IUCr-XAFS, Madrid, 22-8-2011

# APPLICATIONS OF X-RAY SPECTROSCOPY IN CHEMISTRY

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# APPLICATIONS OF X-RAY SPECTROSCOPY IN CHEMISTRY

- Summary

- General Introduction XAFS/XES

Overview XANES/EXAFS utility in Chemistry

- XAFS analysis of materials genesis

- XAFS analysis of industrial-related chemical properties

# APPLICATIONS OF X-RAY SPECTROSCOPY IN CHEMISTRY

- **XAFS (XES) Techniques: XANES and EXAFS**

**Fit Chemical needs (Atmosphere, P, T)**

**Local order sensitive (around each component)**

**Independent of crystallinity**

**XANES: high S/N ratio (absence thermal effects)**

## NANO-CHEMISTRY

**Control of Structure and Morphology (primary particle size, shape)**

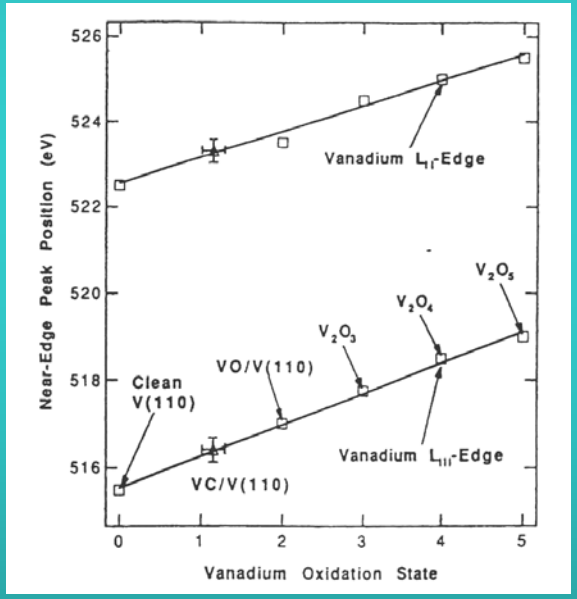
**Structure / Morphology <> Chemical Properties**

## OVERVIEW XANES APPLICATION: CHEMISTRY

**Electronic Properties**

- **Edge**
- **Pre-edge**
- **CRs**

$$\Delta E = \Delta \sum_{j}^{val} \left\langle e^2 / r_j \right\rangle + E(exchange)$$



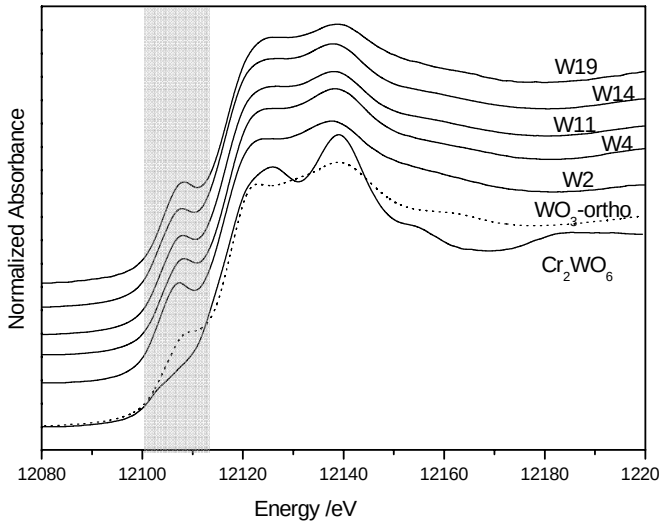

**Average Oxidation State**

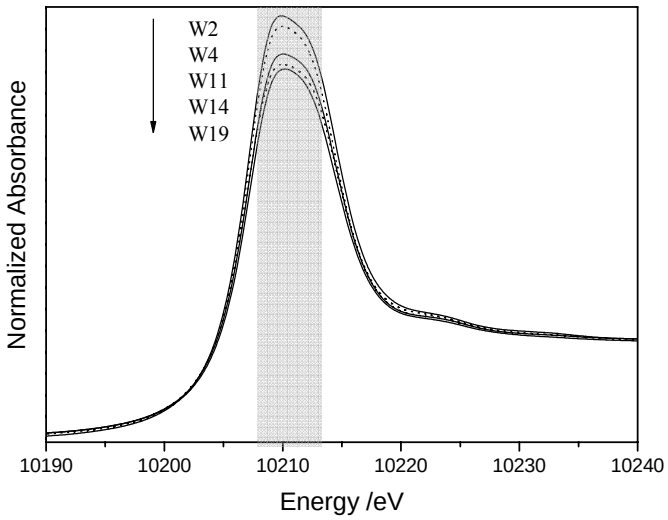
## OVERVIEW XANES APPLICATION: CHEMISTRY

### Electronic Properties

- Edge
- Pre-edge
- CRs

### W: $TiO_2$ W $L_I$ $L_{III}$-edge




**Pre-edge Position and Intensity: Ox. State + Local symmetry**

**CRs: "Projected" Empty (s,p,d) Density of States**

J. Phys. Chem. B 109 (2005) 6075

# OVERVIEW XANES APPLICATION: CHEMISTRY

## Electronic/Structural Properties

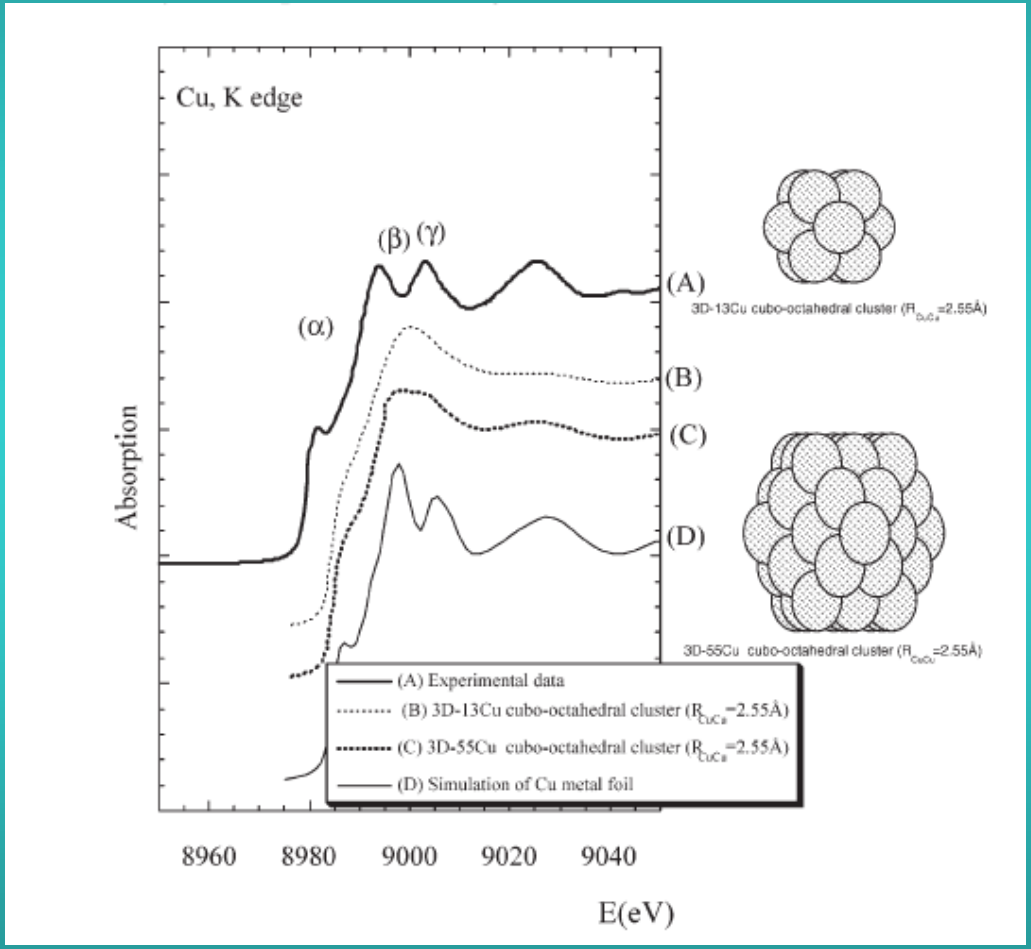
- **Pre-edge**
- **CRs**

Nanophases

Th. Calculations

Size/Shape dependence

## Cu nanoparticles

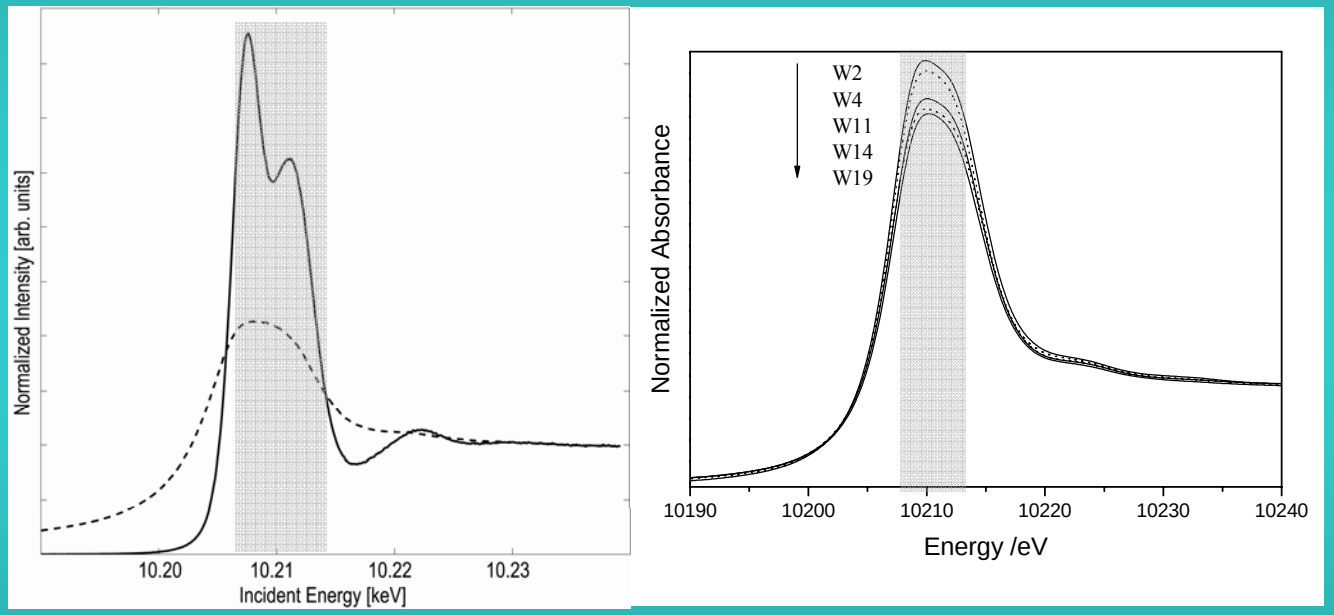


## OVERVIEW XANES APPLICATION: CHEMISTRY

### Electronic Properties

- Edge
- Pre-edge
- CRs

### W: $TiO_2$ XES W $L_{III}$-edge




**High Resolution => Fine electronic details**

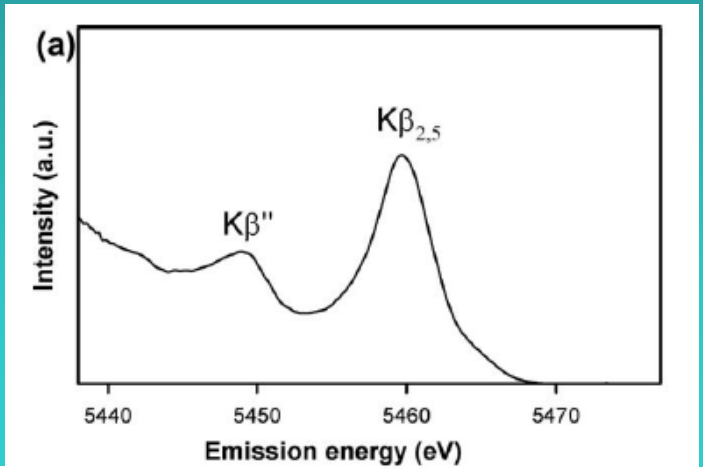
Eur. J. Phys 169 (2010) 207

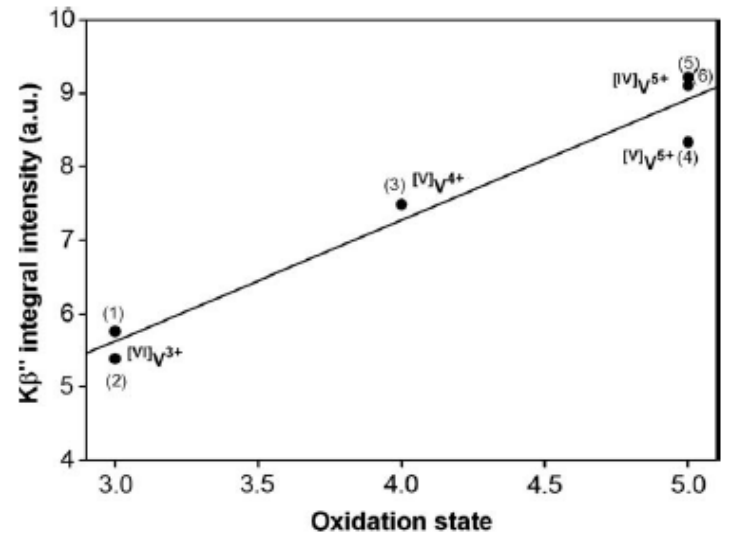
# OVERVIEW XAFS APPLICATION: CHEMISTRY

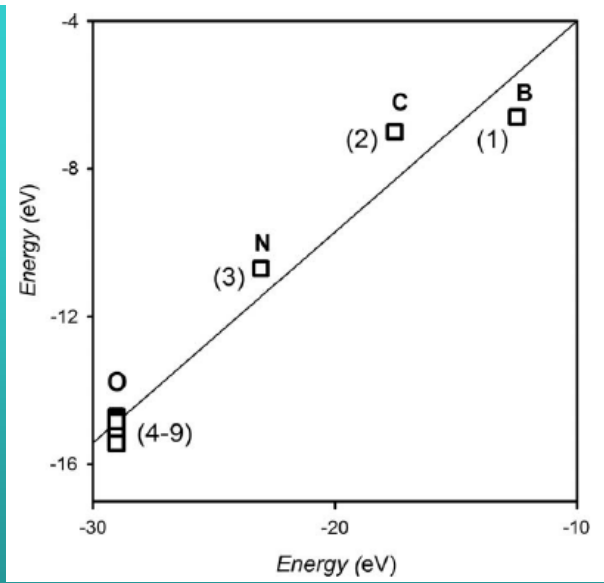
## XES: selective spectra

## Electronic Properties

- XANES




**Oxidation State and Ligand Selective Electronic details**

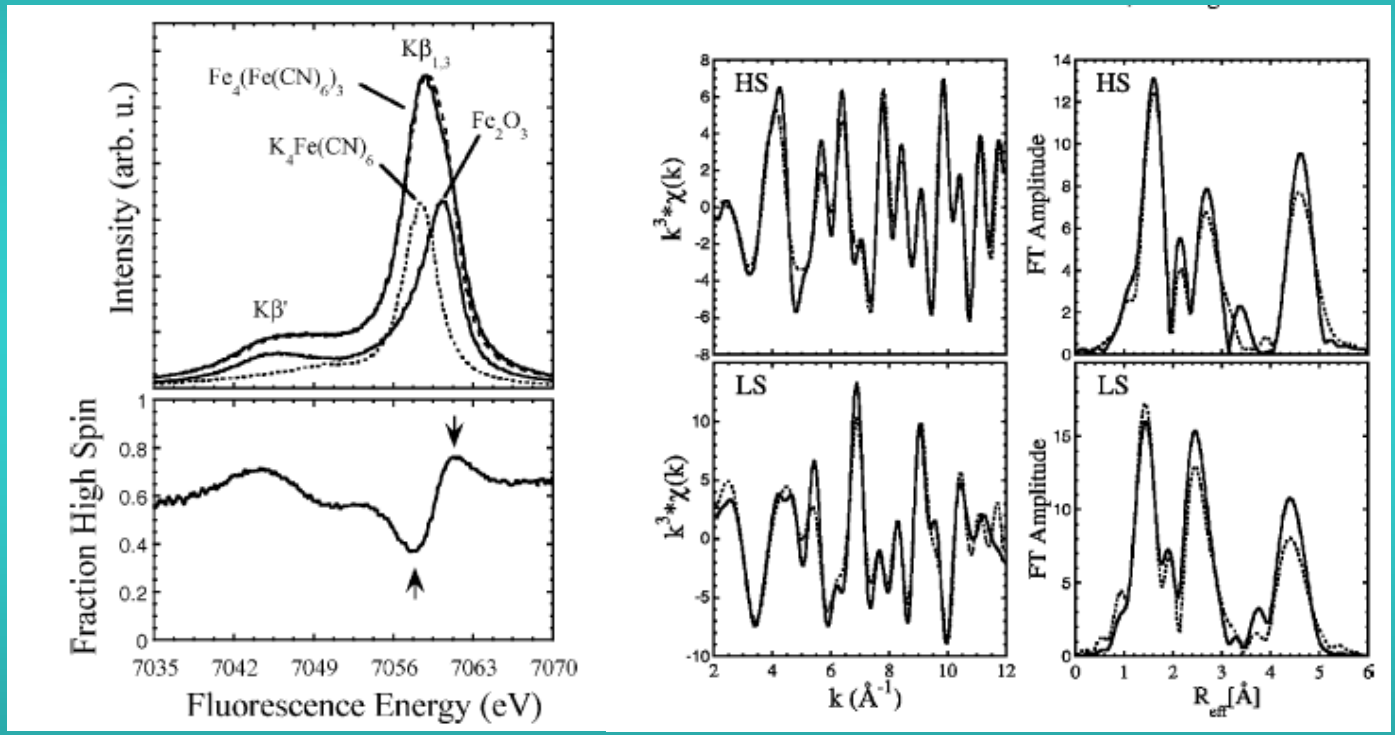
Eur. J. Phys 169 (2010) 207

## OVERVIEW XAFS APPLICATION: CHEMISTRY

### Structural Properties

- **EXAFS**

**XES: selective spectra**




**Site (Local St.) Selective Structural details**

Coord. Chem. Rev. 249 (2005) 65

# OVERVIEW XANES APPLICATION: CHEMISTRY

## Structural Properties

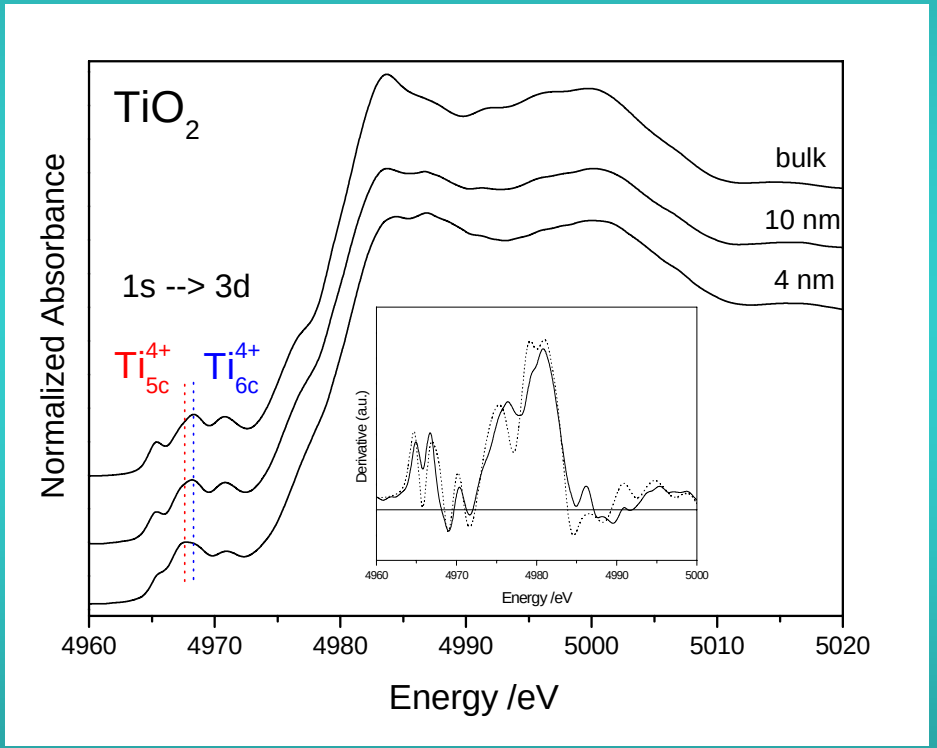
- Pre-edge (s -> p/d)

**Undercoordinated Metal**

**$Ti^{4+}_{5c}$**

**Number of Oxygen Vacancies**

### Metal Oxides (1st Transition Series)




X-Ray Spectrom. 37 (2008) 572

# OVERVIEW XANES APPLICATION: CHEMISTRY

## Metal Oxides (1st Transition Series)

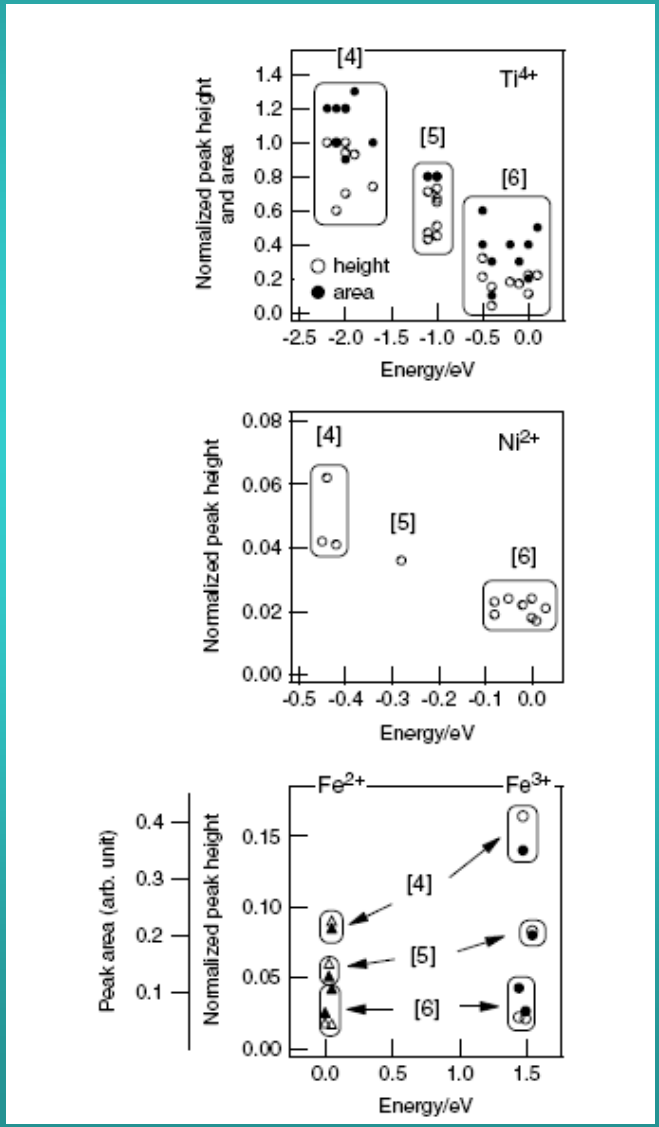
## Structural Properties

- **Pre-edge (s -> p/d)**

**Partially Reduced**
**And/or**
**Undercoordinated**
**Metal**

$M^{n+}_{xc}$

**Number**
**Defects/Vacancies**



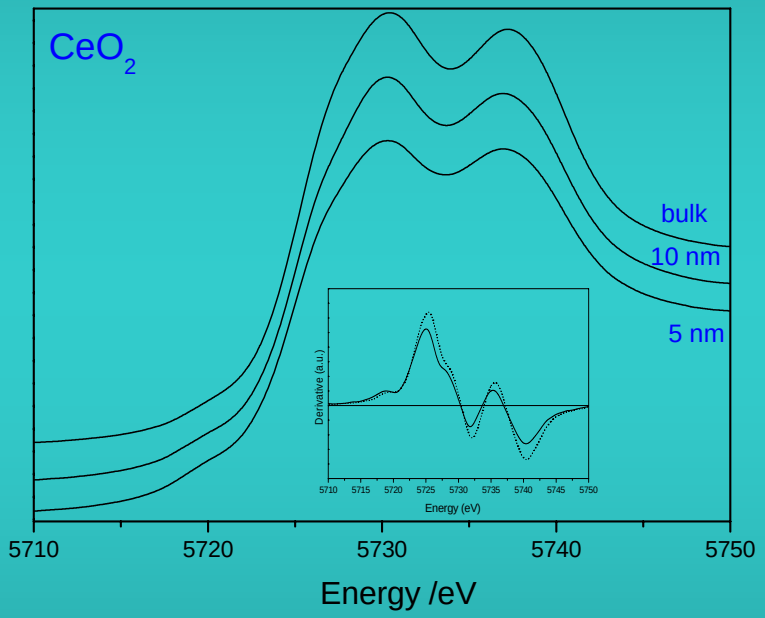

X-Ray Spectrom. 37 (2008) 572

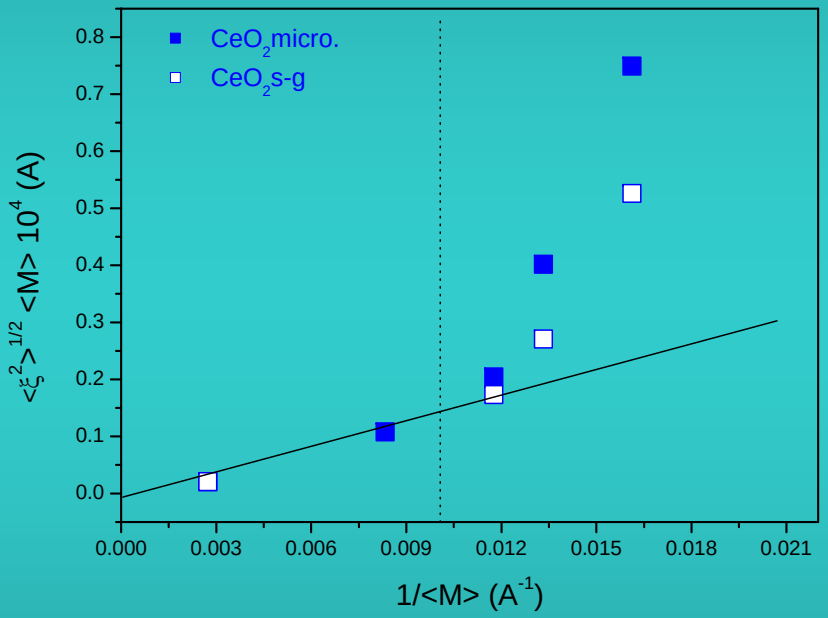
## OVERVIEW XANES APPLICATION: CHEMISTRY

# Structural Properties

### $Ce^{3+}$ in quasi-stoichiometric particles

- **CRs**




- **$Ce^{3+}$ <> Vacancies below 5 at. %**

- **Strain from $Ce^{3+}$ presence Raman ($Ce^{3+}$ < 1.6 at. %)**

**XANES: Relatively Poor Detection Limit**

*PCCP 6 (2004) 3524*

# OVERVIEW XANES APPLICATION: CHEMISTRY

## Structural Properties

- CRs

$E \propto 1/R^2$

Phase behavior

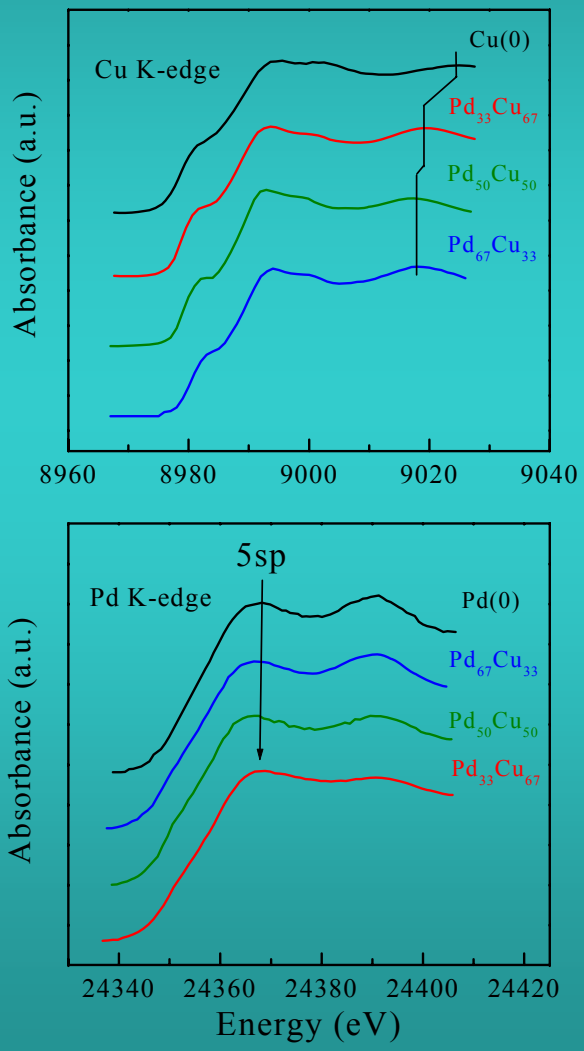
Analysis
CR 9020 eV

↓

disordered FCC alloys

Local ordering
Pd/Cu ≤ 1

### Pd-Cu alloys




J. Phys. Chem. 99 (1995) 12565

# OVERVIEW EXAFS APPLICATION: CHEMISTRY

## Structural Properties

- **Primary p. size and shape for nano-particles**

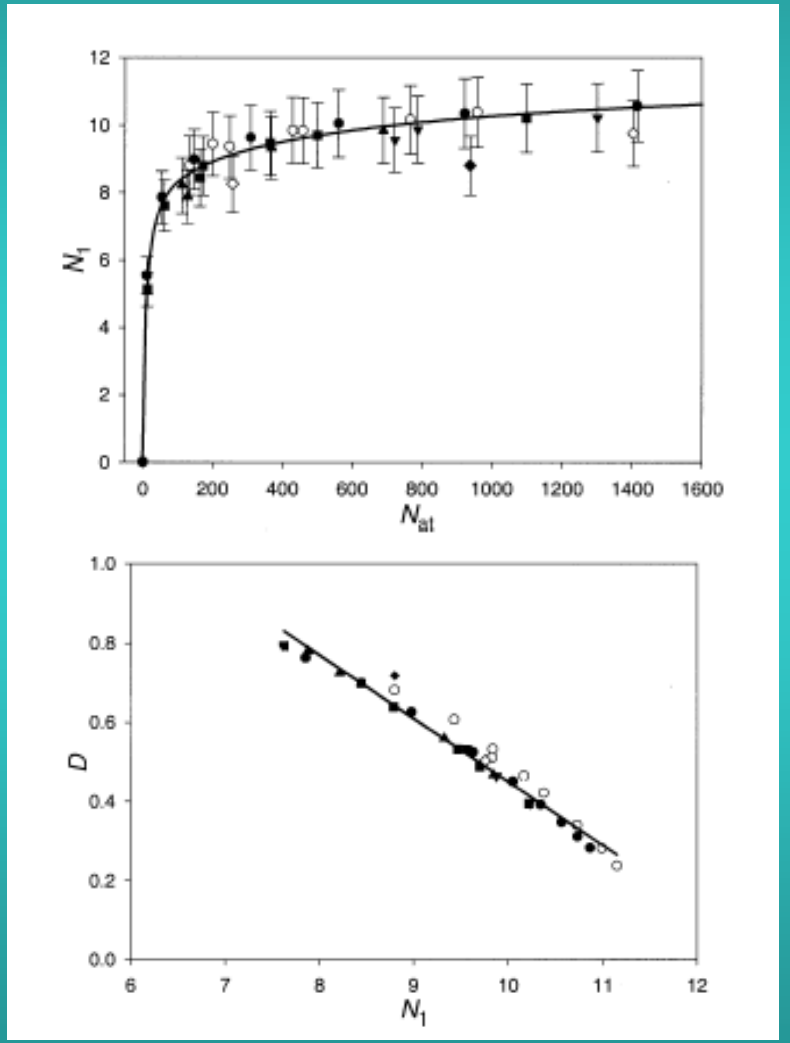
1st Shell CN

Size

Dispersion (Surf. vs. Bulk)

High Sensitivity < 300 at.

**Nano-metals**




PCCP 1 (1999) 4059; 12 (2010) 5562

# OVERVIEW EXAFS APPLICATION: CHEMISTRY

## Structural Properties

- **Primary p. size/shape**

1st Shell CN

Size

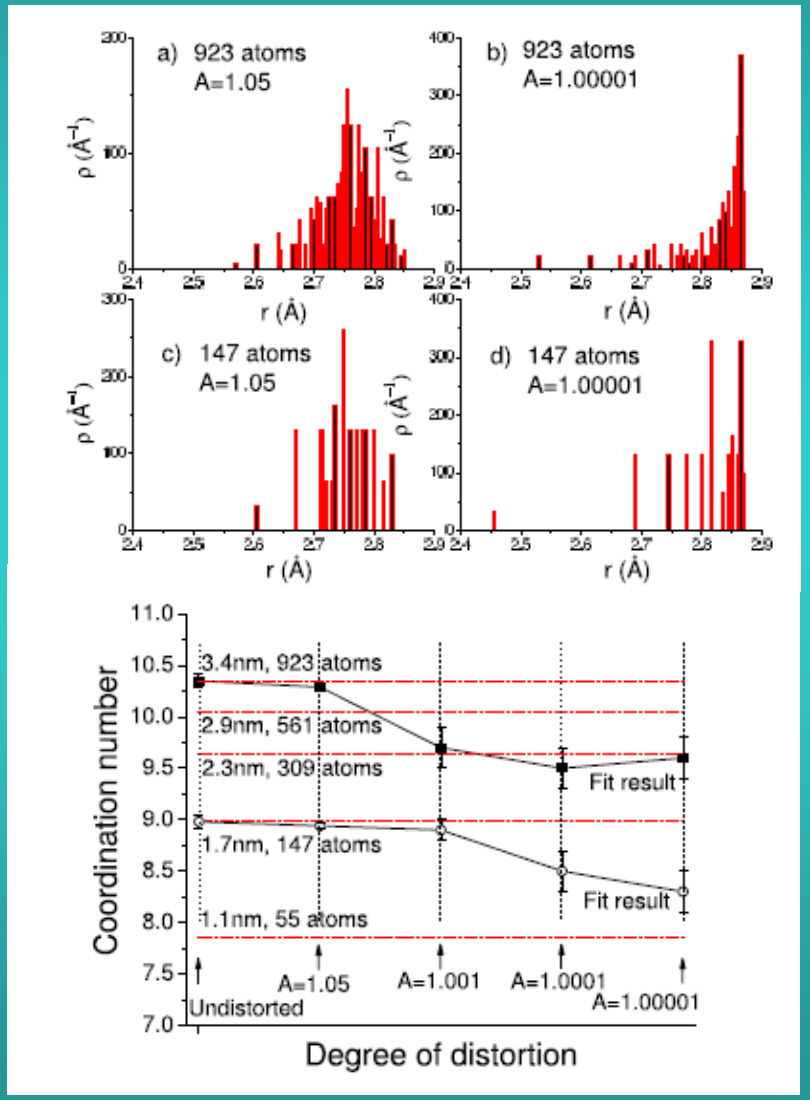
Surface Disorder

Size < 5 nm

Limited validity
Usual Analytical Approach

Underestimation CN

## Nano-metals




Phys. Rev. B 81 (2010) 115451

# OVERVIEW EXAFS APPLICATION: CHEMISTRY

## Structural Properties

- Primary p. size and shape for nano-particles (metals)

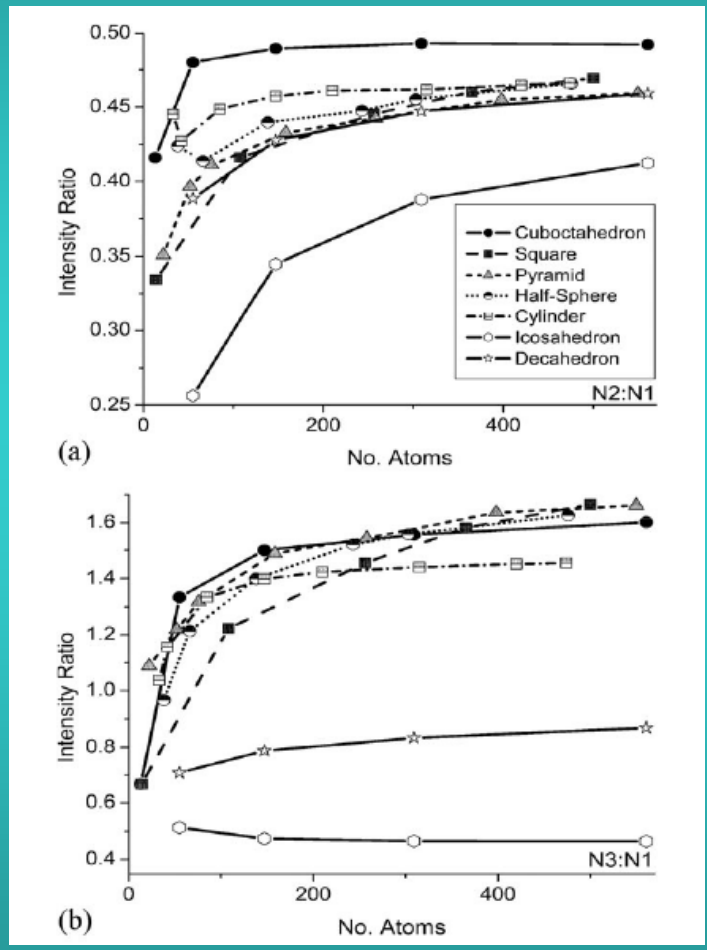
1st Shell CN; size

CNn: CN1; shape

Fcc; hcp OK

Bcc; only CN1 > 4

## Nano-metals




PCCP 1 (1999) 4059; 12 (2010) 5562

# OVERVIEW EXAFS APPLICATION: CHEMISTRY

## Structural Properties

## Homogeneity

$$\alpha = \frac{1 - N_{PtPd}/N_{\sum PtPt + PtPd}}{X_{Pd}}$$

$\Delta = \alpha_{M1} - \alpha_{M2}$ $\Sigma = \alpha_{M1} + \alpha_{M2}$

Combination

Degree of interaction/mixing

## Nano-alloys

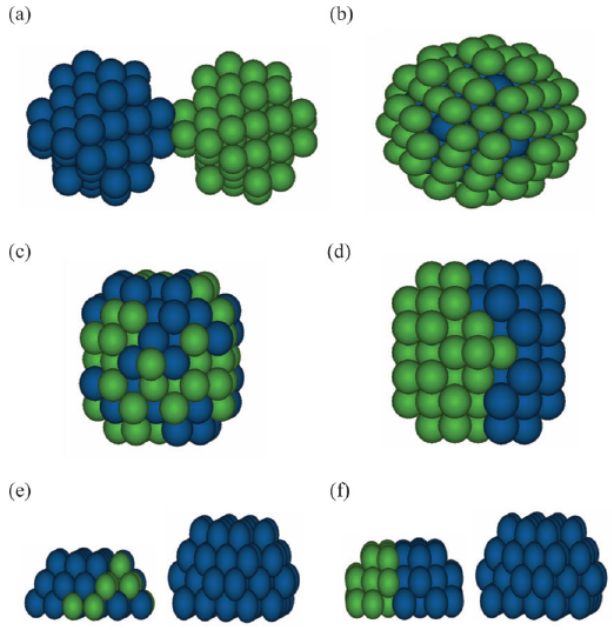



Fig. 9 Hypothetical bimetallic clusters (Pt = blue, Pd = green): (a) bi-cluster; (b) core–shell; (c) random; (d) single-half; (e) bi-cluster homo; (f) bi-cluster inhomo.

Table 5 1st shell coordination numbers for PtPd bimetallic systems

| Cluster Type | Pt–Pt | Pt–Pd | $\sum N_{PtP}$ | Pd–Pd | Pd–Pt | $\sum N_{PdP}$ | $x_{Pt}$ | $x_{Pd}$ | $\alpha_{Pt}$ | $\alpha_{Pd}$ | $\Delta\alpha$ | $\sum\alpha$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Bi-cluster | 8.73 | 0.07 | 8.80 | 8.73 | 0.07 | 8.80 | 0.5 | 0.5 | −0.98 | −0.98 | 0 | −1.96 |
| Single-Half | 7.08 | 1.58 | 8.66 | 7.85 | 1.19 | 9.04 | 0.43 | 0.57 | −0.68 | −0.69 | 0.01 | −1.37 |
| Core–shell | 7.73 | 3.86 | 11.59 | 3.90 | 2.92 | 6.82 | 0.43 | 0.57 | −0.42 | 0 | −0.42 | −0.42 |
| Random | 3.63 | 4.80 | 8.42 | 5.59 | 3.63 | 9.22 | 0.43 | 0.57 | 0 | −0.08 | 0.08 | −0.08 |
| Decorated | 3.43 | 3.00 | 6.43 | 8.73 | 0.77 | 9.50 | 0.21 | 0.78 | −0.18 | −0.9 | 0.72 | −1.08 |
| Random (50/50) | 5.41 | 4.26 | 9.68 | 4.20 | 3.88 | 8.09 | 0.5 | 0.5 | −0.12 | −0.08 | −0.04 | −0.2 |
| Bi-cluster homo | 7.63 | 0.92 | 8.55 | 3.25 | 4.33 | 7.58 | 0.82 | 0.18 | −0.39 | −0.31 | −0.08 | −0.7 |
| Bi-cluster inhomo | 7.63 | 0.24 | 7.88 | 5.92 | 1.17 | 7.08 | 0.82 | 0.18 | −0.82 | −0.8 | −0.02 | −1.62 |

PCCP 12 (2010) 5562

# APPLICATIONS OF X-RAY SPECTROSCOPY IN CHEMISTRY

- **Summary**

**- General Introduction XAS/XES**

**Overview XANES/EXAFS utility in Chemistry**

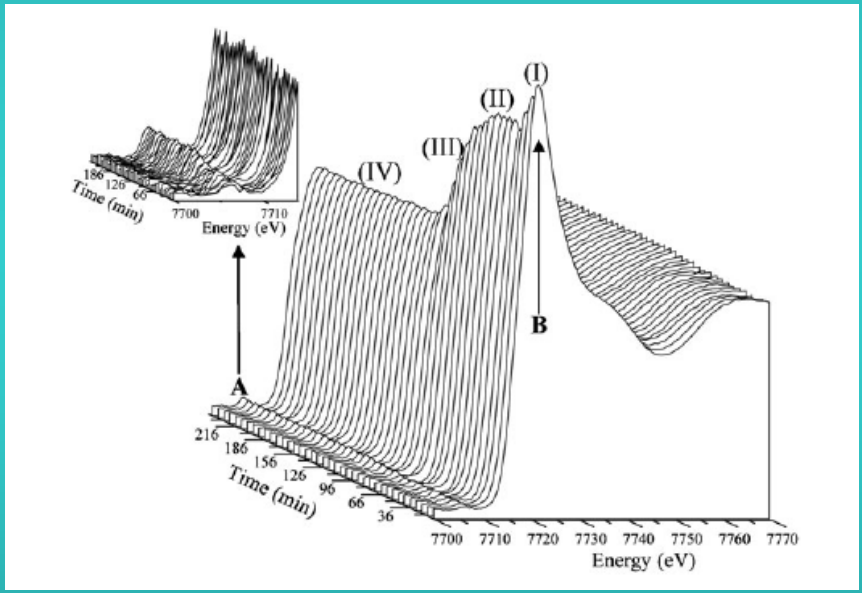
***- XAFS analysis of materials genesis***

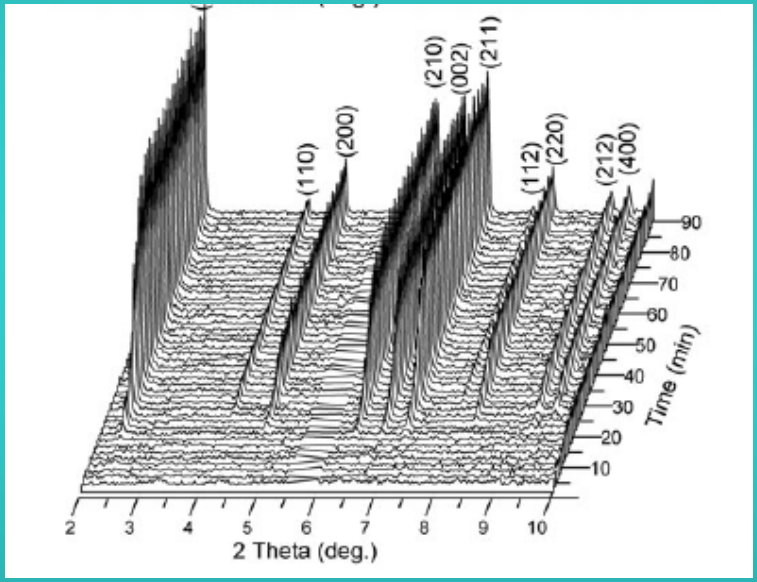
**- XAFS analysis of industrial-related chemical properties**

## CONTROL OF STRUCTURE AND MORPHOLOGY: SYNTHESIS

# Liquid Phase; synthesis of Zeotypes (Co-AlPO)

## XAS - XRD Analysis



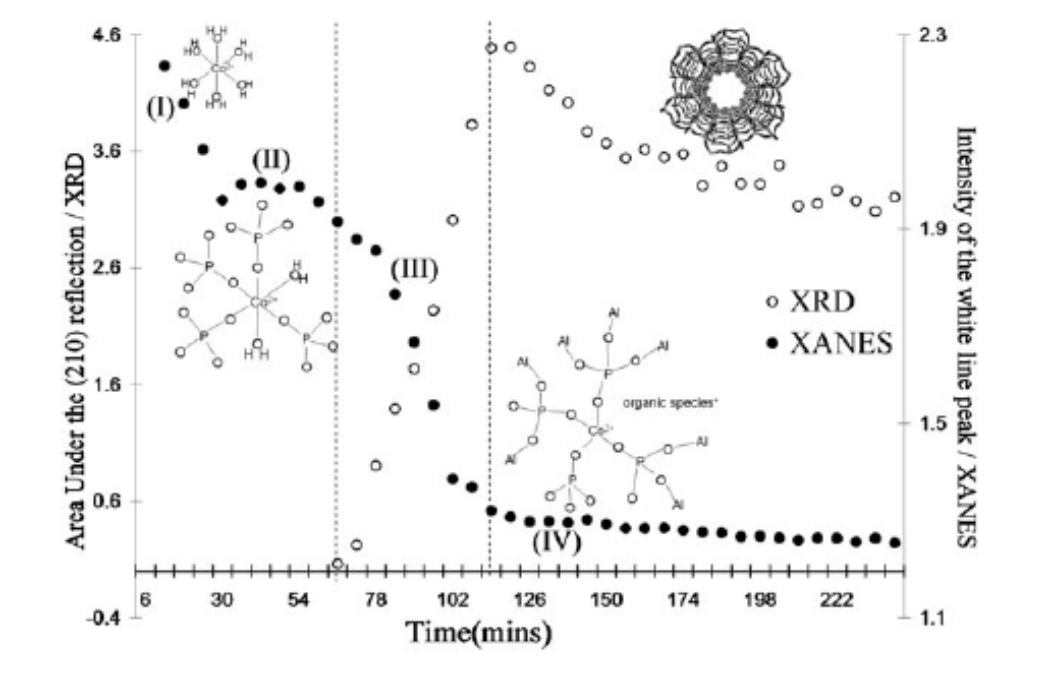

**Complementary analysis of the local/long range order evolution**

PCCP 12 (2010) 559

## CONTROL OF STRUCTURE AND MORPHOLOGY: SYNTHESIS

# Liquid Phase; synthesis of Zeotypes

## XAS XRD Analysis




**Detection of four different regions**
**(Initial) Intermediate only detected by XAS**

PCCP 12 (2010) 559

## CONTROL OF STRUCTURE AND MORPHOLOGY: SYNTHESIS

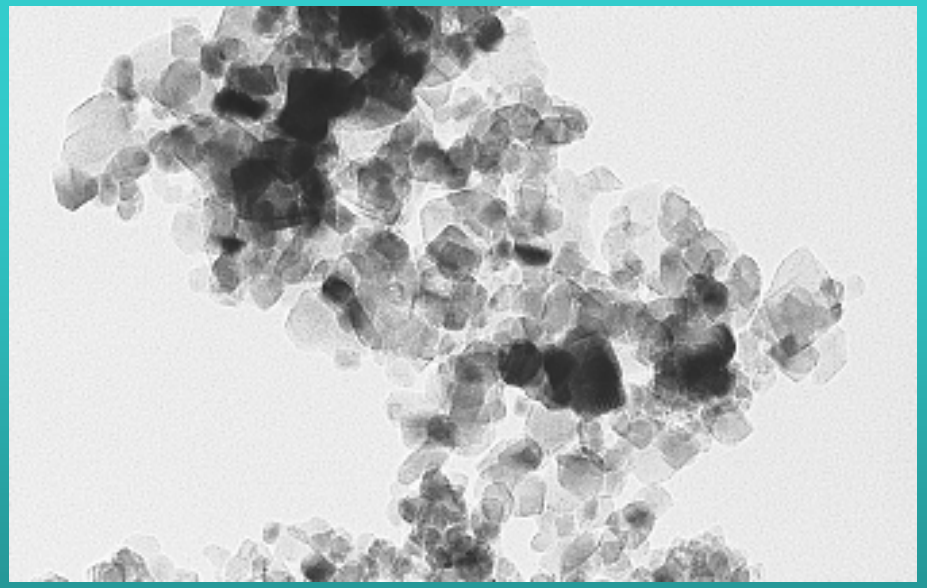
### Synthesis of Oxides

| Surfactant | Triton X-100 | | | Tween 85 | |
|---|---|---|---|---|---|
| $H_2O$ / Surf. | 18 | 4.5 | 3 | 18 | 3 |
| Samples / 773 K | T | TA | TB | TW | TWB |
| Samples / 873 K | T1 | T1A | T1B | T1W | T1WB |

**Solid state treatment**

↓

**High Surface Area**
**Nanostructured Anatase materials**

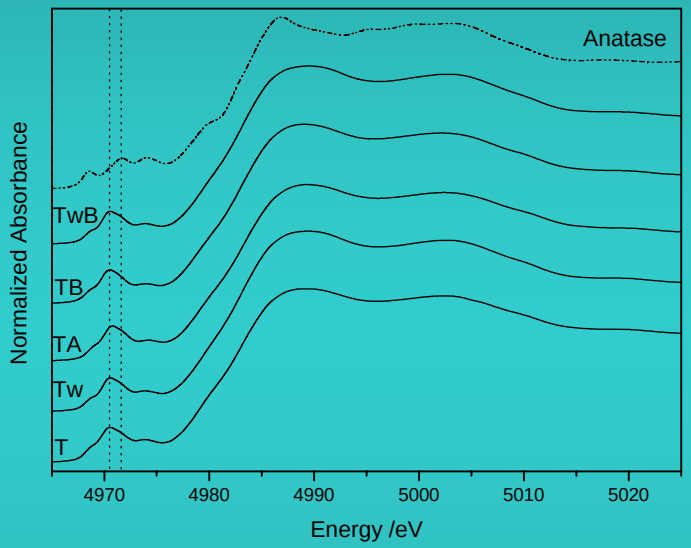


J. Phys. Chem. C 111 (2007) 674

## CONTROL OF STRUCTURE AND MORPHOLOGY: SYNTHESIS

### Solid phase: Initial Precursors

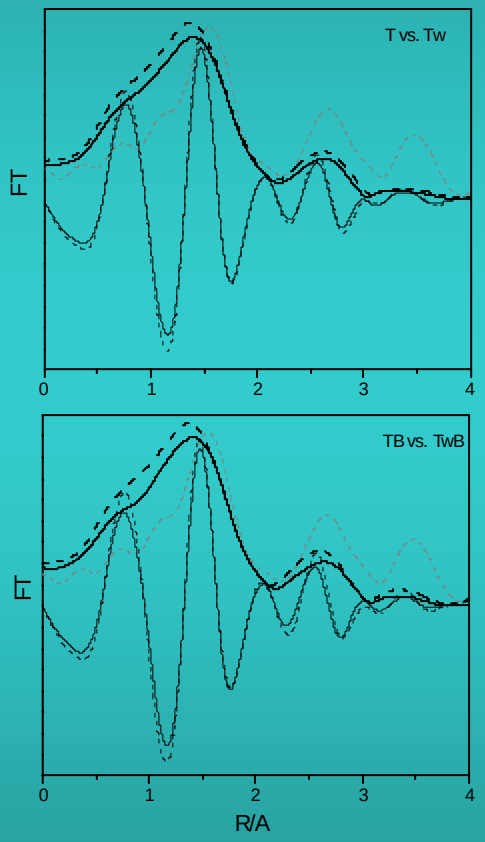
#### XANES Spectra: Pre-edge




**Anatase-type Structure**

$Ti_{5c}^{4+}$

#### EXAFS Spectra



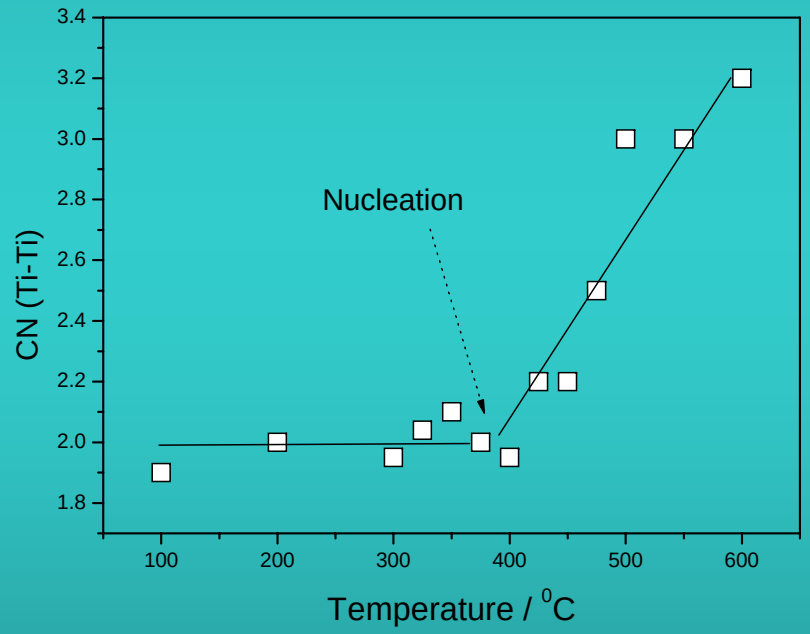

**Ti-Ti C.N. 2.2 ± 0.5**

**Precursors lack 3D connectivity**

## CONTROL OF STRUCTURE AND MORPHOLOGY: SYNTHESIS

# Treatment of Solid precursors; synthesis of Oxides

## EXAFS Spectra: Ti-Ti 2nd Shell CN



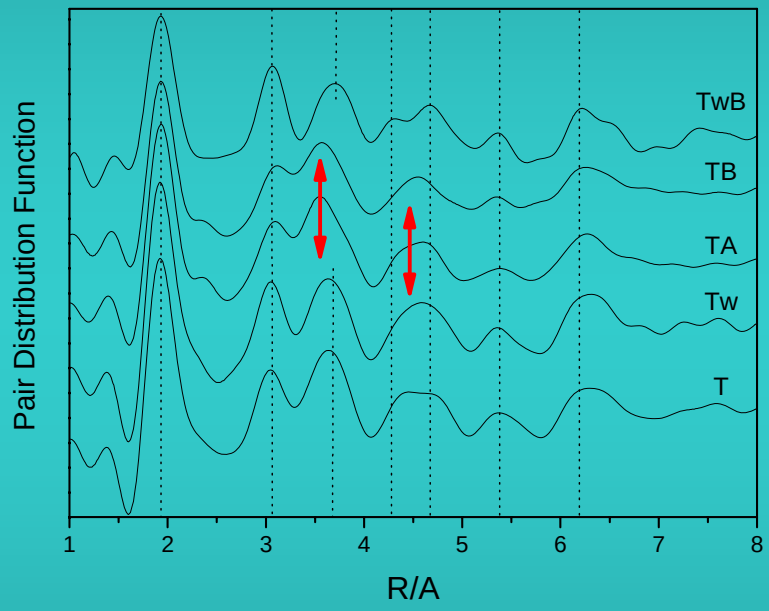

**R < 4 Å may inform about the *nucleation* step**

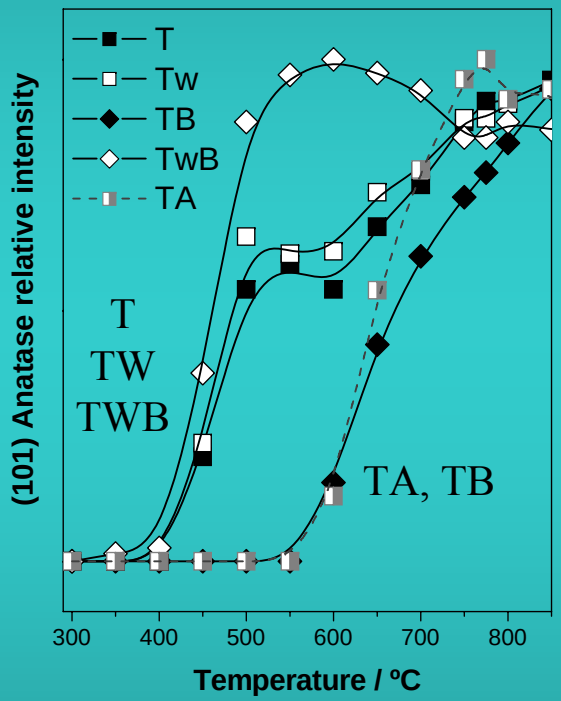
J. Am. Chem. Soc. 129 (2007) 13604

## CONTROL OF STRUCTURE AND MORPHOLOGY: SYNTHESIS

# Treatment of Solid precursors; synthesis of Oxides

## Multitechnique XAS; XRD-PDF




**3-5 Å local order → control *nucleation* and primary particle size**

**Thermodynamic factor**

J. Am. Chem. Soc. 129 (2007) 13604

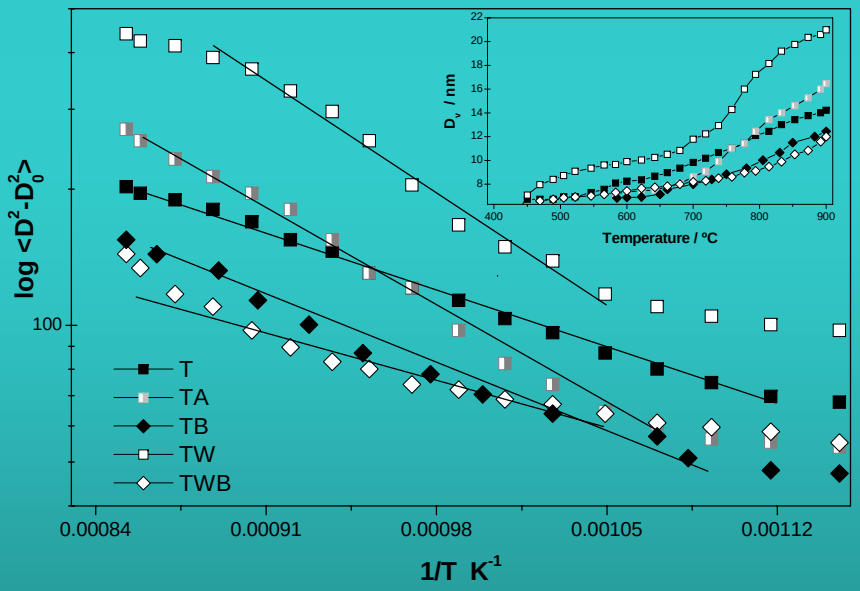
## CONTROL OF STRUCTURE AND MORPHOLOGY: SYNTHESIS

# Treatment of Solid precursors; synthesis of Oxides

## XAS Analysis

**R > 4 Å may inform about the *growth* process (at low T)**

## XRD Analysis

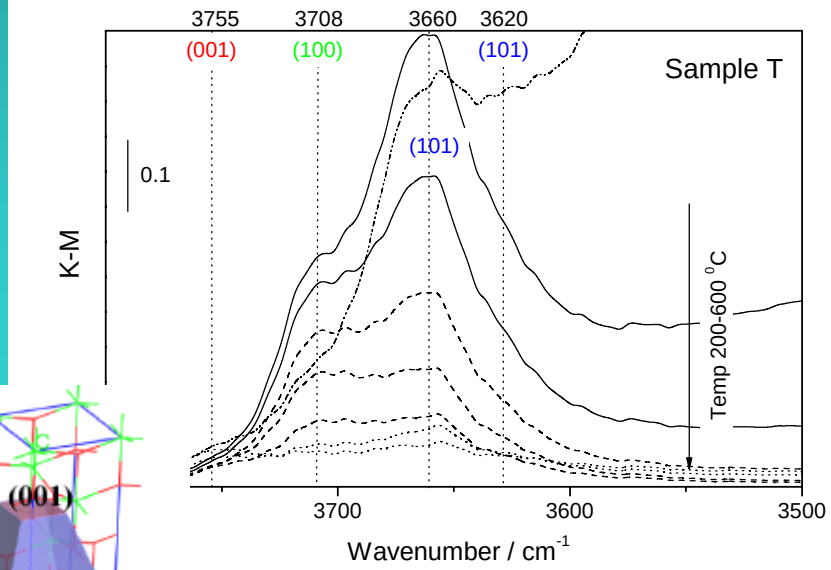


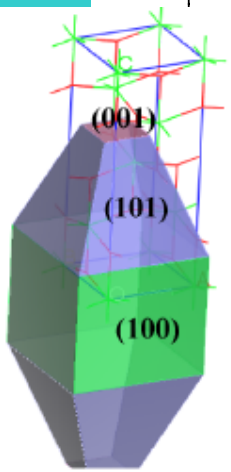

***Growth*** **($D^2$-$D_0^2$) = kT; 15-30 kJ mol$^{-1}$ ; hydration surface layers**

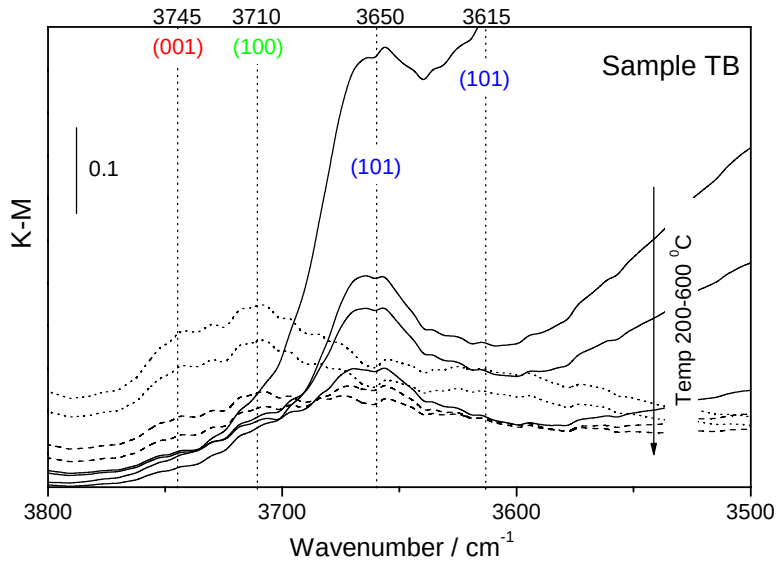
J. Phys. Chem. C 111 (2007) 674

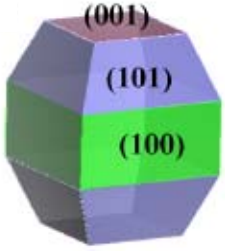
# CONTROL OF STRUCTURE AND MORPHOLOGY: SYNTHESIS

## Surface "sensitive" DRIFT Spectra



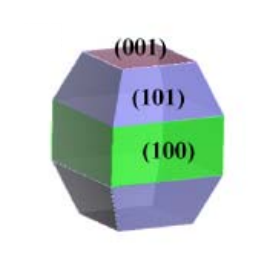



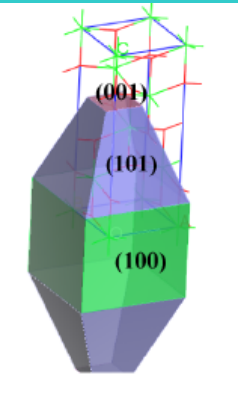

**Control particle shape: complex phenomenon (thermo/structure)**

# CONTROL OF STRUCTURE AND MORPHOLOGY: SYNTHESIS

## $TiO_2$ Anatase Nanomaterials: Size and Shape




Shape




T1A T1B

T1W T1WB

TA TB T1

T TW TWB

4 27

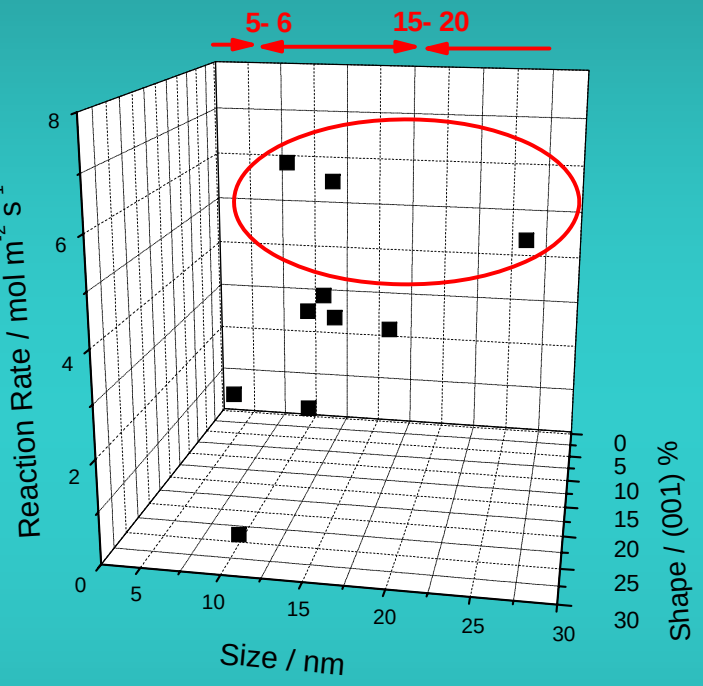
Size / nm

**Morphology control :** Size (Triton)
Shape ("Tween")

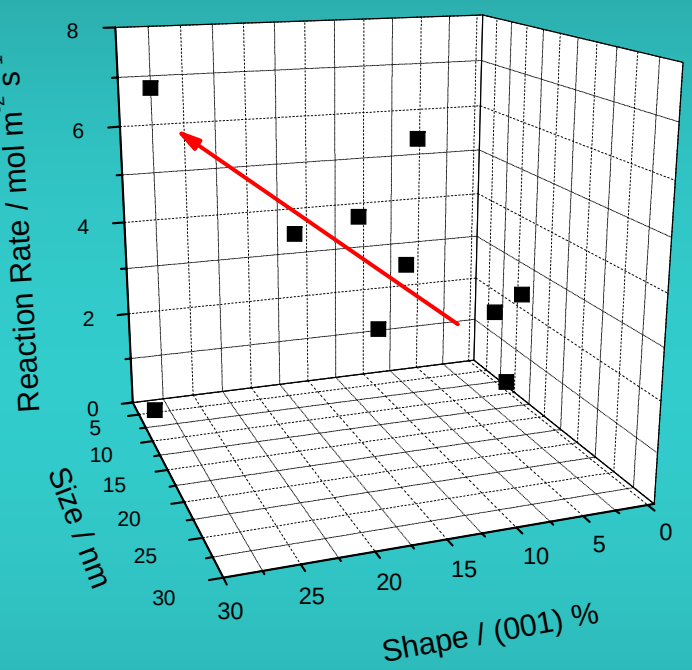
J. Am. Chem. Soc. 129 (2007) 13604

# CONTROL OF STRUCTURE AND MORPHOLOGY: ACTIVITY

## Size




## Shape




**3 Size Regions**
**Size < 5-6 nm; low activity**
**NO clear differences a/b 15 nm**

**Shape**
**Above 6 nm**
**Isotropic Shape enhances Photoactivity**

# APPLICATIONS OF X-RAY SPECTROSCOPY IN CHEMISTRY

- **Summary**

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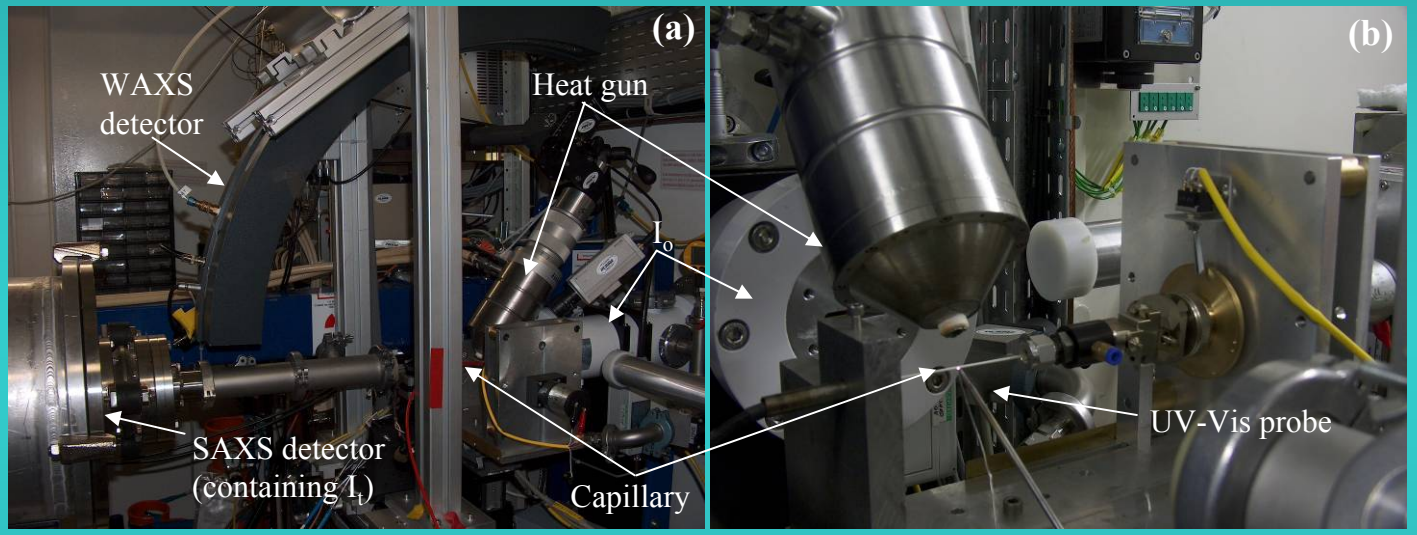
**- XAFS analysis of materials genesis**

***- XAFS analysis of industrial-related chemical properties***

## CHEMICAL ACTIVITY OF MATERIALS

### Mutitechnique SYNCHRONOUS approach




**XAFS-SAXS-WAXS; XAFS-UV (MS) approaches**

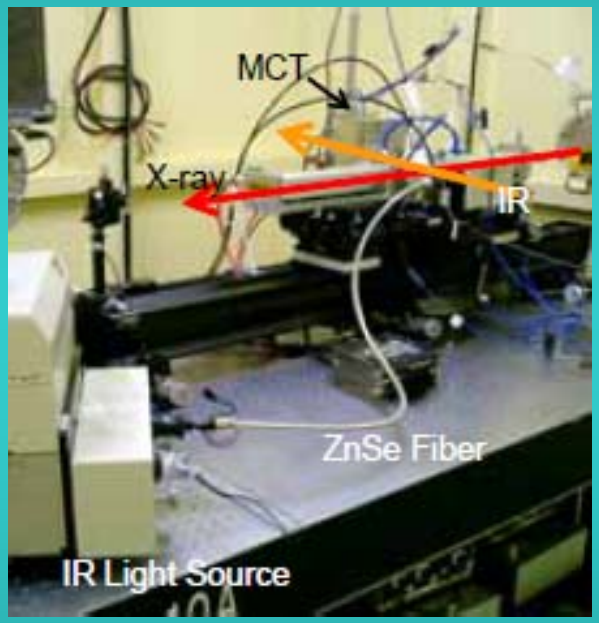
**Real "operando" conditions**

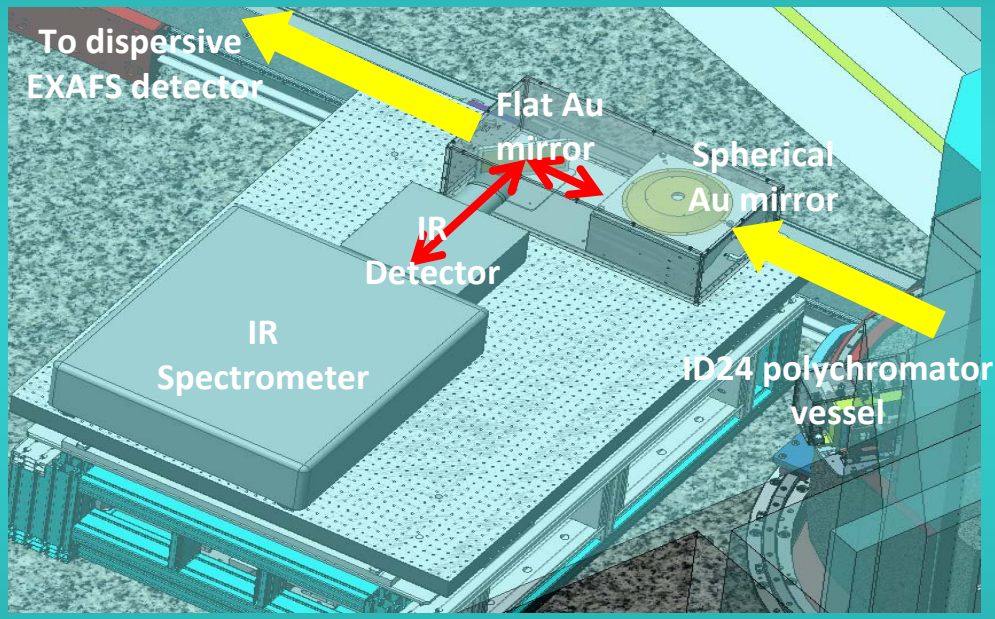
**Time dependent Structure – Chemical Activity**

Catal. Today 145 (2009) 204

## CHEMICAL ACTIVITY OF MATERIALS

### Mutitechnique SYNCHRONOUS approach
### Modern requirements



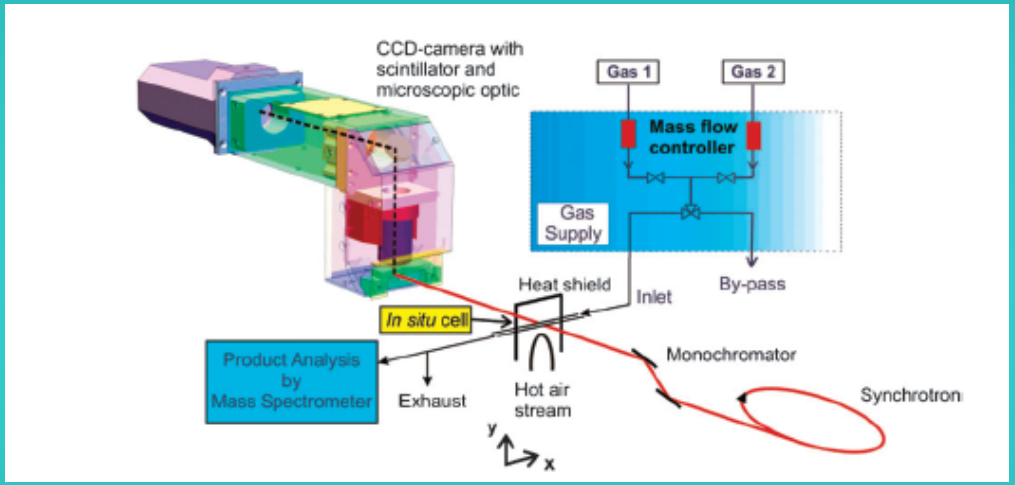

**Energy Dispersive ED-XAFS-IR (MS)**

**μs "real" single-shot Time Resolved experiment; TOFs**

Catal. Today 145 (2009) 204

## CHEMICAL ACTIVITY OF MATERIALS

# Mutitechnique SYNCHRONOUS approach
# Modern requirements



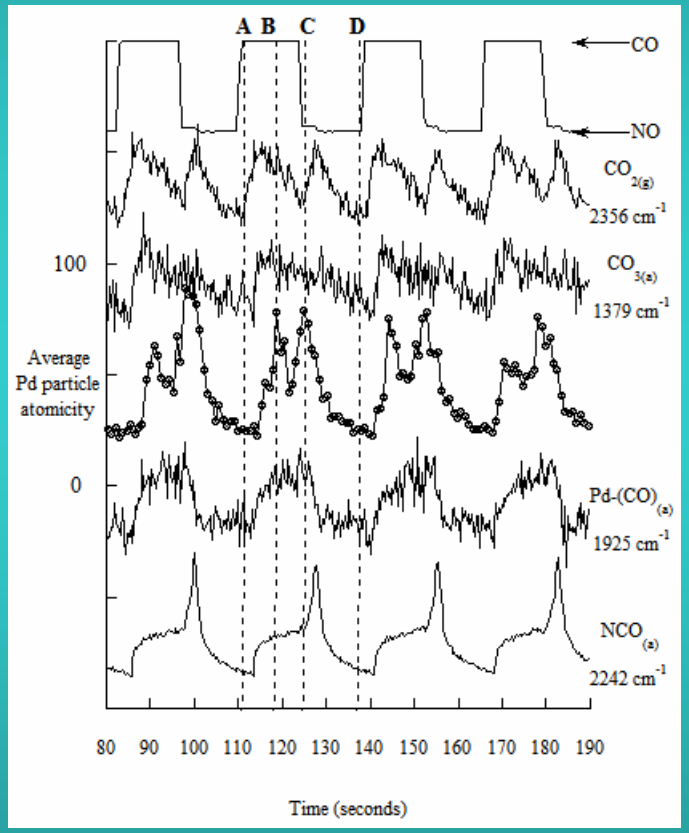

## Spatial Resolved ED-XAFS-IR (MS)

## 2D (3D) sub-μm analysis of industrial Structures (pellets, monolith)

Chem. Soc. Rev. 39 (2010) 4741

# CHEMICAL ACTIVITY OF MATERIALS

## XAS techniques; novel experiment




### Summary

Fast (ms-μs) easy track of structural-electronic properties

Combination Surface-Bulk

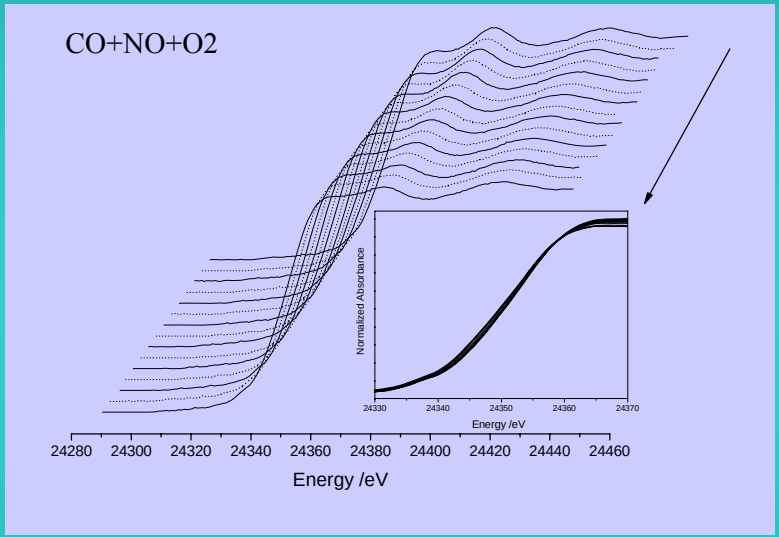
(Spatial-resolved) Information

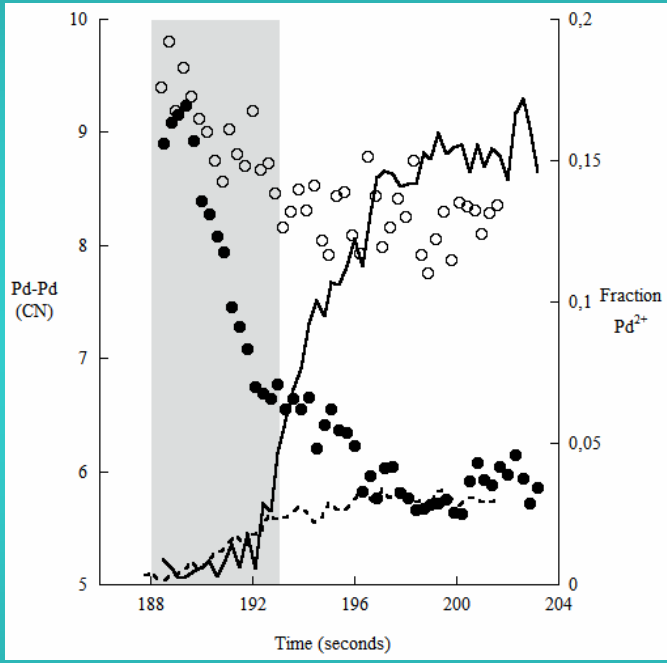
Link with Chemical Activity

Nat. Mater. 6 (2007) 528

## CHEMICAL ACTIVITY OF MATERIALS

# XANES technique; time-resolved studies



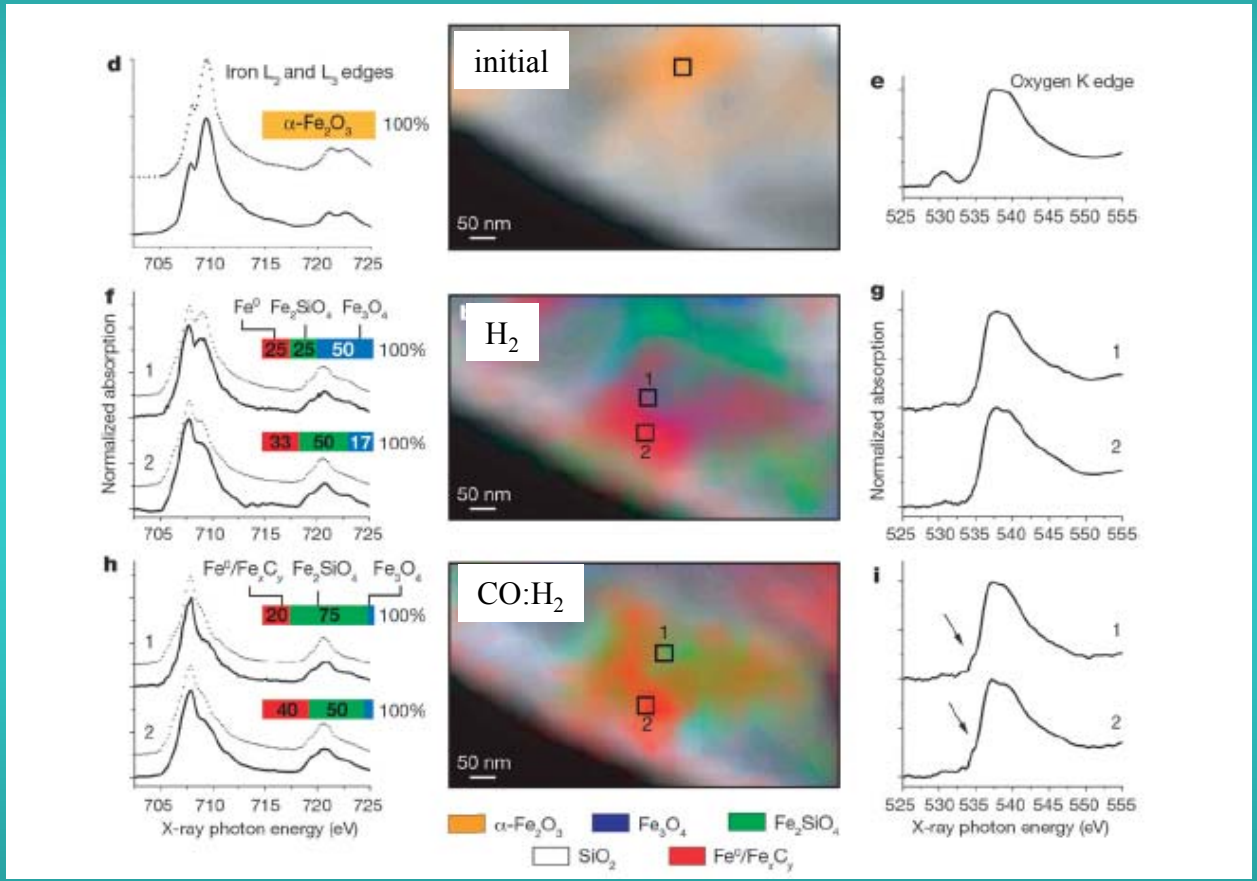

**Size-dependence => Fitting procedures**

**Statistical Analysis: Self-resolving or multivariate curve resolution**

Angew. Chem. 46 (2007) 8629

## CHEMICAL ACTIVITY OF MATERIALS

## XANES-Fluorescence microscopy technique; Spatial Resolution

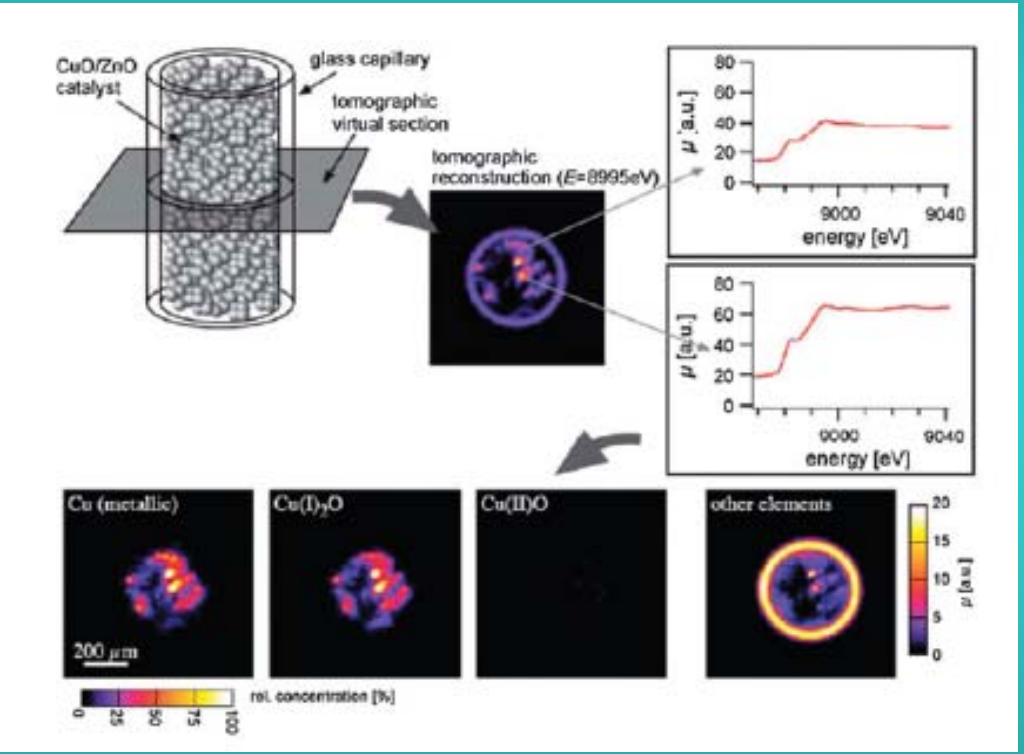



**2D Chemical (10 x 10 nm x 10-100 μm) imaging of "active" species**

Nature 456 (2008) 222

## CHEMICAL ACTIVITY OF MATERIALS

# XANES (XRD) microtomography technique; Spatial Resolution




**3D Chemical (10x10 nm x 360 $^{0}$) imaging of "active" species**

Appl. Phys. Lett. 82 (2003) 3360

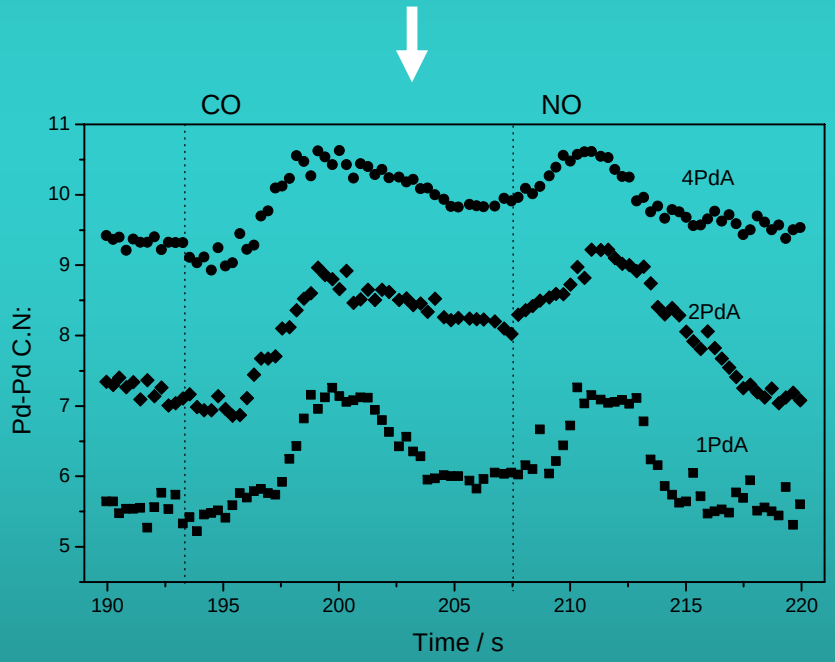
## CHEMICAL ACTIVITY OF MATERIALS

## EXAFS technique; time-resolved studies

**Pd size-dependence; cycling CO/NO at 673 K**

**EXAFS analysis assumptions**

**$\sigma^2$ constant and/or R harmonic distribution**



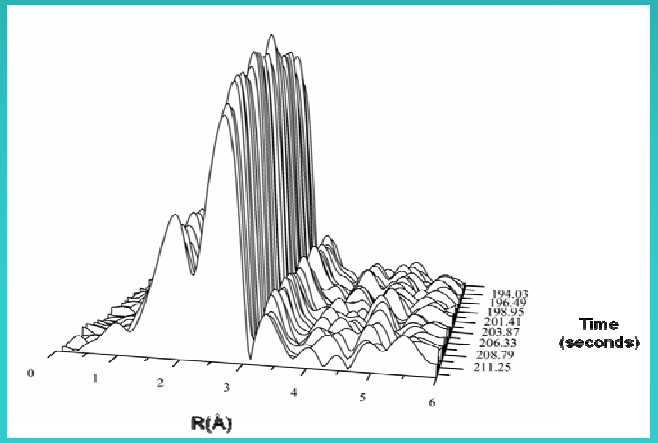

**Incorrect Information**

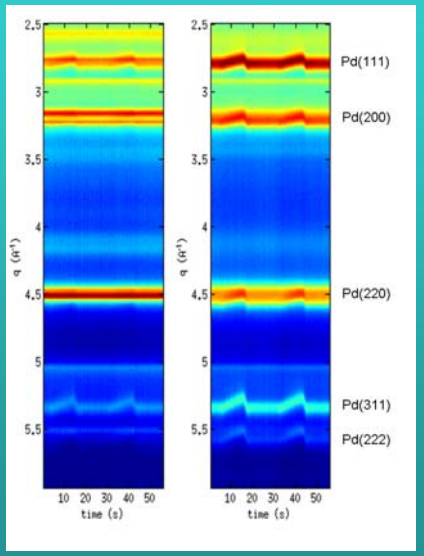
J. Am. Chem. Soc. 132 (2010) 4540

# CHEMICAL ACTIVITY OF MATERIALS

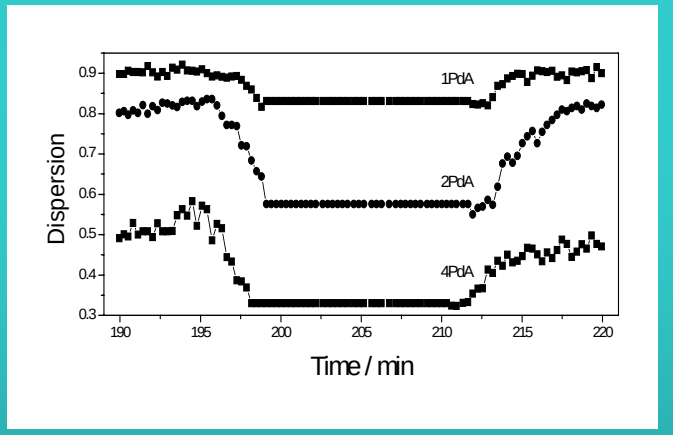
## EXAFS technique; time-resolved studies

## Pd size-dependence; cycling CO/NO at 673 K




**XAS; XRD Information**



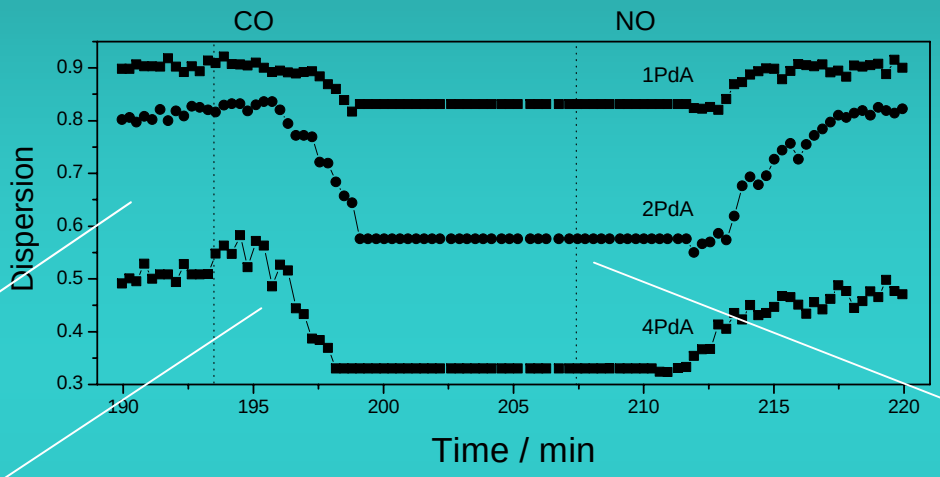

J. Am. Chem. Soc. 132 (2010) 4540

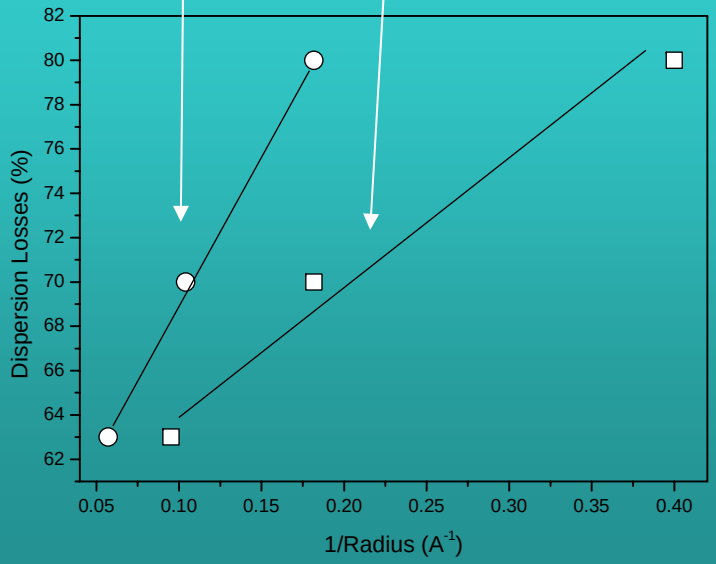
J. Catal. 270 (2010) 275

# CHEMICAL ACTIVITY OF MATERIALS

## EXAFS technique; time-resolved studies

## Pd size-dependence; cycling CO/NO at 673 K




**Dynamic Size modification**

**1/R dependence**

**Dispersion Loss Increases as Size increases**

**Phase Composition**

**Pd -> $PdC_x$**

**Size is constant**

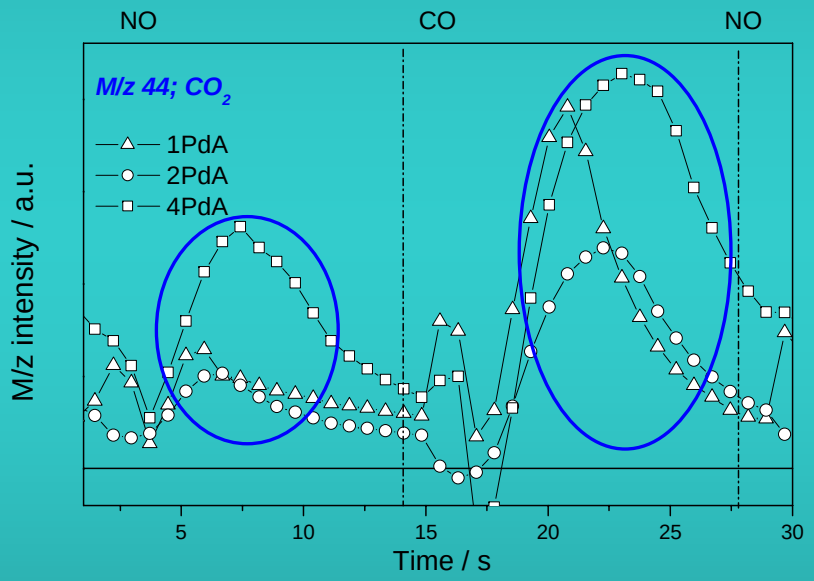
J. Catal. 270 (2010) 275

# CHEMICAL ACTIVITY OF MATERIALS

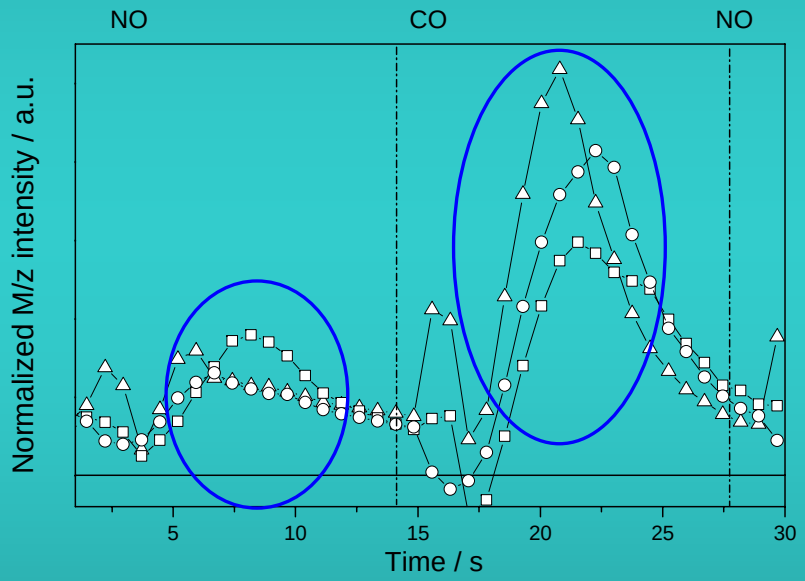
## EXAFS technique; time-resolved studies

## Pd size-dependence; cycling CO/NO at 673 K

### Raw Data




### Dynamic Dispersion




**"Dynamic" Surface Normalized**

↓

**(TOFs) "True"Activity**

J. Catal. 270 (2010) 275

# APPLICATIONS OF X-RAY SPECTROSCOPY IN CHEMISTRY

## XANES/EXAFS

Tools for dynamic structural-electronic characterization of nano-solids

## CONTROL PHASE AND MORPHOLOGY

## CHEMICAL ACTIVITY

# ACKNOWLEDGEMENTS


## Collaborators

Dr. A. Kubacka
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Dr. M.A. Newton
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ESRF; France

## XAS experiments

All staff at:

- *7.1, 9.2, 9.3 at SRS*

- *ID15, BM23, ID24, ID26, BM29 at ESRF*

- *X7B, X19A at NSLS*

## Financial sources

EU program for Large Scale Installations
Spain-MICINN (CTQ2010-14872)