Ecole Polytechnique Fédérale de Lausanne

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Catalysis for Emission Control and Energy Processes - ChE-410

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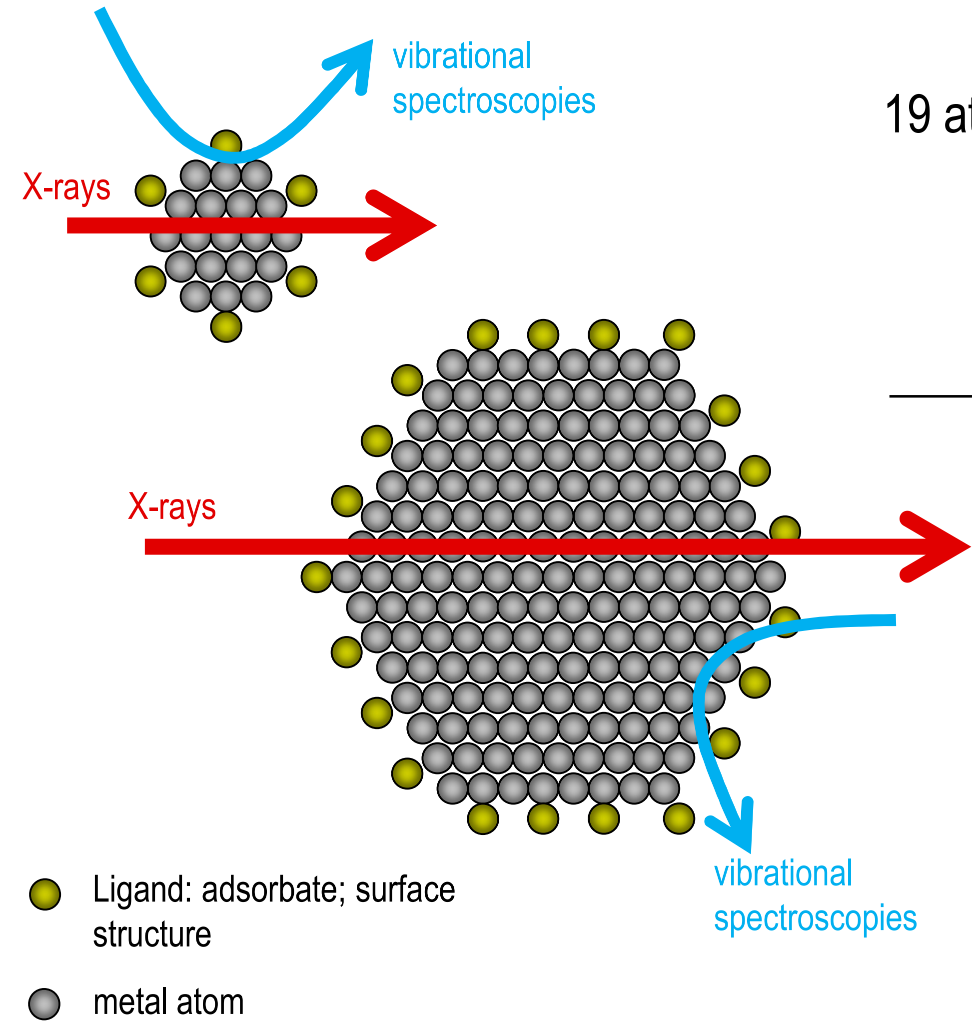
Surface vs. bulk information

Catalysis is a surface phenomenon – XRD and XAS probe the bulk



19 atoms (Ø 1.4 nm)	169 atoms (Ø 4.3 nm)
Surface coverage 50%	
# ligands : # catalyst	
31%	12%

Advantages of X-rays

very good penetration through a number of materials

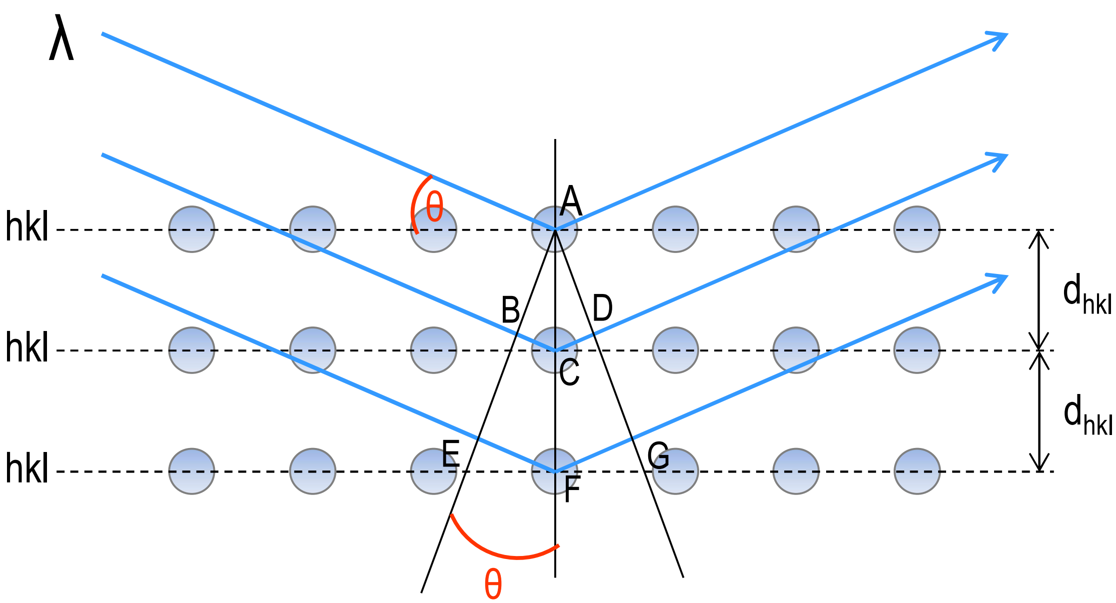
- *in situ* cells similar to catalytic reactors or synthesis vessels can be built up
- well suited for following *in situ* formation of active catalyst phases

X-ray diffraction

Bragg's condition

Distance between the lattice planes about the same as the wavelength of the X-rays

constructive interference between scattered X-rays



$BC = d_{hkl} \sin\theta$

but $BCD = \lambda$

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

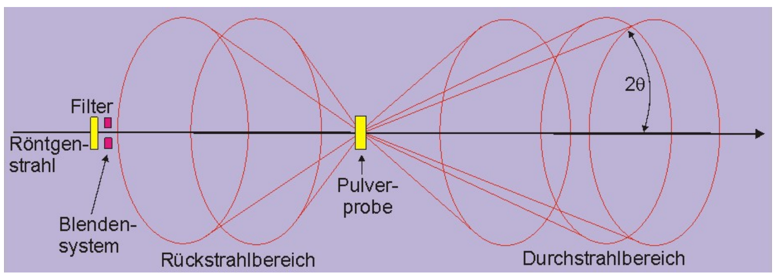
or

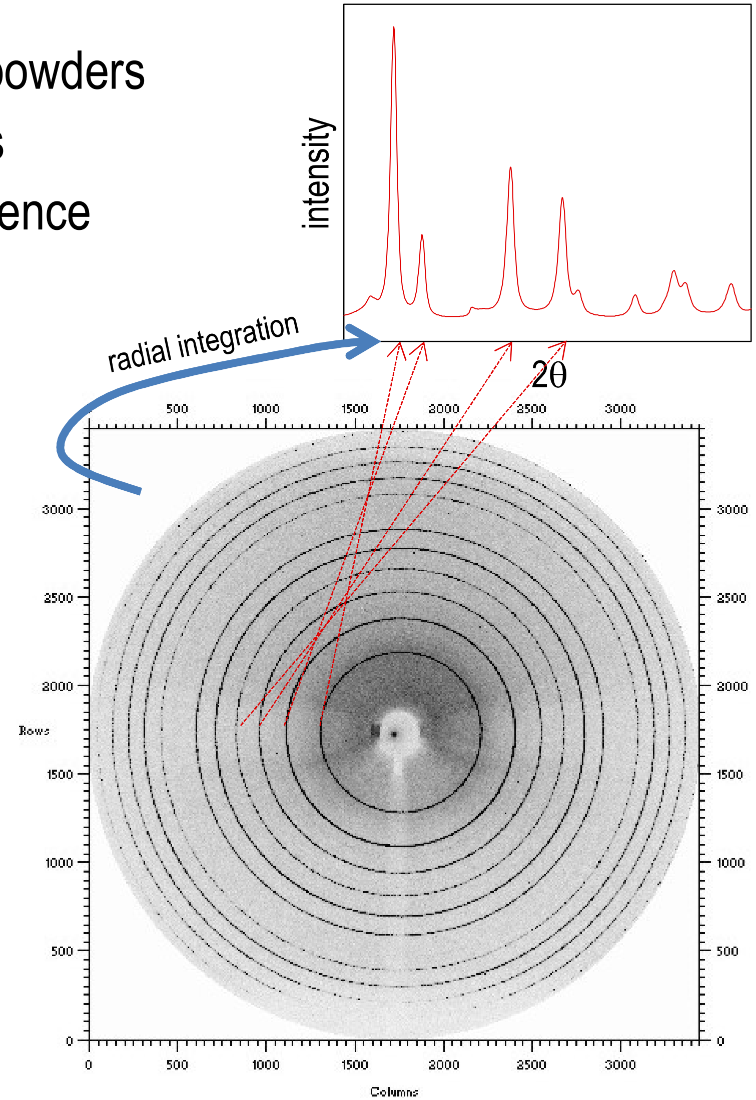
$\lambda = 2d_{hkl} \sin\theta$

Powder diffraction

Heterogeneous catalysts: no single crystals but powders

- hundreds of single crystals in all directions
- diffraction lines, just if constructive interference
- cone with half opening angle 2θ





What is needed?

- fine powders
- or, rotation of the sample

Information contained in the XRD pattern

Peak positions

- Crystal system
- Space group symmetry
- Unit cell dimensions
- Qualitative phase identification

Peak intensities

- Unit cell contents
- Quantitative phase fractions

Peak shapes and widths

- Crystallite size (3-200 nm)
- Non uniform micro-strain
- Extended defects

Line broadening

- SIZE effect: imperfection in size (i.e. no infinite crystal)
- GRAIN effect: imperfection in periodicity

- Small crystal → small nr. periods → larger imperfection → larger line

- Evident for size < 100 nm
- Lower limit: < ca. 3 nm

- Dislocations, vacancies, substitutional defects, interstitial defects

Disadvantages

- amorphous phases cannot be detected
- sufficient concentration
- small particles (2-3 nm) with high dispersion and low concentration not be detected
- bulk, not surface sensitive

Crystallite size

Crystallite size can be estimated from line width

$$D = \frac{K \cdot \lambda}{B \cdot \cos\theta}$$

Scherrer equation

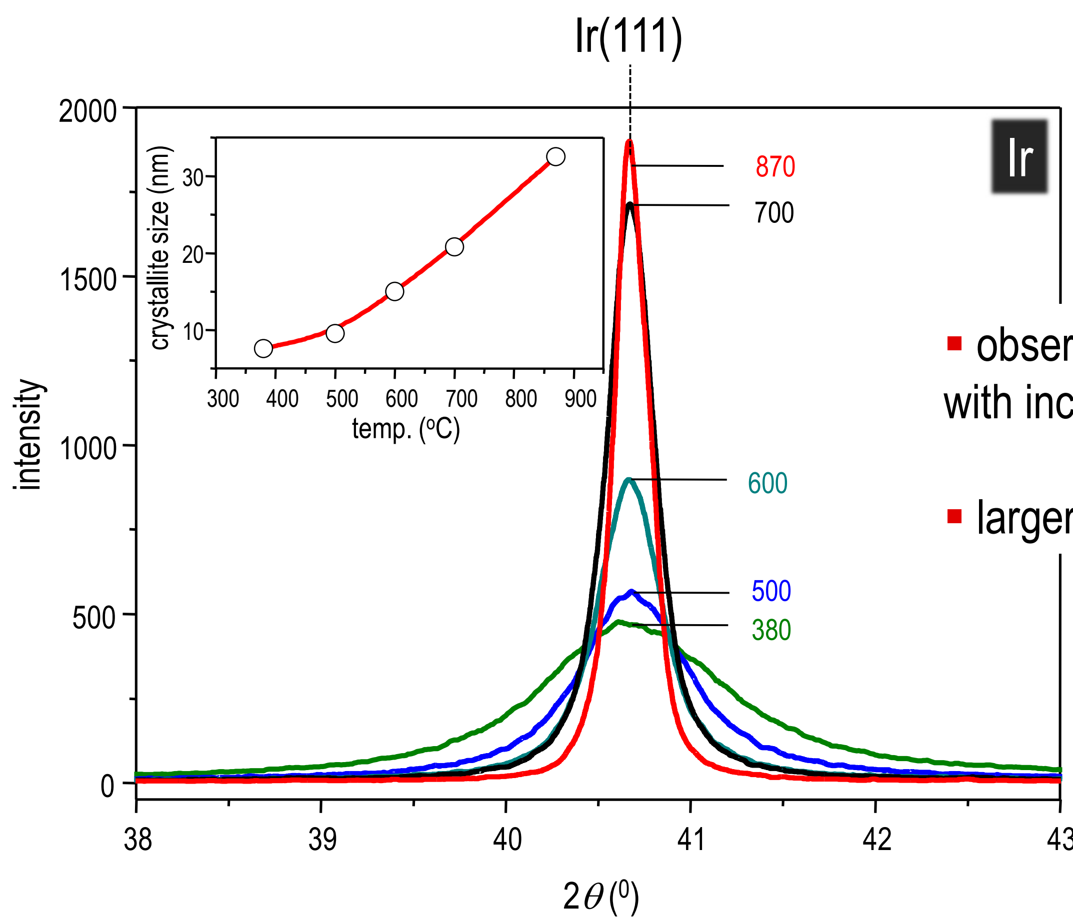
$$B = (B^2_{measured} - B^2_{instrument})^{1/2}$$

- K often taken as 0.9
- Wavelength, λ
- Diffraction angle, θ (rad)
- Instrumental half-width, $B_{instrument}$

Q *Calculate the copper particle size in two different Cu-catalysts (at $2\theta=40^0$), that show a FWHM of 0.12^0 and 2.50^0. The instrumental resolution is 0.10^0. The widely applied X-ray source with a Cu-anode and Ni-filter has been used.*

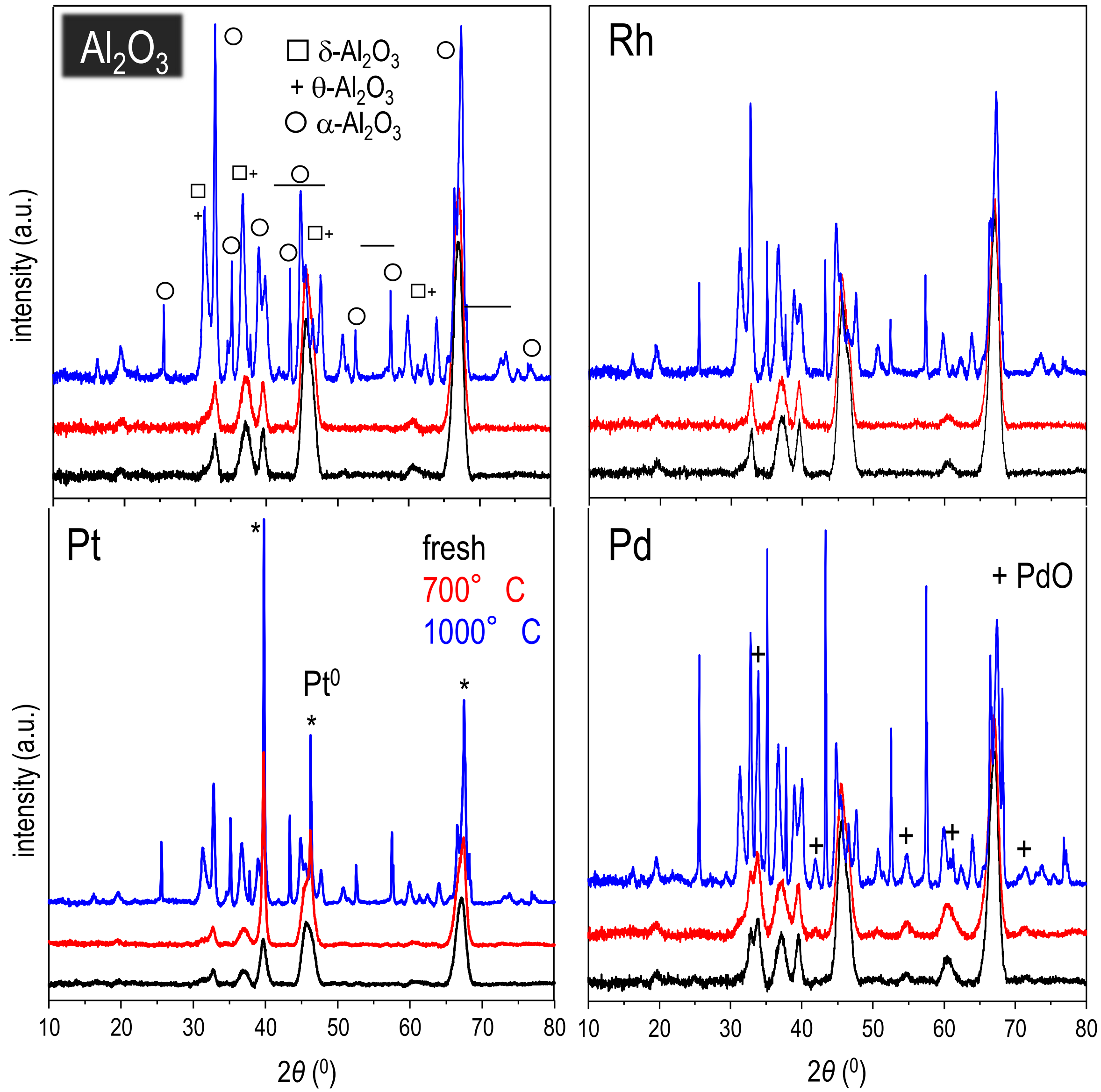
Crystallite size

- Dispersed metal nano-particles



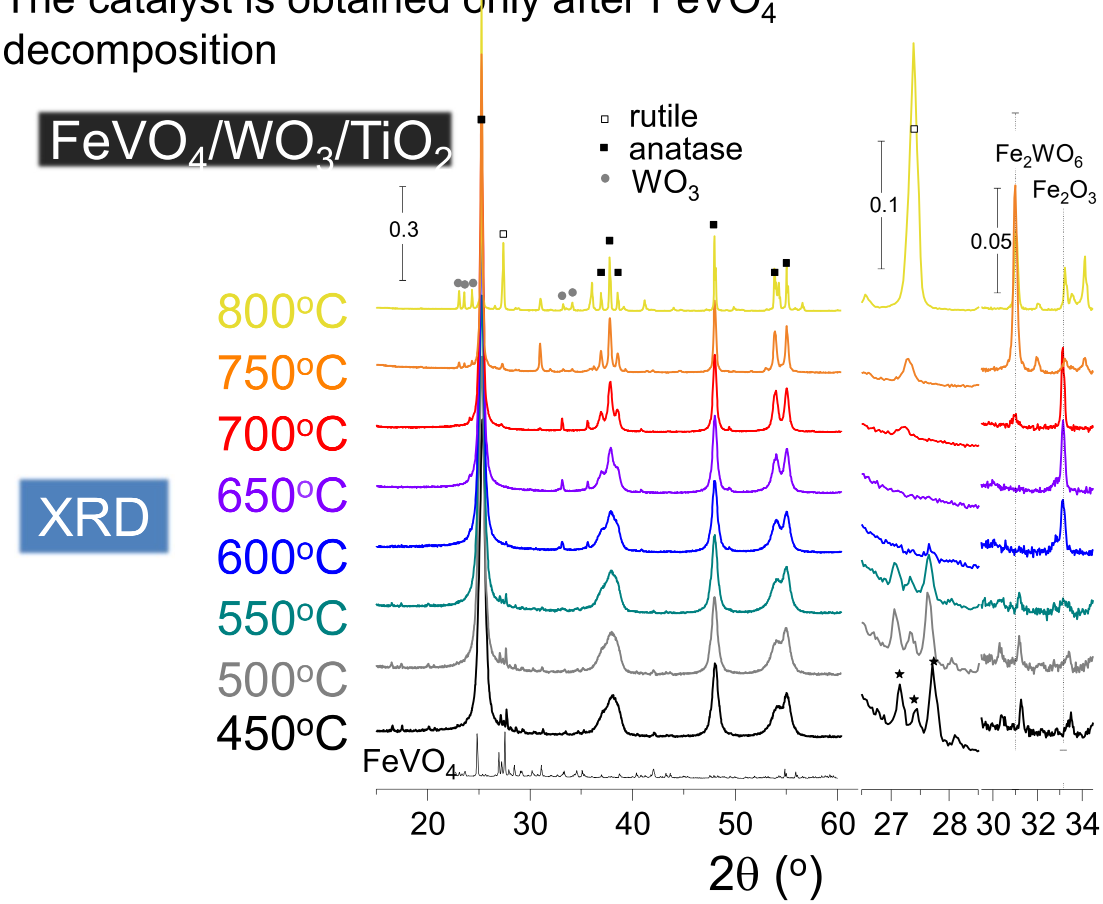
- observed increase of selectivity with increasing T
- larger crystallite size at higher T

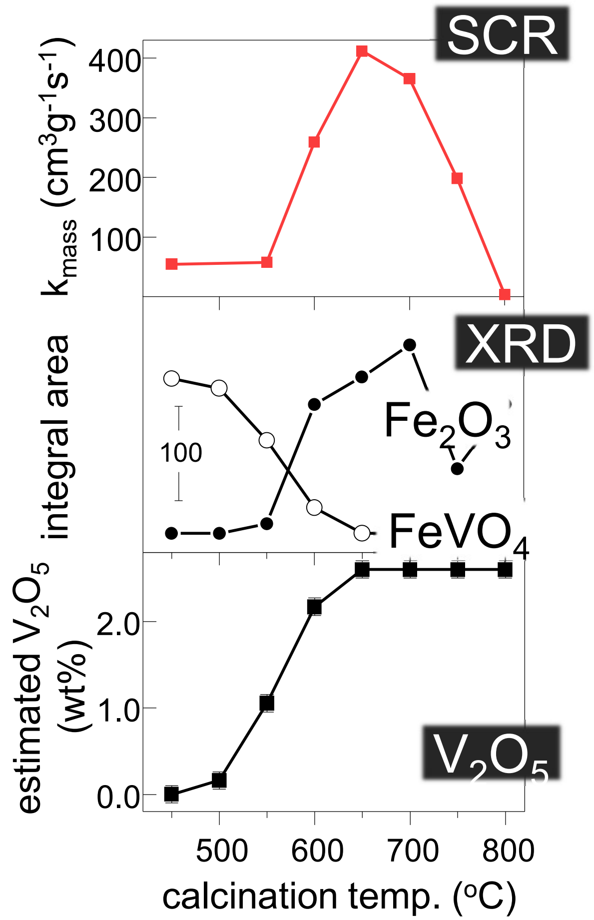
Phase composition



Phase composition

- Unsupported $FeVO_4$ stable up to 700° C
- The catalyst is obtained only after $FeVO_4$ decomposition





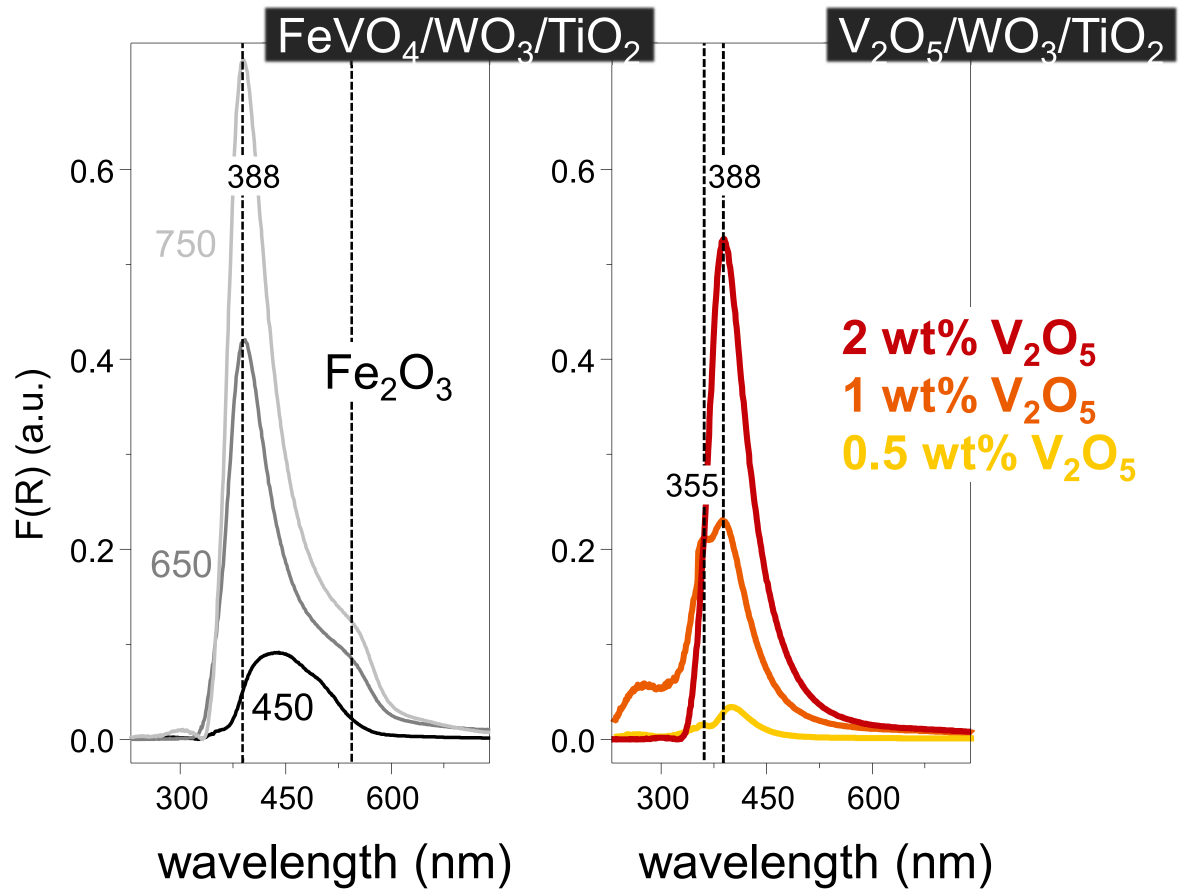
- What about Vanadium species?

Phase composition

- Unsupported $FeVO_4$ stable up to 700° C
- The catalyst is obtained only after $FeVO_4$ decomposition

- Fresh supported $FeVO_4$: no V_2O_5 species
- After heat treatment: V_2O_5 formation – 388 nm

UV-vis



similar VO_x species to ref. catalyst

XRD and TEM

XRD

- averaging over the whole sample
- limited to larger crystallites (> 3 nm)
- amorphous material invisible
- 3D distribution of d-spacings (but collapsed into 1D)
- usually no beam damage

TEM

- local
- limited to smaller crystallites (beam transparency required)
- amorphous material visible
- 2D projection of d-spacing
- beam damage possible

Synchrotron radiation

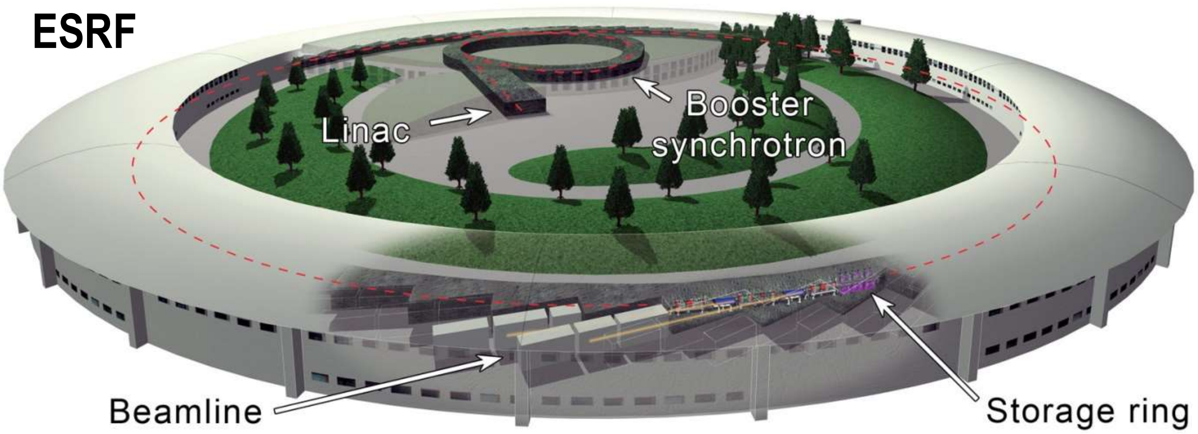
Synchrotron light is the electromagnetic radiation emitted when electrons, moving at velocities close to the speed of light, are forced to change direction under the action of a magnetic field.
The electromagnetic radiation is emitted in a narrow cone in the forward direction, at a tangent to the electron's orbit.

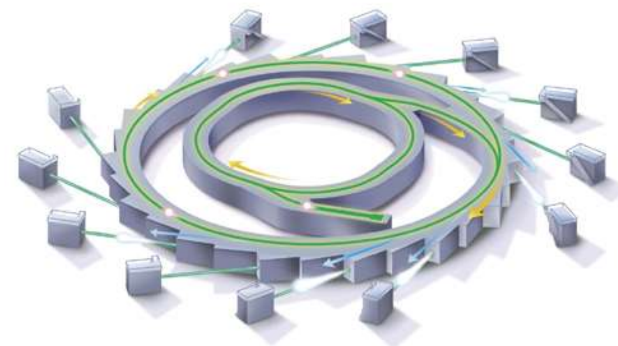
Properties

- **High brightness:** synchrotron light is extremely intense (hundreds of thousands of times more intense than that from conventional x-ray tubes) and highly collimated
- **Wide energy spectrum:** synchrotron light is emitted with energies ranging from infrared light to hard x-rays
- **Tunable:** it is possible to obtain an intense beam of any selected wavelength
- **Highly polarized:** the synchrotron emits highly polarized radiation, which can be linear, circular or elliptical
- **Emitted in very short pulses:** pulses emitted are typically less than a nano-second (a billionth of a second), enabling time-resolved studies

Synchrotron radiation

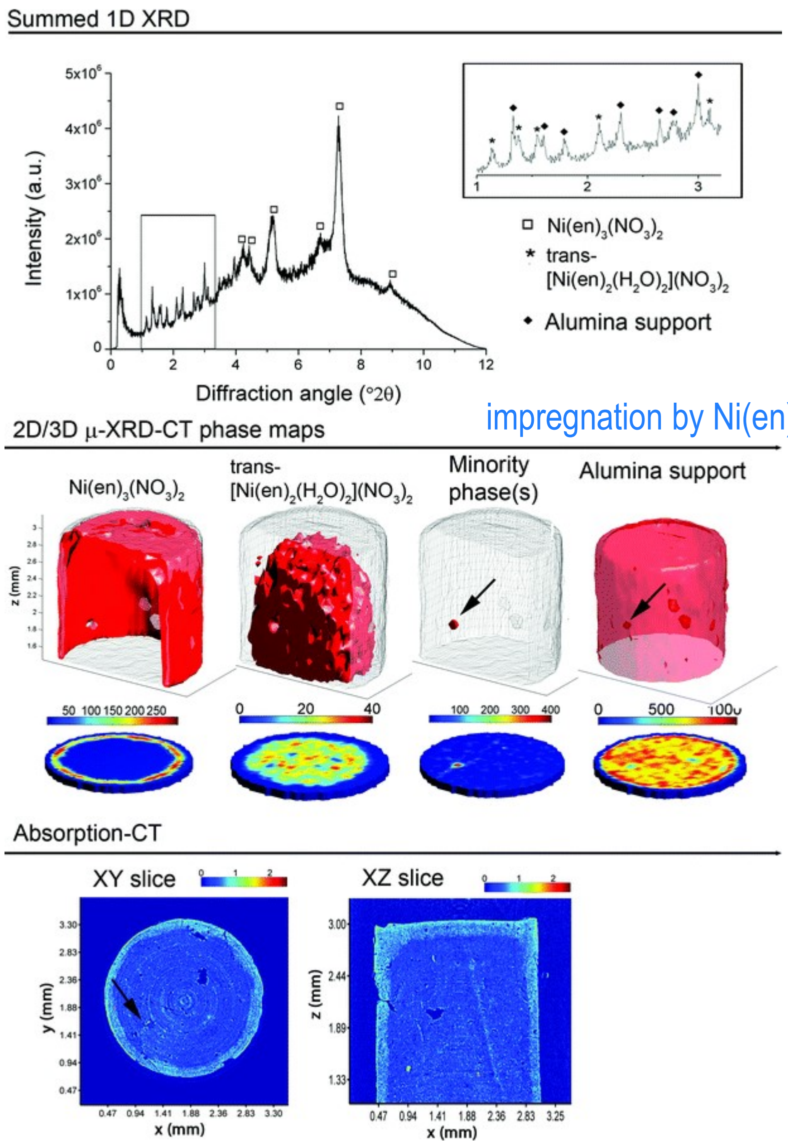
ESRF





ASLS

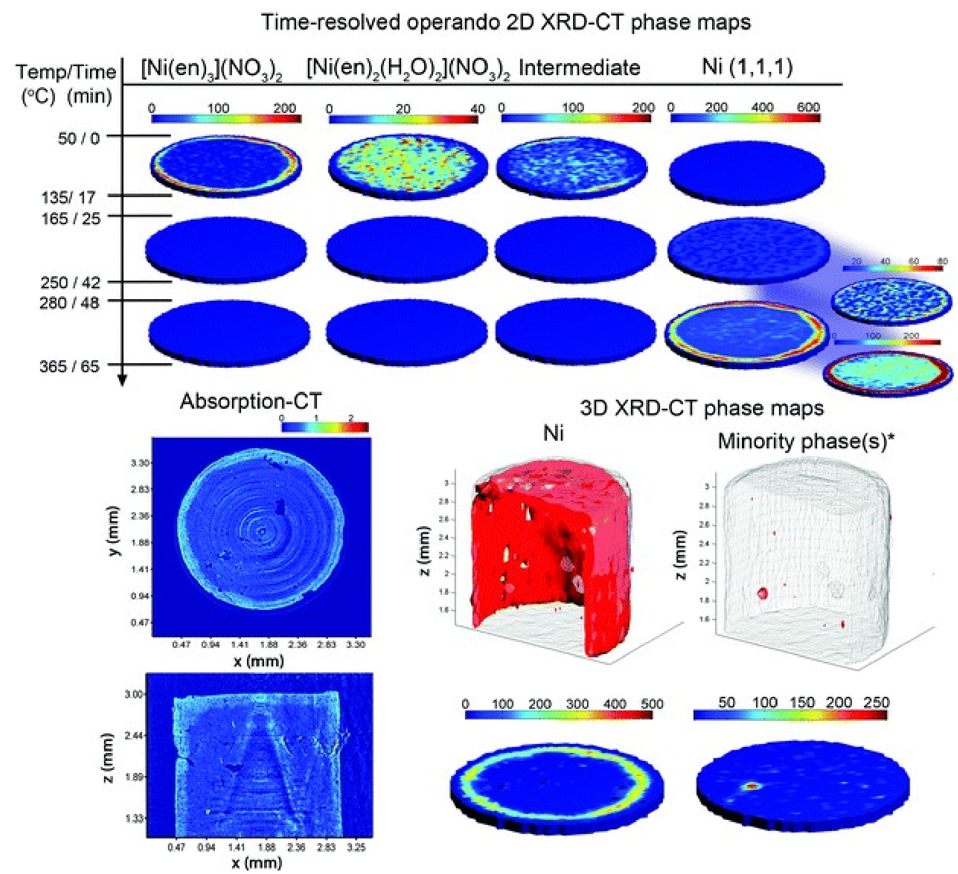
XRD│µ-Tomography of catalyst bodies



impregnation by Ni(en)Cl$_2$

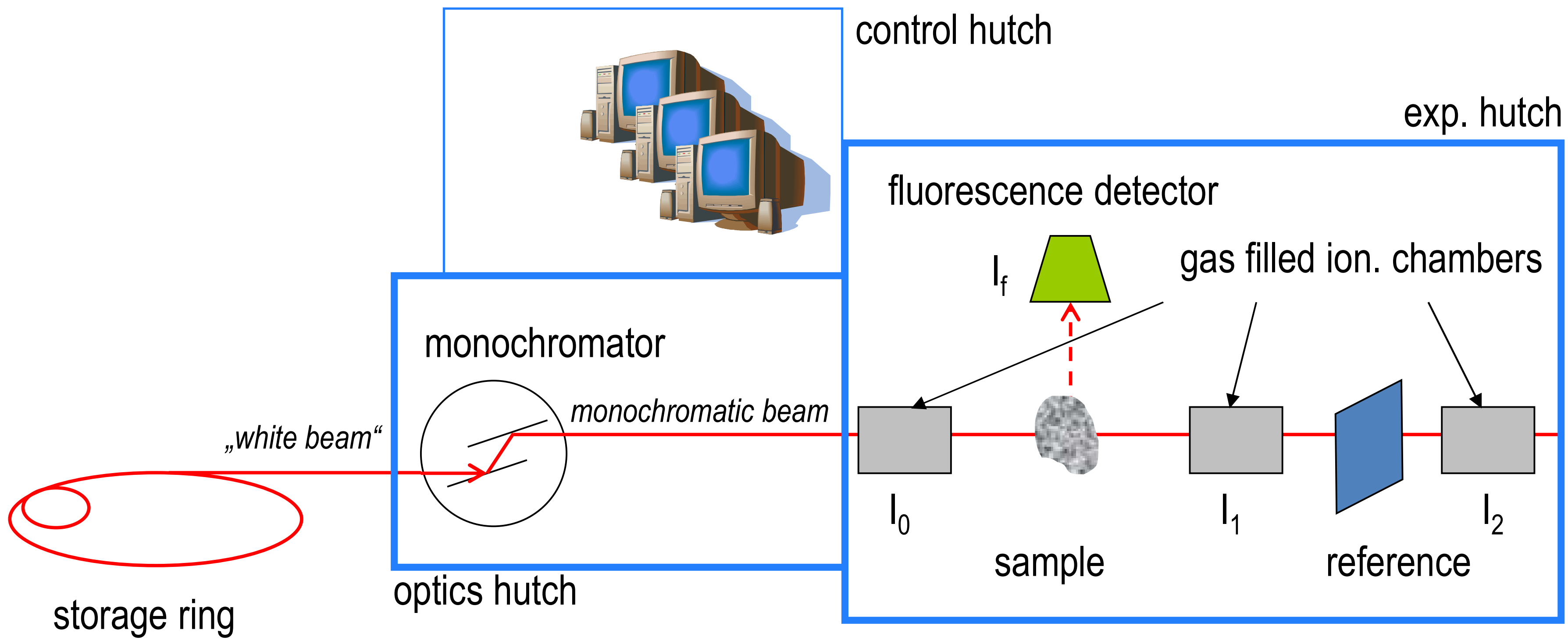
beam size: 50x100 µm
pixel res.: 50 µm
Al_2O_3 pellet: 3x3 mm

activation in N_2 flow



O'Brien et al., *Chem. Sci.* 3 (2012) 509

Simplified beamline layout

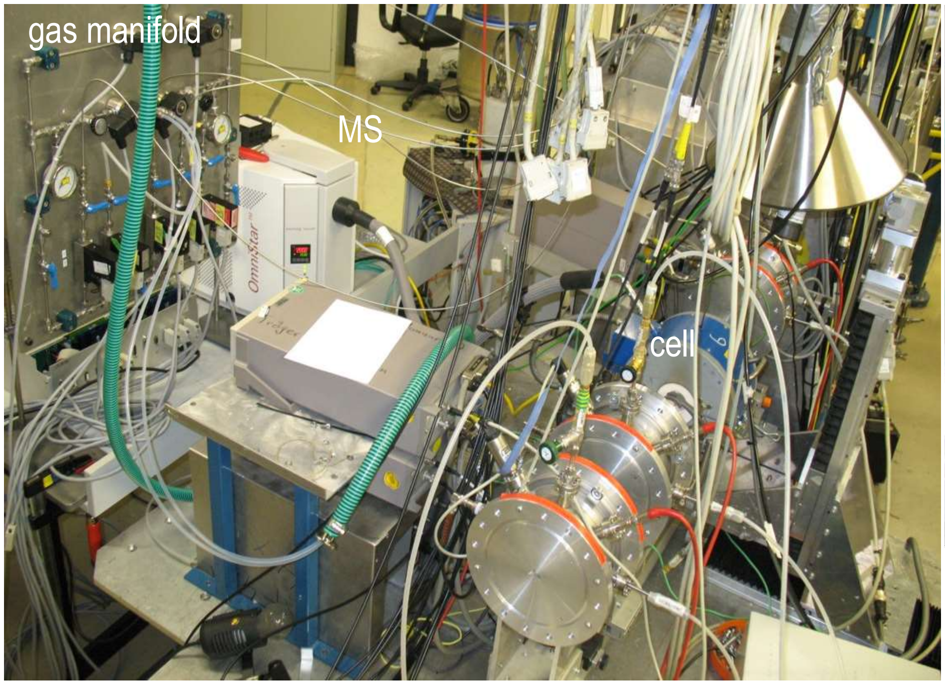


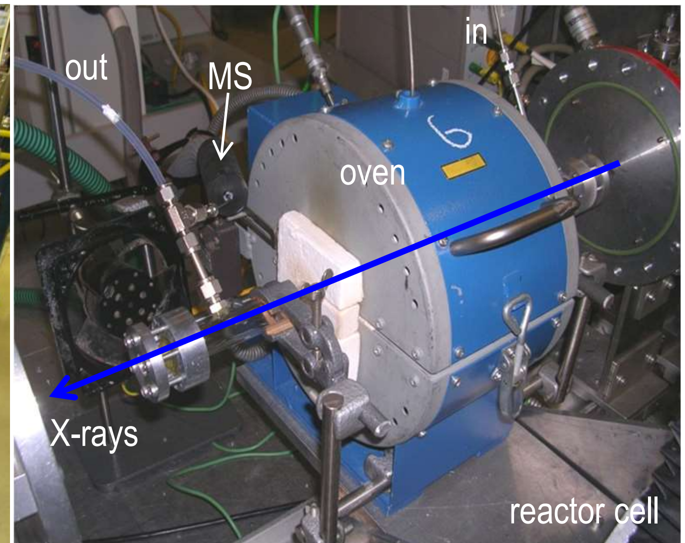
Some things to consider:

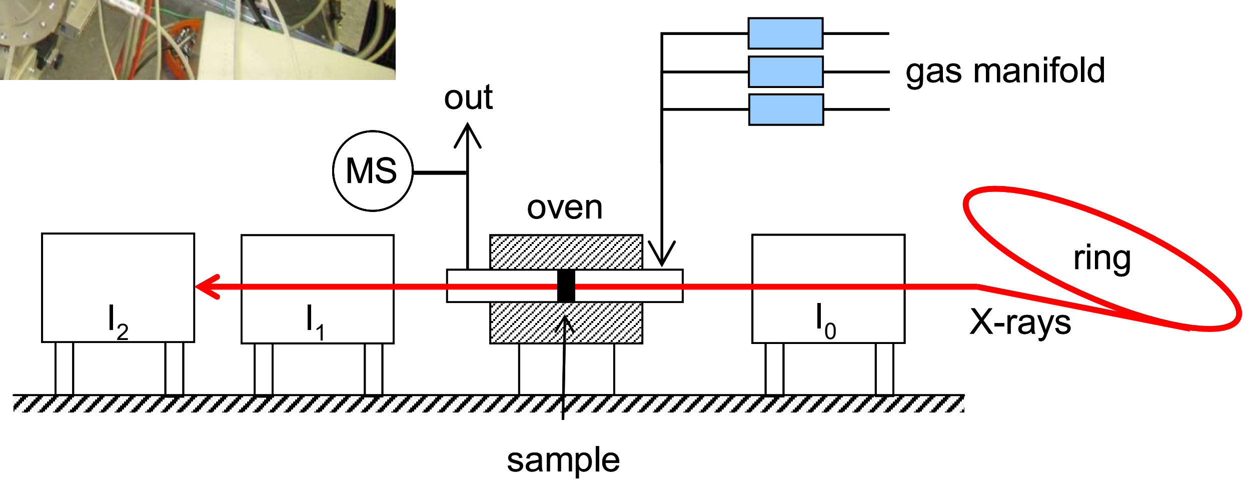
- which elements/edges → *energy range*
- absorption too high/low → *element concentration*
- kinetics of process → *time resolution*
- absorption of environment (reactor, gases)

- fluorescence detector is needed if the sample absorbs too much/too little
- measuring the reference (e.g. a metal foil) simultaneously allows for a precise energy calibration
- typically enough space around sample

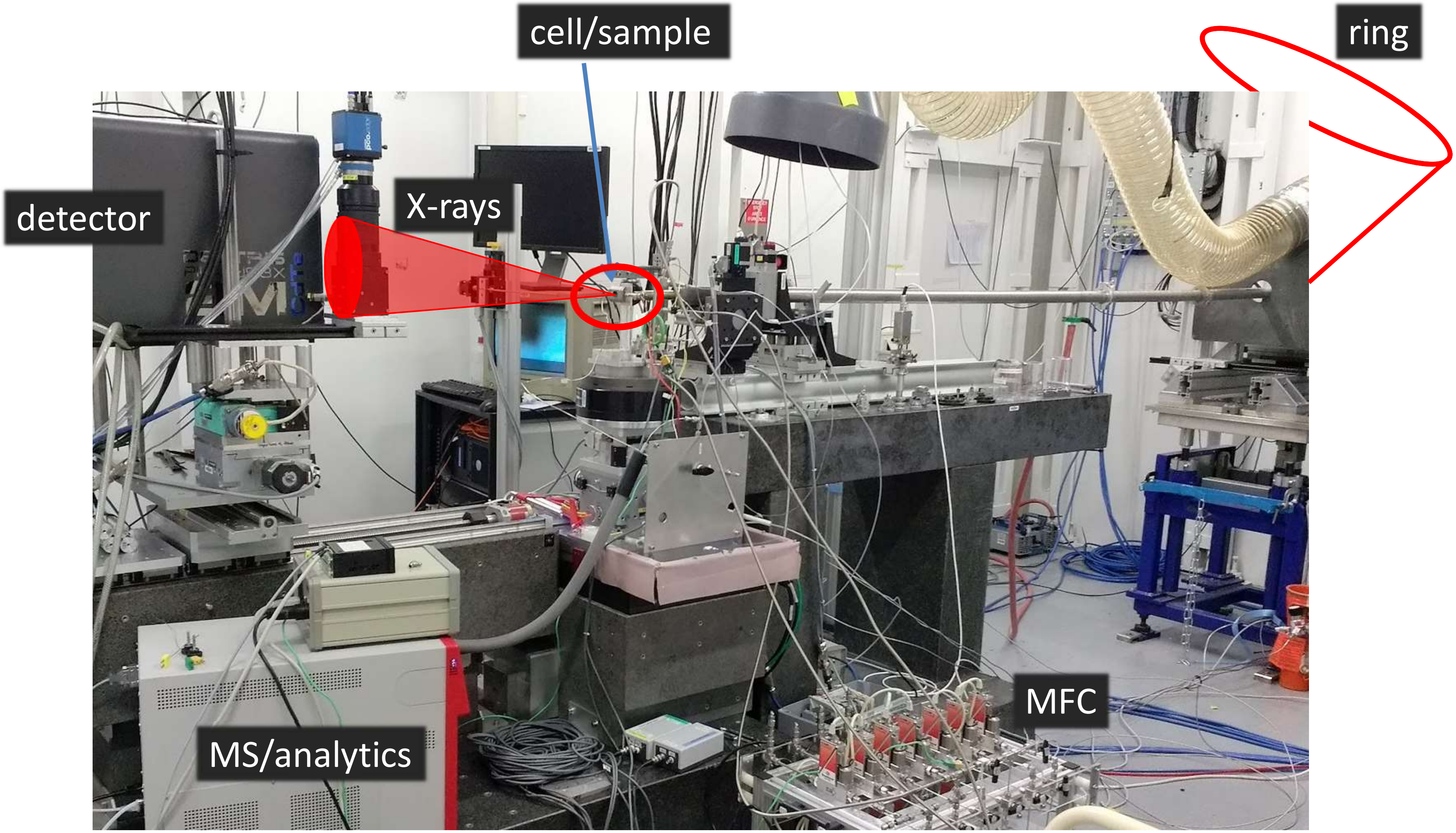
X-ray absorption spectroscopy



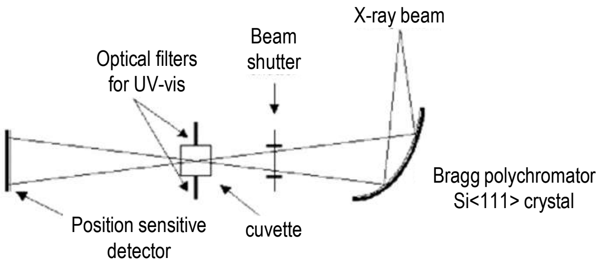


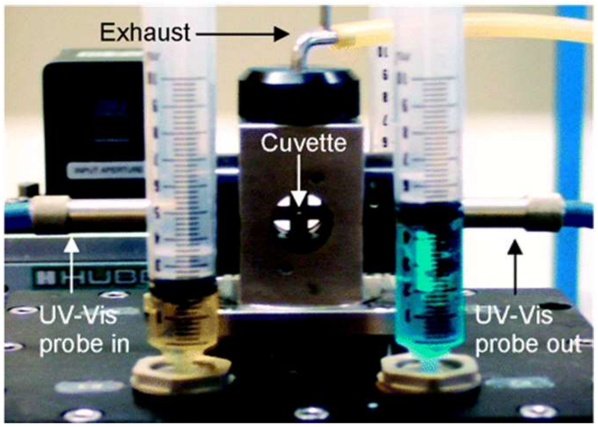


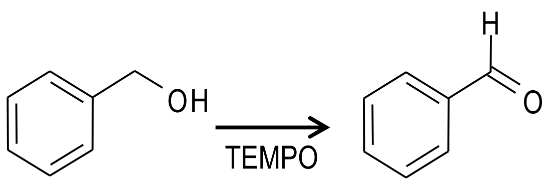
Time-resolved X-ray diffraction



Sample damage by X-rays

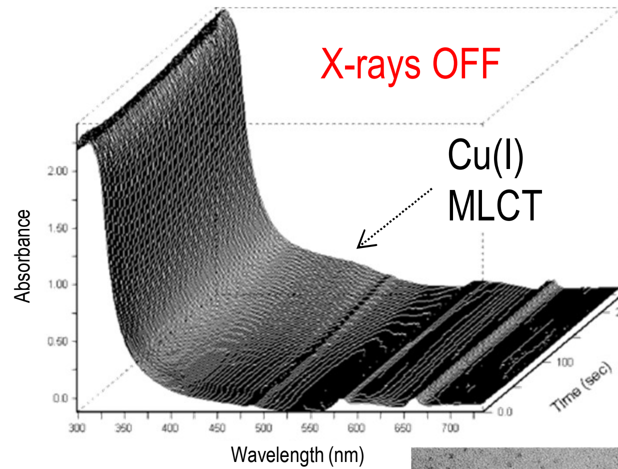


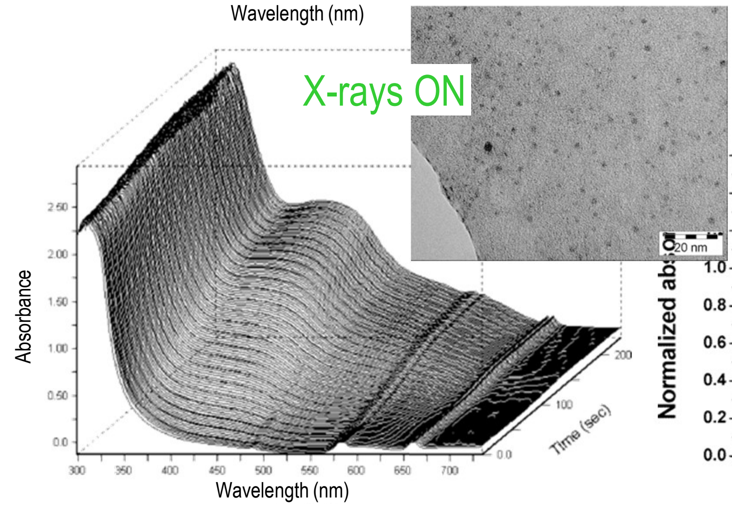




CuBr$_2$/bipyridine, benzyl alcolhol, TEMPO, TEAOH 1:1:1:1
NMP/H$_2$O 1:1; rt

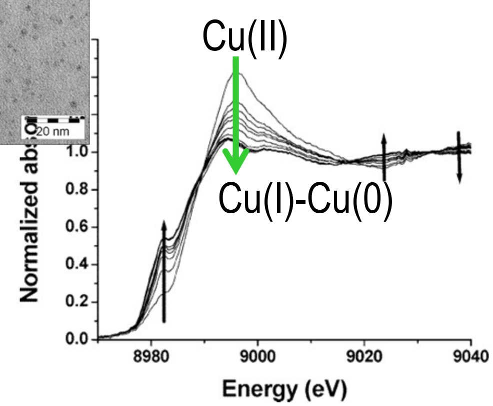
UV-vis





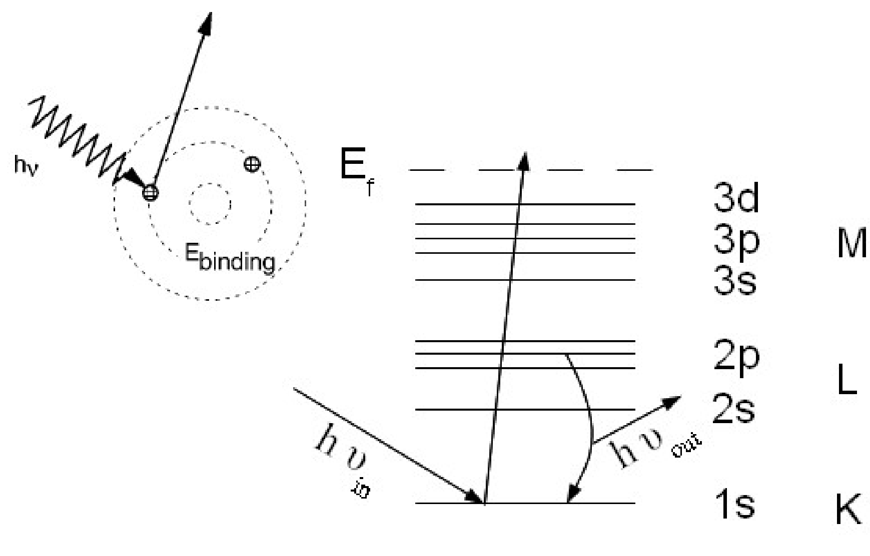
XANES

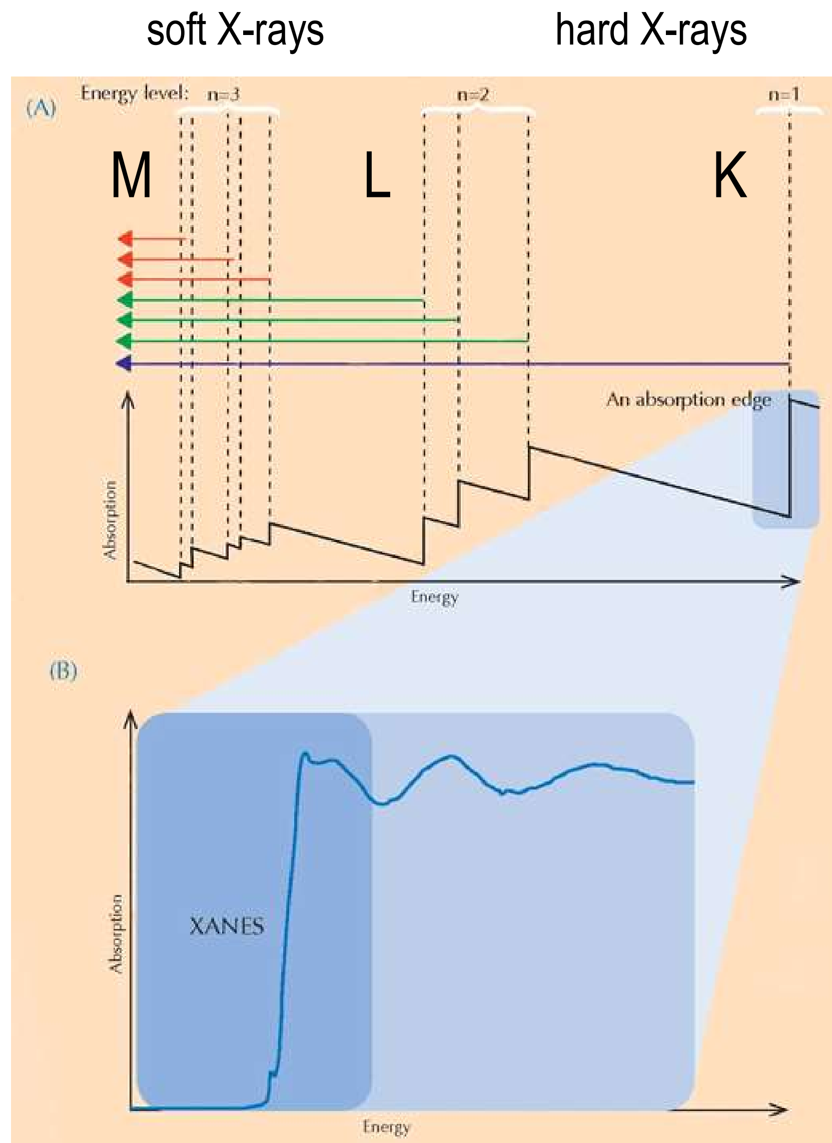
- CuBr$_2$/bipyridine, stable w/o X-rays
- **Cu(0) formed with X-rays**
- CuBr$_2$ and CuCl$_2$ sensitive to X-rays
- reducing effect of X-rays



Gerbrand Mesu et al., *J. Phys. Chem. B* 109 (2005) 4042; Tinnemans et al., *Catal. Today* 113 (2006) 3

X-ray absorption spectroscopy





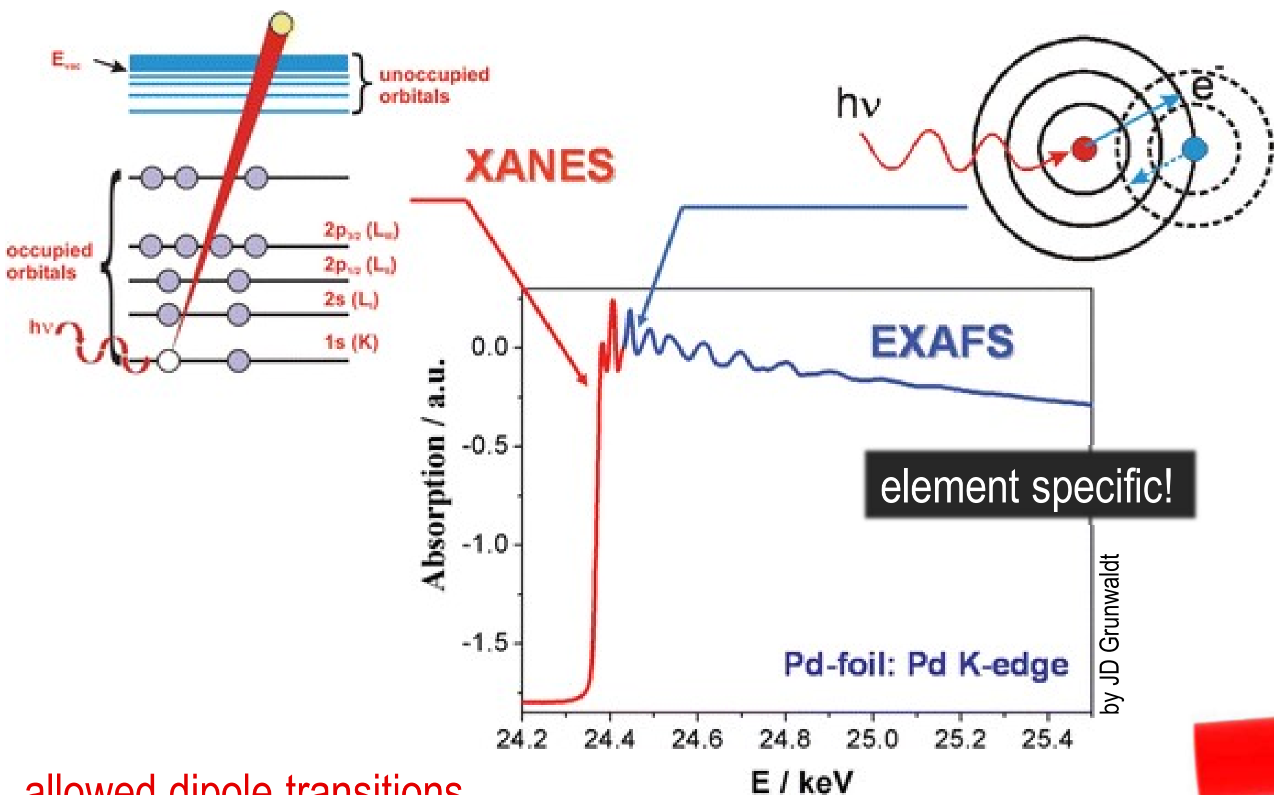
http://www.scienceinschool.org/2011/issue19/vangogh/german; M Blank: Bildquelle; Wikimedia Commons;

if energy of incoming photon matches binding energy of electron

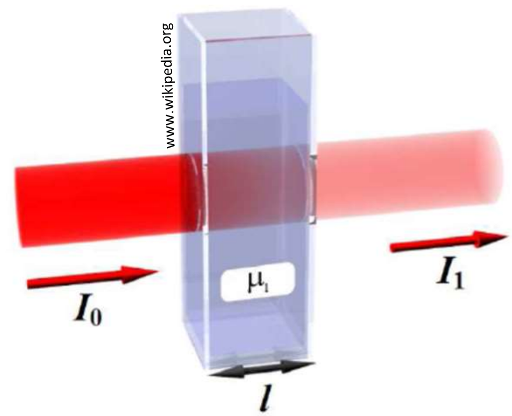
- photon is absorbed
- photoelectron is created
- photoelectron probes the environment

$$E_{kinetic} = E_{photon,in} - E_{binding}$$

X-ray absorption spectroscopy



Quantification possible:
Lambert-Beer law



allowed dipole transitions
K-edge 1s→p
L-edge 2s→p and 2p→s,d

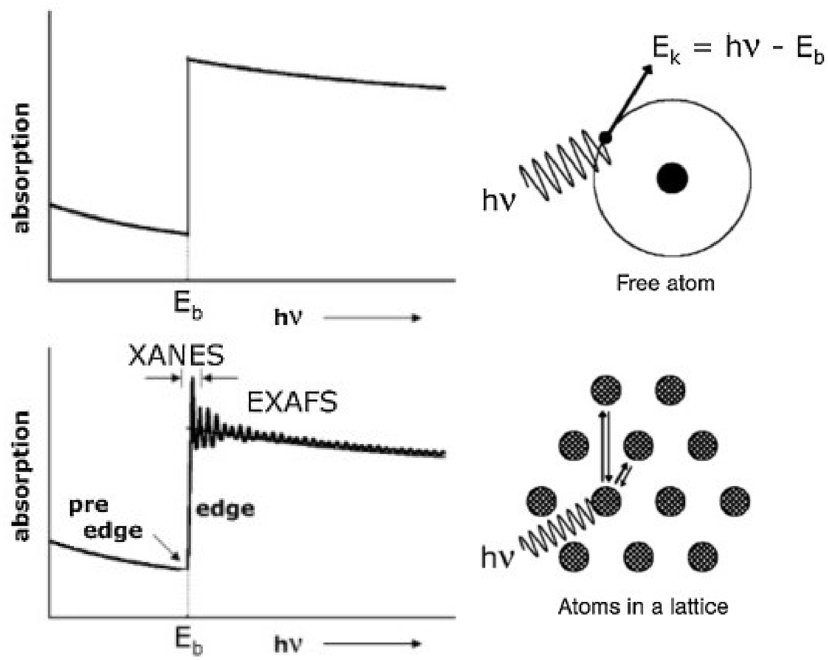
EXAFS single (+multiple) scattering
XANES multiple scattering+electronic transitions

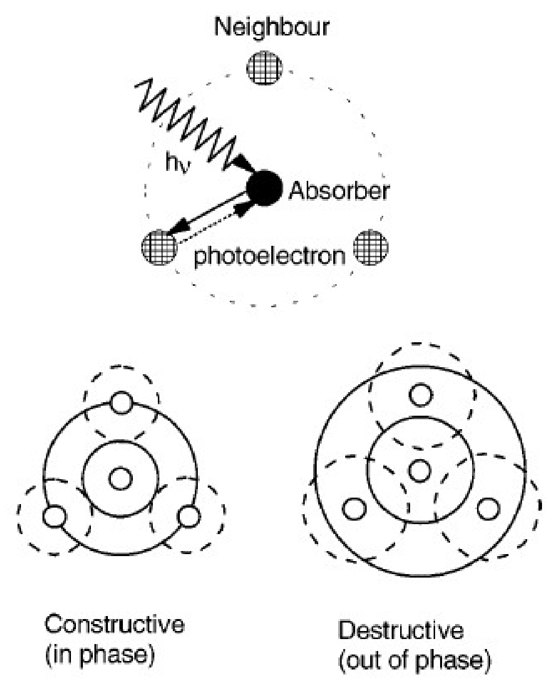
$$I(l) = I_0 e^{-\mu_l l}$$ μ: absorption coefficient

X-ray absorption spectroscopy

There is a difference in the absorption spectrum between a gas and a solid/liquid sample

- gas: photon hits sample, photoelectron is emitted, no interference
- solid matter (not necessarily crystalline): photoelectron is scattered back on neighbouring atoms, it interferes with absorbing atom



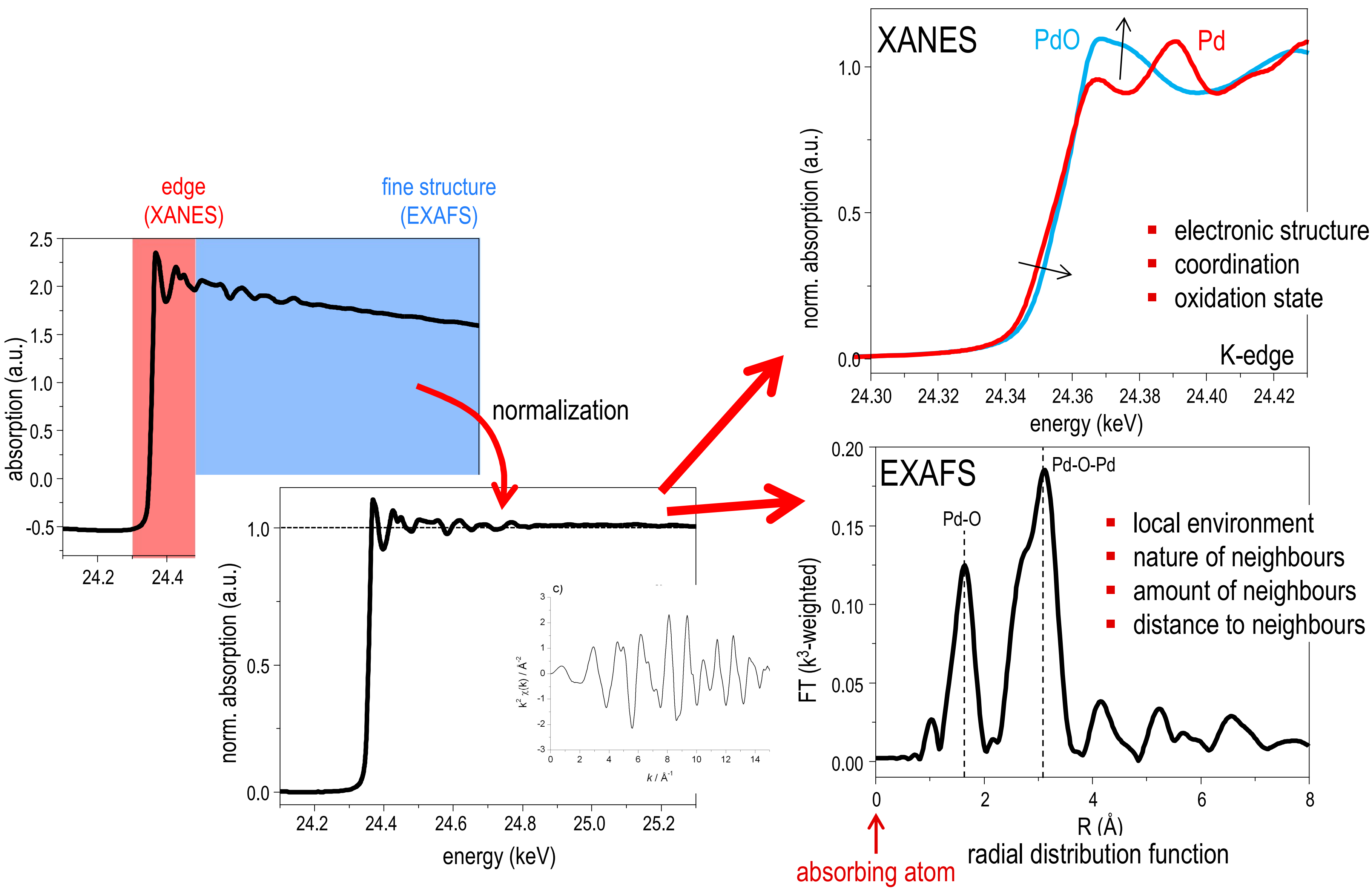


Koningsberger, *Top. Catal.* 2000

courtesy Dr. König

Gogate, *Appl. Catal. A* 514 (2016) 203

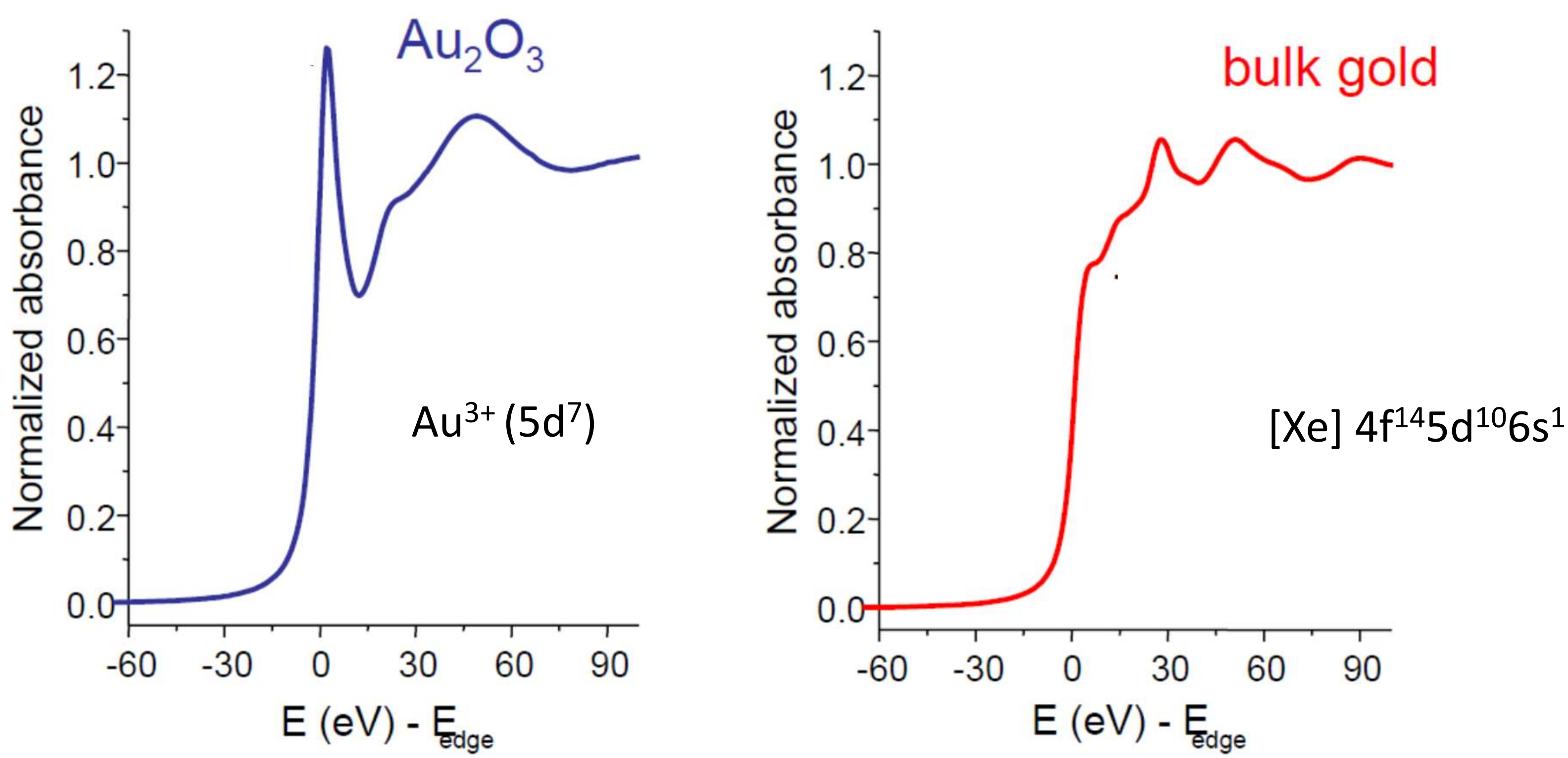
X-ray absorption spectroscopy



X-ray absorption spectroscopy

- Shape of XANES spectra: intensity of whiteline (L-edge)

Au L_3-edge (11.919 keV)



whiteline reflects holes in d-band → unoccupied d orbitals

courtesy Prof. van Bokhoven

X-ray absorption spectroscopy

- EXAFS equation

$\chi(k) = \mu(E) - \mu_0(E)/\mu_0(E_0)$

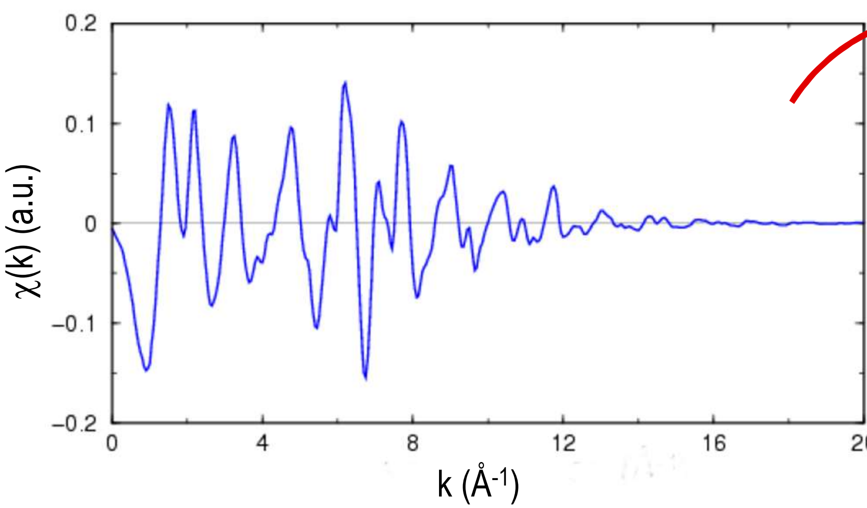
$\chi(k) = \sum N_i F_i(k) S_0^2/R_i^2 \exp(-2R_i/\lambda) \exp(-2\sigma_i^2 k^2) \sin(2kR_i + \varphi(k))$

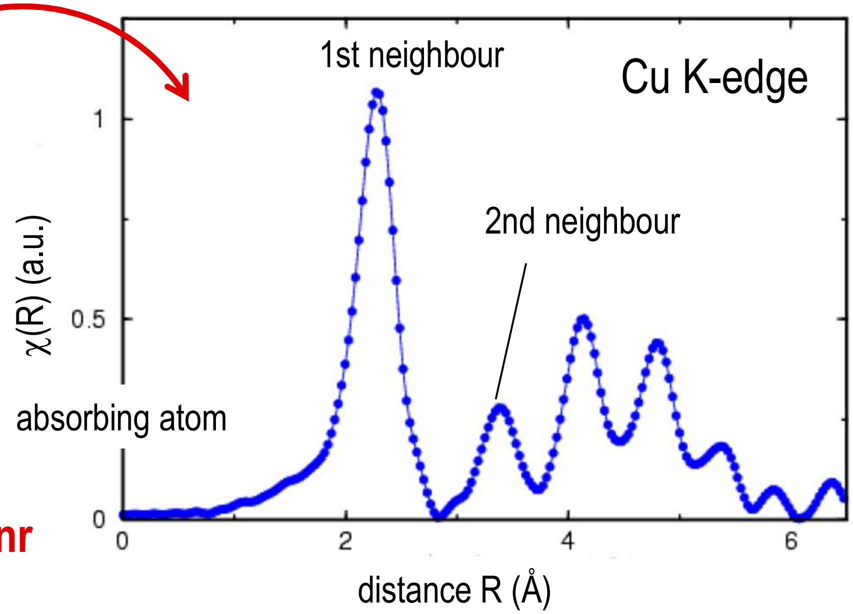
scatter power — damping — disorder

- EXAFS signal $\chi(k)$ is sum of sin functions
- FT changes $\chi(k)$ into the space domain (**bond distances**)

- μ, absorption coefficient
- μ_0, atomic absorption coefficient
- E_0, edge energy
- N, number of scattering atoms
- F, scattering amplitude
- S_0, passive electron reduction factor
- R, interatomic distance
- λ, mean free path
- σ^2, Debye-Waller factor
- φ, phase shift
- k, photo-electron wave function

FT





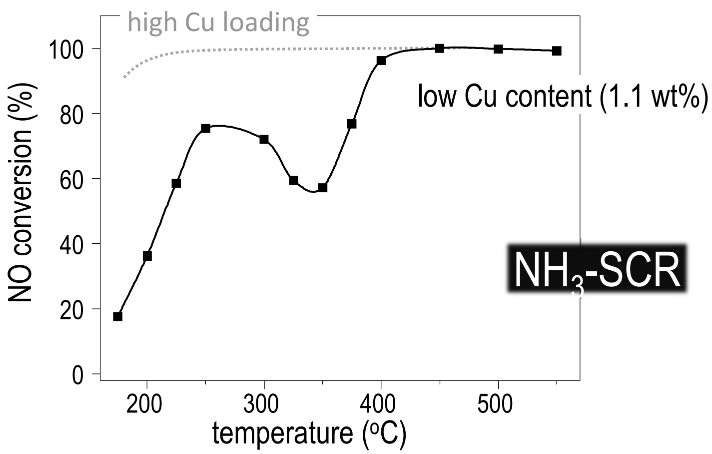
- Quantification: **bond distances/coordination nr**

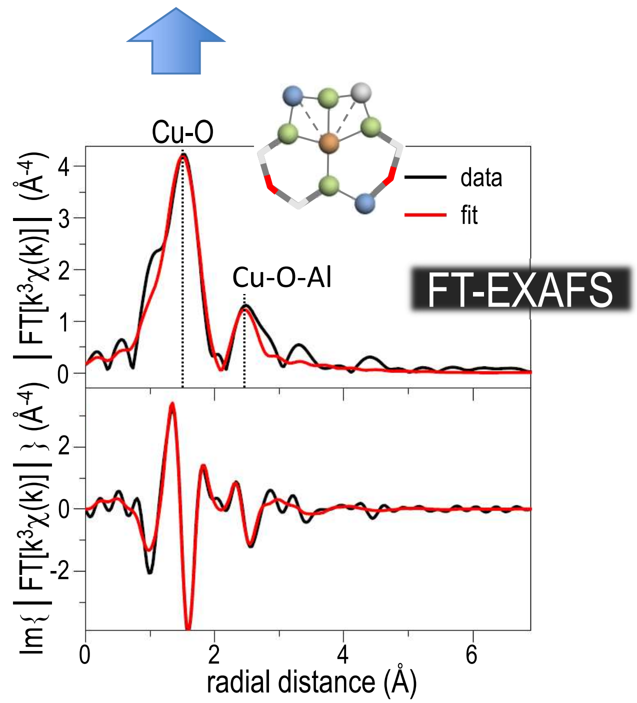
Example

- NH_3-SCR on Cu-SSZ13

- Low Cu content, Si/Al= 14 and Cu/Al= 0.17
- Well dispersed Cu ions

compare with spectra of references
e.g. CuO, Cu_2O, supported CuO and inorganic compounds



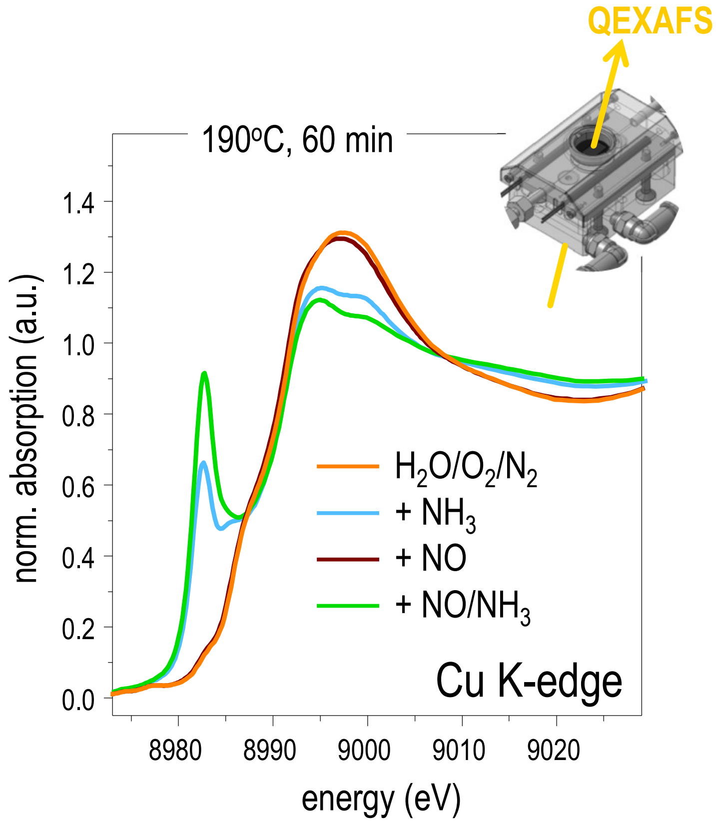


500 ppm NH_3 + 500 ppm NO, 10 vol% O_2, 6 vol% H_2O, bal. N_2; 50,000 h^{-1}
Marberger et al., *Nat. Catal.* 1 (2018) 221

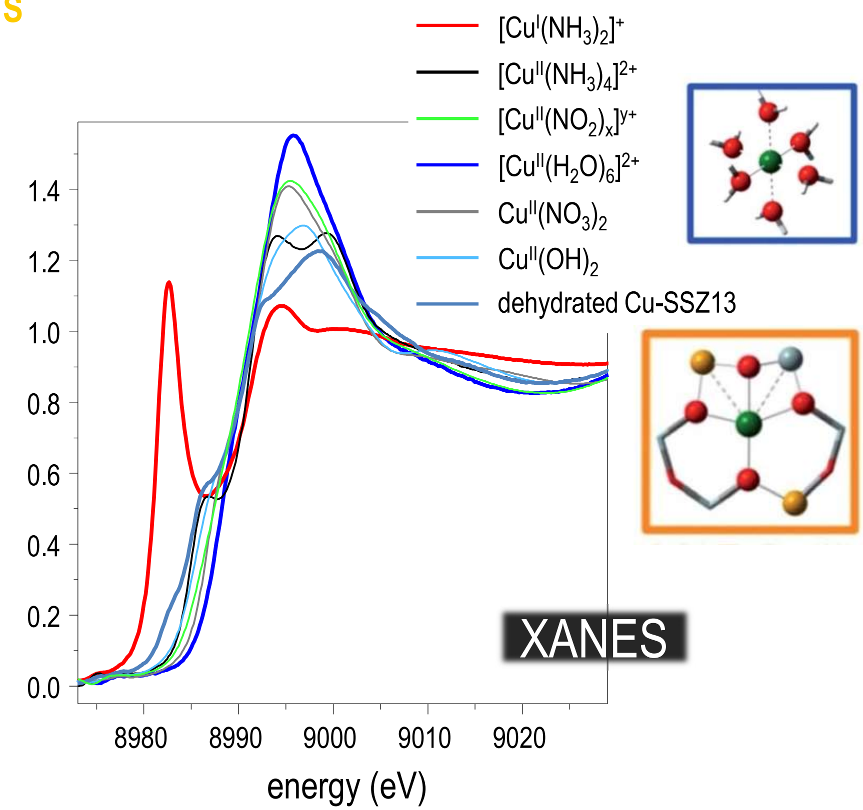
Example

- NH_3-SCR on Cu-SSZ13
- Choice of reference compounds

operando XANES spectra

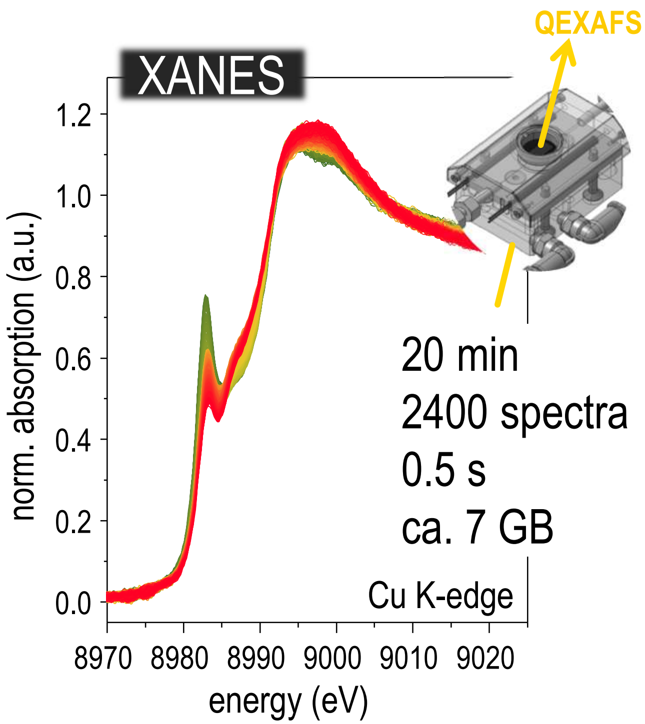


spectra of tentative references



Example

- NH_3-SCR on Cu-SSZ13
- Operando experiment, single transient



linear combination fit (LCF)
subject to intuition

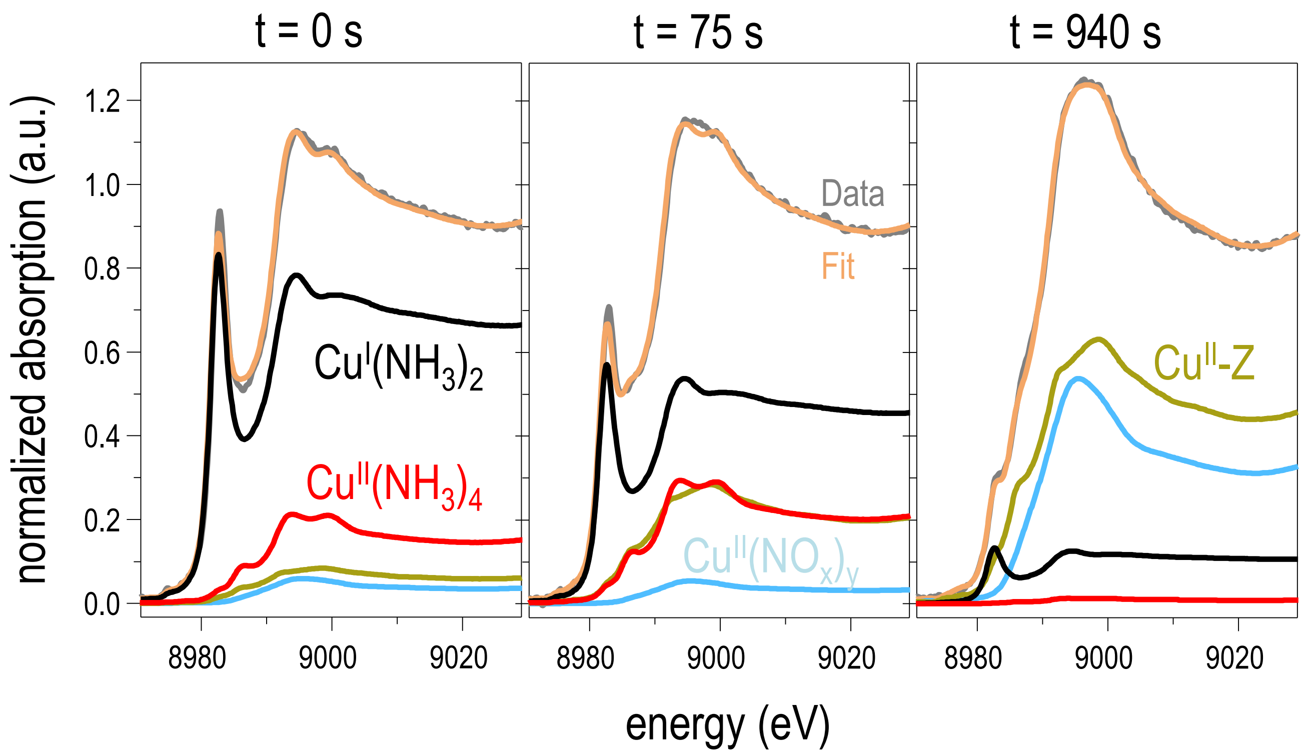
SuperXAS

Athena XAS
data processing…

500 ppm NH_3 + 500 ppm NO, 10 vol% O_2, 6 vol% H_2O, bal. N_2; 50,000 h^{-1}
Marberger et al., *Nat. Catal.* 1 (2018) 221

Example

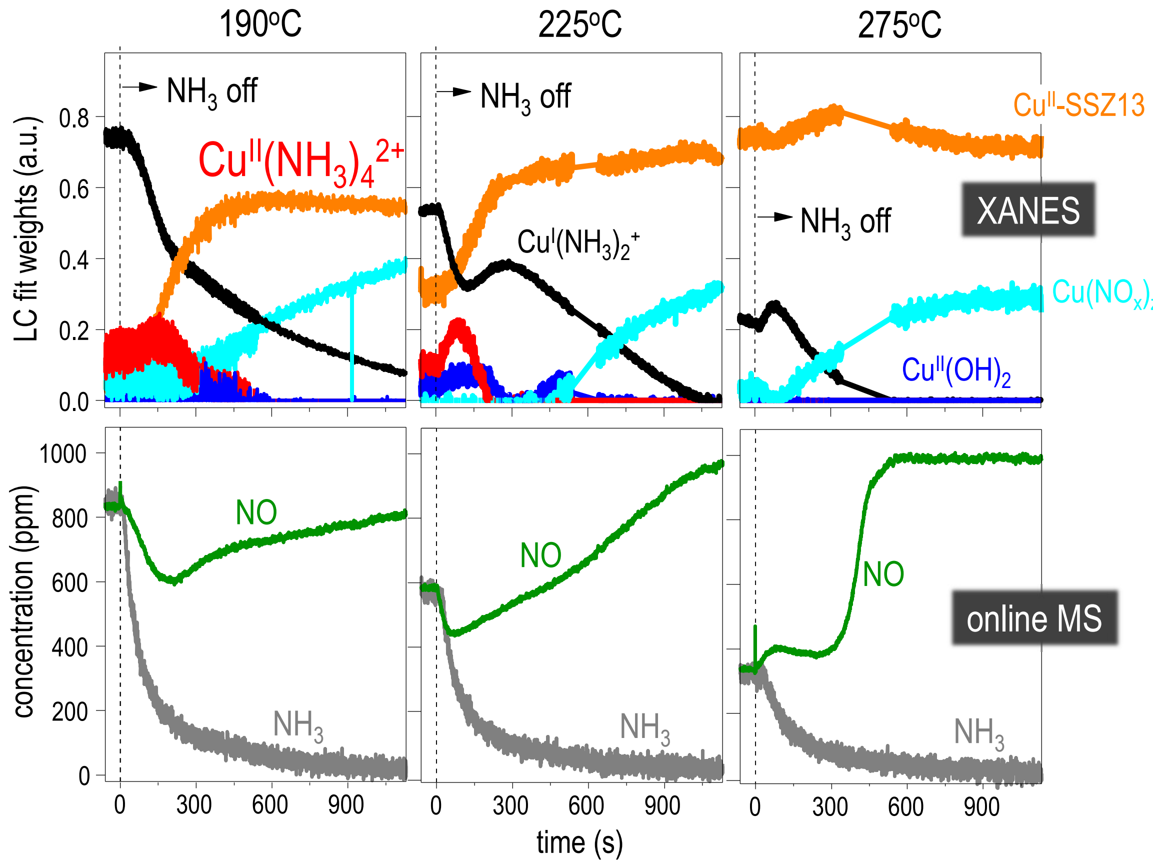
- NH_3-SCR on Cu-SSZ13
- Linear combination fit of spectra of predefined reference compounds



Example

- NH_3-SCR on Cu-SSZ13
- LCF of spectra of selected reference compounds

- time resolution enables following precisely evolution of species
- transient exp enables seeing behaviours not visible in steady state



QEXAFS, 0.5 s/spectrum; 1000 ppm NH_3 + 1000 ppm NO, 6 vol% O_2, 2 vol% H_2O, N_2

XRD and XAS

XRD

- analysis of long range order
- limited to crystalline material
- not element specific
- distinguishes different crystallographic sites
- averages over different elements on the same crystallographic site
- distinguishes different (crystalline) phases

- BOTH: carefuly planning of experiments necessary for synchrotron use

EXAFS

- analysis of short range order
- both crystalline and amorphous material
- element specific
- averages over different sites (for the same element)
- distinguishes different elements on the same crystallograpohic site
- averages over different phases (containing the same element)