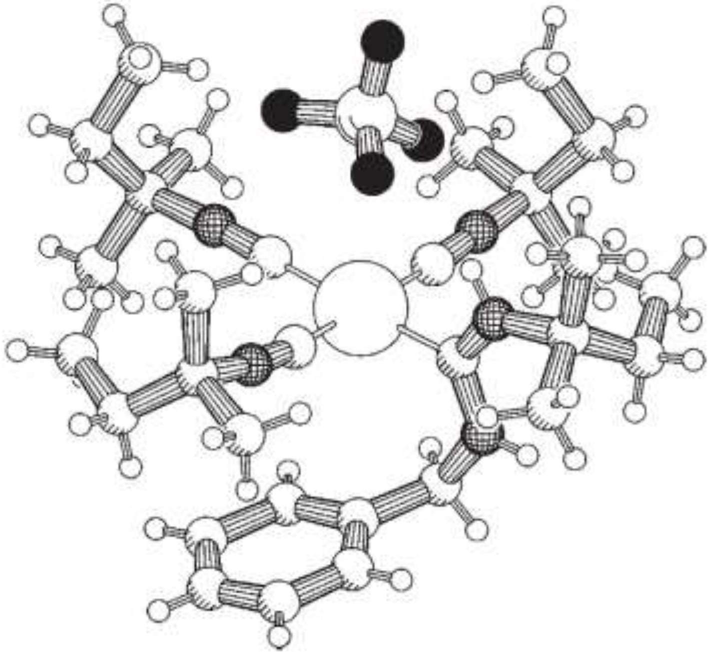


Science **2001**, *293*, 676

Example of EXAFS

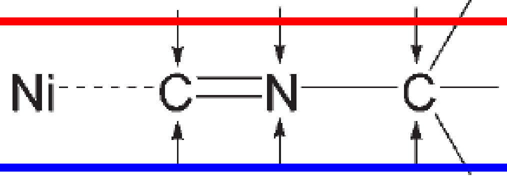




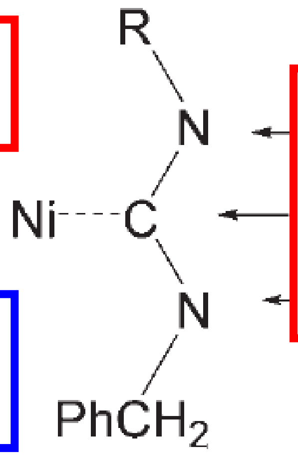


X-ray of **2b**

XRD **1a**: 4 x 1.833, 2.989, 4.378 (2 O, 2.739) Å
2b: 3 x 1.845, 2.983, 4.444 (1 O, 3.061) Å



EXAFS **1a**: 4 x 1.869, 3.002, 4.291 (2 O, 2.803) Å
1b: 4 x 1.866, 3.020, 4.332 (2 O, 3.090) Å
2b: 3 x 1.862, 2.999, 4.363 (1 O, 3.110) Å



XRD	2b EXAFS
2.741	2.812Å
1.920	1.907Å
2.807	2.812 Å

ChemPhysChem **2007**, *8*, 1850

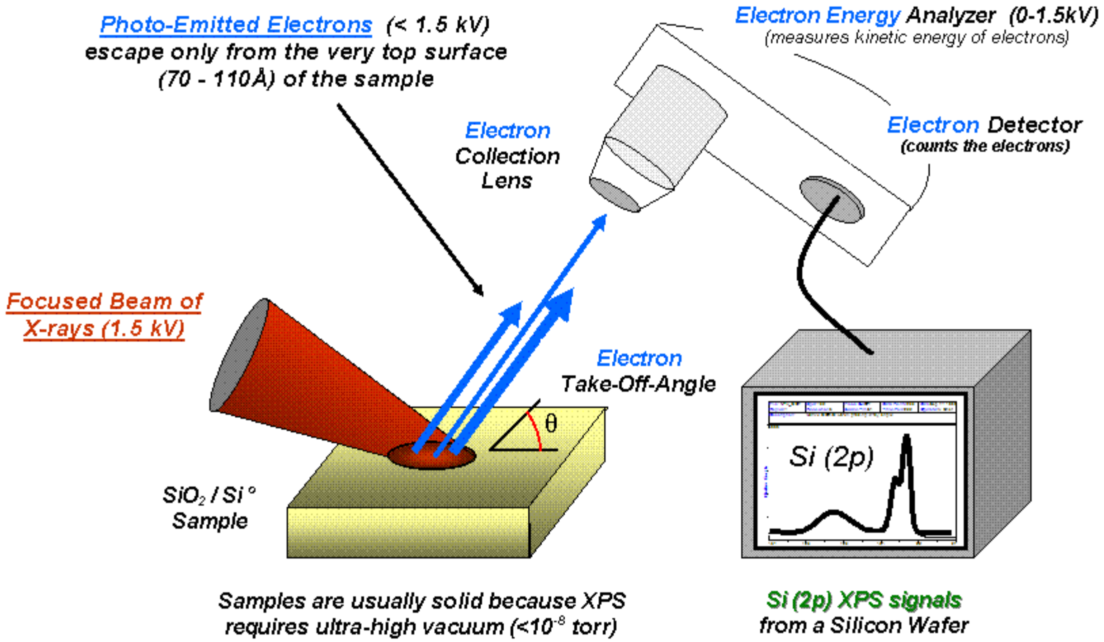
X-ray Photoelectron Spectroscopy (XPS)

Electromagnetic radiation with *E* ~1.5 keV

- Generated by interaction of high energy electrons with the surface of a (catalytic) material
- Excitation of electrons (including core) of which $E_{kinetic}$ is measured
- Binding energy of excited electron can be determined:

$$E_{binding} = E_{photon} - (E_{kinetic} + \varphi)$$

- Can provide several material properties:
  - Elemental composition (from $E_{binding}$)
  - Empirical formula of pure material (from intensity and surface areas of the peaks)
  - Electronic properties of elements (oxidation states)
  - Distributions (uniformity) of elements across a surface
  - Identification of contaminants on the surface



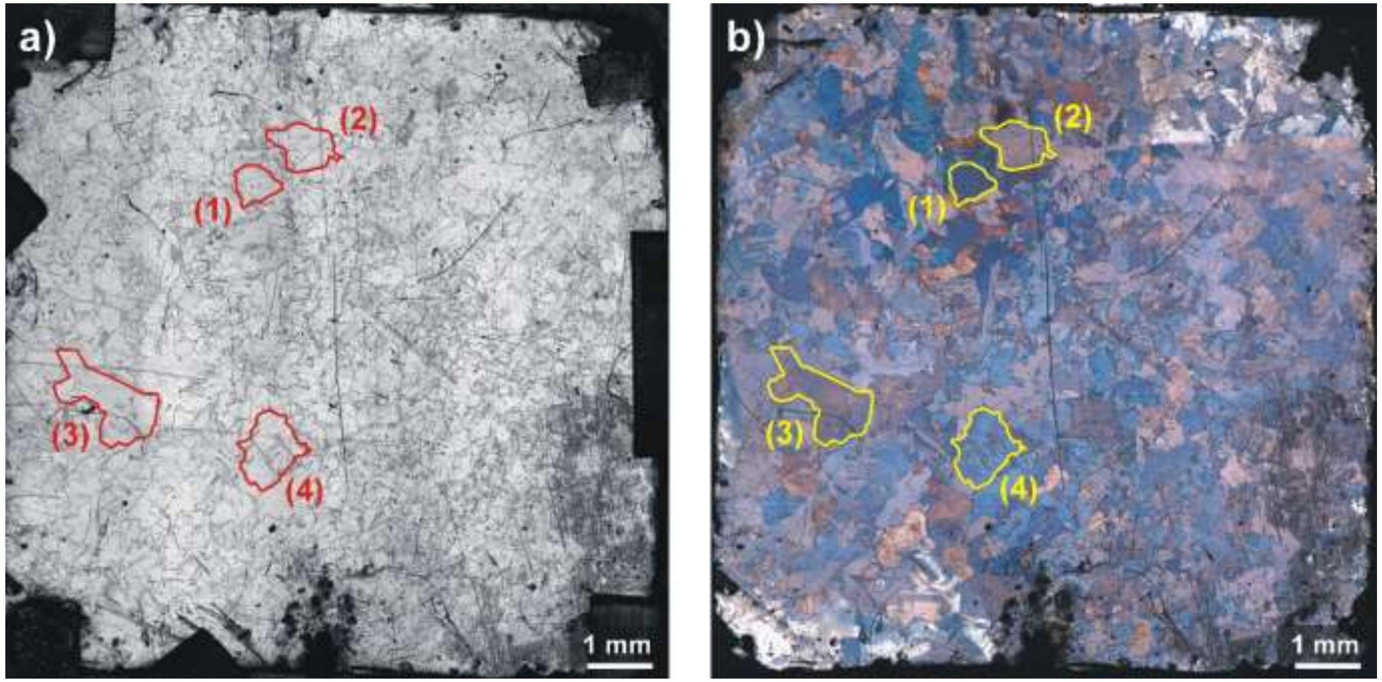
Limitations

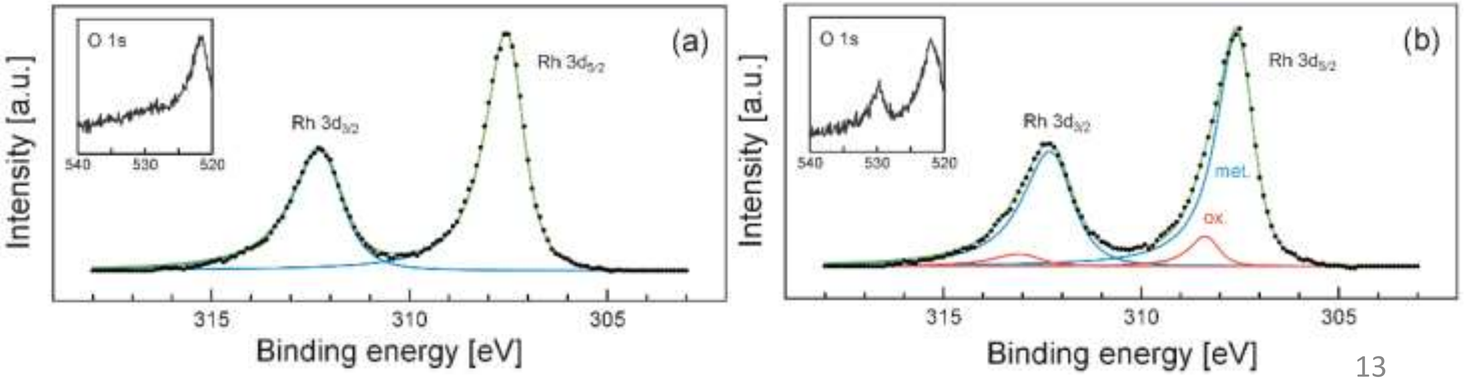
- Vacuum environment required
- Electron escape depth limited. Technique only surface-sensitive

Example of XPS

Oxidation of a Rh catalyst surface

- Present in automotive exhaust catalysts
- Study on polycrystalline Rh films
- Resolution at sub-milimeter level



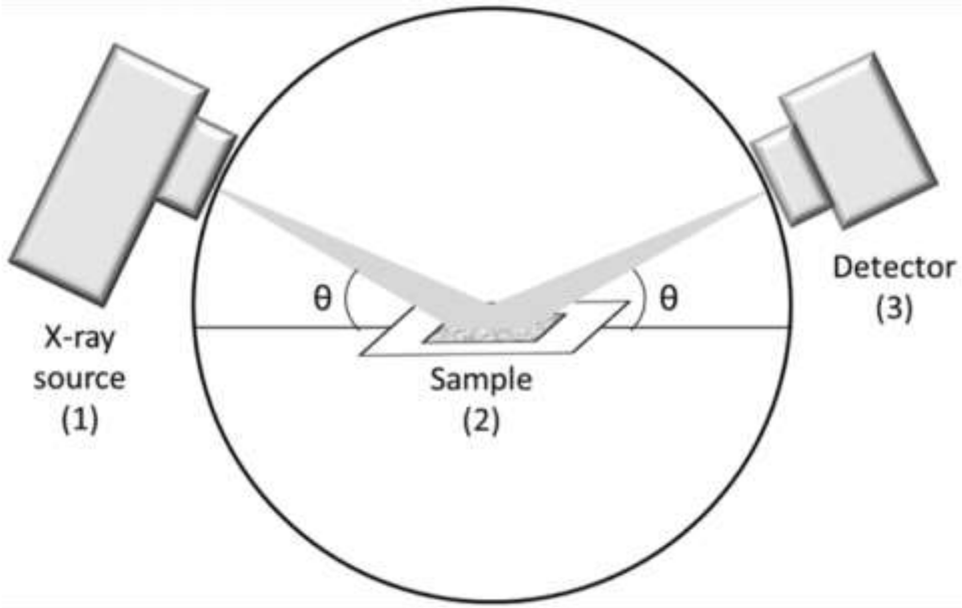


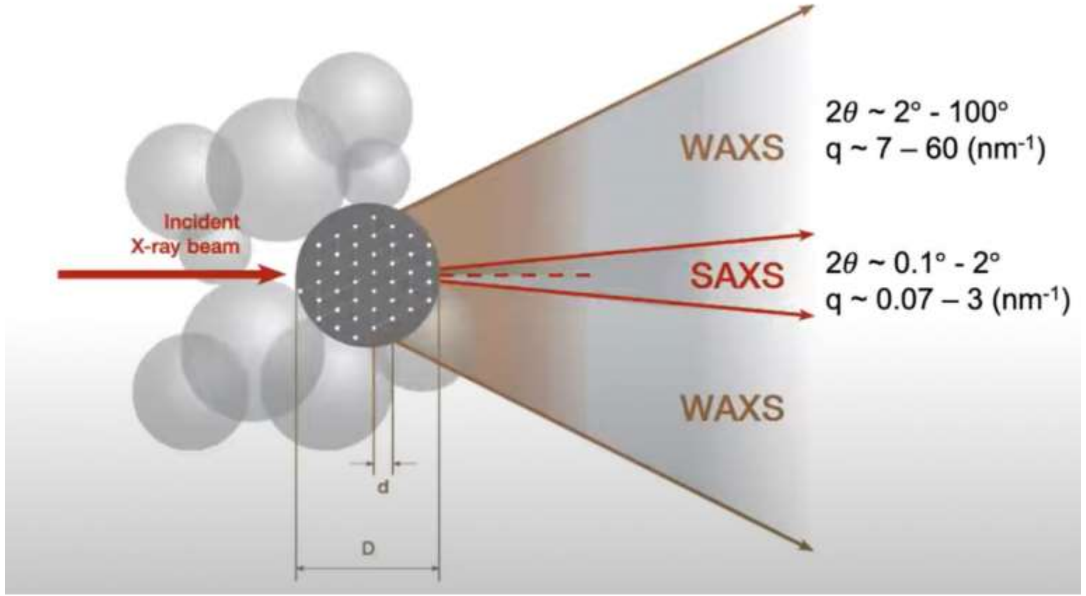
Catalysts **2020**, *10*, 617

X-ray scattering

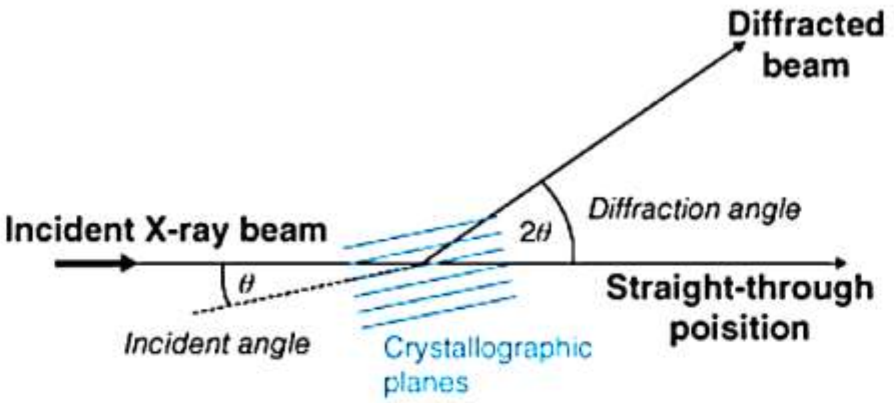
Incident x-rays are scattered elastically by electrons of the material

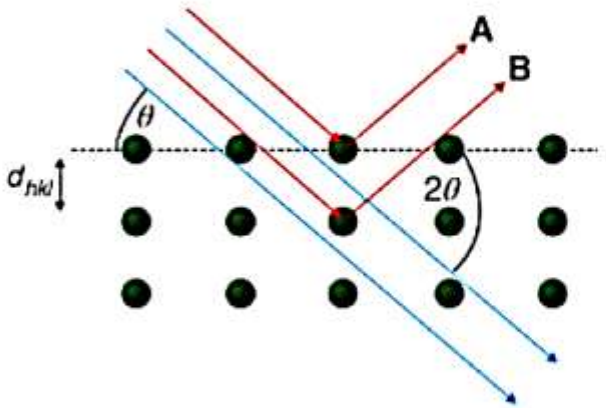
- Wide-angle X-ray scattering (WAXS) (or X-ray diffraction, XRD): information on the periodic crystal structure (*intra*molecular – interatomic – subnanometer level). Atomic resolution.
- Small-angle X-ray scattering (SAXS) : information on the *inter*molecular level – shape and size of particles from nanometer to micrometer size. No atomic resolution.





WAXS

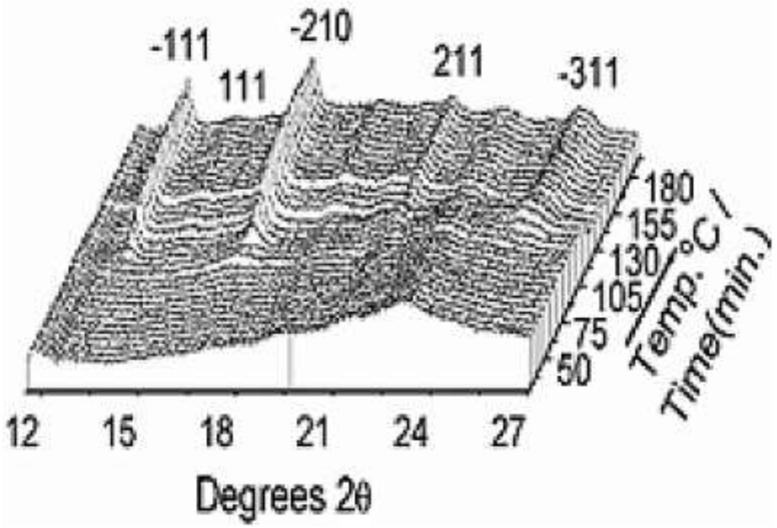




- Long-range order → constructive interference of scattered waves → Bragg's law: $2d\sin(\vartheta) = n\lambda$
- Homogeneous/biocatalysis: single-crystal structure determination of isolated catalysts and enzymes
- Heterogeneous catalysis: *in situ* monitoring of structural transitions during catalysis and catalyst preparation

Example

Observation of zinc-substituted microporous aluminophosphate formation at time resolution of minutes



J. Am. Chem. Soc. **2006**, *128*, 12386

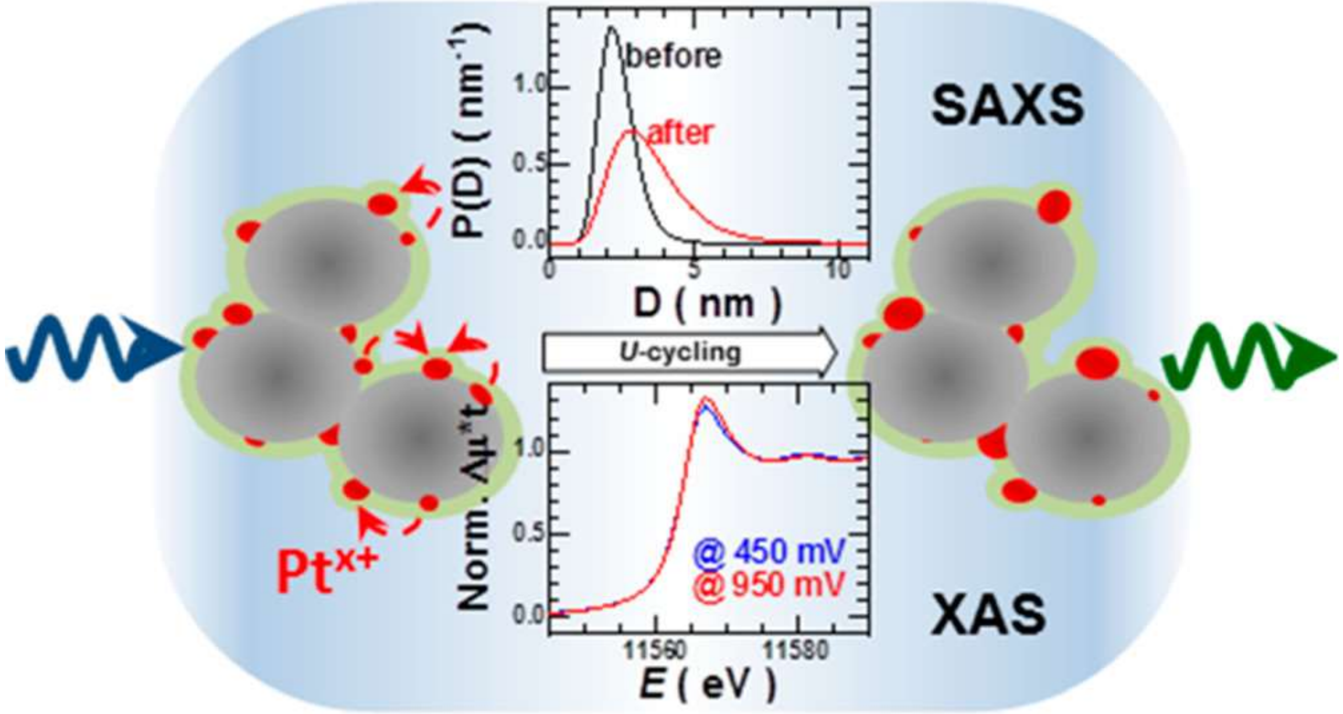
SAXS

- Operates at much smaller angles than WAXS
- Mainly applied in polymer science. In heterogeneous catalysis for determination of particle sizes, porosity, formation mechanisms of supports and catalyst materials

Example

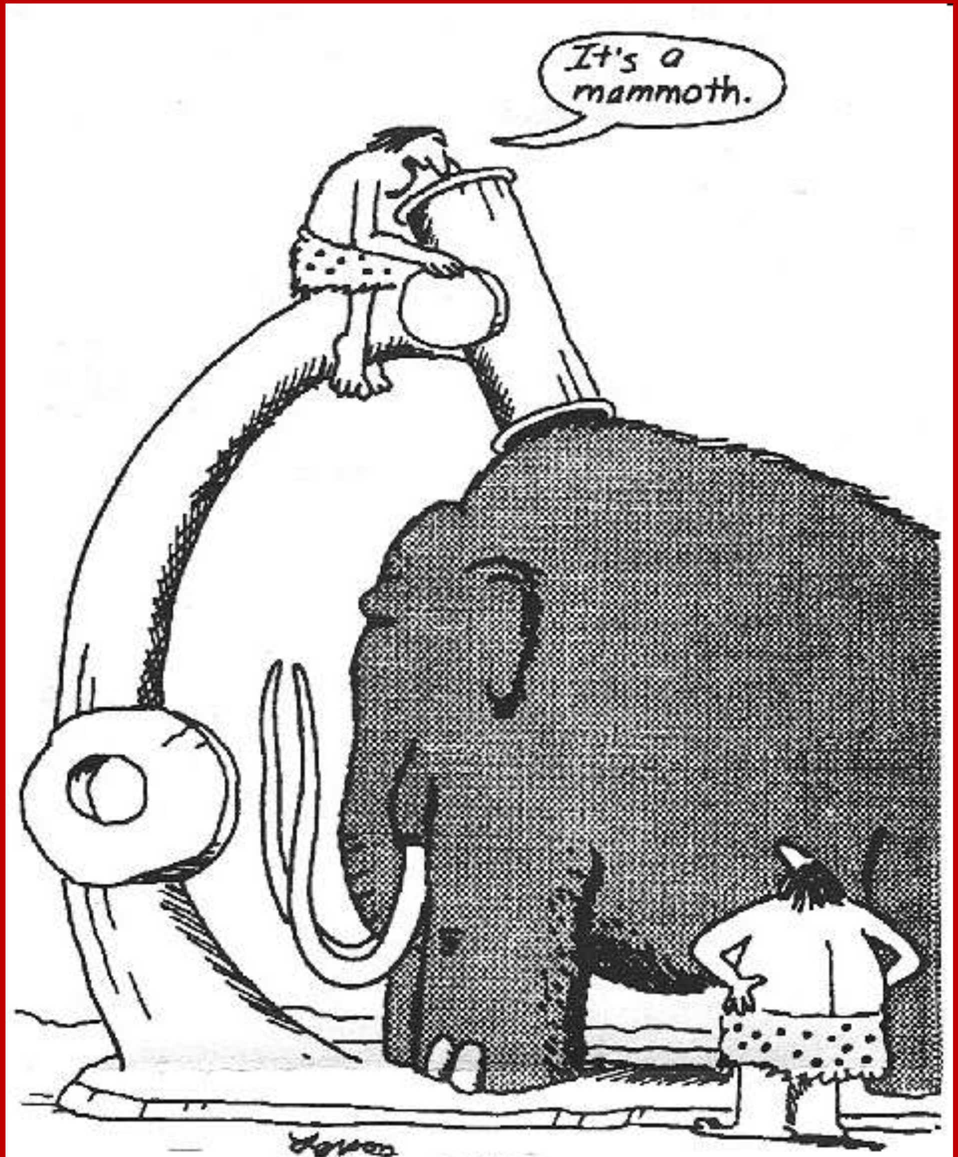
In operando degradation of carbon-supported Pt-nanoparticle (Pt/C) catalysts in polymer electrolyte fuel cells.

- SAXS: On average particles become larger
- EXAFS: when particles become larger, Pt-Pt distances in nanoparticles increase



ACS Catal. **2018**, *8*, 7000

Microscopic Characterization

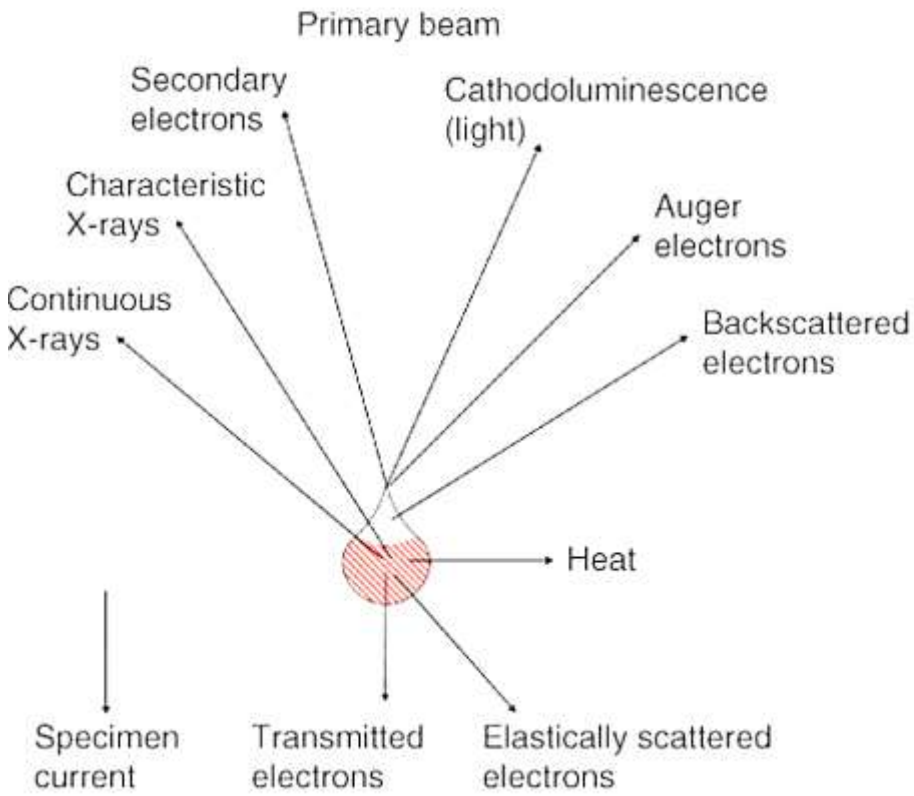


Early Microscope

Electron microscopy

Visualization of surface structure, homogeneity, and of materials/particles adsorbed to surfaces

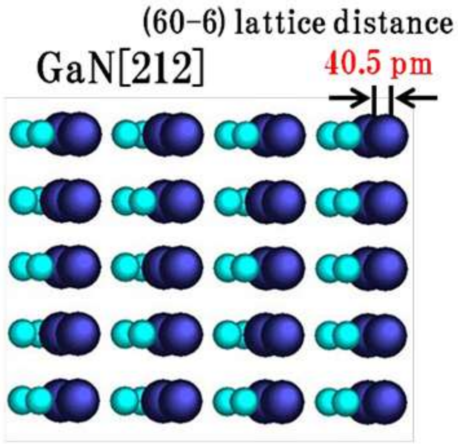
- Surface exposed to primary electron beam, most often in high vacuum (but in recent years also in gases and liquids)
- Sample information may be extracted from variety of response of electron to interactions with material
- Two main types: Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM)

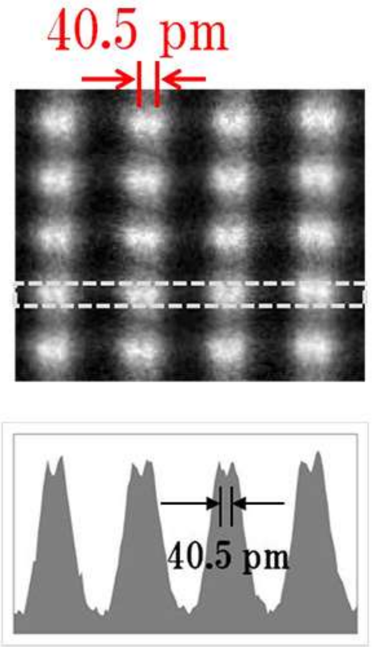


Electron microscopy

Transmission electron microscopy (TEM)

- Information about the bulk of the sample
- Surface is exposed to primary electron beam, most often in high vacuum
- Electrons pass through sample (which must be very thin): absorption contrast image
- Electrons can also be scattered by sample: diffraction image → information about crystalline vs. defect sites, edges, etc.
- High resolution TEM (HRTEM): atomic resolution (<0.5 Å) possible.





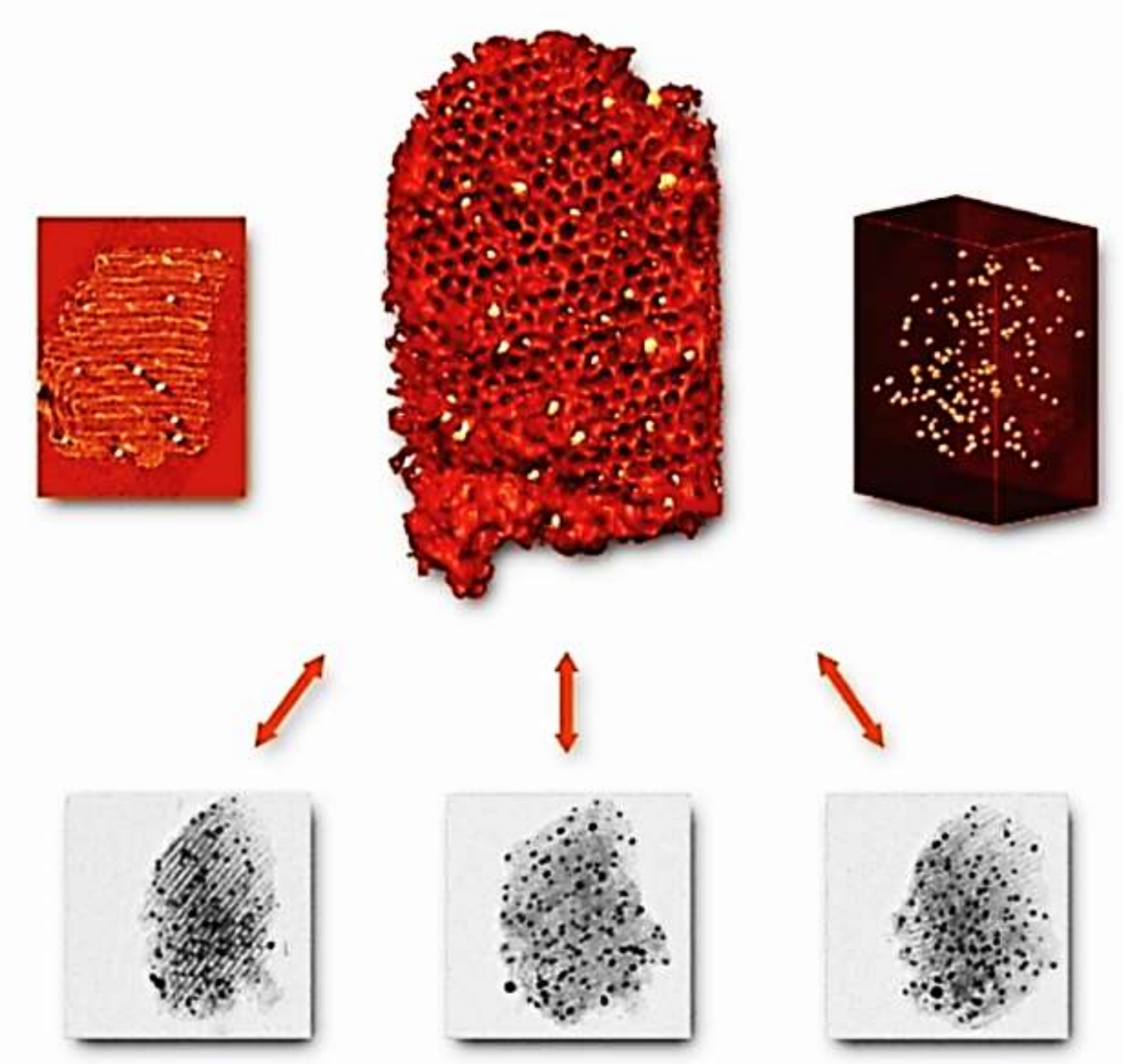
Limitations

- Not always possible to get very thin samples
- Beam may change or damage the sample
- Time-consuming to obtain large overview
- Generally high vacuum needed

Electron microscopy

Electron tomography

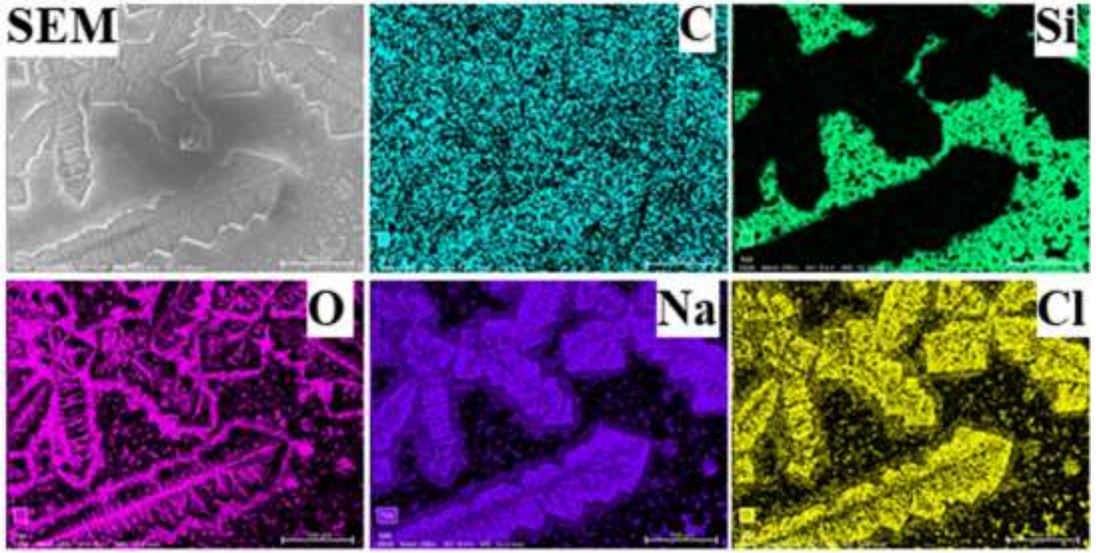
- Rotation of sample inside TEM under varying angles to construct a 3D image
- Powerful tool to investigate solid catalysts (pore structures, active metal particles etc.)



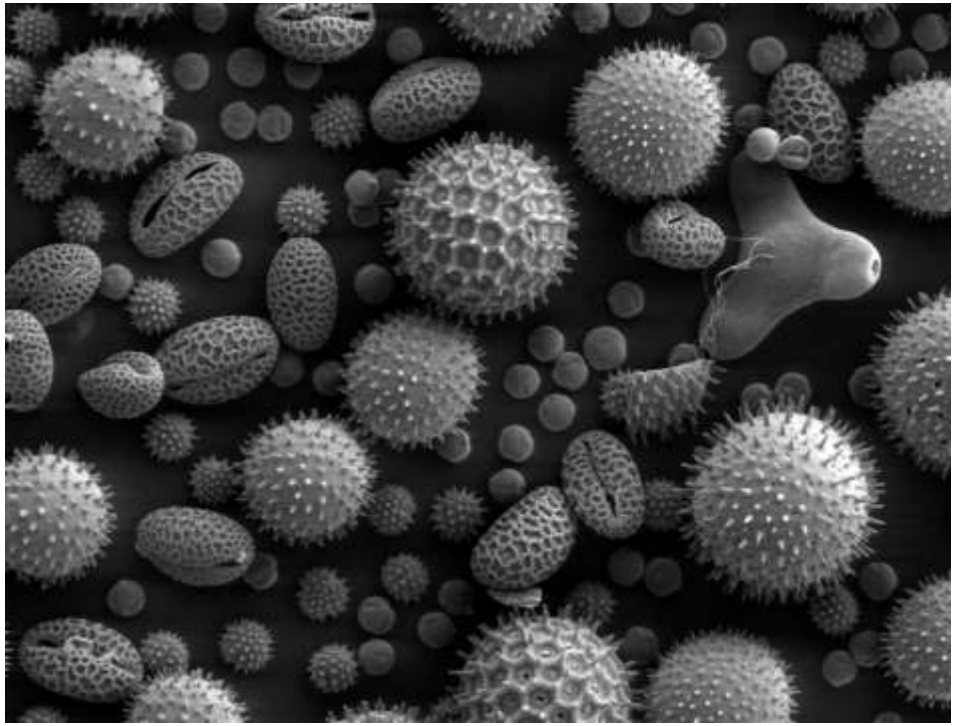
Electron microscopy

Scanning electron microscopy (SEM)

- Smaller electron beam is scanned (rastered) along a surface
- No transmission but emission of secondary electrons from the sample → information about outer surface
- Samples can be tilted so 3D-like images are obtained ⇨
- Detection of X-rays (Energy-Dispersive X-ray (EDX) analysis → 'elemental analysis'



Sci. Rep. **2019**, *9*, 1284



Limitations

- Only information about top part of surface
- Scanning of a surface takes time
- High resolution more difficult than with (HR)TEM
- Generally high vacuum needed