Structure-Function Studies in Heterogeneous Catalysis

Marcos Fernández-García

Instituto de Catálisis y Petroleoquímica

ICP-CSIC

Energy-dispersive XAS Workshop ESRF, Grenoble, February, 2009

XAS-based Structure-Function Studies

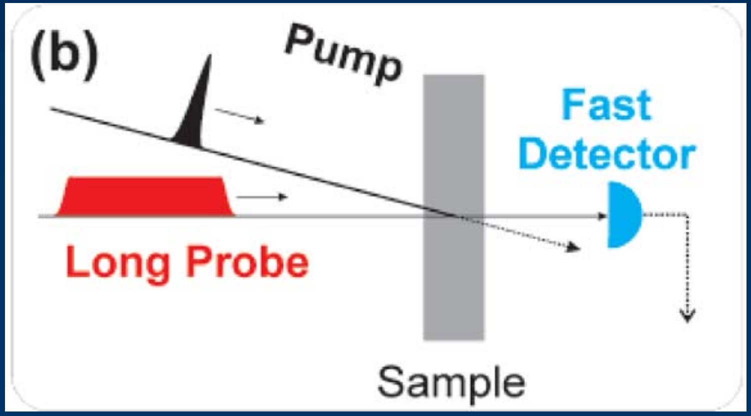
Spatial-resolved XAS

- Focal spot 50 - 100 nm; 1 x 1 μm (acquisition time; “in-situ”)

Time-dependent XAS

- Ejection, backscattering, and interference **≈ 1 fs**
- Synchrotron incident X-ray pulse **≈ 100 ps**
  Brown (J. Chem. Phys. 1999)

Pump-probe XAS



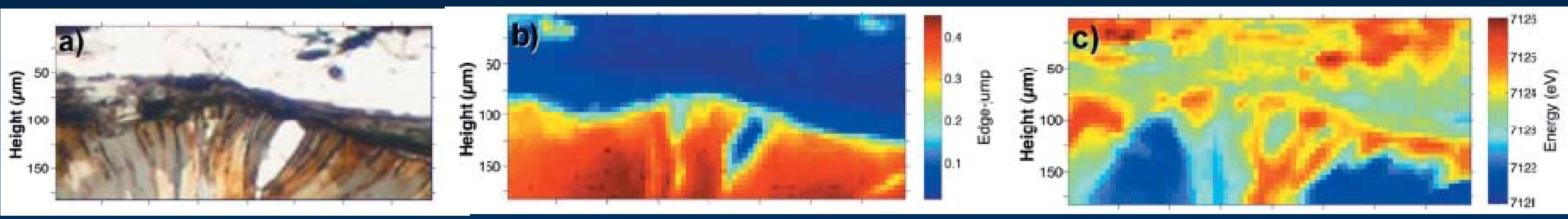
XAS-based Structure-Function Studies

Spatial resolution in XAS

- Spatial Domain

- Focal spot 50 nm (conventional) 1 µm (ED)
  10^2 nm → 2D, 3D Chemical /Structural mapping

Optical — Concentration/M — Ox. State



•*J. Synchr. Radiat. (2006) 13, 351*

- Differential technique
  Femtometre-resolution x 100 !!!!

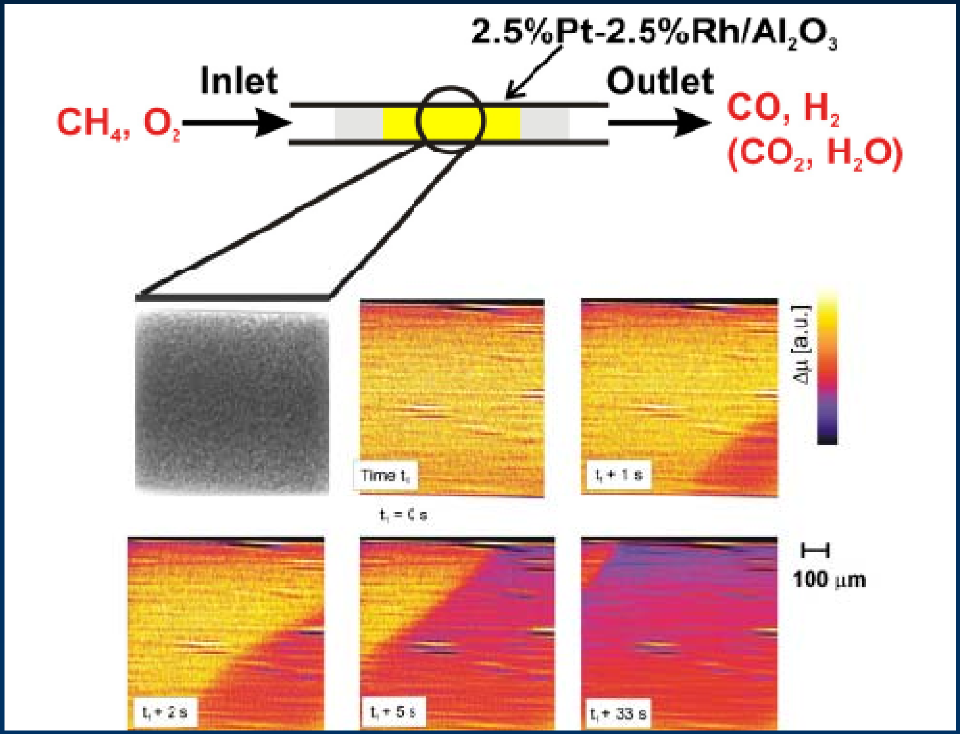
•*Nature* (2005) *435*, 78

XAS-based Structure-Function Studies

Representative examples; spatial domain

- Behavior of catalytic systems in "industrial conditions"

Spatial-time resolved XAS studies



• *Catal. Today. (2008) doi: 10.1016/jcatod.2008.11.002*

XAS-based Structure-Function Studies

Time-resolved XAS

- Time domain analyzed

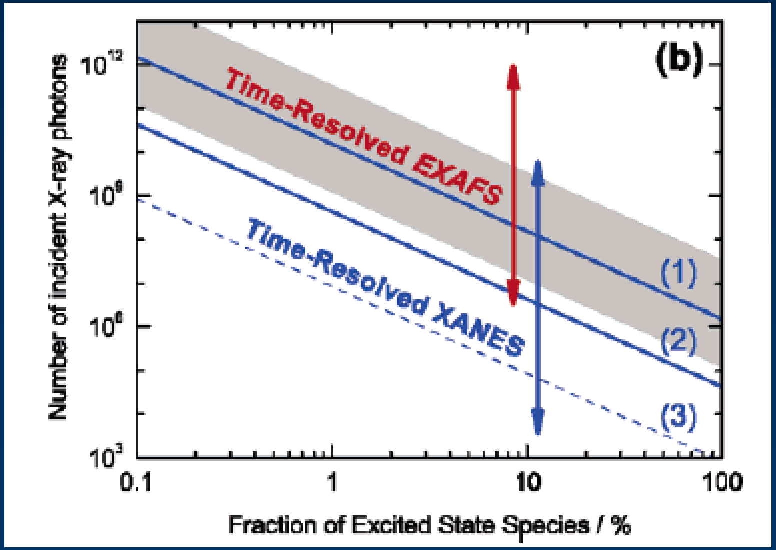
  ps/ns → h/days

  nature of the phenomenon

- Experimental set-up and procedure

  - microscopic reversibility (aging)

  - S/N ratio



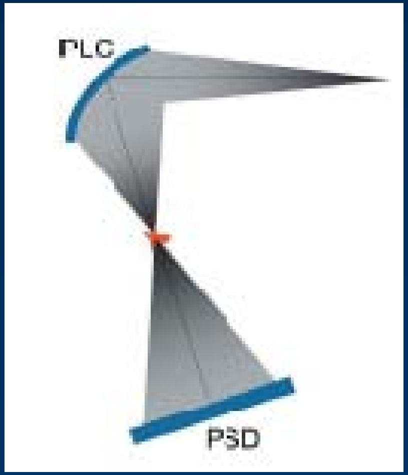
• *Bressler, Chergi, Chem. Rev. 104 (2004) 1781*

Catalysis: Time-resolved XAS

In-situ conditions (T, P; atmosphere)

XAS set-up	Time domain
"Conventional"	min to days
"Quick"	1 s to min
"Energy dispersive"	1 ms to 10 s

ED-XAS



- Absence of movement
  - Constant energy scale
  - Stable focal point / spatial resolution
  - High time resolution

- Application
  - All catalysts (0.5 wt. % NM)
  - Suitable ref. materials
  - S/N ratio limited (2^{nd} shell EXAFS)

XAS-based Structure-Function Studies

Representative examples; time domain

- Minimize "averaging" / "Instantaneous" picture chemical species

  Similar chemical species (ox. state, local symmetry)

  Short existence (intermediate)

  High number of species (4,5) ; demanding systems

  Cu-Rh/Al_2O_3

- Unique choice

  Homogeneous catalysis: exchange of ligands

  Heterogeneous catalysis: **Redox**; T- Lambda **TWCs**

TPR of Rh-Cu/Al_2O_3 CATALYSTS

Main Characteristics

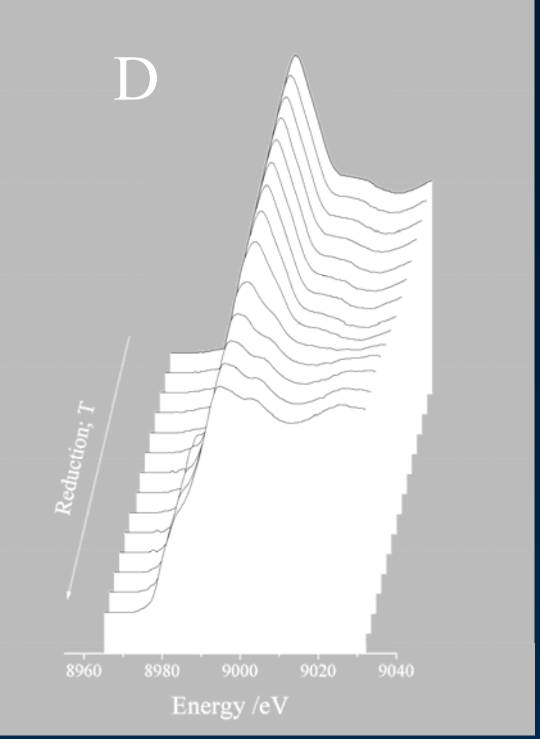
- Methane conversion (synthesis gas or higher HCs)

$$CO_2 + CH_4 \rightarrow 2CO + 2H_2$$

$$XCH_4 \rightarrow C_XH_{2X+2} + (x/2)\ H_2$$

- Cu beneficial effect:

- Interaction with the Support (Al_2O_3)
- Presence/Absence of Alloy
- Oxidation State changes under reaction

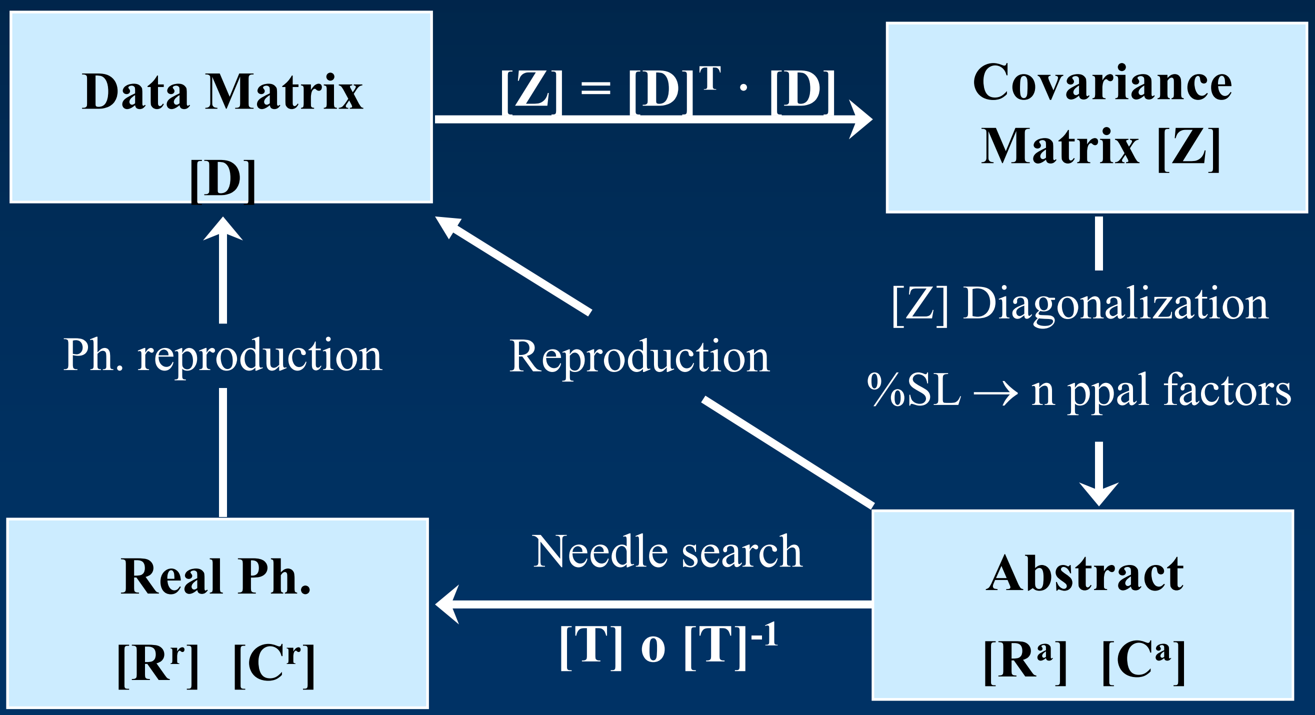


Cu/Al_2O_3 XANES-TPR: FACTOR ANALYSIS

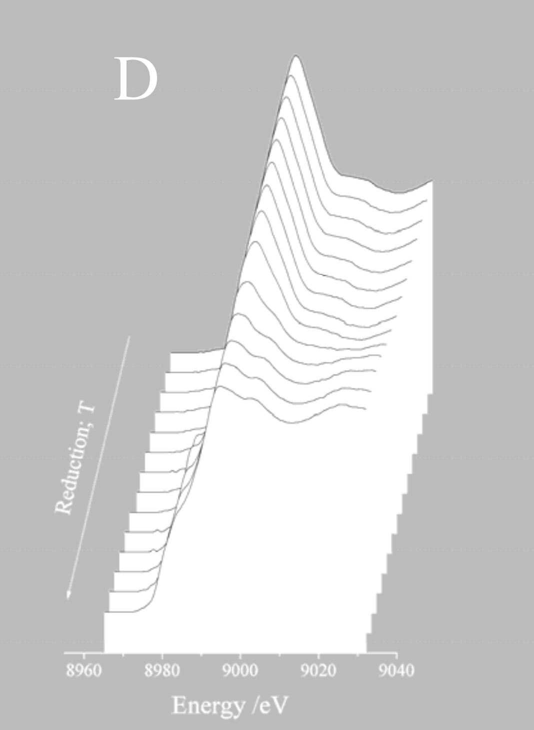
Identify and follow Chemical Species during Reaction

$$\{D\} = \sum_{i}^{n} C_i \{R_i\} + E$$

$$D = R \cdot C$$

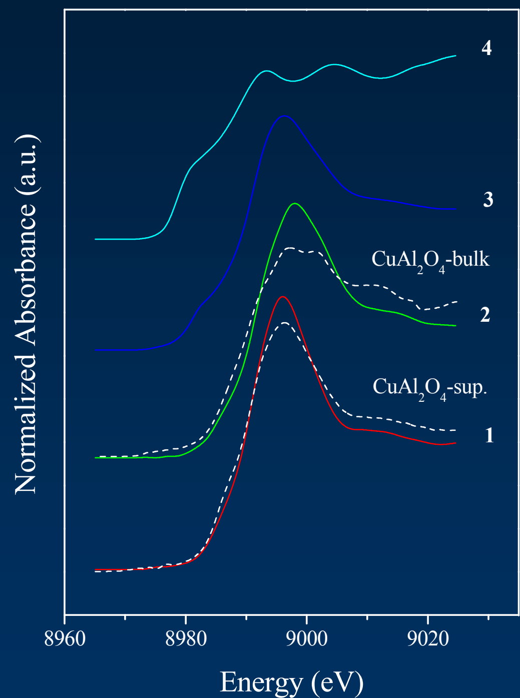


•*J. Phys. Chem. (1995) 99, 12565*

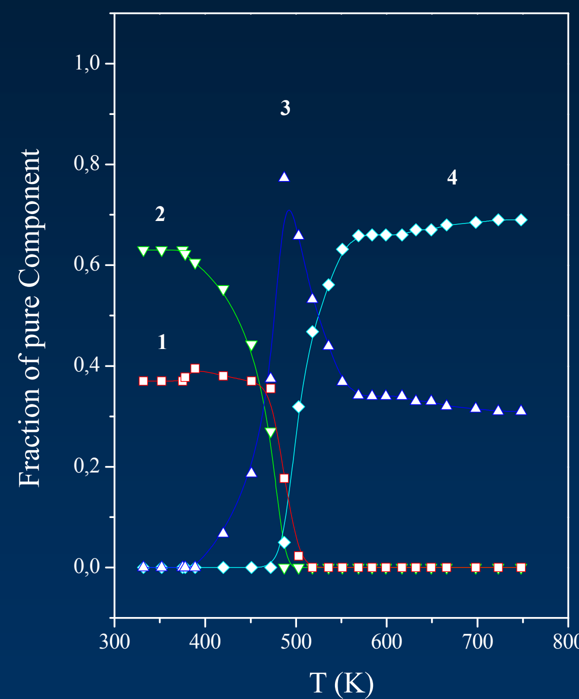


Cu/Al_2O_3 ED-XANES-TPR: Factor Analysis

[Rr]

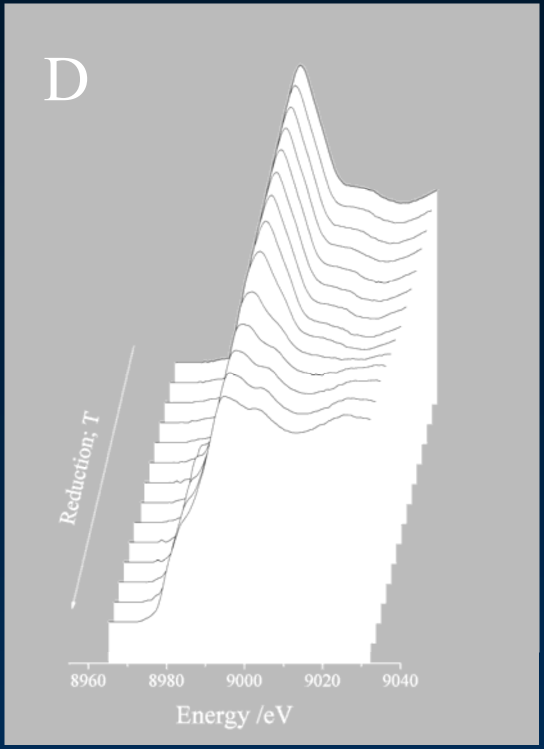


[Cr]



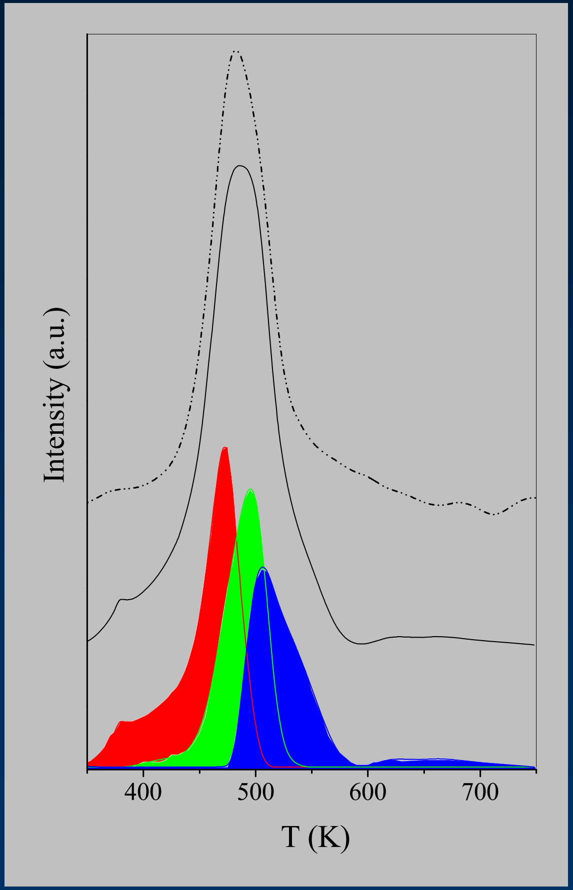
Two similar chemical phases
$CuAl_2O_4$-sup $CuAl_2O_4$-bulk
Strong (T,C) overlapping

•*J. Catal. (1998), 178, 253*



Cu/Al_2O_3 ED-XANES-TPR

H_2 consumption

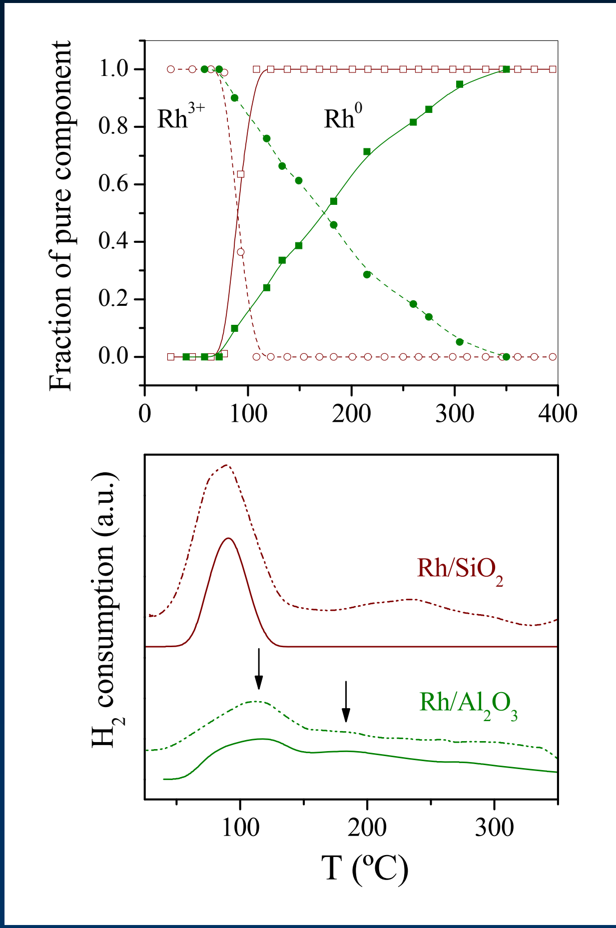


•*J. Catal. (1998), 178, 253*

Correct simulation of phys-chem observables

Rh/Al_2O_3 ED-XANES-TPR

H_2 consumption

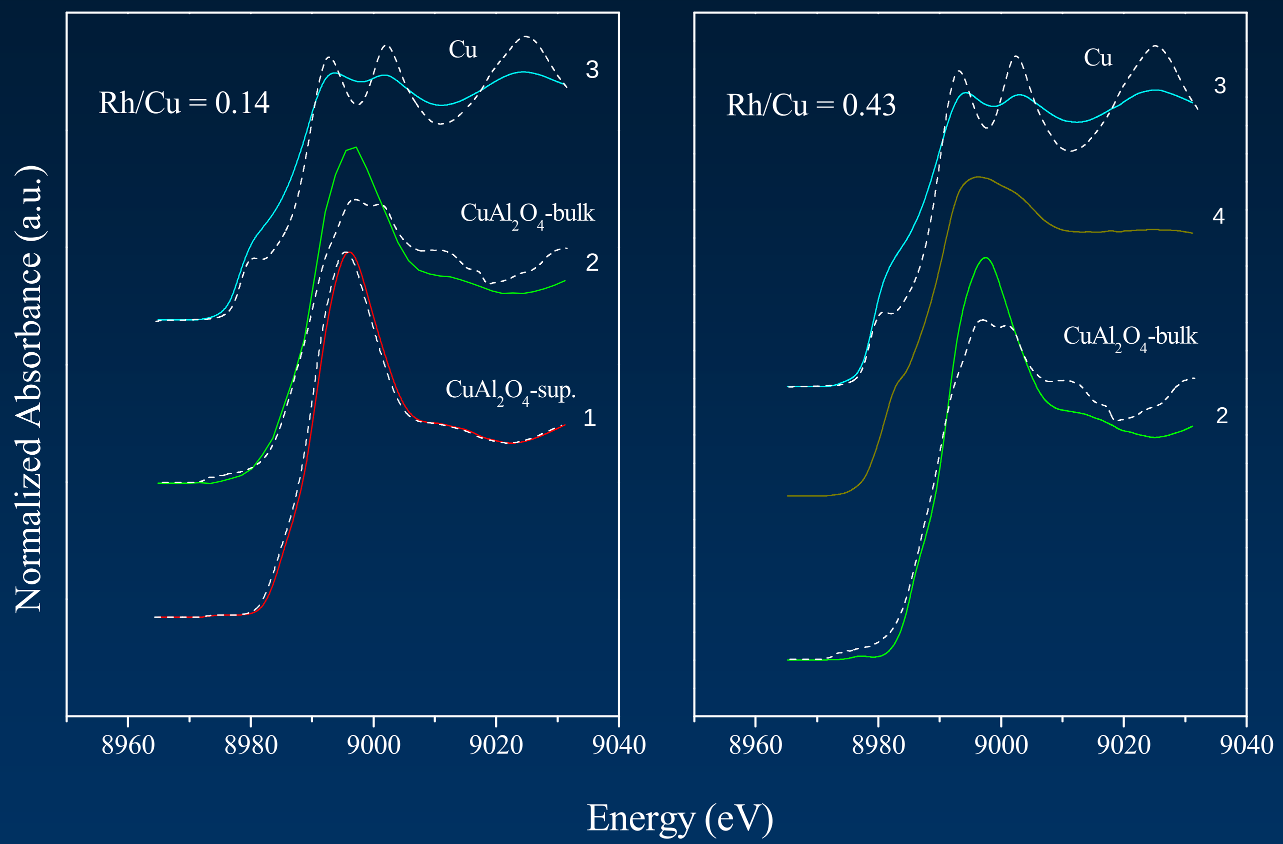


Rh-O-Al bonds; competition for alumina surface

•*Caztal. Lett. (1997), 45, 163*

Rh-Cu/Al_2O_3 ED-XANES-TPR

Cu K-edge Chemical Species



Rh/Cu > 0.15

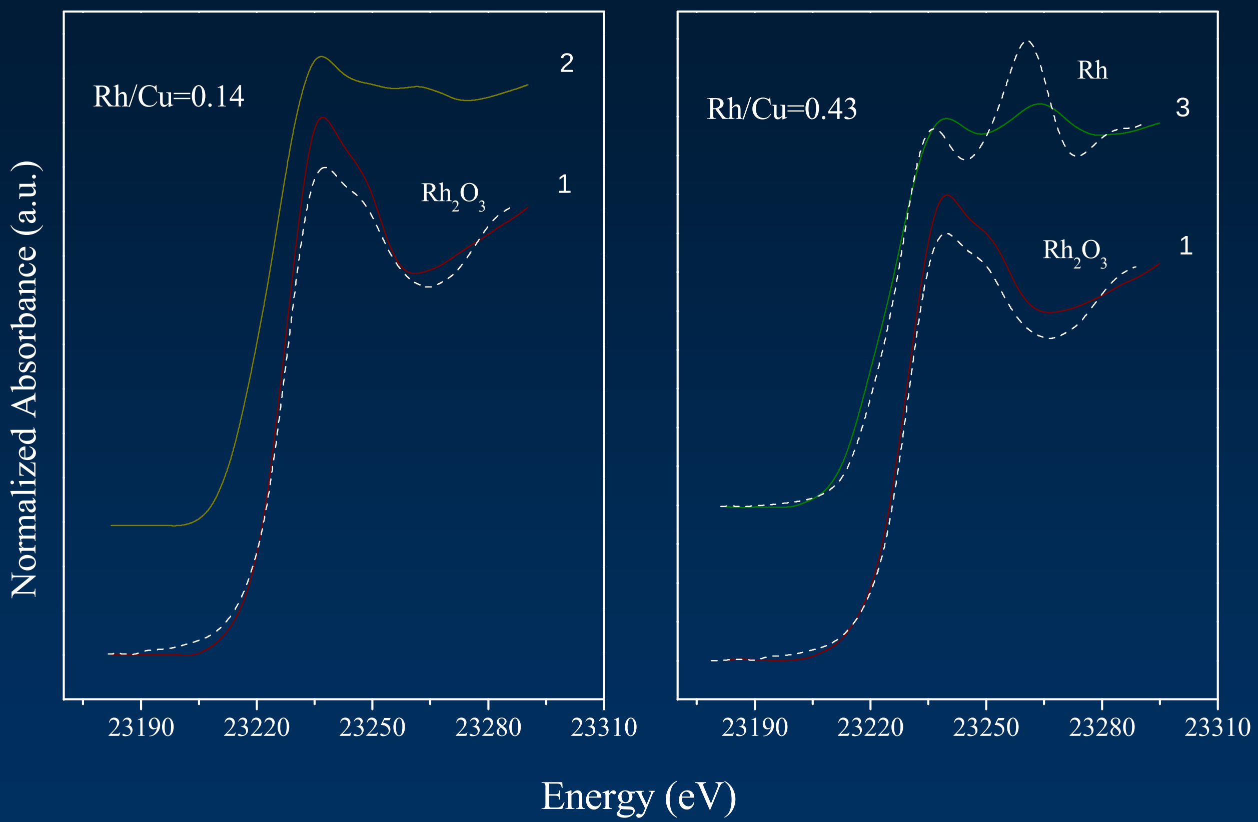
$CuAl_2O_4$-sup absent

Cu(I) intermediate

•*Langmuir. (1999), 15, 5295*

Rh-Cu/Al_2O_3 ED-XANES-TPR

Rh K-edge Chemical Species



Rh/Cu < 0.15

formation disordered FCC alloy

Rh positively charged

•*Langmuir. (1999), 15, 5295*

CO_2 Dry Reforming Activity x 3

M-Ce MIXED OXIDES

Main Characteristics

- Chemistry dominated by interface effects between M / Ce species

Mixed oxides; modulation redox activation

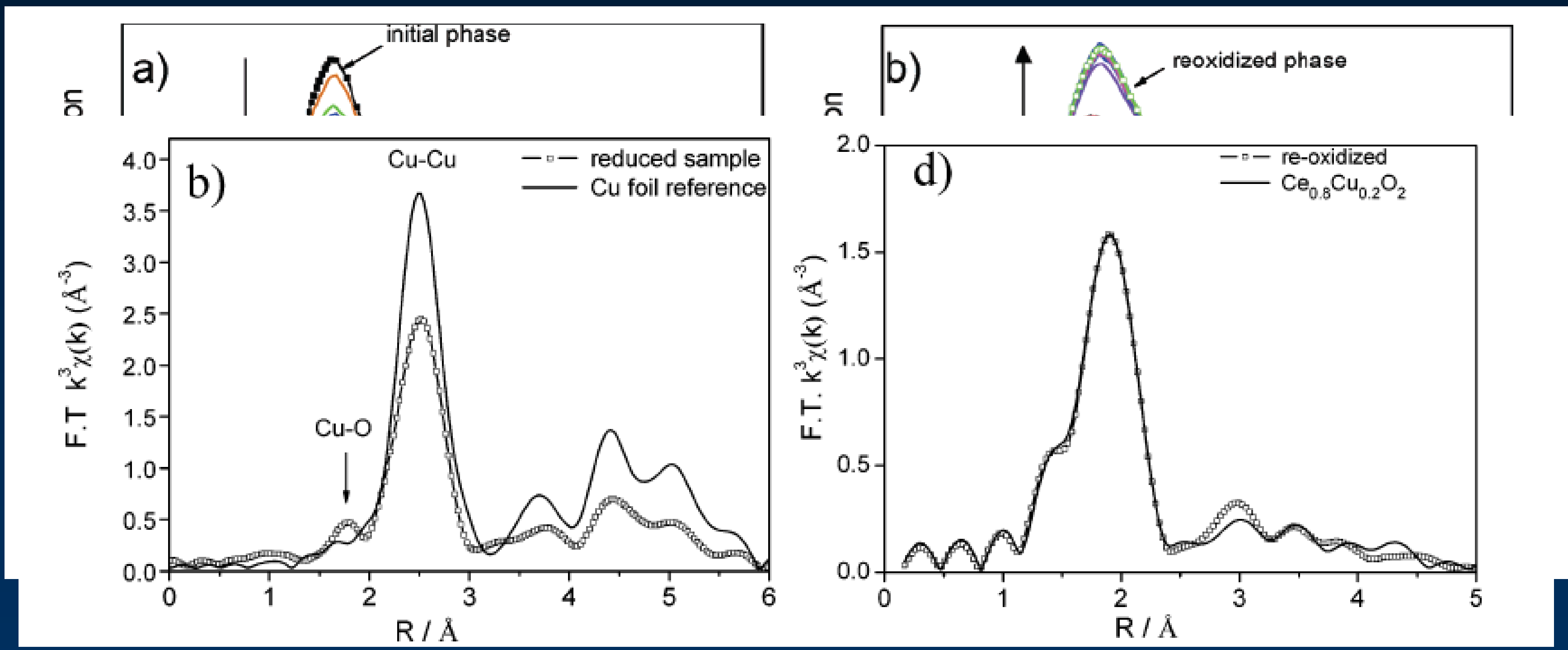
- **Cu-Ce:** Chemical activity

WGS: $CO + H_2O \rightarrow CO_2 + H_2$

CO-PROX: $CO + O_2 (H_2) \rightarrow CO_2$

Cu-Ce MIXED OXIDES

Cu K-edge: Redox Chemistry



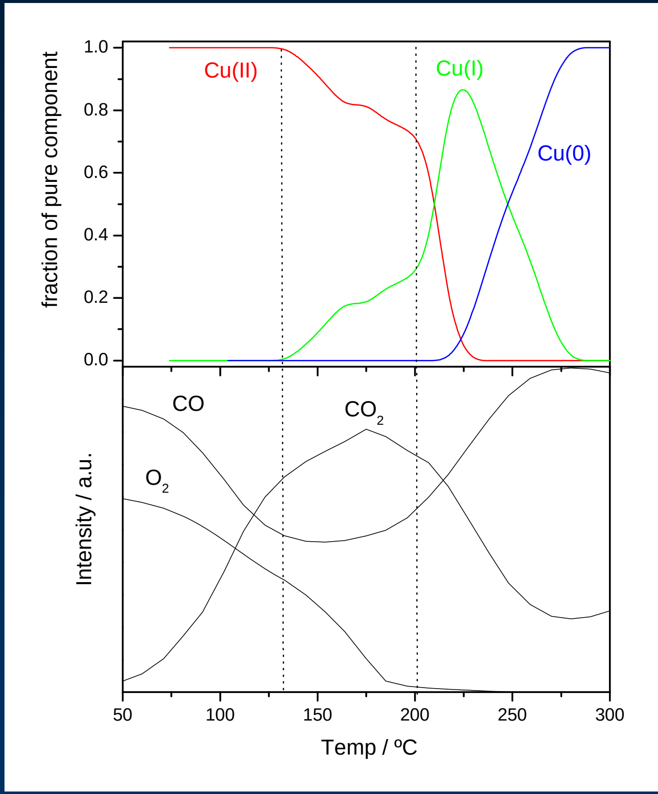
Cu(II)-Ce(IV) Fluorite Network ⇄ Cu(O)//CeO_x Binary system

•*J. Phys. Chem. B. (2005), 109, 19595*

Cu-Ce MIXED OXIDES

CO-PROX; Dependence on Cu Chemical State

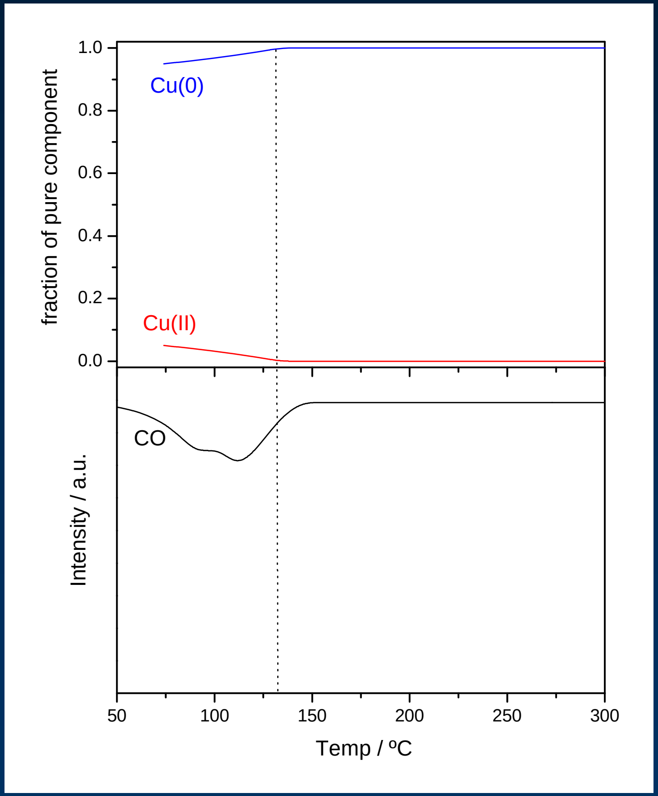
Cu-Ce Fluorite Network



Active System

Cu(I)-Ce(IV) Interface

Cu(0)//CeO_x Binary system



No Active System

Cu(0)

•*J. Am. Chem. Soc. (2007), 129, 12054*

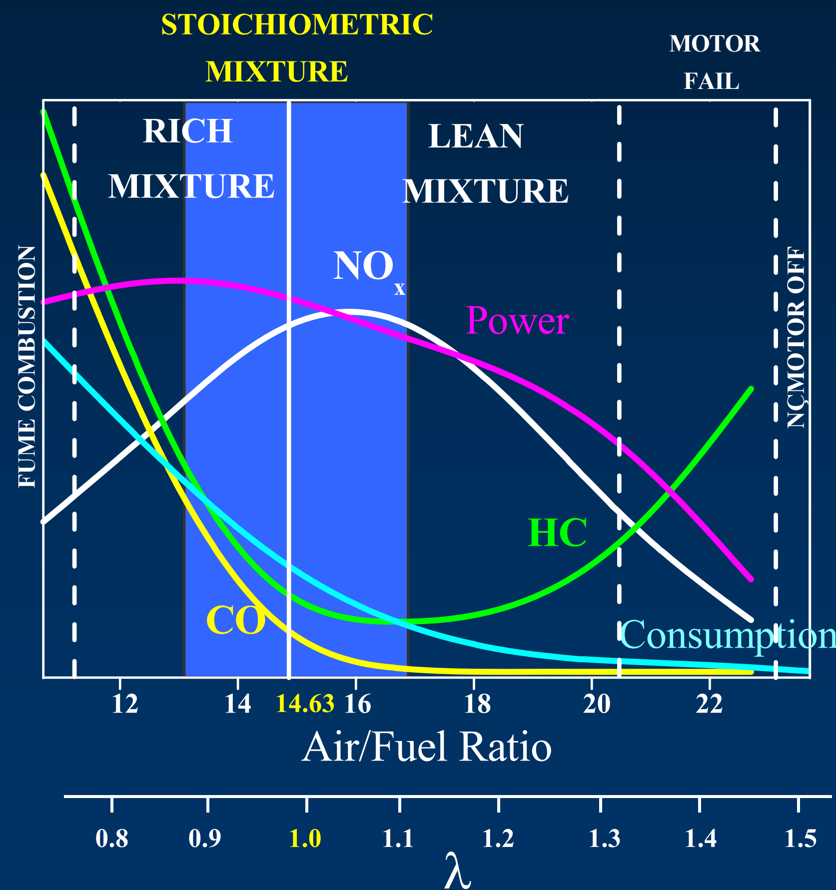
CONTROL OF POLLUTANTS EMISIONS FROM AUTOMOBILES

The main pollutants from automobile engines are CO, HC and NO

The nature and amount of the emissions vary as a function of air-fuel (A/F) ratio in the engine.

Petrol engines working with stoichiometric A/F mixtures

THREE WAY CATALYSTS (TWCs)



$$\lambda = \frac{A/F}{A/F \text{ stoichiometric}}$$

THREE WAY CATALYSTS (TWCs)

Main Characteristics

- Zr-Ce Component

  $(Zr,Ce)O_x$, Zr/Ce≈1 → higher OSC and durability.

- Pd-based system

  Substitution of Rh CO, HC oxidation (low temperatures)
  NO elimination

- Dynamic behavior and thermal degradation

  Temperature/Lambda Cycling

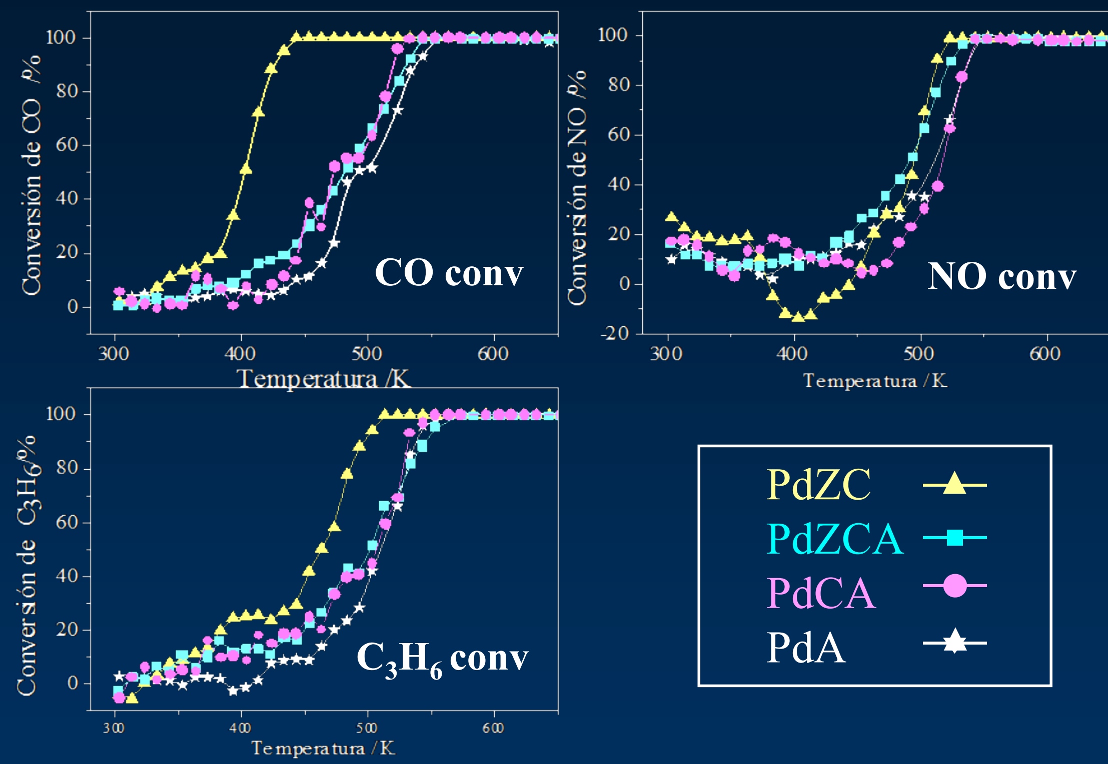
MULTITECHNIQUE APPROACH

Redox and structural behavior

Conventional and Energy dispersive

Catalytic activity: “stoichiometric-static” conditions

$C_3H_6+CO+NO+O_2$



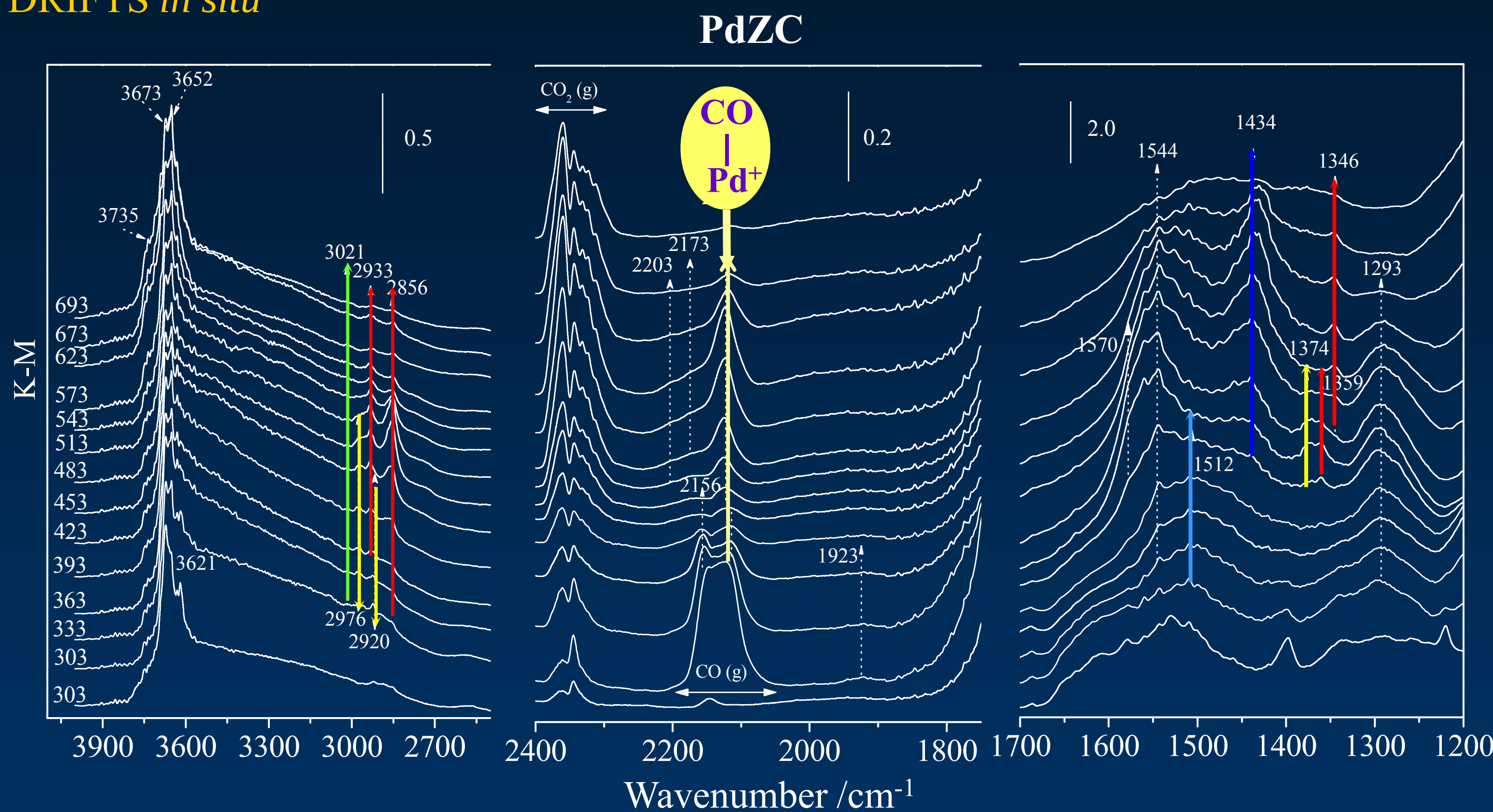
- The presence of the HC diminishes the activity for CO and NO conversion
- PdZC converts CO and C_3H_6 at lower temperatures
- PdZC also reaches 100% of NO conversion at slightly lower temperatures

•*J. Catal. (2004), 221, 594.*

Catalytic activity: "stoichiometric-static" conditions *TWC*

$C_3H_6+CO+NO+O_2$

DRIFTS *in situ*

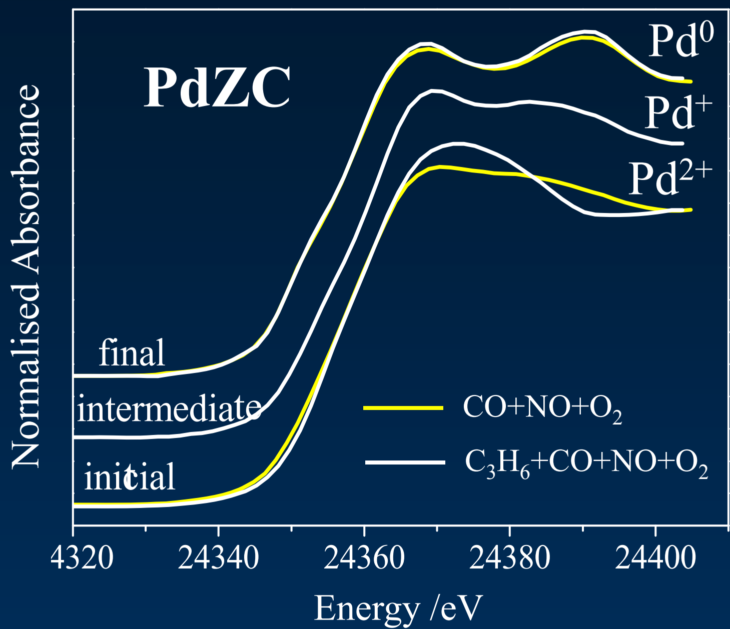


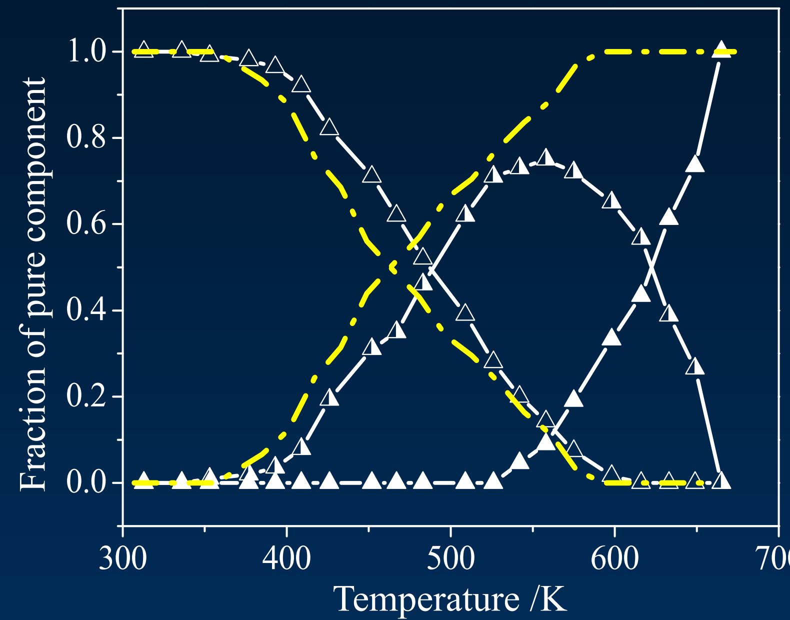
$$O - Pd^{2+} - O - Pd^{2+} - O \xrightarrow{+\,C_3H_6} O - Pd^{+} - O - Pd^{+} - O$$

$[C_3H_5^{+}]$ H^{+} $[C_3H_6]$

C_3H_6+CO+NO+O_2

XANES *in situ*





- HC presence affects Pd from RT

  Evolution to Pd^0 through an "**oxycarbide**" intermediate species, Pd^+

- HC-Pd interaction stabilises a π-allylic complex; the active species

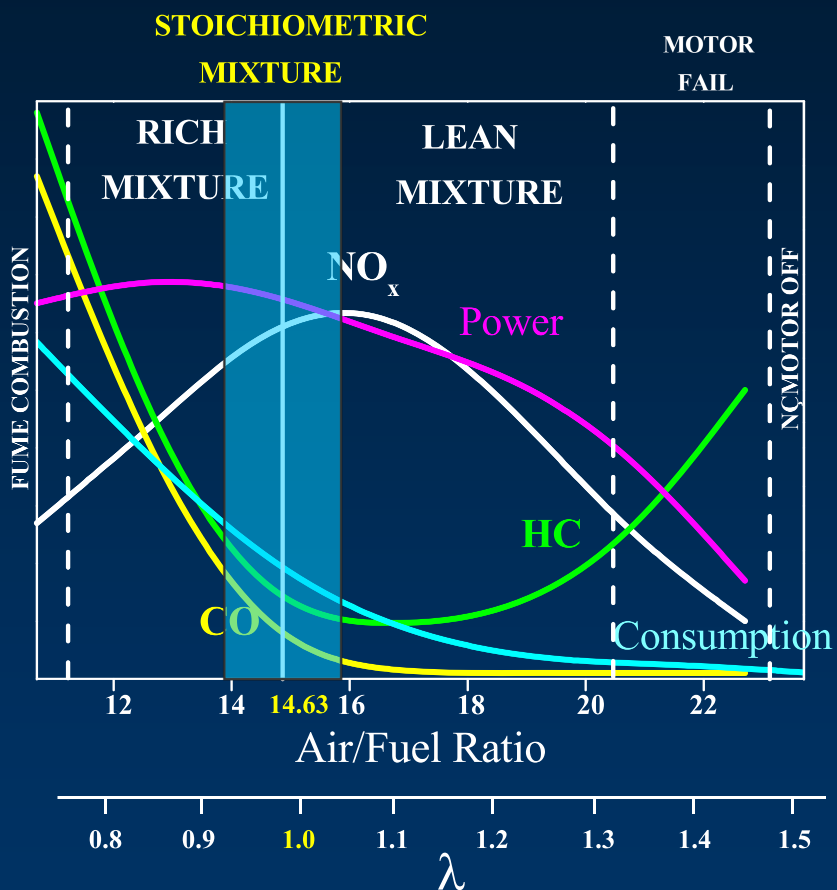
Pd-3D(Zr-Ce) contacts contribute to

- effectively eliminate the HC of the emissions from low temperatures by stabilizing partially "oxidized" Pd species

- eliminate CO/"NO" with the help of surface/bulk Pd^0 reduced species

•*J. Catal. (2004), 221, 594.*

LAMBDA OSCILLATIONS



- Rich

  CO, HC max. conc.

  Lean

  NO in presence of excess O_2

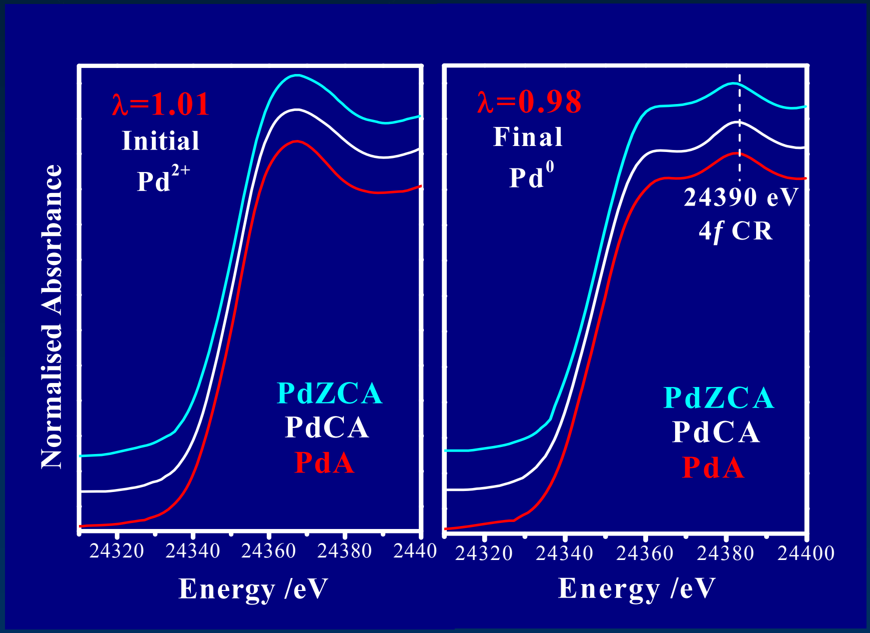
REDOX; STRUCTURAL

$$\lambda = \frac{A/F}{A/F\ \text{stoichiometric}}$$

TIME RESOLVED STUDY OF Pd REDOX BEHAVIOR UNDER OSCILLATING CONDITIONS

In situ ED-XANES

Pd K-edge results



Energy position (eV) of the edge and 4f Continuum Resonance (CR) present in XANES spectra. Values relative to the Pd foil.

Sample	Series /Condition	Edge	4*f* CR
PdA	A/lean	4.3	—
	B/rich	0.0	39.5
PdCA	A/lean	4.0	—
	B/rich	0.0	39.6
PdZCA	A/lean	3.7	—
	B/rich	0.0	37.9

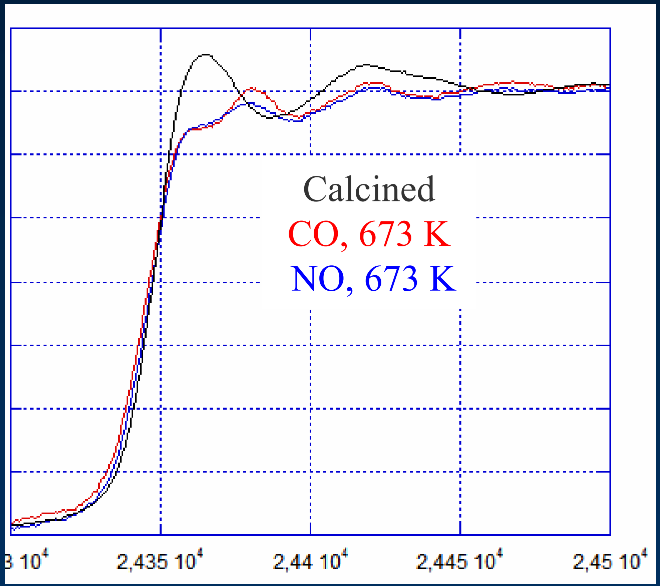
•PdZC 4*f* CR small red shift: increase of the Pd–Pd nearest distance most likely associated with the dissolution of C atoms in the Pd *fcc* structure

"Different" Oxycarbide/Carbide Chemical Phases

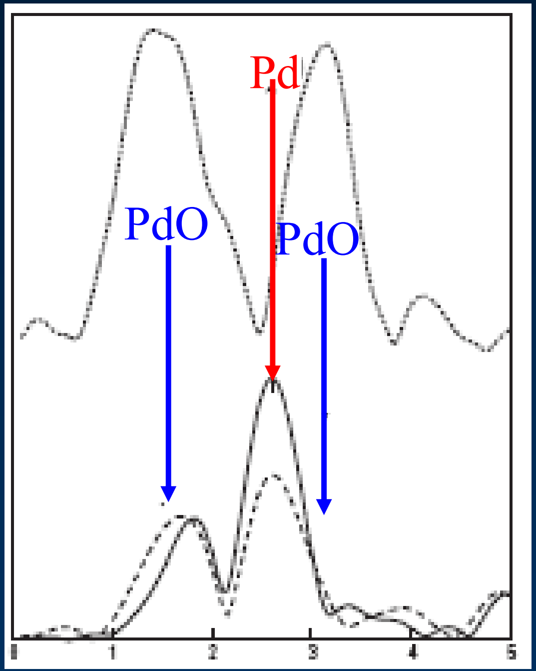
•*Chem. Commun. (2005) 2, 4092-4094*

TIME RESOLVED STUDY OF Pd STRUCTURE UNDER λ FLUCTUATIONS

ED-EXAFS (Pd K-edge) *in situ:* CO + NO



Energy /eV



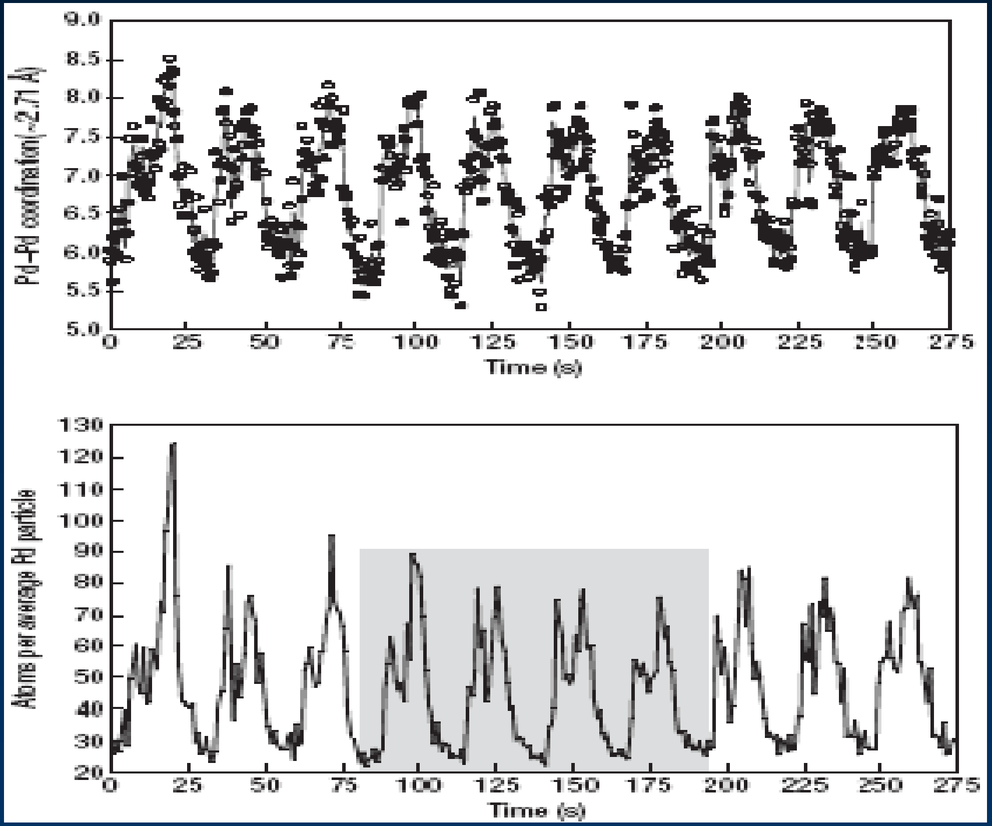
R (A)

- Combination of $Pd^0 \rightarrow PdO$ and size/shape variations

•*Nature Mater. (2007) 6, 528-532*

TIME RESOLVED STUDY OF Pd STRUCTURE UNDER λ FLUCTUATIONS

ED-EXAFS (Pd K-edge) *in situ:* CO + NO

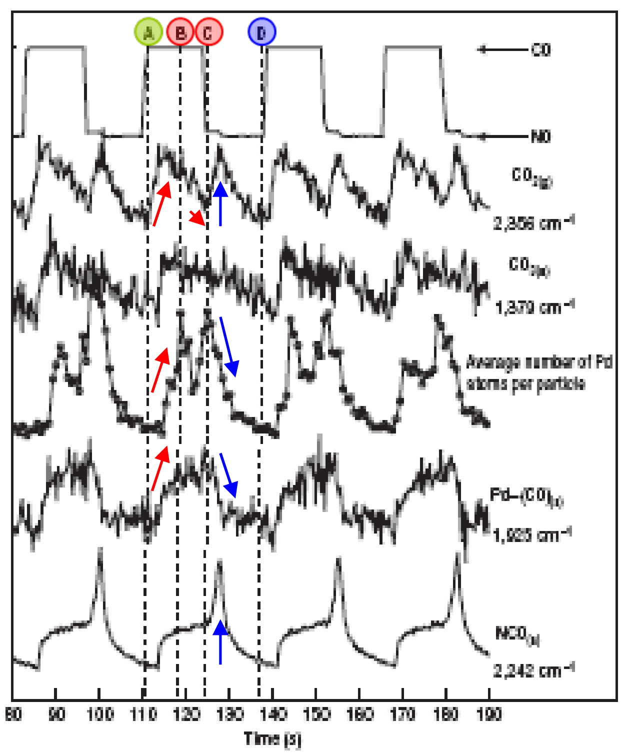


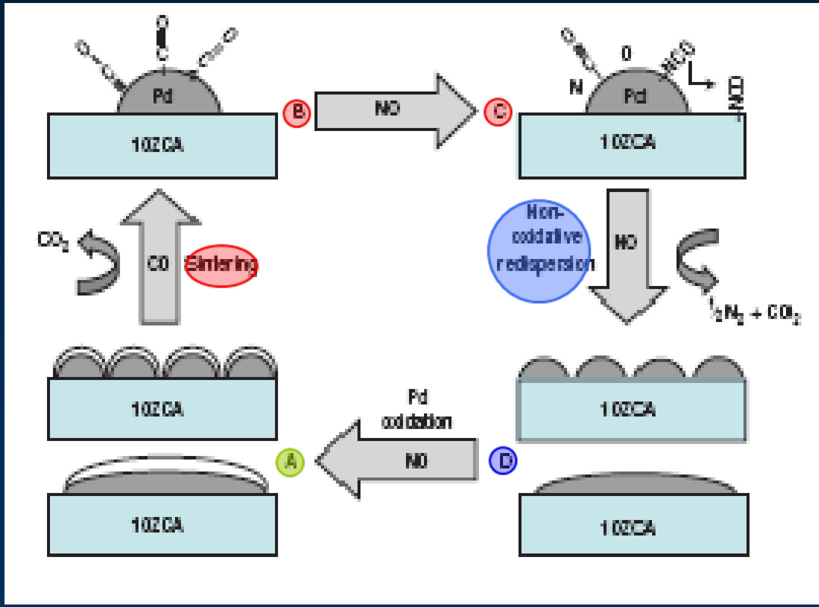
- **Strong and reversible** structural modification under Lambda Oscillations

Particles from 30 to 70 NM atoms

TIME RESOLVED STUDY OF Pd STRUCTURE UNDER λ FLUCTUATIONS

Synchronous ED-EXAFS and IR: CO + NO



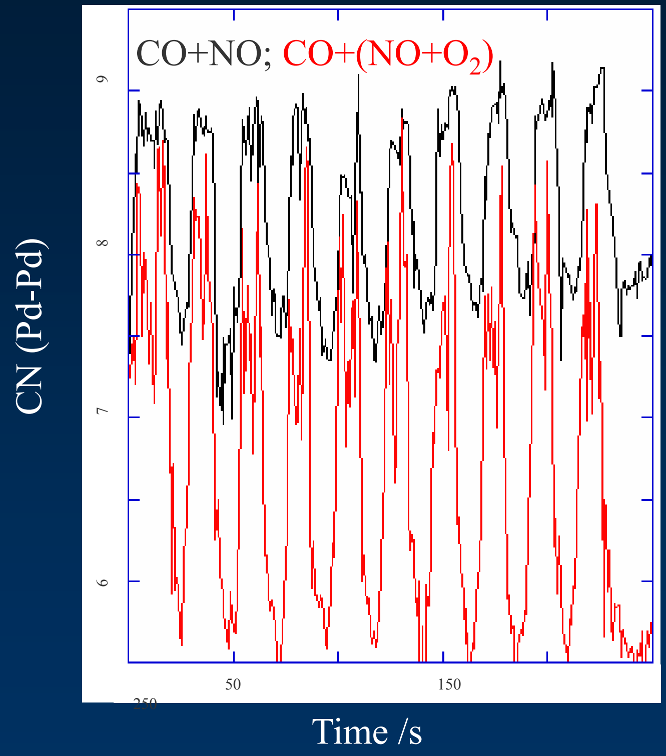


- **Dynamic surface-bulk NM changes** during operation

•*Nature Mater. (2007) 6, 528-532*

TIME RESOLVED STUDY OF Pd STRUCTURE UNDER λ FLUCTUATIONS

ED-EXAFS (Pd K-edge) *in situ:* CO + NO + O_2



- **Strong and reversible** structural changes under Lambda Oscillations

O_2 enhanced phenomenon

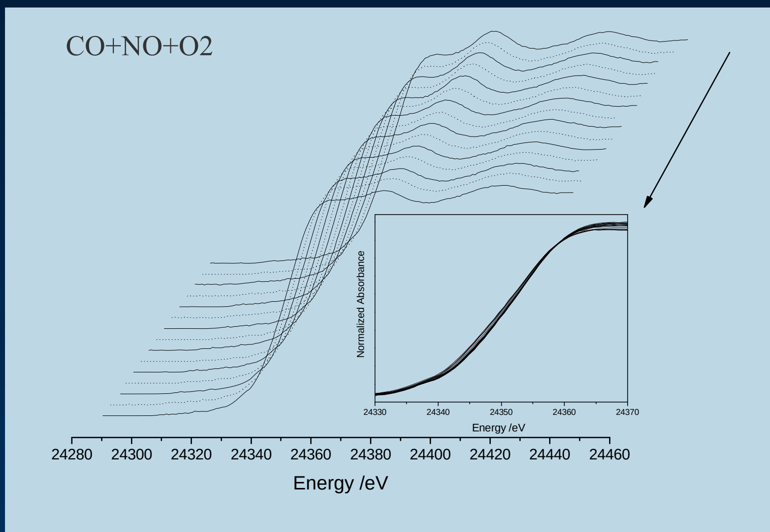
Aggregated state under CO: similar

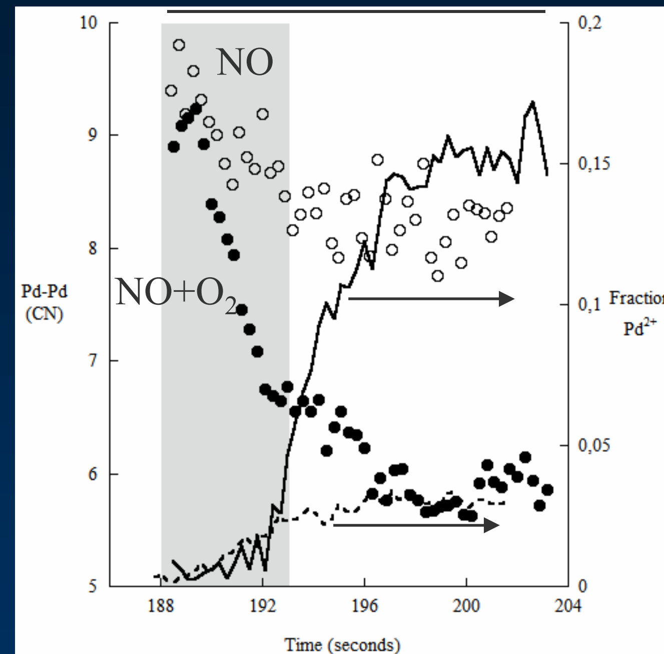
Dispersed state under Ox. Conditions: O_2-promoted

• *Angew. Chem. Int. Ed. (2007) 46, 8629-8631*

TIME RESOLVED STUDY OF Pd STRUCTURE UNDER λ FLUCTUATIONS

ED-XAS (Pd K-edge XANES/EXAFS) *in situ:* CO + NO + O_2



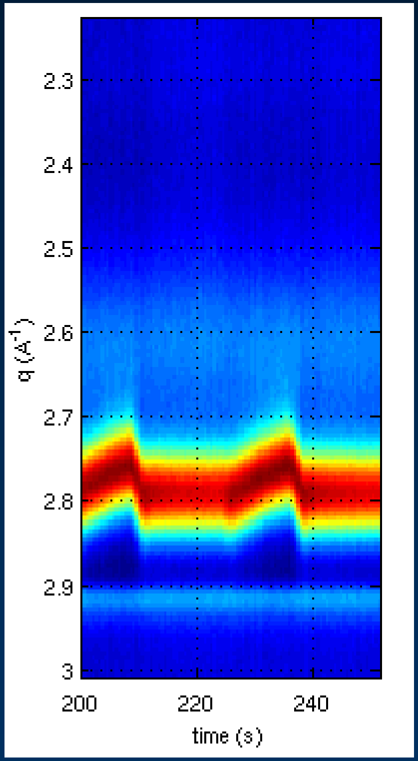


- **Non-oxidative redispersion** enhanced in presence of oxygen

• *Angew. Chem. Int. Ed. (2007) 46, 8629-8631*

SYNCHRONOUS TIME-RESOLVED MULTI-SPECTROSCOPIC STUDY

High Energy XRD



- **Dynamic surface-bulk NM structural: size, shape, lattice**
- **Dynamic redox changes**

Catalytic Activity

Energy-dispersive XAS

Future challenges

- Spatial Domain (time efficiency)

    - 2D, 3D Chemical /Structural nano-mapping
    - Angstrom/Sub-angstrom resolution

- Time Domain

    - Gas-solid
    - Light-solid

    Solid elemental process kinetics (µs)

Opening Novel perspectives in Catalysis

- Nucleation and growth of nano-phases
- Dynamic of radiation-mater (photocatalysis)
- "Operando" analysis of TON (10^4-10^6 s^{-1})

ACKNOWLEDGEMENTS

Collaborators

-Dr. M. A. Newton

-- Dr. M. Di Michel

- Dr. A. Iglesias-Juez

-Dr. A. Martínez-Arias

-Dr. C. Belver

- Dr. D. Gamarra

- Dr. A. Kubacka

DRIFTS experiments

- Prof. J. A. Anderson

Ce experiments

- Dr. J.A. Rodríguez
- Dr. J.C. Hanson

XAS experiments

All staff at:

-*7.1, 9.2 and 9.3 at SRS*

- *ID15, BM-29 and* ***ID-24*** *at ESRF*

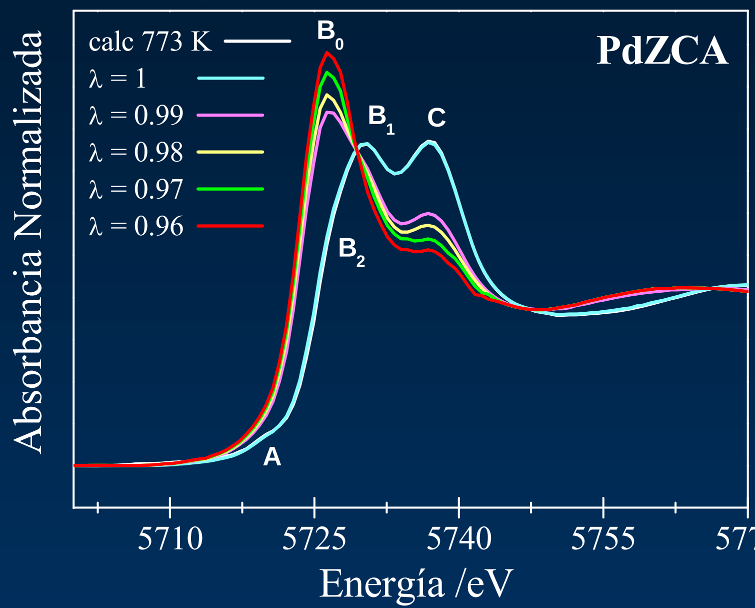
Financial sources

EU program for Large Scale Installations

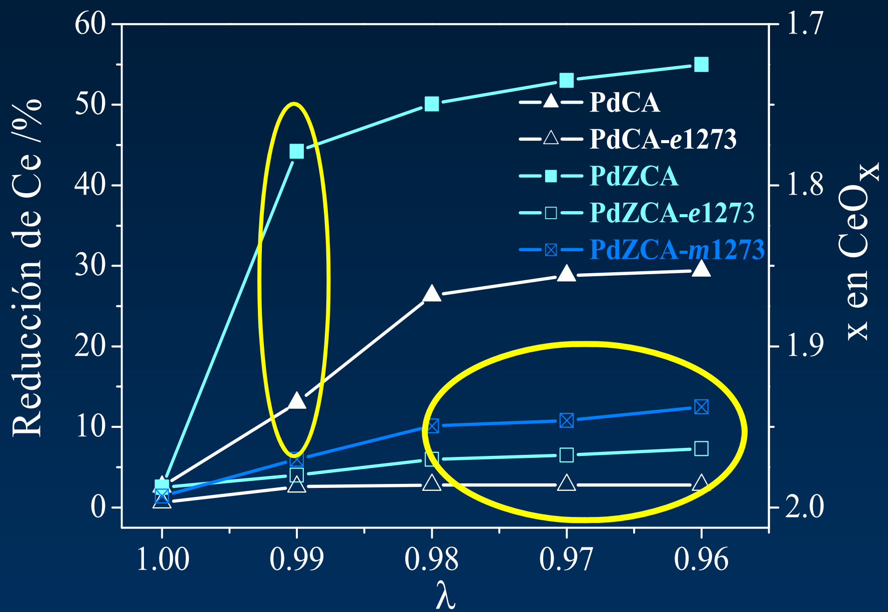
Spain-MEC (CTQ2004-3409; CTQ2006-60480)

Ce^{4+}/Ce^{3+} REDOX BEHAVIOR
Oxygen Storage Capacity

Ce L_{III} edge



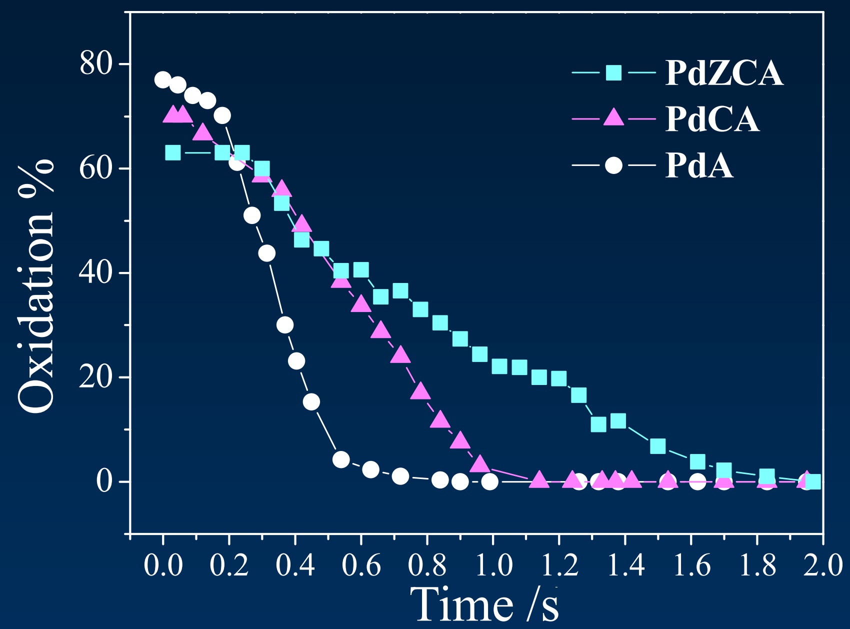
XANES *in situ*



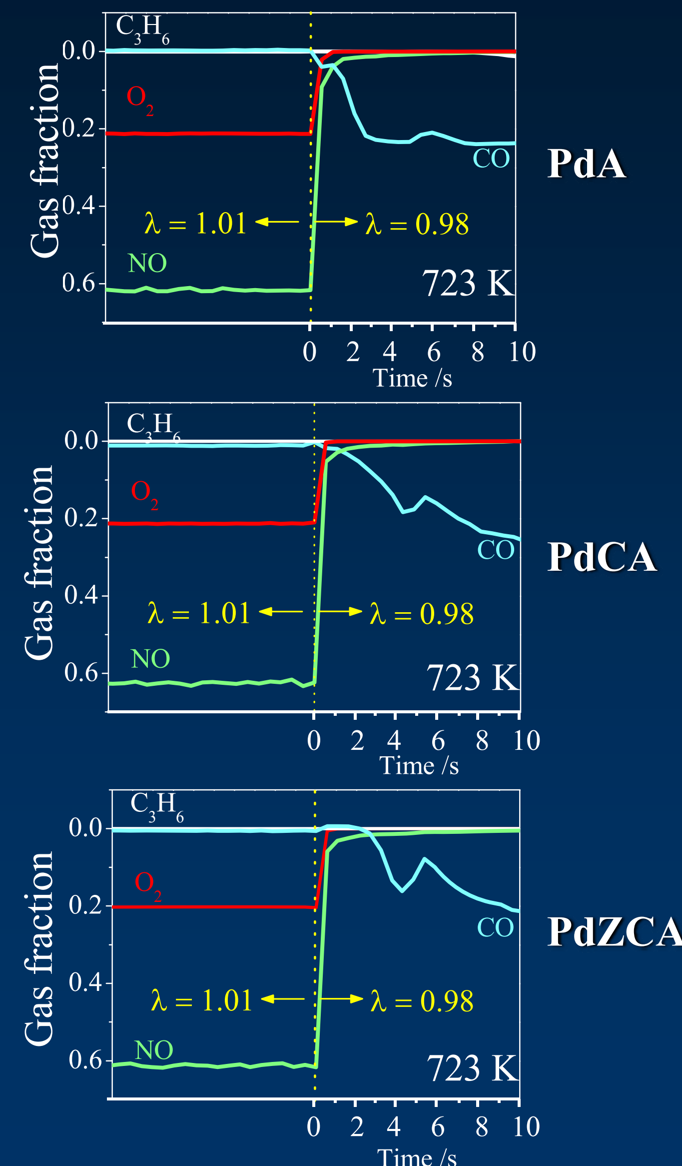
- The presence of Zr increases the oxygen storage capacity
- This occurs in fresh and aged catalysts

TIME RESOLVED STUDY OF Pd REDOX UNDER λ FLUCTUATIONS

ED-XANES (Pd K-edge) *in situ*



MS signals



- PdO → Pd^0 transformation is delayed by effect of the promoter component, especially when Zr is present

- Zr increases the amount of oxygen transferred by the promoter oxide, limiting the loss of CO conversion in reducing conditions

LAMBDA OSCILLATIONS: DYMANIC "EFFECTS"