XPS

Topias Jussila

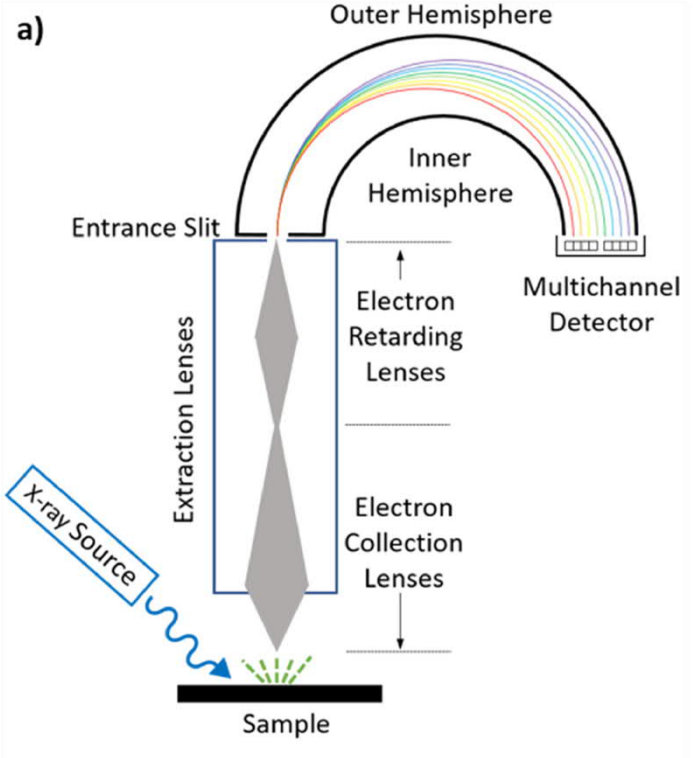
Table of content

X-ray photoelectron spectroscopy (XPS)

- Also known as ESCA (Electron spectroscopy of chemical analysis)
- Widely used surface analysis method
  - Elemental composition
  - Chemical and electronic state of atoms
    - Oxidation state
    - Valence band structure
  - qualitative and quantitative analysis
- Basic principle
  - Sample surface is exposed to x-ray beam
  - Photoelectric effect
  - Electrons are emitted from the top 10 – 20 nm of the sample
  - Analysis based on kinetic energies of the emitted electrons

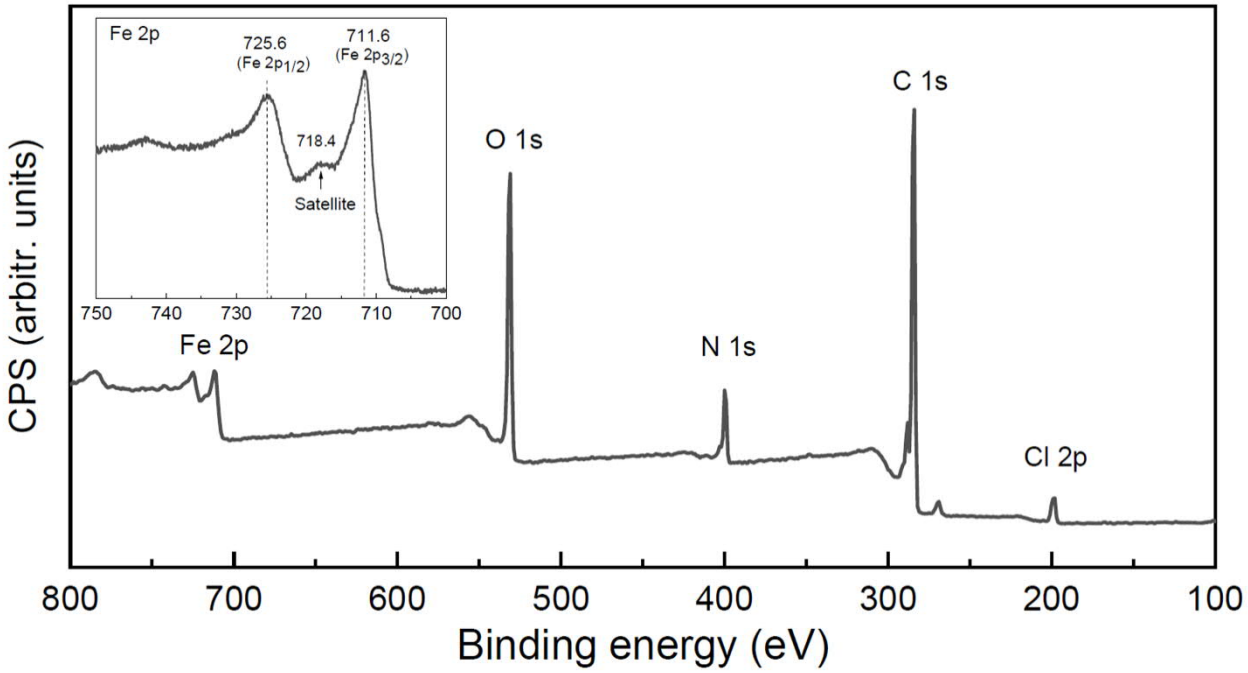
Instrumentation

- ultra-high vacuum chamber (10^{-9}/10^{-10} mbar)
  - Prevent electron from scattering from air
  - Prevent surface contamination
- X-ray source (>1 keV)
  - Electron created by heating a filament (e.g., tungsten) and accelerated towards high voltage anode (e.g., aluminium)
  - Monochromator typically used → only x-ray with certain wavelength (Al K_α) and narrower linewidth
- Extraction lenses
  - Define the angle range on electrons and area of the sample
  - Energy of electrons is often decreased as smaller energy results in higher energy resolution
- Electron energy analyzer
  - Concentric hemispherical analyzer
  - Detectors with electron multipliers



What do we get out of the analysis?

- Number of ejected electrons as function of their binding energy
  - Binding energies give qualitative information
  - Number on electrons (peak intensity) give quantitative information



Binding energy (BE)

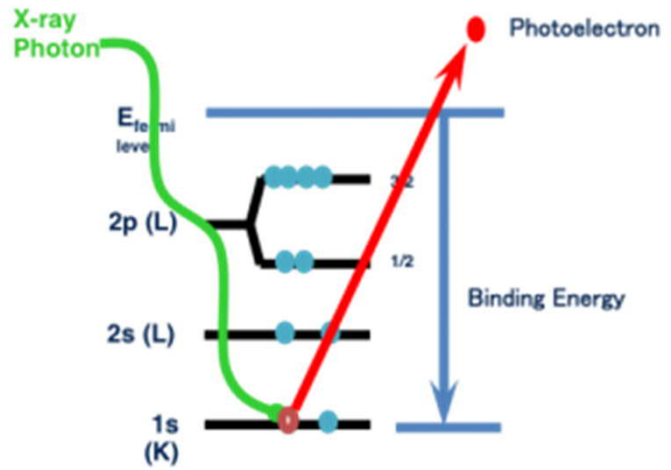
- Attraction energy between the ejected electron and nucleus
- Photoelectric effect

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

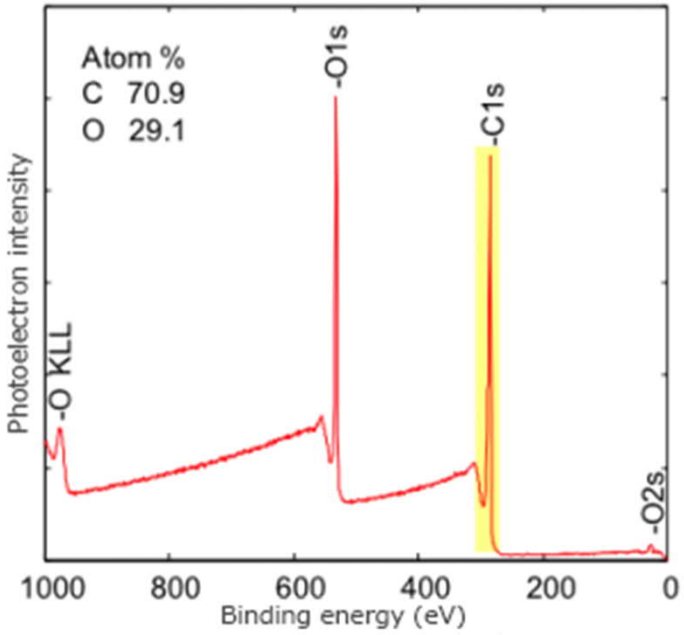
- Each electron configuration has specific binding energies

→ Elemental analysis

- Comparation of the results to tabulated data



Core level



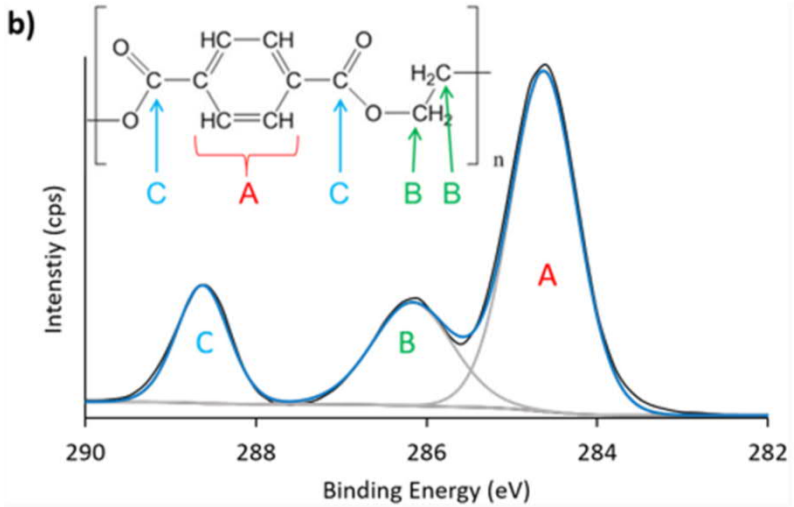
Techniques:What is XPS? I ULVAC-PHI, Inc.

Chemical shift

- Orbital energies (binding energies) depends also on the chemical environment

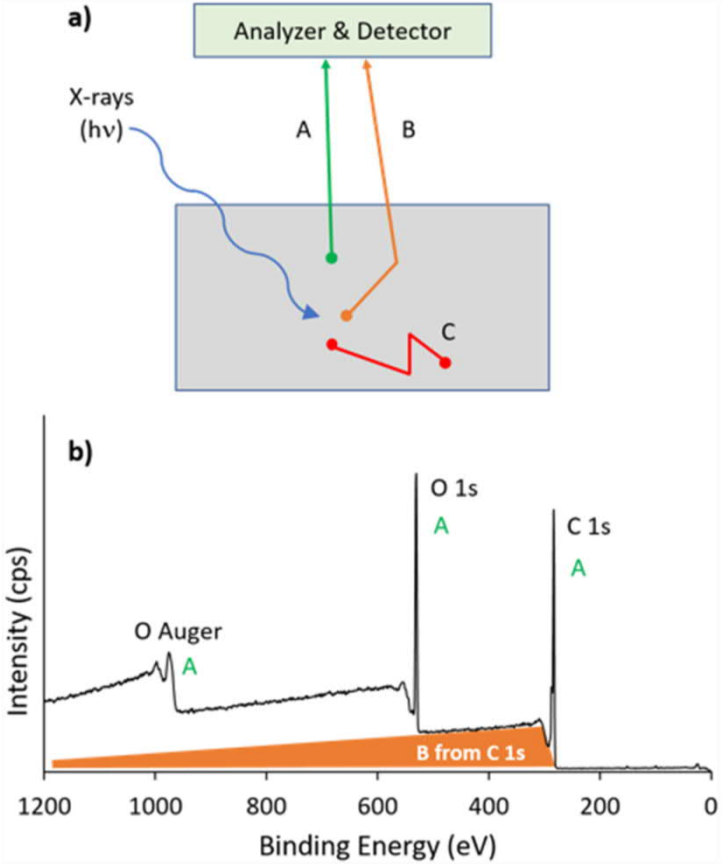
  → chemical/electronic state, empirical formula

- peaks shift according to the environment
  - Higher the oxidation state of a transition metal, higher the BE
  - Carbon attached to electronegative oxygen has higher BE than carbon attached to hydrogen



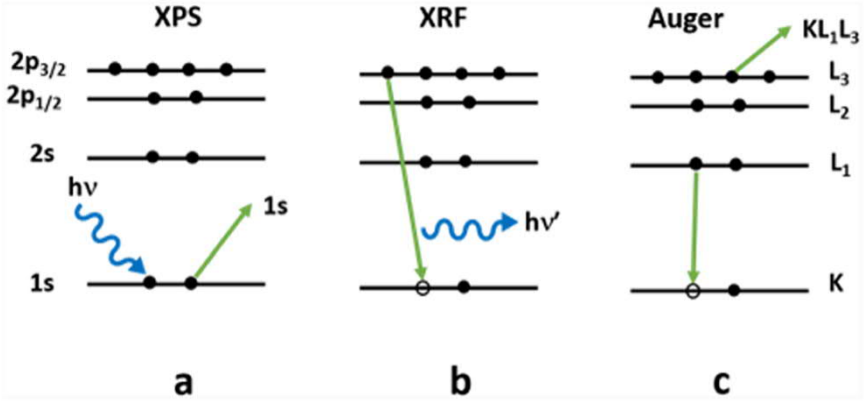
Surface sensitivity

- X-rays penetrate quite deep to the sample (few µm)
  - Ejected electron face several inelastic collisions → loss on energy
- “C” electrons are ejected deep in the sample → energy loosed before reaching the surface
- “B” electrons created a bit closed to surface → some collisions → some energy loss
  - Background signal
- “A” electrons escape the material with no inelastic collision
  - Characteristic photoelectron peaks
- Higher x-ray energy source results in electrons detected deeper from the surface



Other considerations

- Auger electrons
  - Electron ejection from higher orbitals after relaxation
  - Does not depend on x-ray energy
  - Sometimes useful in qualitative analysis
- Satellite peaks
  - Due to multiple x-ray energies
- Shake-up peaks (“loss peaks”)
  - Ejected core electron excites valence electron
- Plasmon lines
- Spin-orbit coupling

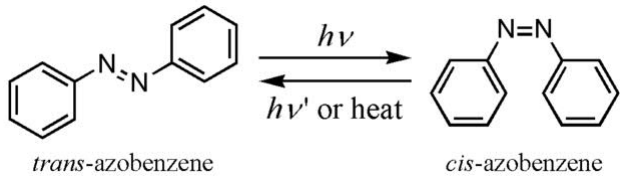


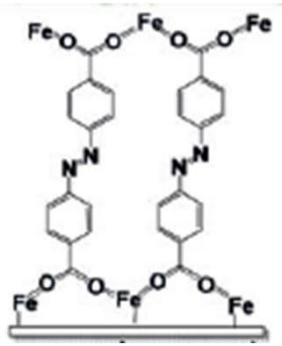
Pros and Cons

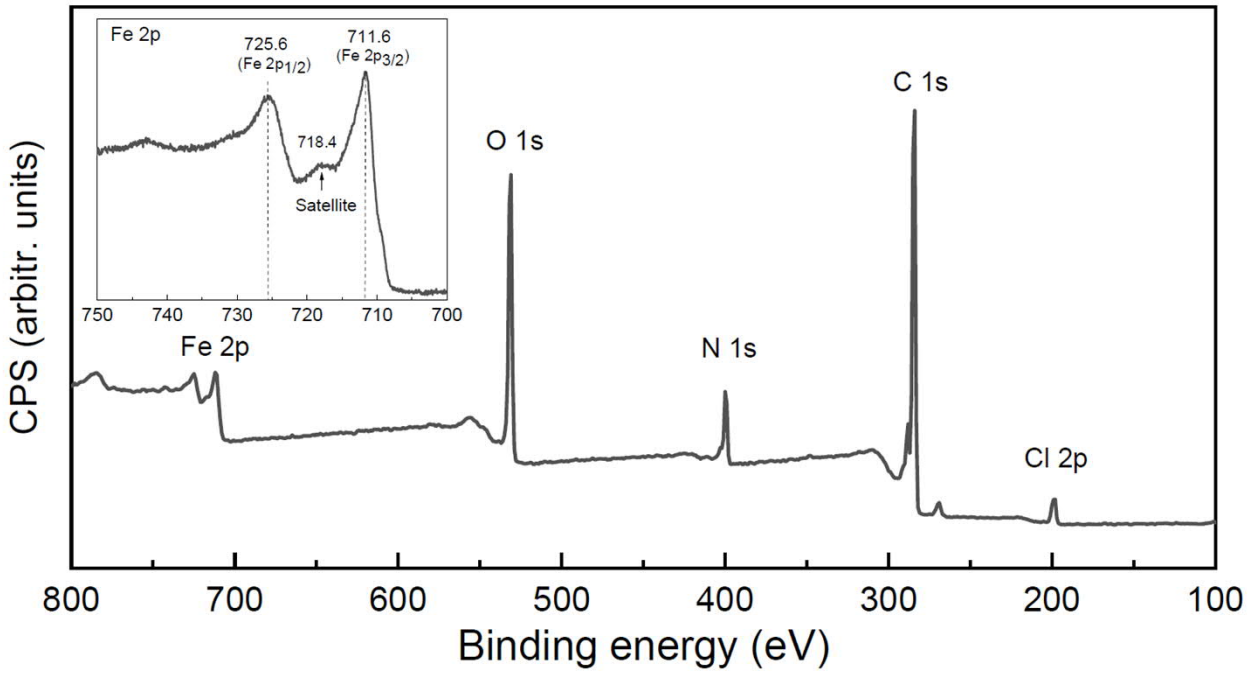
- Pros
  - Highly surface sensitive
  - Information about chemical states
  - Various material types can be analyzed
    - Organic, inorganic, composite, alloys, conducting, insulating, coatings…
- Cons
  - x-ray interaction with electrons
    - Hydrogen, helium cannot be seen
  - Only surface analysis
  - Sample must endure ultra-high vacuum
  - Surface charge creation of insulating sample
    - Charge neutralizers

Case 1: Iron-azobenzene MOF thin films

- ALD/MLD fabrication of sequential inorganic and organic layers
  - $FeCl_3$
  - azobenzenedicarboxylic acid
- Photoactive azobenzene
  - Cis-trans isomerism
    - Cis isomer by UV irradiation
  - Remote controlled of gas molecule capture
- Characteristic Fe $2_{p1/2}$ and Fe $2p_{3/2}$ peaks of trivalent iron
  - Characteristic satellite peak, too
- N:Fe ratio 2.6
  → azobenzene:Fe ratio 1.3
  - High CN and bridging type bonding
- Cl impurity



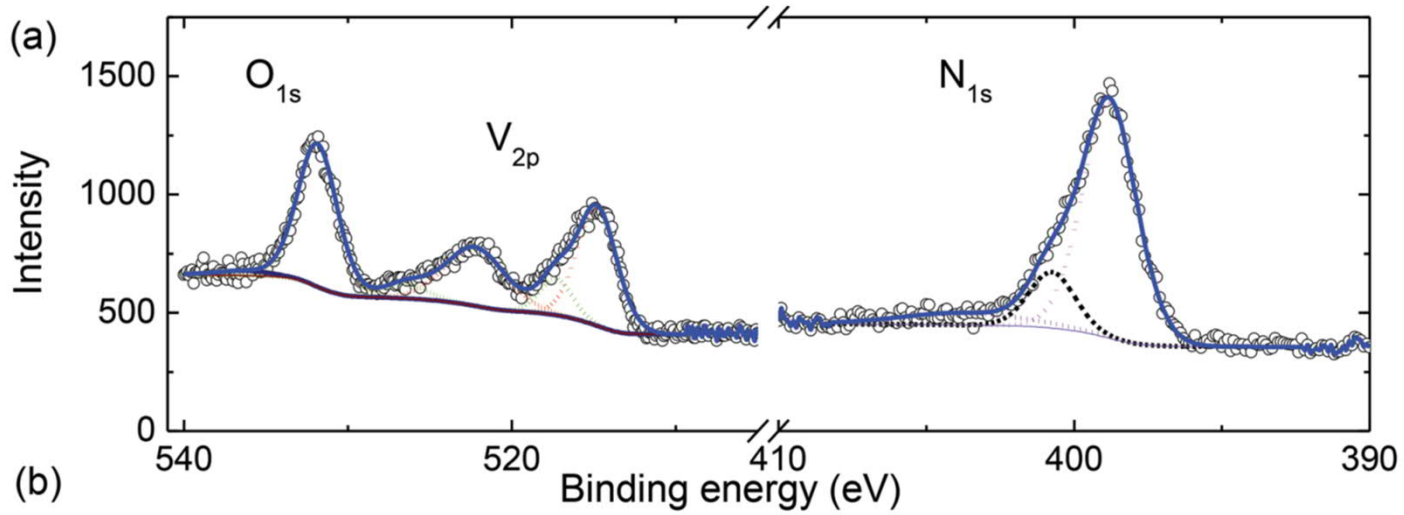




Khayyami, A., Philip, A., & Karppinen, M. (2019). doi: 10.1002/ange.201908164

Case 2: Organometallic thin films

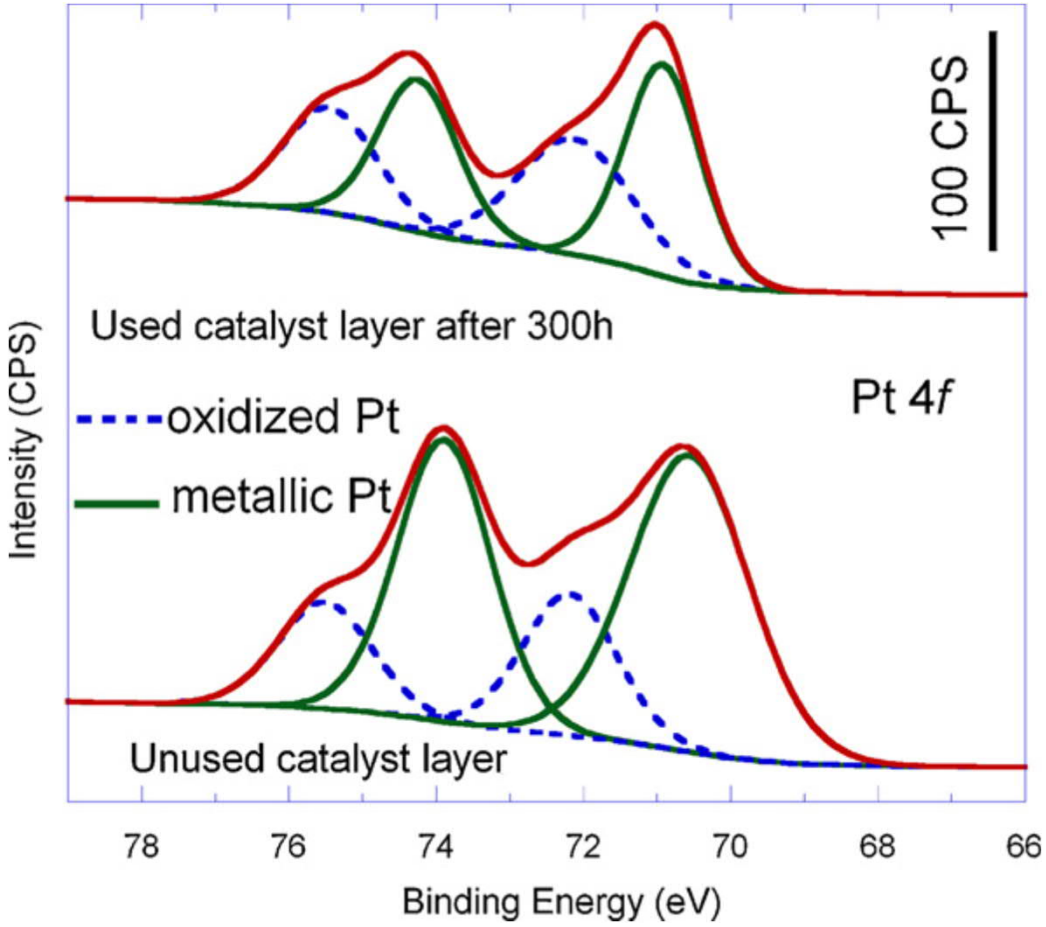
- Organic based magnet by CVD
  - $V(CO)_6$ and MeTCEC precursors
  - $V[MeTCEC]_x$ thin films
- Air sensitive → Ar sputtering before XPS measurement
- Composition: $VC_{15.6}N_{4.3}O_{2.5}$
  - Stoichiometry $V[MeTCEC]_{1.5}$
- V_{2p} peak split (spin-orbit coupling)
  - Both peaks have two different binding energies
    - V^{2+} and V^{5+} (due to oxidation)
- N_{1s} peak with characteristic shakeup peak



Lu, Y., Harberts, M., Kao, C., Yu, H., Johnston-Halperin, E., & Epstein, A. (2014). doi: 10.1002/adma.201403834

Case 3: Catalyst degradation

- degradation of a fuel cell catalyst studied by XPS
  - Dispersed Pt nanoparticles supported by carbon particles
  - Pt as the active catalyst material
- Oxidized and metallic Pt
  - Total amount of Pt decreased from 0.4% to 0.3%
  - Portion of metallic Pt decreased and oxidized Pt increased → catalyst degradation
- Surface chemistry of catalysts extremely important → XPS suitable characterization method



Zhang, F., Advani, S., Prasad, A., Boggs, M., Sullivan, S., & Beebe, T. (2009). doi: 10.1016/j.electacta.2009.02.028

References

X-Ray Photoelectron Spectroscopy | Thermo Fisher Scientific – FI

X-ray Photoelectron Spectroscopy (XPS) - Chemistry LibreTexts

X-ray photoelectron spectroscopy – Wikipedia

Stevie, F., & Donley, C. (2020). Introduction to x-ray photoelectron spectroscopy. *Journal Of Vacuum Science & Technology A*, *38*(6), 063204. doi: 10.1116/6.0000412

Khayyami, A., Philip, A., & Karppinen, M. (2019). Atomic/Molecular Layer Deposited Iron–Azobenzene Framework Thin Films for Stimuli-Induced Gas Molecule Capture/Release. *Angewandte Chemie*, *131*(38), 13534-13538. doi: 10.1002/ange.201908164

Lu, Y., Harberts, M., Kao, C., Yu, H., Johnston-Halperin, E., & Epstein, A. (2014). Thin-Film Deposition of an Organic Magnet Based on Vanadium Methyl Tricyanoethylenecarboxylate. Advanced Materials, 26(45), 7632-7636. doi: 10.1002/adma.201403834

Zhang, F., Advani, S., Prasad, A., Boggs, M., Sullivan, S., & Beebe, T. (2009). Quantitative characterization of catalyst layer degradation in PEM fuel cells by X-ray photoelectron spectroscopy. *Electrochimica Acta*, *54*(16), 4025-4030. doi: 10.1016/j.electacta.2009.02.028