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# Exploration of X-ray Absorption Spectroscopy (XAS) in Catalysis

*Ph.D. course “Elements of X-ray Physics” : 11-06-2024*



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- How XAS came into being?
- XAS Principle
- XANES & EXAFS -*Three distinct features in XAS spectra; EXAFS equation.*
- XAS measurement -*Experimental modes;*
- Time resolved XAS- *MEMS & capillary reactors*
- Case studies
  1. Incomplete formation of bimetallic alloy- Difference approach
  2. Importance of catalyst preparation protocol-XAS-CT.

# How XAS came into being?



1913

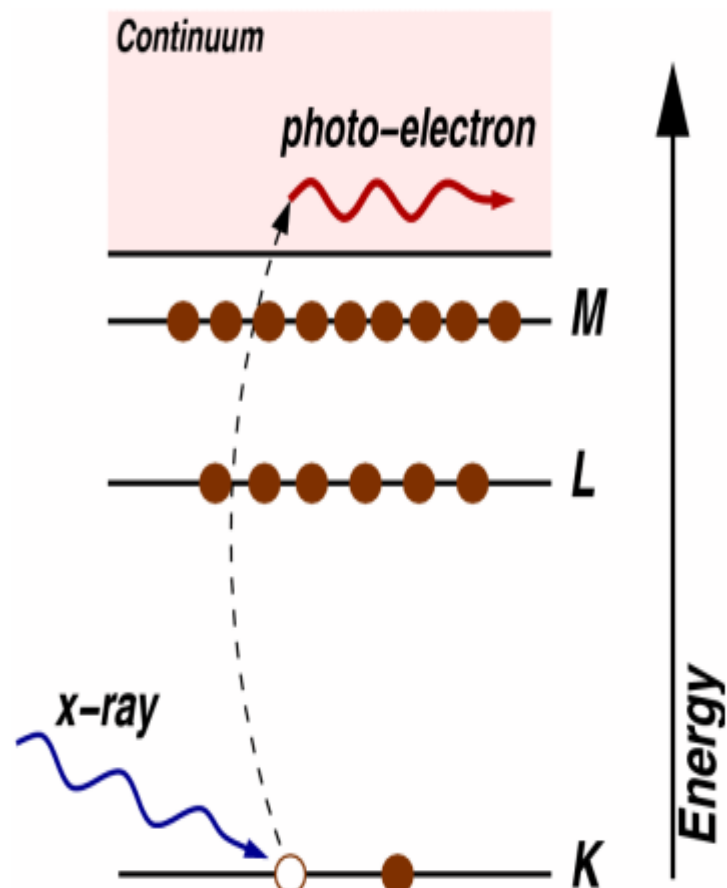


*Maurice de Broglie*

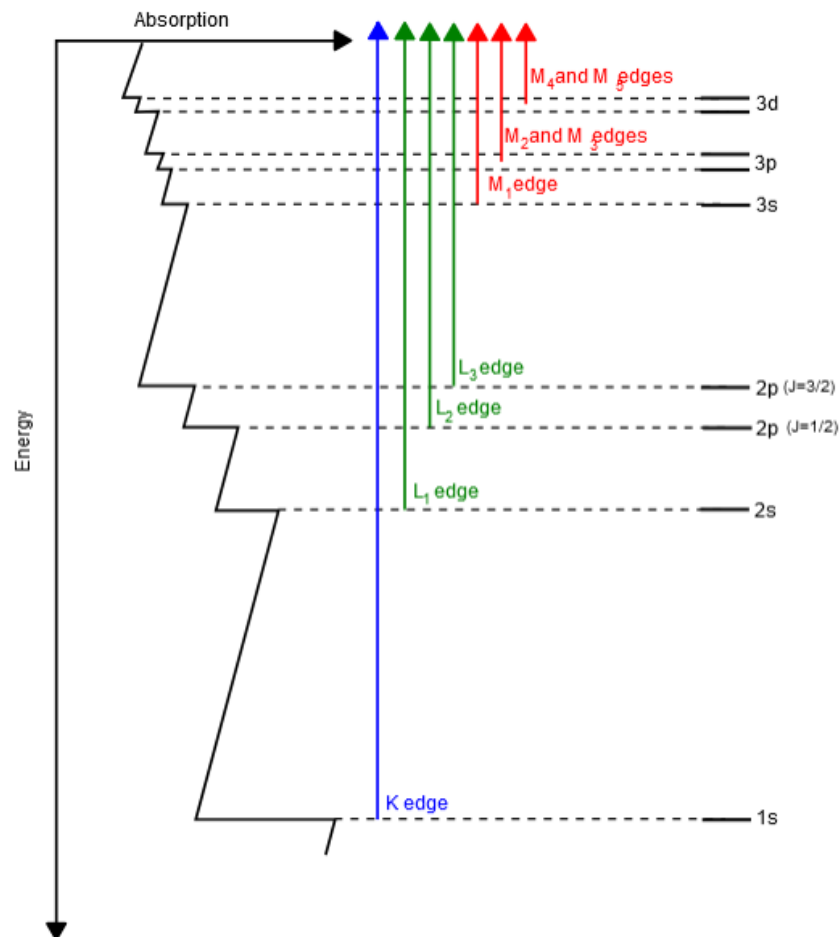
**Table: EXAFS Family Tree.**

|                                  |   |
|----------------------------------|---|
| Röntgen (1895)                   | Discovered X-rays   |
| Maurice de Broglie (1913)        | Measured first absorption edge  |
| World War I (1914–1918)          |   |
| Fricke (1920)                    | Observed first fine structure   |
| Kossel (1920)                    | First theory of XANES   |
| Hanawalt (1931)                  | EXAFS in gases, temperature effect  |
| Kronig (1931)                    | First theory of EXAFS   |
| Cauchois (1932)                  | Curved crystal transmission spectrograph                                  |
| Hayasi (1936, 1949)              | Theory of EXAFS   |
| World War II (1941–1945)         |   |
| Sawada (1955)                    | Amorphous/crystalline polymorphs  |
| Shiraiwa (1958)                  | Improved theory   |
| Kostarev (1939, 1946)            | Theory and measured EXAFS in single crystals                              |
| Kozlenkov (1960)                 | Improved theory   |
| Van Nordstrand (1960)            | Instrumentation, fingerprint ID, used XAS to characterize catalysts       |
| Lytle (14 July 1960)             | Starts work at Boeing (BSRL)  |
| Krogstad (1960)                  | Personal communication  |
| Lytle (1962)                     | Particle-in-a-box model   |
| Prins (1964)                     | Helped name EXAFS   |
| Parratt (1965)                   | Personal communication;<br><i>Rev. Mod. Phys.</i> (1959). <b>31</b> , 616 |
| Sayers, Stern, Lytle (1968–1971) | Modern theory, Fourier transform of EXAFS                                 |
| Sayers, Stern, Lytle (1974)      | First trip to synchrotron (SSRL)  |

# XAS Principle



*The photoelectric effect, in which an x-ray is absorbed and a core level electron is promoted out of the atom. (1)*



*Transitions that contribute to XAS edges. (2)*

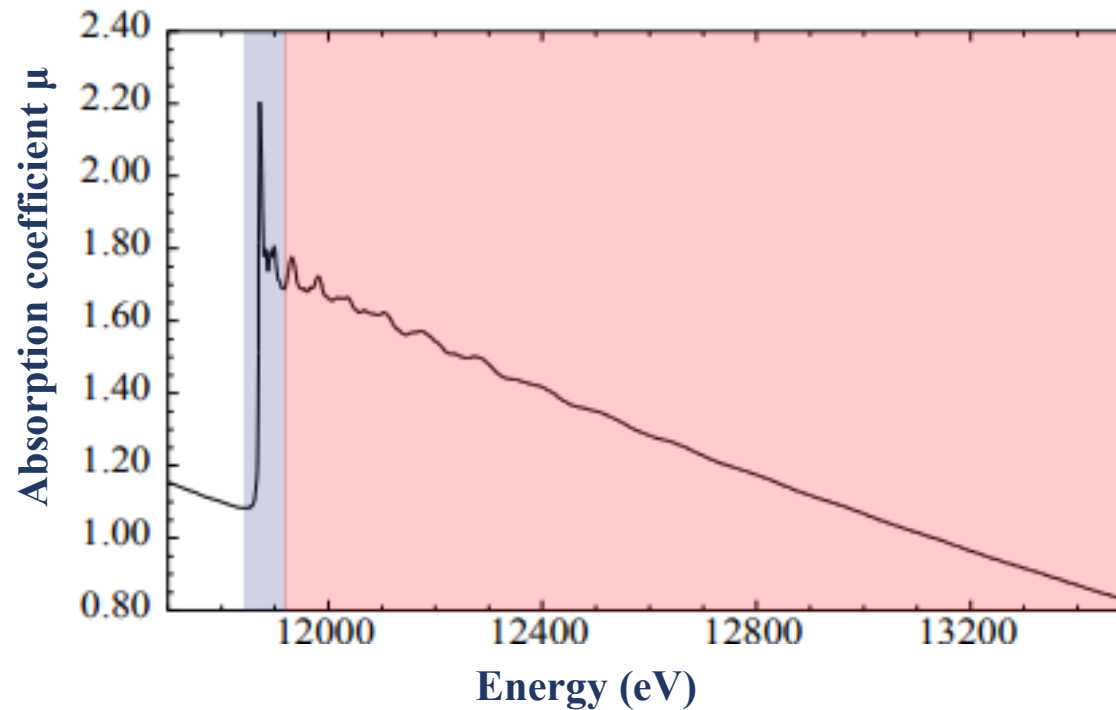
X-ray Absorption Spectroscopy (XAS) is divided into 2 regimes:

**XANES:** X-ray Absorption Near-Edge Spectroscopy

**EXAFS:** Extended X-ray Absorption Fine-Structure

**XANES** : transitions to unfilled bound states, nearly bound states, continuum - **low energy photoelectrons**

**EXAFS**:  $\sim 50 - 1000$  eV from edge, transitions to continuum – **high energy photoelectrons**



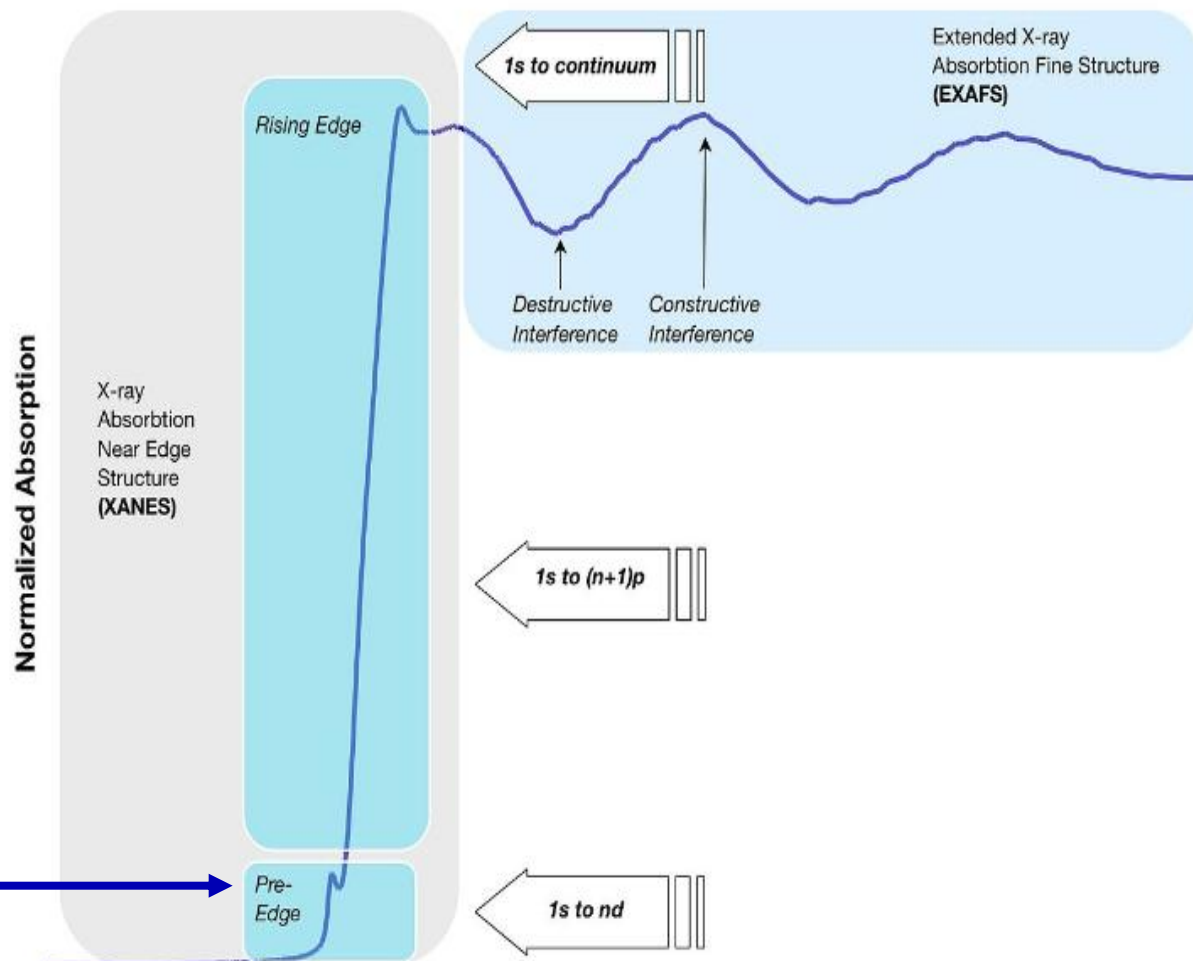
*Example of XAS spectrum*

# Three major events – distinct features

## 1. Pre-edge

The threshold of absorption which is distinct for **excitations into the lowest unoccupied states.**

**XANES**



Example XAS spectrum showing the three major data regions.

# Three major events – distinct features

## XANES

### 2. Rising edge

Here **core transitions to quasi-bound** states occur.

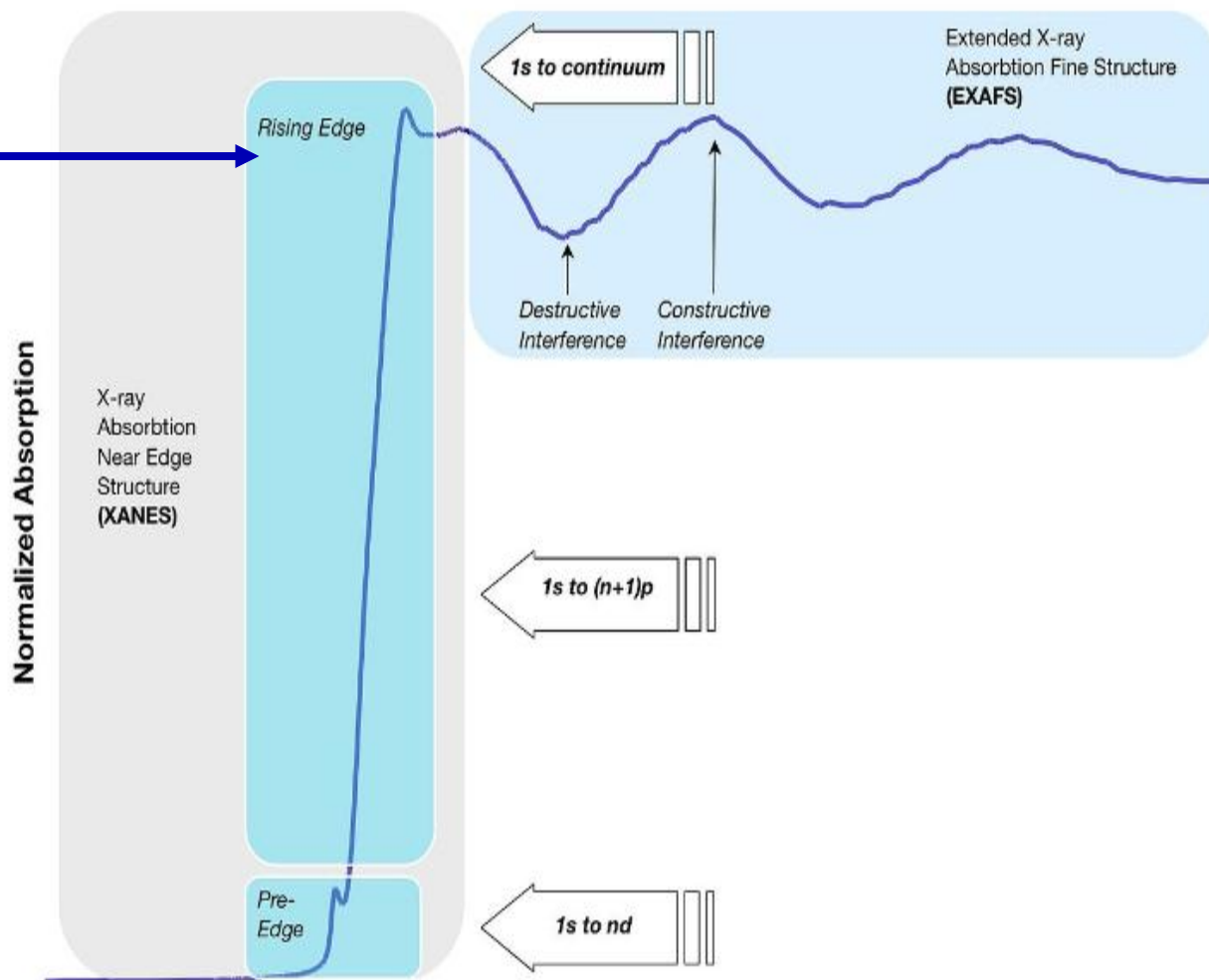
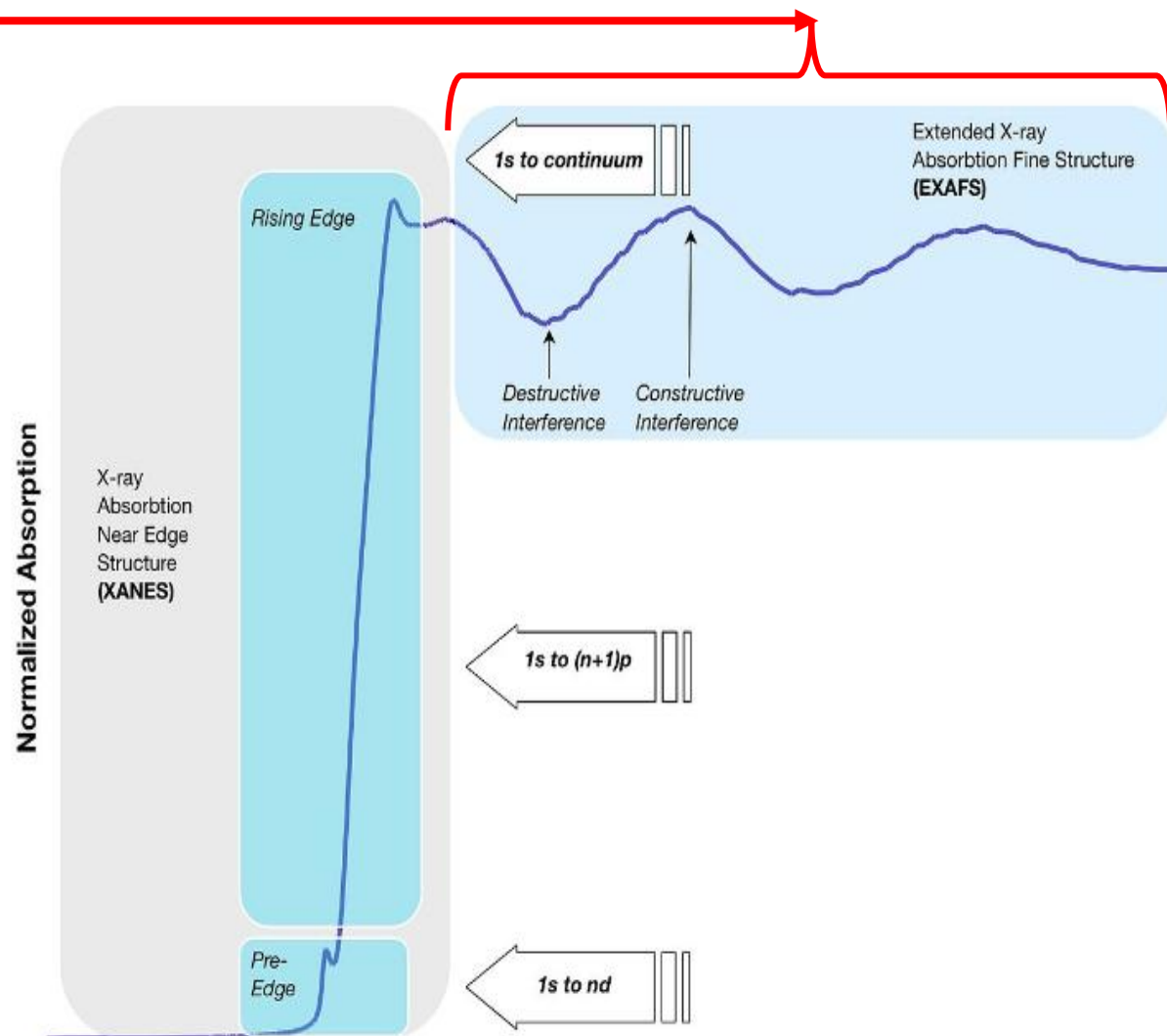


Figure : Example XAS spectrum showing the three major data regions.

# Three major events – distinct features

## EXAFS

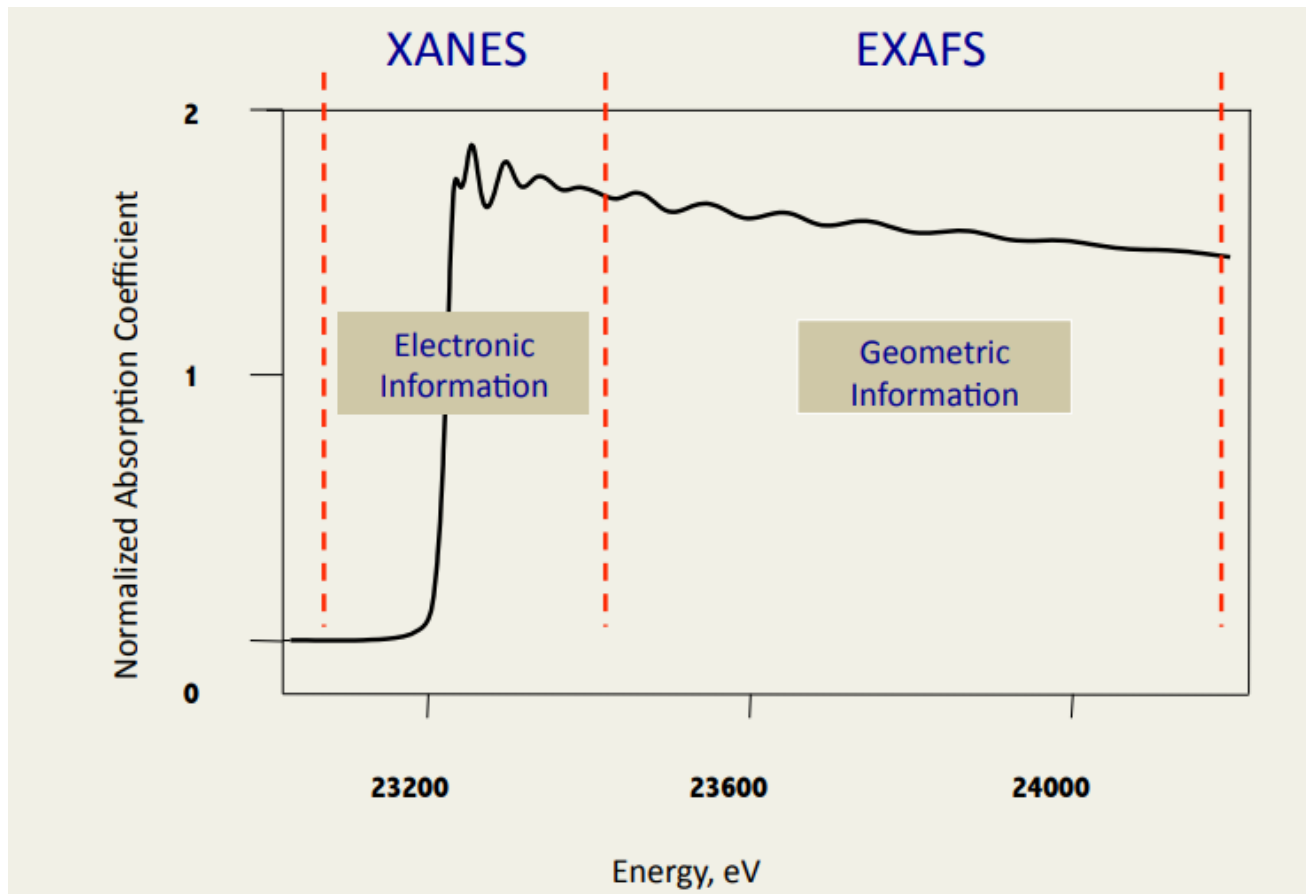
**3.Scattering of electrons** with neighboring atoms. In the high-kinetic-energy range, the **constructive and destructive interference** of the resonance of **excited electrons** at fixed positions of **neighboring atoms** gives rise to clearly distinguishable absorption features (oscillations).



*Example XAS spectrum showing the three major data regions.*

**XANES**-estimations of ligand fields, spin states, or the charge on a metal carrier (oxidation state).

**EXAFS**- Identity, Coordination number (N), Interatomic distances (R) of backscattering atoms.



*Example of XAS spectrum*

# The EXAFS Equation

$$\chi(k) = \sum_j \frac{N_j S_0^2 f_j(k) e^{-2R_j/\lambda(k)} e^{-2k^2 \sigma_j^2}}{k R_j^2} \sin[2k R_j + \delta_j(k)]$$

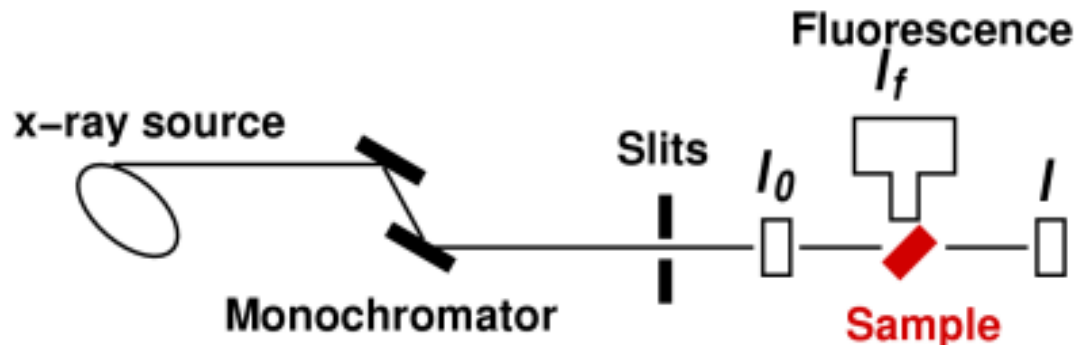
Diagram illustrating the EXAFS equation with annotations:

- Amplitude reduction term**: Points to  $S_0^2$ .
- Photo-electron mean-free path (including core-hole lifetime)**: Points to  $e^{-2R_j/\lambda(k)}$ .
- Thermal and static mean-square disorder in R**: Points to  $e^{-2k^2 \sigma_j^2}$ .

If we know the **scattering** properties of the neighboring atom:  $f(k)$  and  $\delta(k)$ , and the mean-free-path  $\lambda(k)$  we can determine:

- R** distance to neighboring atom.
- N** coordination number of neighboring atom.
- $\sigma^2$**  mean-square disorder of neighbor distance.

The scattering amplitude  $f(k)$  and phase-shift  $\delta(k)$  depend on **atomic number**, so that XAFS is also sensitive to **Z** of the neighboring atom



*XAS measurement setup*

**XAS** measures the energy dependence of the **x-ray absorption coefficient**  $\mu(E)$  at and above the absorption edge of a selected element.

$\mu(E)$  can be measured in two ways:

**Transmission:**

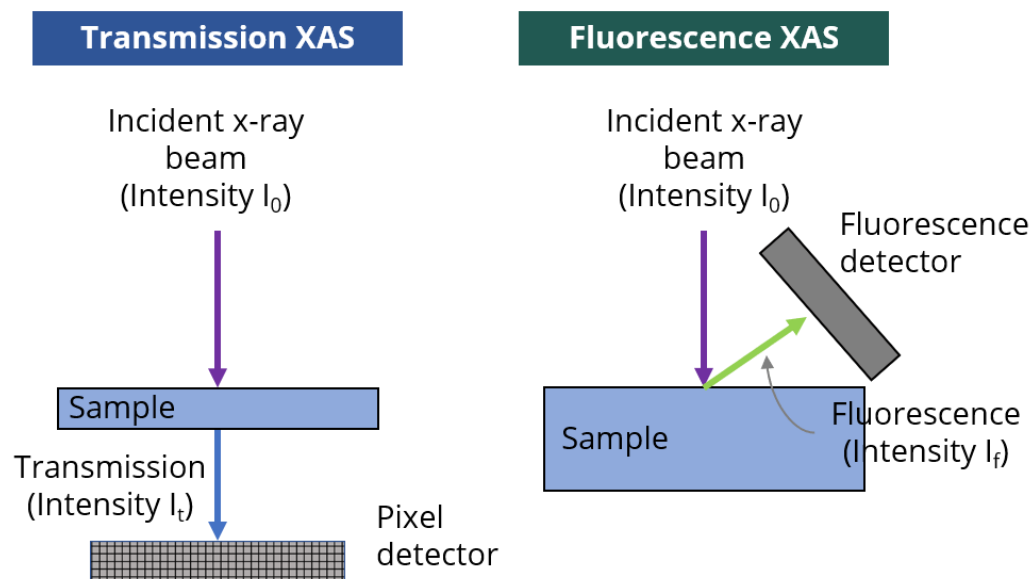
$$I = I_0 e^{-\mu(E)t}$$
$$\mu(E)t = -\ln(I/I_0)$$

**Fluorescence:**

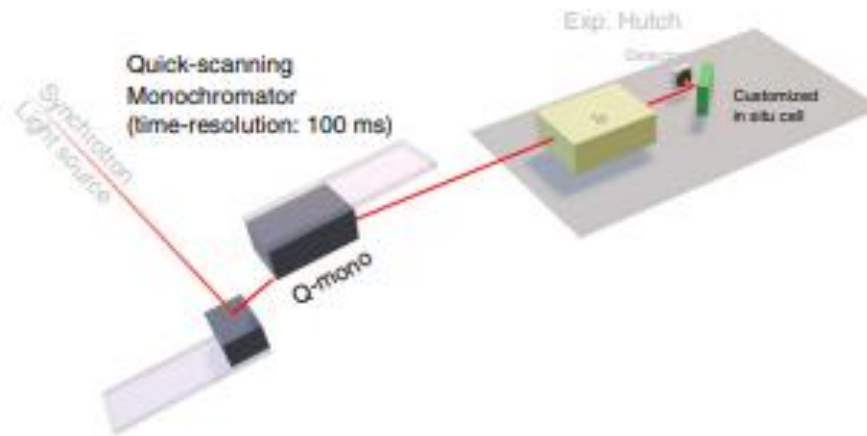
$$\mu(E) \propto I_f / I_0$$

# Choosing the Correct Experimental Mode

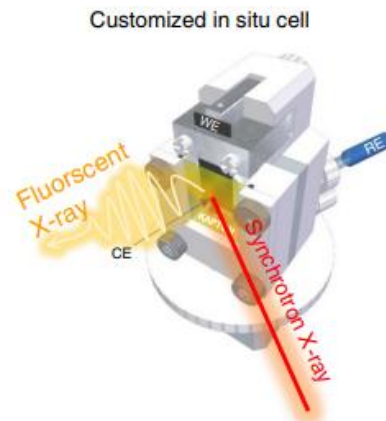
- **Choosing the right Measurement Mode:** Transmission or Fluorescence
- **Key Considerations:** element of interest, its absorption edge energies, its concentration and distribution, and the physical state of the sample.
- **Transmission Experiments:** pass through straight line-Sample uniformity- *Rule of thumb*  $\sim 4$  absorption lengths.
- **Fluorescence Mode:** concentration of the element of interest - emission is detected-detector is placed at an angle.
- **Detector Placement:** to maximize emission yield and minimize noise from scattering.



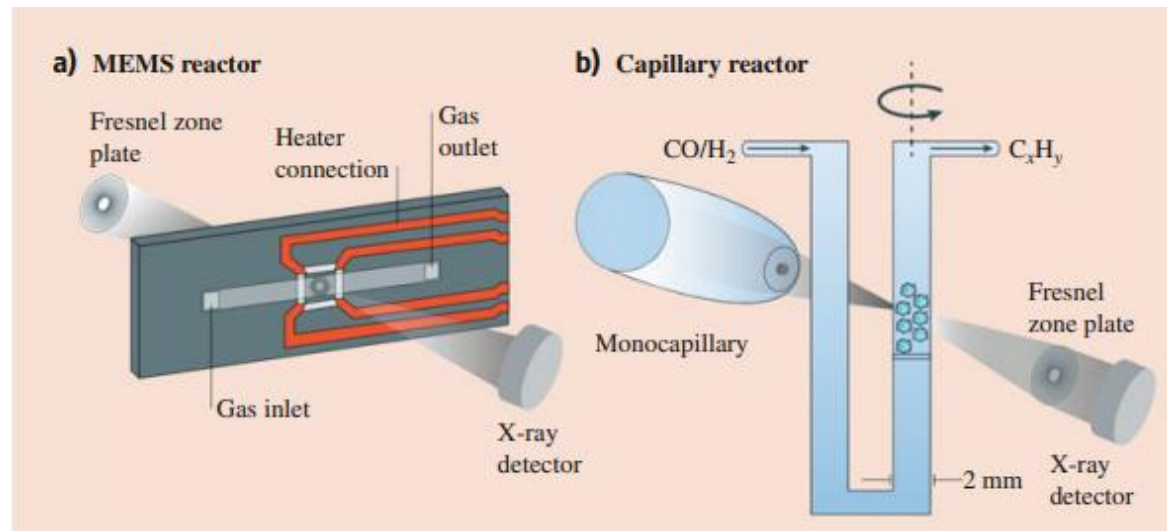
*Experimental modes in XAS*



*The schematic diagram of the setup of operando time-resolved XAS experiments*



*Representation of customized operando XAS cell.*



*Two reactor designs used for time-resolved long-duration in situ or operando*

## Microelectromechanical system reactor

- Experiments using **soft** XAS.
- Both for **liquid** and **solid** studies (the attenuation length < total absorption).

## Capillary reactor

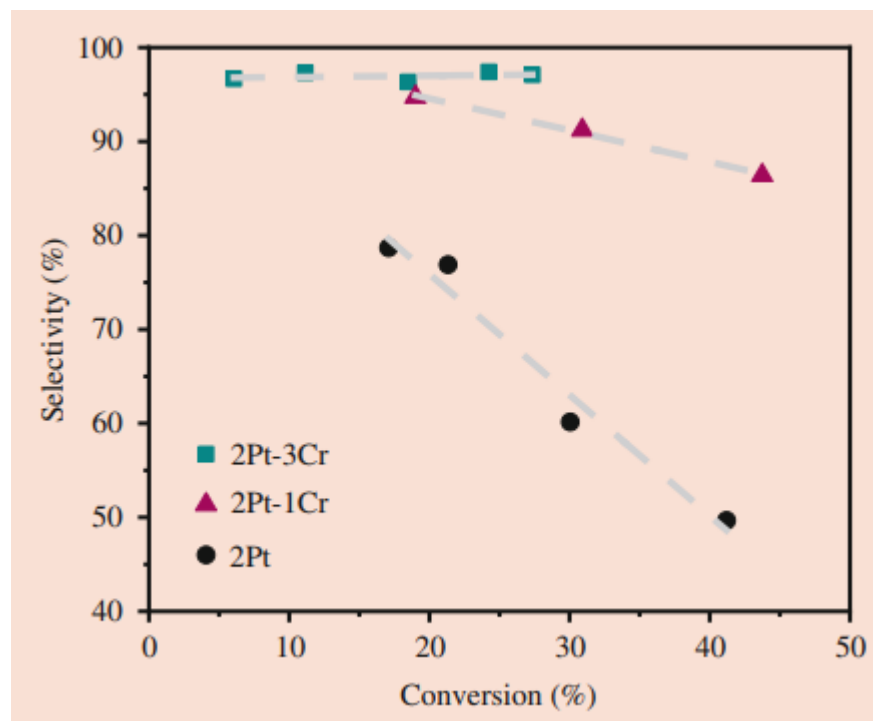
- Solid catalysts using **hard** XAS.
- Operando studies choose **heterogeneous catalyst powders** reacting mainly with gases.

# Case Study 1: Incomplete Formation of a Pt<sub>3</sub>Cr Alloy



- Bimetallic catalysts of Pt-Cr **propane dehydrogenation**, achieving **propylene selectivity** greater than 95%, which is superior to monometallic Pt nanoparticles.
- Preparation- **incipient wetness impregnation** method.

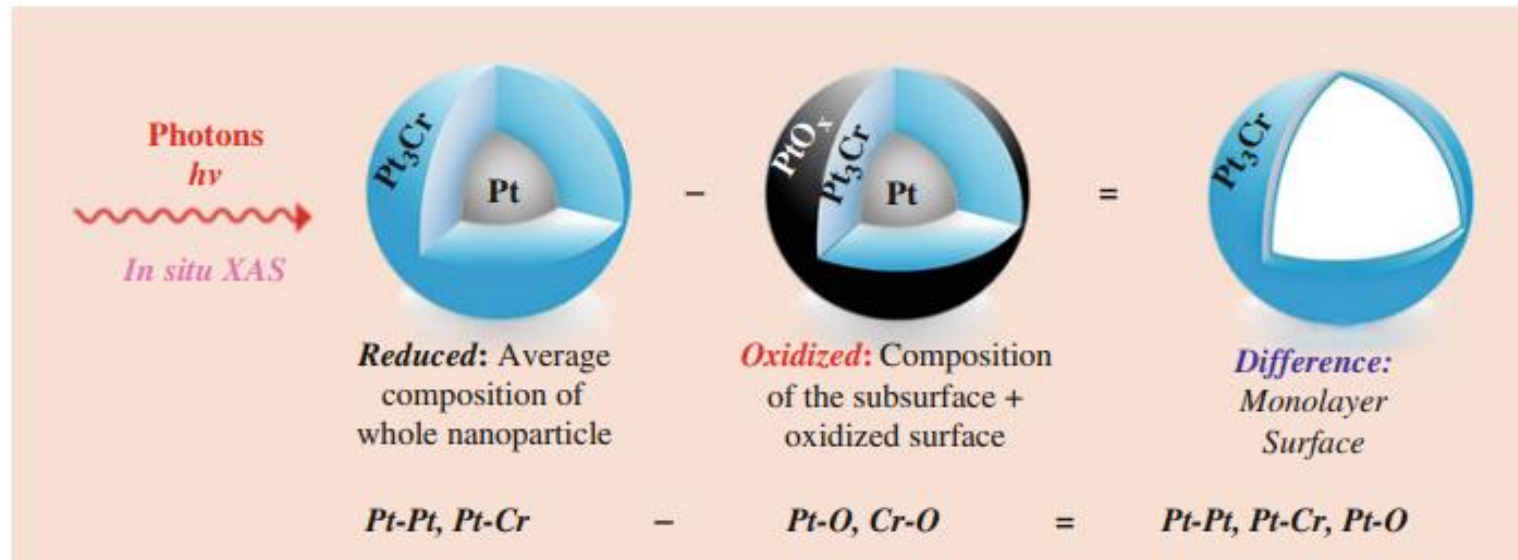
| Catalysts                   | Denotation | Selectivity (%) | Particle size  |
|-----------------------------|------------|-----------------|----------------|
| 2%Pt/SiO <sub>2</sub>       | 2Pt        | 75              | ~2 nm by STEM. |
| 2%Pt-1%Cr/ SiO <sub>2</sub> | 2Pt-1Cr    | 95              |                |
| 2%Pt-3%Cr/ SiO <sub>2</sub> | 2Pt-3Cr    | 98              |                |



*Propylene selectivity as a function of propane dehydrogenation conversion at 550 °C, 2.5% C<sub>3</sub>H<sub>8</sub> and 2.5% H<sub>2</sub>.*

*Why it is necessary to determine the surface structure and how this can be determined using the surface EXAFS analysis?*

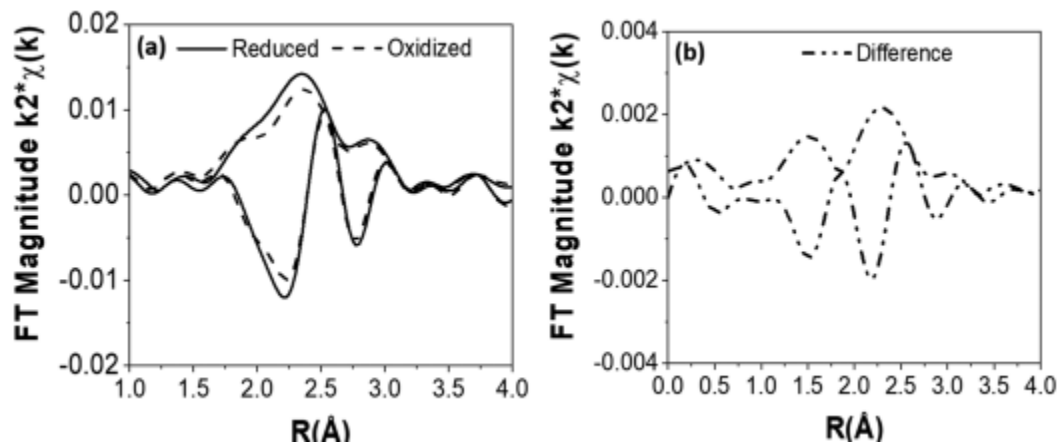
# Case Study 1: Incomplete Formation of a Pt<sub>3</sub>Cr Alloy



*Approach for difference analysis, where reduced Pt-Cr nanoparticles are subsequently oxidized and the EXAFS ( $\chi$ ) data is subtracted to isolate the surface atoms*

The **metallic bonds** of the **oxidized nanoparticles** are **identical** to those of the particle interior of the **reduced sample**, the **difference spectrum** represents the bonds only from the surface.

# Case Study 1: Incomplete Formation of a Pt<sub>3</sub>Cr Alloy



*2Pt3Cr/SiO<sub>2</sub> after reduction at 550 °C: (a) Fourier transform magnitudes and imaginary components of the reduced and oxidized catalysts. (b) Difference EXAFS.*

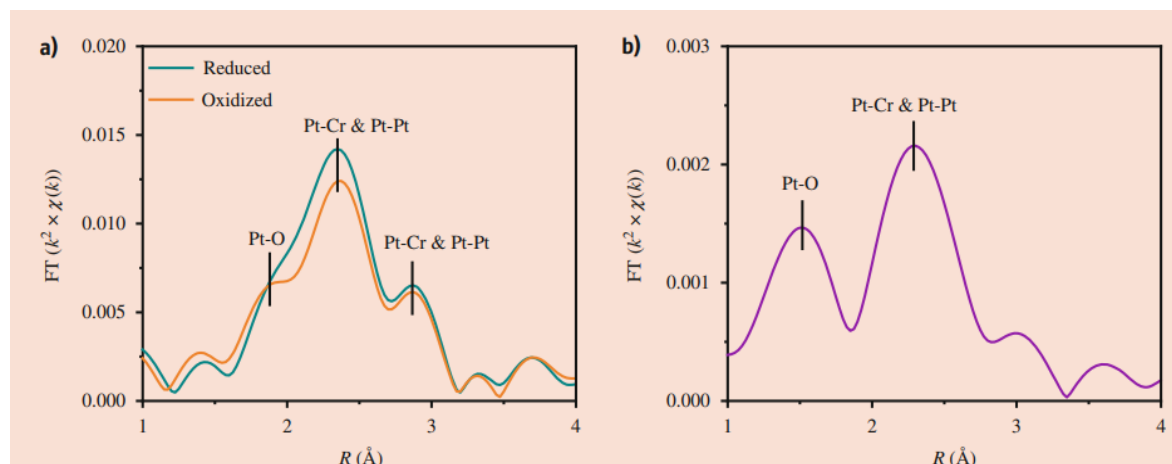
XRD of **2Pt-3Cr** -reduction at **550°C** – Pt and Pt<sub>3</sub>Cr phases ; **800 °C** – bimetallic phase Pt<sub>3</sub>Cr .

**2Pt-1Cr** reduced at **550°C**, the XRD pattern and EXAFS **CN<sub>Pt-Cr</sub>: Pt-Pt** ratio and bond distances - nearly identical to that of **2Pt-3Cr** indicating that both catalysts **have very similar average structures**.

Both **2Pt-1Cr** and **2Pt-3Cr** form bimetallic catalysts with **similar average compositions and structures**, the **differences in catalytic selectivity** indicate that the **surface compositions are not equivalent**.

**Table.** *Difference EXAFS fits for 2Pt-1Cr and 2Pt-3Cr*

| Catalyst | Scattering pair | CN  | <i>R</i> (Å) |
|----------|-----------------|-----|--------------|
| 2Pt-1Cr  | Pt-Pt           | 1.5 | 2.75         |
|          | Pt-Cr           | 0.6 | 2.71         |
|          | Pt-O            | 0.4 | 2.05         |
| 2Pt-3Cr  | Pt-Pt           | 0.9 | 2.73         |
|          | Pt-Cr           | 0.5 | 2.73         |
|          | Pt-O            | 0.3 | 2.05         |

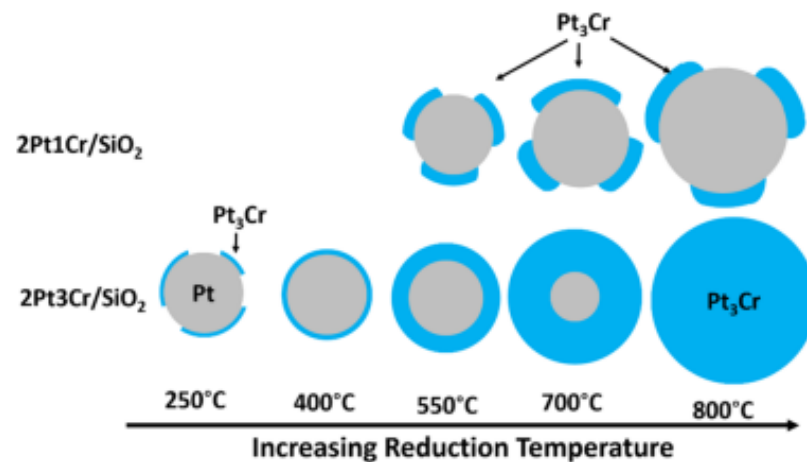


**The  $k^2$  -weighted Fourier transform of chi of 2Pt-3Cr after reduction at 550°C; (a) the reduced, oxidized, and (b) difference EXAFS**

# Case Study 1: Incomplete Formation of a Pt<sub>3</sub>Cr Alloy

**Table.** EXAFS Coordination Ratios for the Reduced (*Average*), *Oxidized (Particle Interior)*, and *Difference (Surface)* of Bimetallic Pt–Cr Nanoparticles

| sample                  | reduction temperature (°C) | CN <sub>Pt–Cr</sub> /CN <sub>Pt–Pt</sub> |          |         |
|-------------------------|----------------------------|--|----------|---------|
|                         |                            | average                                  | interior | surface |
| 2Pt1Cr/SiO <sub>2</sub> | 550                        | 0.28                                     | 0.25     | 0.40    |
|                         | 700                        | 0.35                                     | 0.31     | 0.40    |
|                         | 800                        | 0.38                                     |          |         |
|                         |                            |  |          |         |
| 2Pt3Cr/SiO <sub>2</sub> | 250                        | 0.16                                     | 0.11     | 0.31    |
|                         | 400                        | 0.24                                     | 0.14     | 0.45    |
|                         | 550                        | 0.30                                     | 0.22     | 0.56    |
|                         | 700                        | 0.46                                     | 0.43     | 0.71    |
|                         | 800                        | 0.52                                     |          |         |



*Cr incorporation into Pt nanoparticles in 2Pt1Cr/SiO<sub>2</sub> and 2Pt3Cr/SiO<sub>2</sub> with the increasing reduction temperature.*

## Summary

*The average nanoparticle composition of two Pt–Cr alloy catalysts is similar, but their catalytic performance is not, and this difference is related to the surface composition.*

*A precise understanding of the surface structure in alloy nanoparticles, therefore, is critical for relating the active site structure to catalytic performance.*

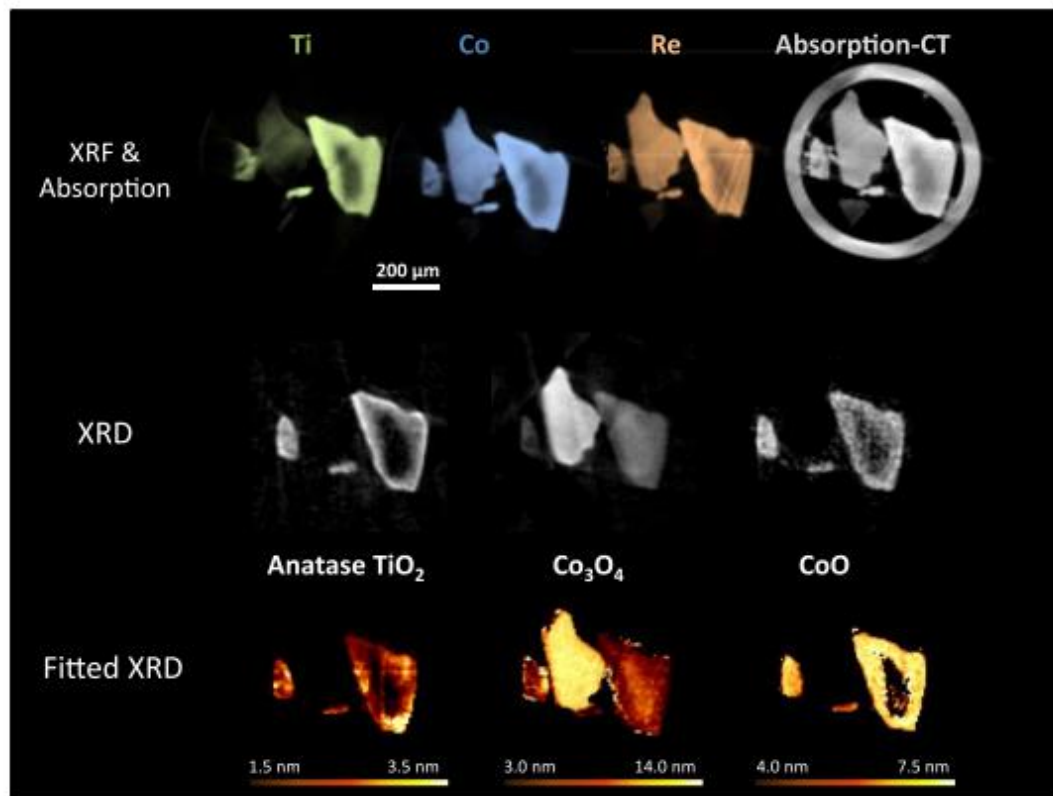
# Case Study 2: Catalyst Preparation protocol

**FTS Catalyst** - consisting of 5% Ti/10% Co/1% Re on SiO<sub>2</sub>

**Five-dimensional (5D) color imaging**

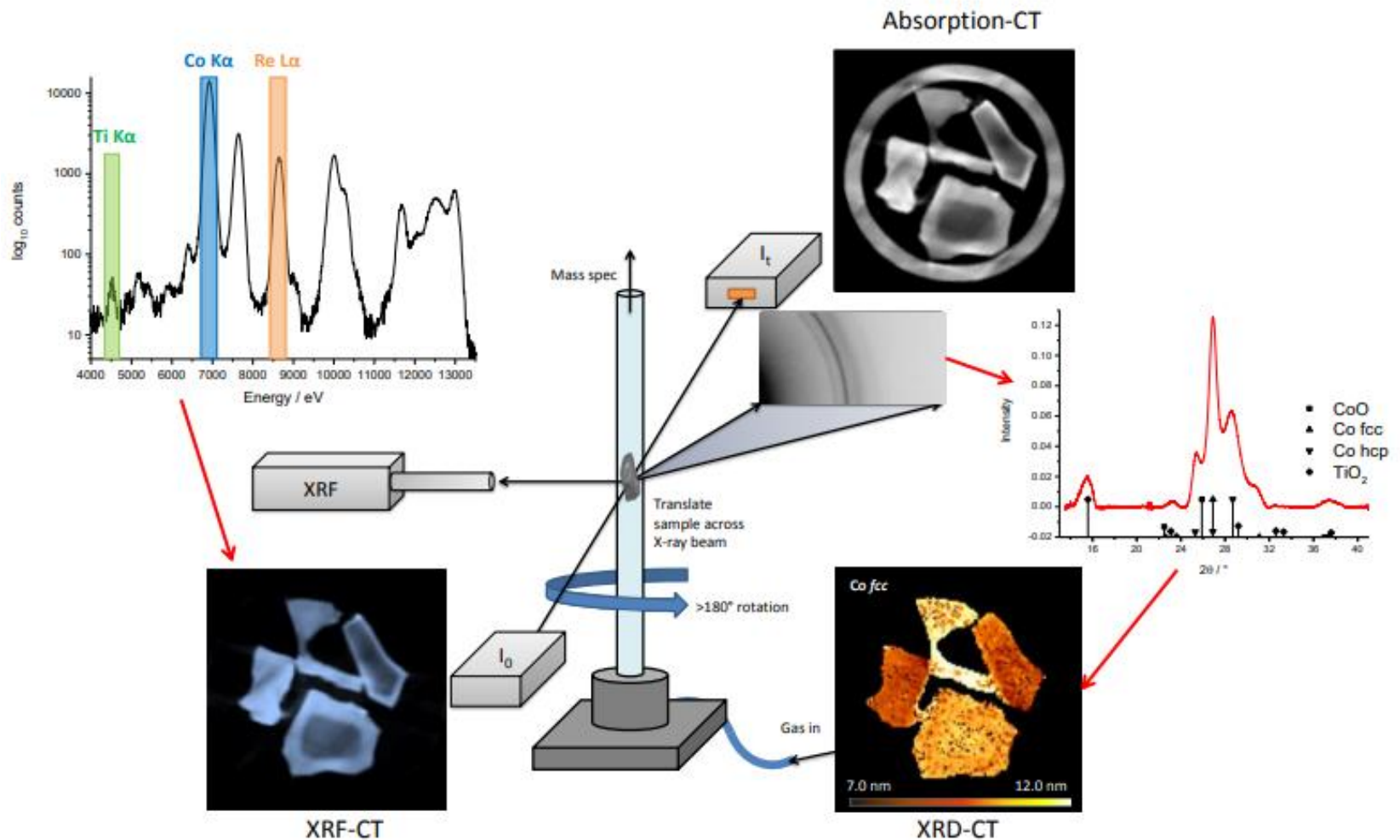
**Operando multimodal imaging techniques** like XRD-CT, XRF-CT, and absorption-contrast CT.

**Different impregnation sequences** yielded materials with the **same chemical compositions**, but the **size and distribution of crystalline species** were significantly altered.



*Conventional catalyst precursor structure.*

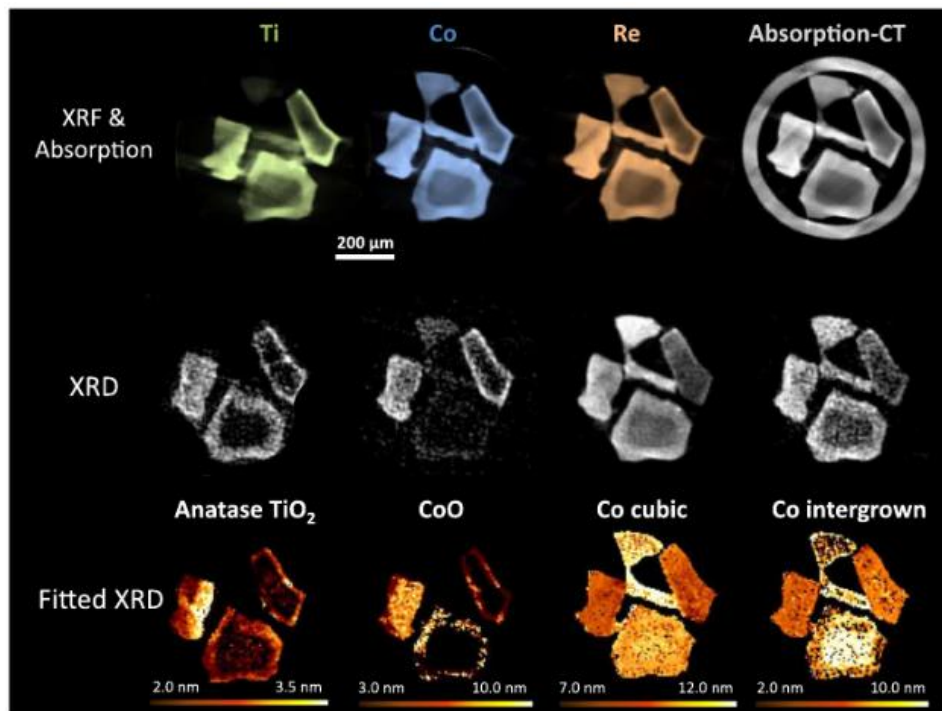
# Case Study 2: Catalyst Preparation protocol



*Schematic of the experimental setup including exemplar XRF spectrum and XRD pattern.*

## Conventional

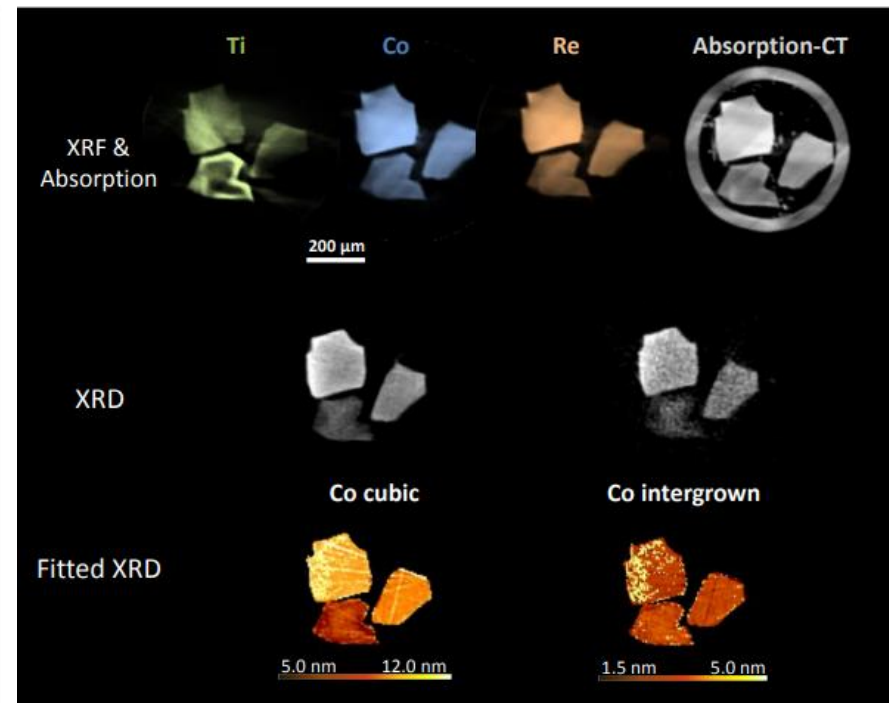
*Suppressed the diffusion/migration of **Co** and **Re** species to the core of catalyst particles.*



*XRF-CT reconstructions showing elemental distributions for conventional catalyst structure during FTS at 4 bar.*

## Inverse configuration

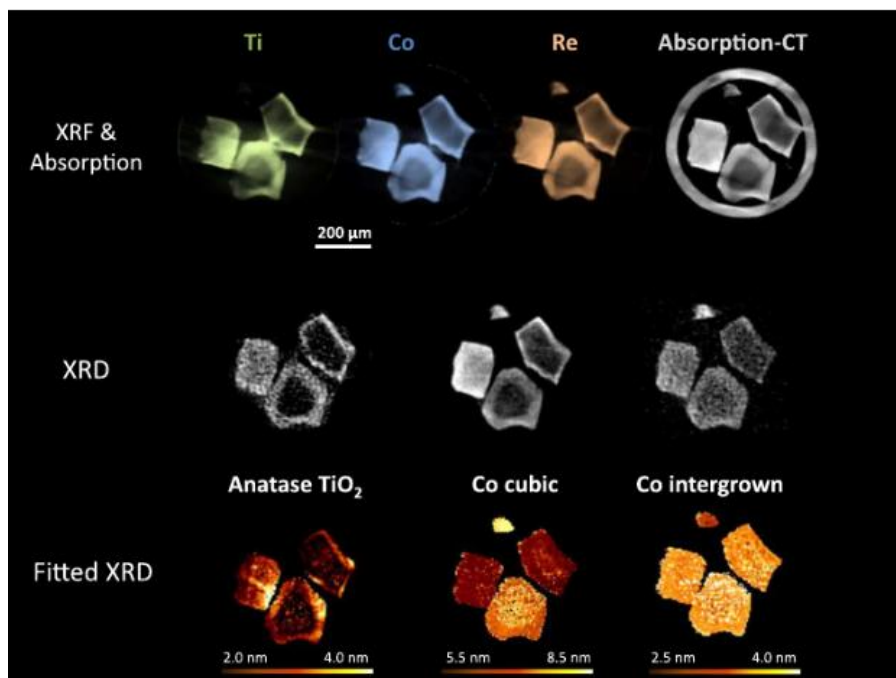
***Co** and **Re** species freely diffused through the support material.*



*XRF-CT reconstructions showing elemental distributions for inverse catalyst during FTS at 4 bar.*

## Conventional

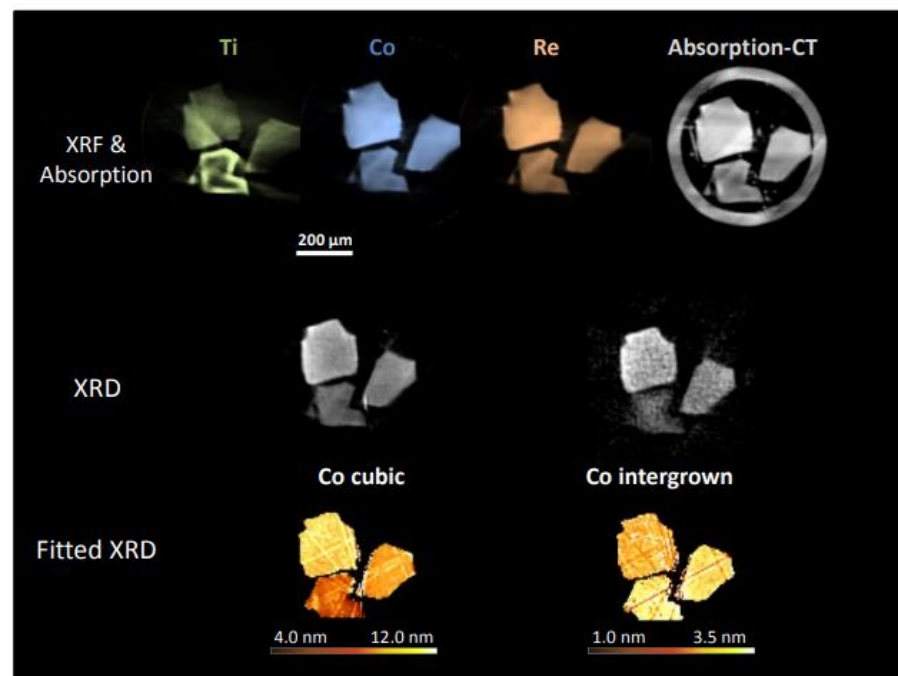
Reduced Co nanoparticles were smaller and more strained due to the *higher degree of intergrowth between hexagonal and cubic Co particles*.



*Conventional catalyst structure after reduction*

## Inverse configuration

Formation of Larger Co Nanoparticles but *less strained*, and the catalyst exhibited *higher stability and selectivity for longer-chain hydrocarbons*.



*Inverse catalyst structure after reduction*

## **Summary**

*Small variations in the deposition sequence can result in catalysts with identical chemical composition, yet differ in spatial distribution of elements, different phases, and crystallite sizes, and, notably, in their activity and selectivity to specific products.*

*Multimodal approach is used here to image the catalysts operando. Represent the first true simultaneous chemical tomography experiment.*

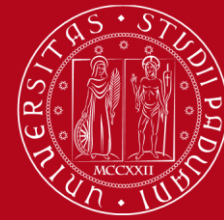
XAS is *element specific* and can *distinguish* between different valences or coordination numbers of an element within this specific range of energies.

XAS therefore *enables the elucidation of how introduced species* change the (average) state of the catalyst.

*In situ* and *operando spectroscopy* offers the possibility to investigate *various aspects of such catalytic processes* in great detail as it is aimed at *characterization of catalysts in their active state*.

An in-depth understanding of *reaction* and *deactivation mechanisms* can lead to the *design of new and improved catalytic processes* in terms of *activity, selectivity, stability*, and as such can have major effects on sustainability and economic factors.

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*Thank you*