Looking into Copper in CO-PROX Catalysts: A Multitechnique Approach

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The participants in the Projects

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Material Science Department, Univ. Cambridge, UK

Chemistry Department, Brookhaven National Laboratory, USA

10 years using $CuO\text{-}CeO_2$ catalysts

for:

- CO total oxidation with O_2 (TOX)

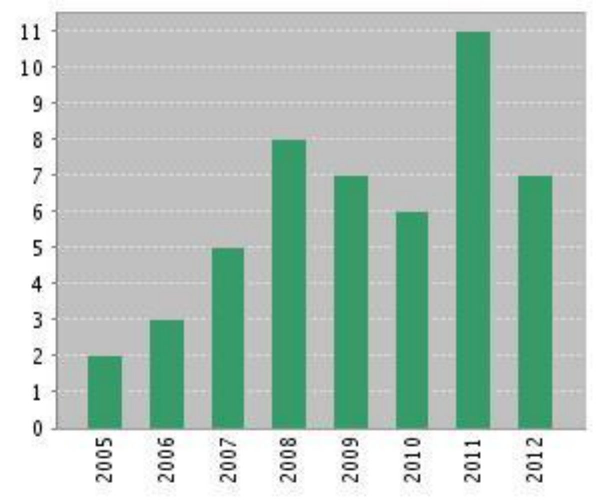
and

- CO preferential oxidation in excess of H_2 (PROX)

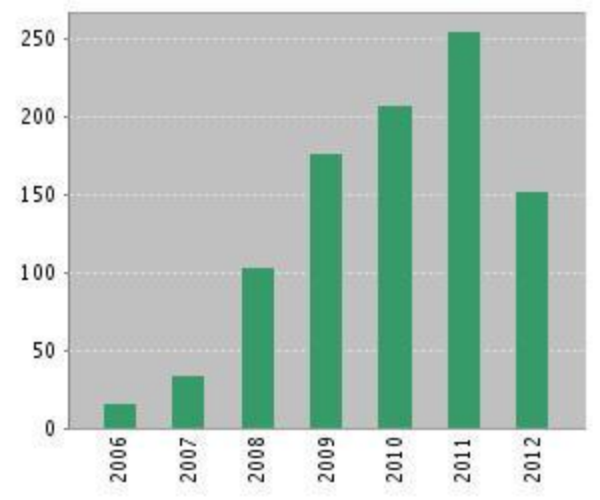
Last 10 years using CuO-CeO_2 catalysts

CO preferential oxidation in excess of H_2 (PROX)

Published Items in Each Year

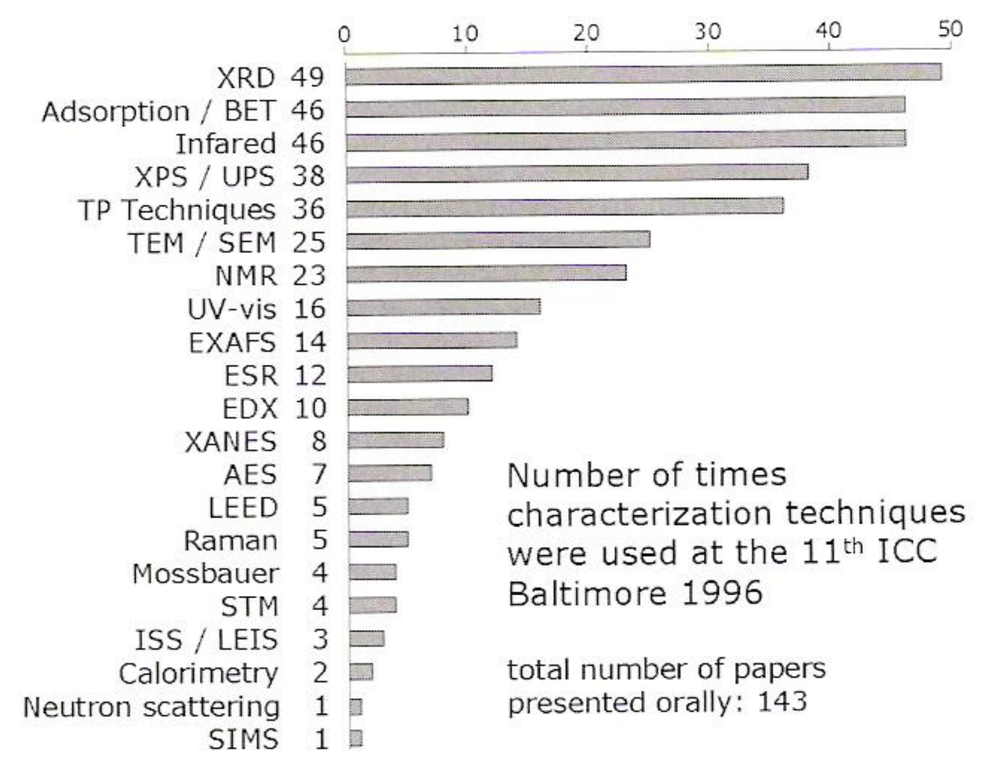


Citations in Each Year



Search: Web of Knowledge
Period: 2002-2012
Topic: "CO-PROX AND CuO AND CeO2"
Results: 49 references
Impact: h-index = 17 (cites/item =19.22)

Looking into Copper in CO-PROX Catalysts: A Multitechnique Approach

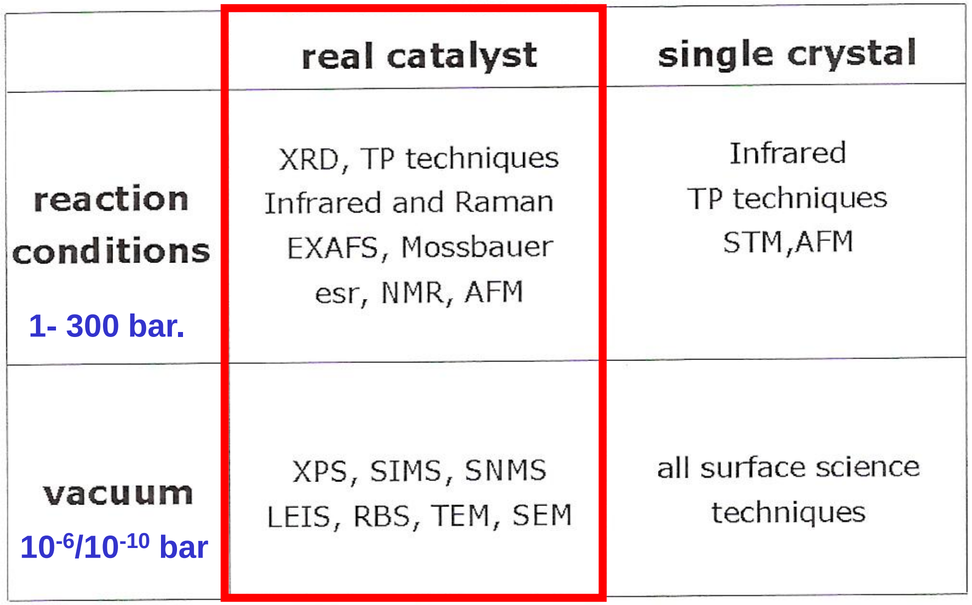


Number of times characterization techniques were used at the 11th ICC Baltimore 1996

total number of papers presented orally: 143

Catalysis: An integrated Approach to Homogeneous, Heterogeneous and Industrial catalysis
J.A. Moulijn, P.W.N.M. Leeuwen, R.A. van Santen,1993

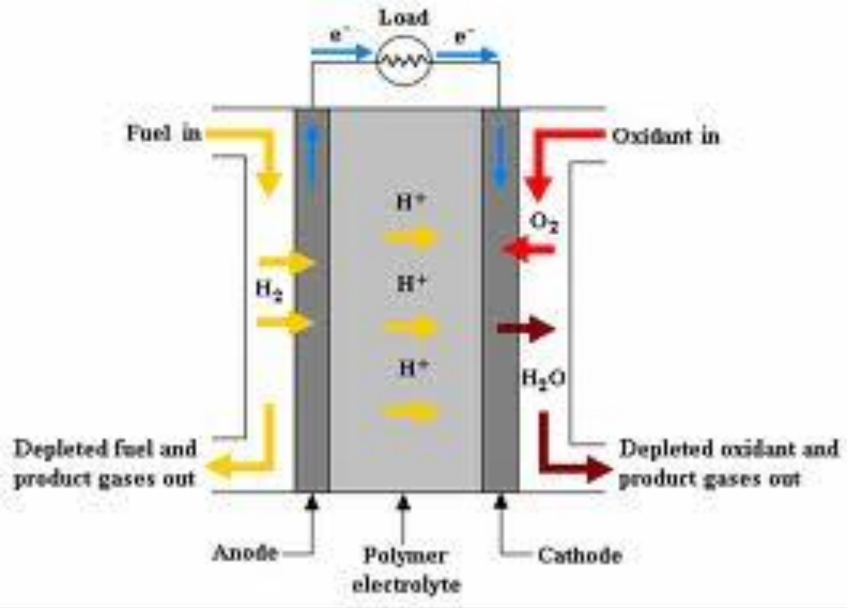
Characterization tecniques used in Catalysis



	real catalyst	**single crystal**
reaction conditions **1- 300 bar.**	XRD, TP techniques Infrared and Raman EXAFS, Mossbauer esr, NMR, AFM	Infrared TP techniques STM,AFM
vacuum **10^{-6}/10^{-10} bar**	XPS, SIMS, SNMS LEIS, RBS, TEM, SEM	all surface science techniques

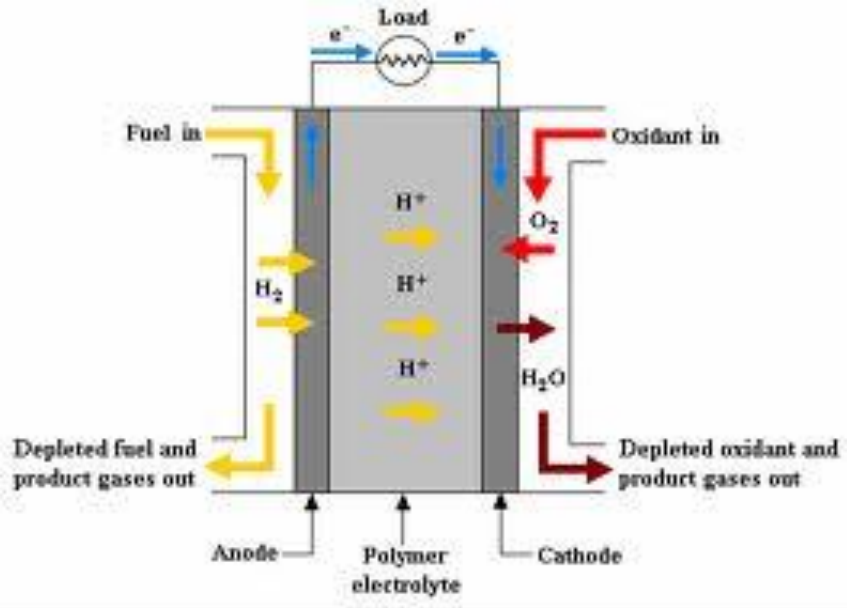
- The *"operando"* techniques
- The *"pressure gap"* debate

Catalysis: An integrated Approach to Homogeneous, Heterogeneous and Industrial catalysis
J.A. Moulijn, P.W.N.M. Leeuwen, R.A. van Santen, 1993



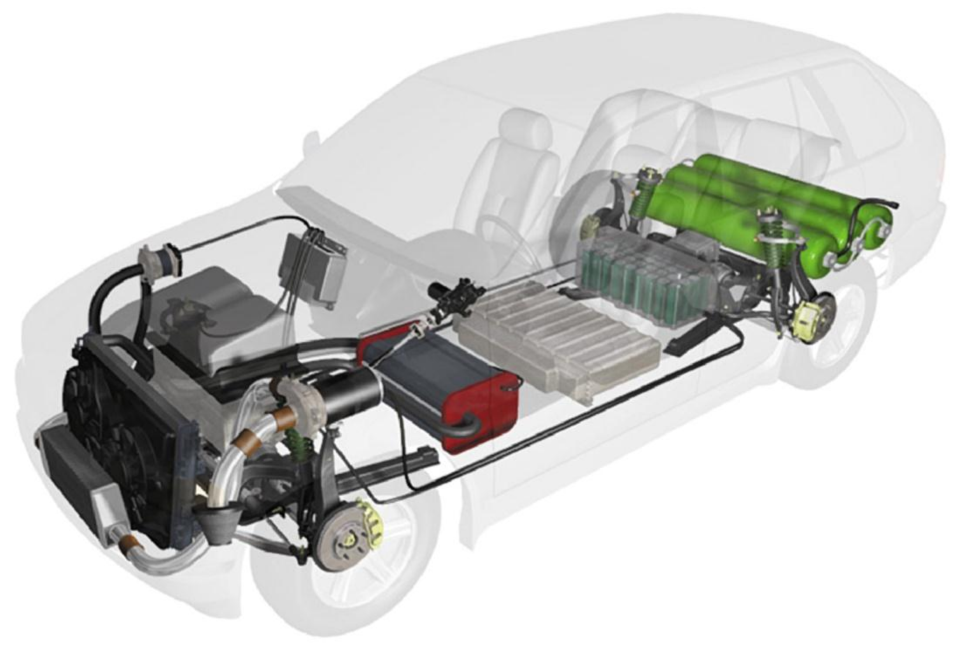
Proton Exchange Membrane Fuel Cell unit

Industrial Aplications

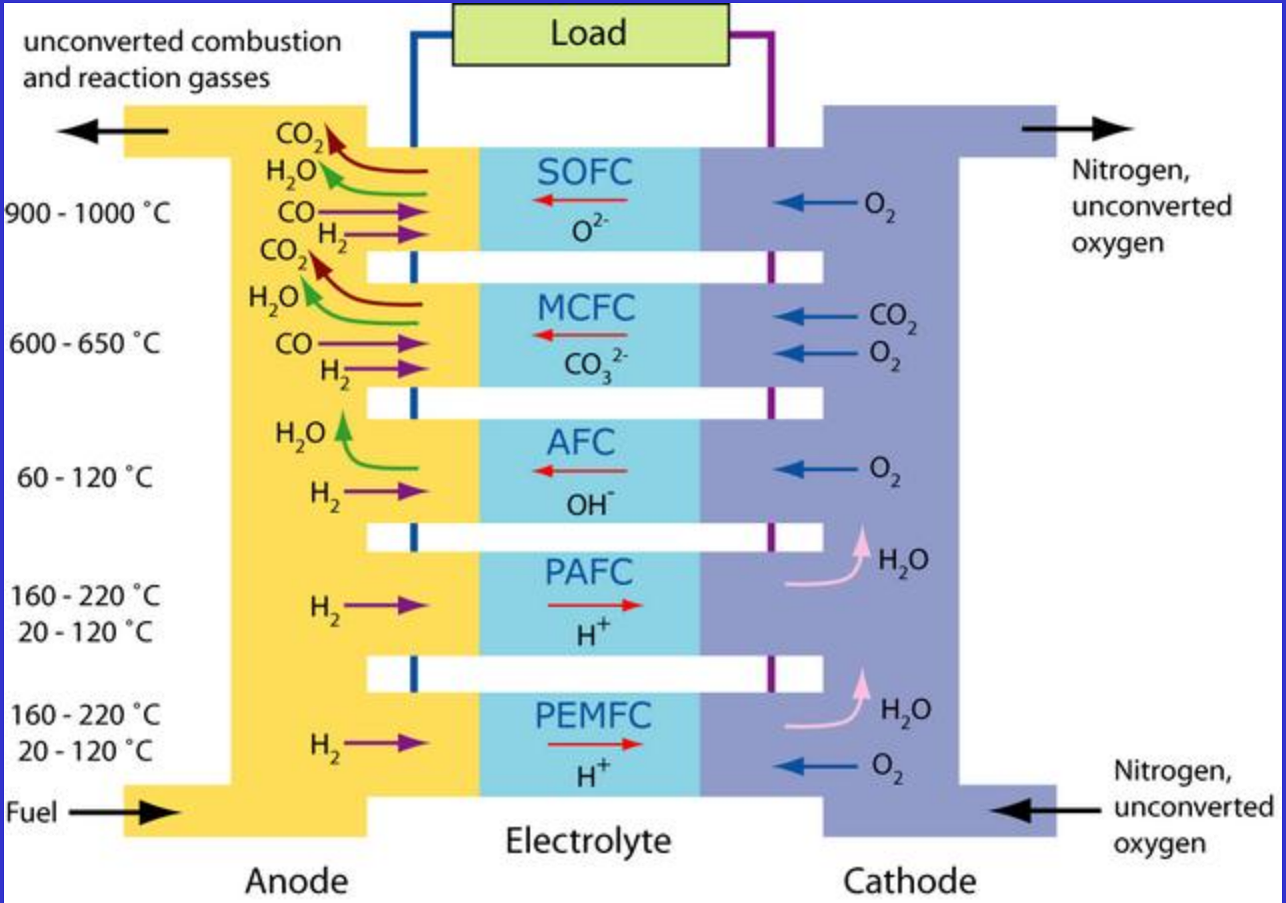


Proton Exchange Membrane
Fuel Cell unit

Hydrogen Powered
automotives



Fuel Cells: From PEMFC to SOFC electrolytes



PEMFC : Proton Exchange Membrane Fuel Cell
SOFC: Solid Oxide Fuel Cell

H_2 generation from HC's for its use in PEMFC

HC

H_2O

Steam Reformer

10 % CO

HT-WGS

3 % CO

LT-WGS

0.5 % CO

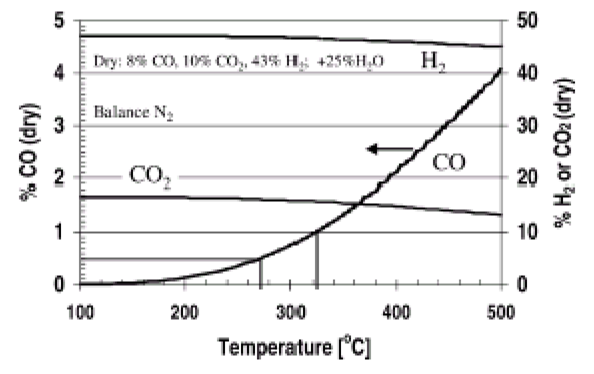
PROX

<100 ppm CO

PEMFC

45-75 % H_2 + 0.5-2 % CO + 15-25 % CO_2 + few % H_2O + HC traces

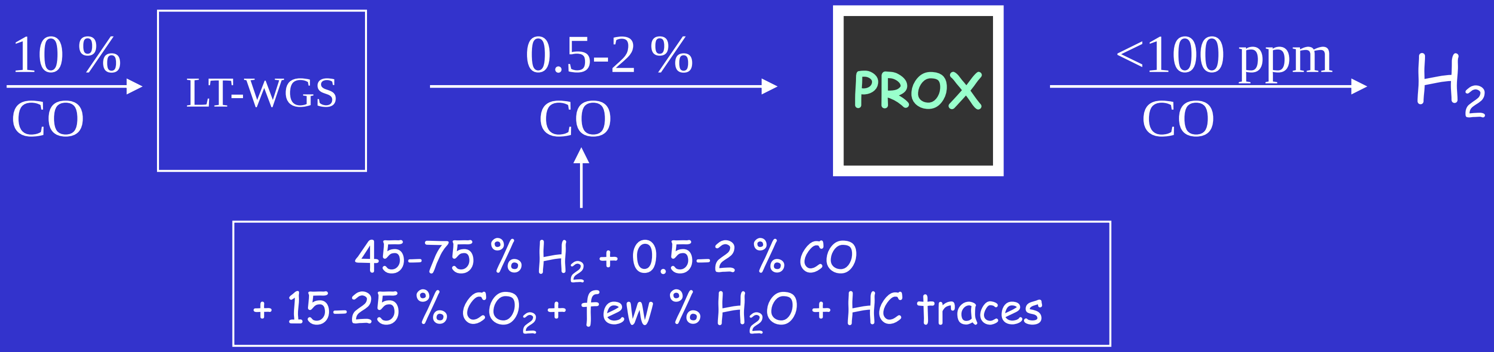
Thermodynamics of the WGS process



$$CO + H_2O = CO_2 + H_2$$

$$\Delta H = -40.6\ \mathrm{kJ\ mol^{-1}}$$

Catalytic Preferential Oxidation of CO



10 % CO → LT-WGS → 0.5-2 % CO → **PROX** → <100 ppm CO → H_2

45-75 % H_2 + 0.5-2 % CO
+ 15-25 % CO_2 + few % H_2O + HC traces

Requirements for CO-PROX catalysts

$$\boxed{\text{CO-PROX: } CO + H_2 + (O_2) = CO_2 + H_2}$$

- High reactivity for CO oxidation

} CO_2-Selectivity

- Low reactivity for H_2 oxidation
- High resistence to poisoning by CO_2 and H_2O

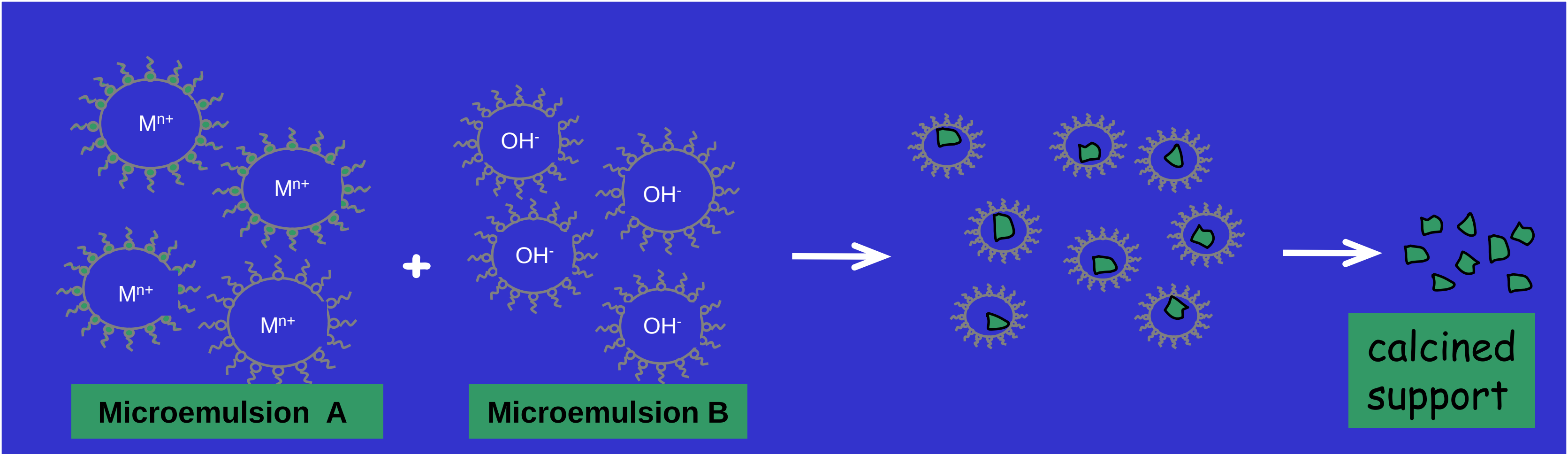
Overview of CO-PROX catalysts

Systems	Supported PtGM Pt; Pt-Ru; Pt-Rh (promoters; Ru, Rh)	Supported gold Au/Fe_2O_3; Au/TiO_2; Au/CeO_2	Copper-ceria CuO/CeO_2; $CuO/(Ce,M)O_x$
Conversion window	100-200 °C	50-100 °C	120-200 °C
Selectivity at full conversion	☺ 50 % (could be enhanced by certain promoters)	50-100 %	80-100 %
Resistance to H_2O-CO_2	good	☺ poor	fair

S. Park, R.J. Gorte , J.M Vohs; Applied Catalysis A : General, 200 (2000) 55-61

How to prepare a $CuO-CeO_2$ catalysts ?

Microemulsion preparation

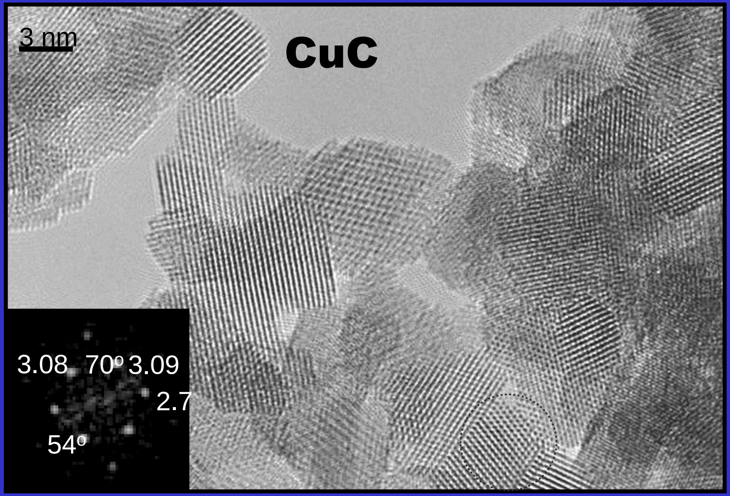


Microemulsion A

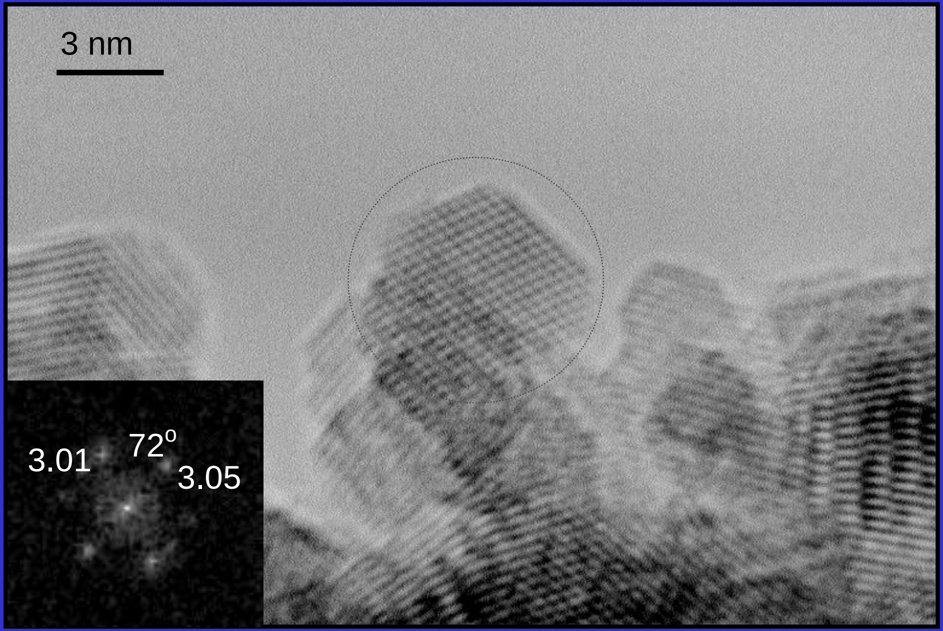
Microemulsion B

calcined support

1% w/w Cu was incorporated by incipient wetness impregnation



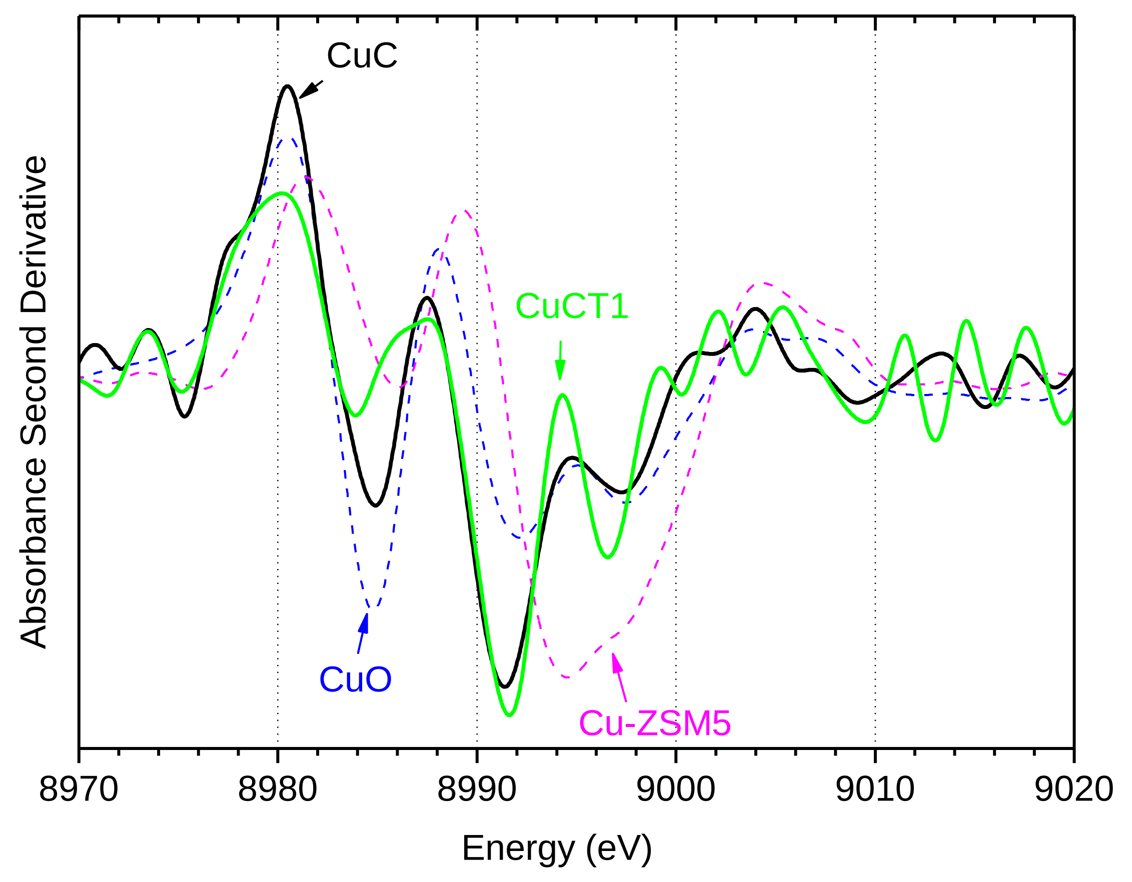
A. Martínez-Arias et al. J. Power Sources 151 (2005) 32



Sample	Cell parameter (Å)[a]	Particle size (nm)		$(Ce/Tb)_{at}$[c] Ratio XPS	S_{BET} (m^2g^{-1})[a]
		HREM[b]	XRD[a]		
CuC	5.413 (5.412)	6.7 (8.2)	8.3 (7.9)	-	92 (92)
CeTb1 50% Tb	5.367 (5.368)	5.5 (6.9)	6.1 (6.0)	0.89 ± 0.13	95 (95)
CeTb4 20% Tb	5.393 (5.392)	6.6 (9.0)	7.2 (7.4)	4.25 ± 0.75	104 (104)

The copper catalysts were prepared on CeO_2 supports contaning 20% and 50% of Tb to examine posible electronic interactions of the support with the CuO active phase of the catalysts during CO-TOX. Data for the respective supports are given in parenthesis

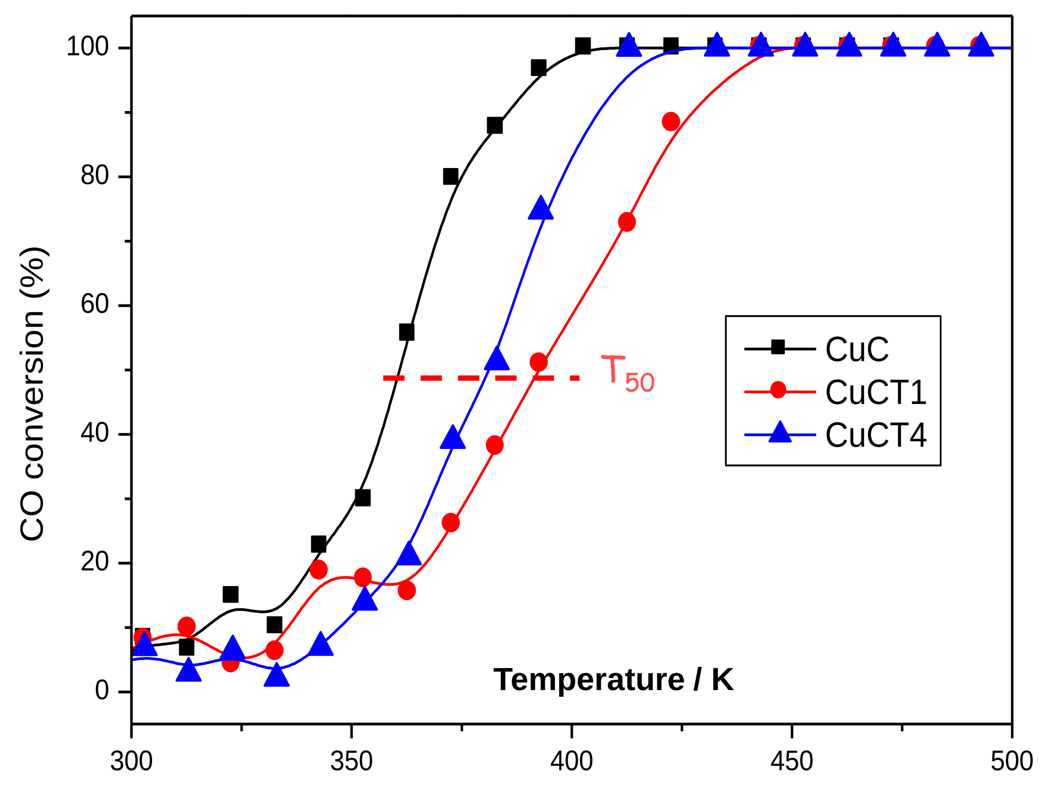
XANES Cu-K edge analysis of calcined CuC and CuCT1



The structure of copper in the original calcined CuC and CuCT1 catalysts is quite different to that Of small clusters of CuO incorporated into ZSM 5 zeolites, it look more like bulk CuO but cannot be seen eithe by XRD or even by HRTEM

Catalytic tests in CO-TOX

CO-TOX: 1% CO + 0.5% O_2 + Ar (balance)



Space velocity: 80.000 h^{-1}; heating ramp: 5 K min^{-1}

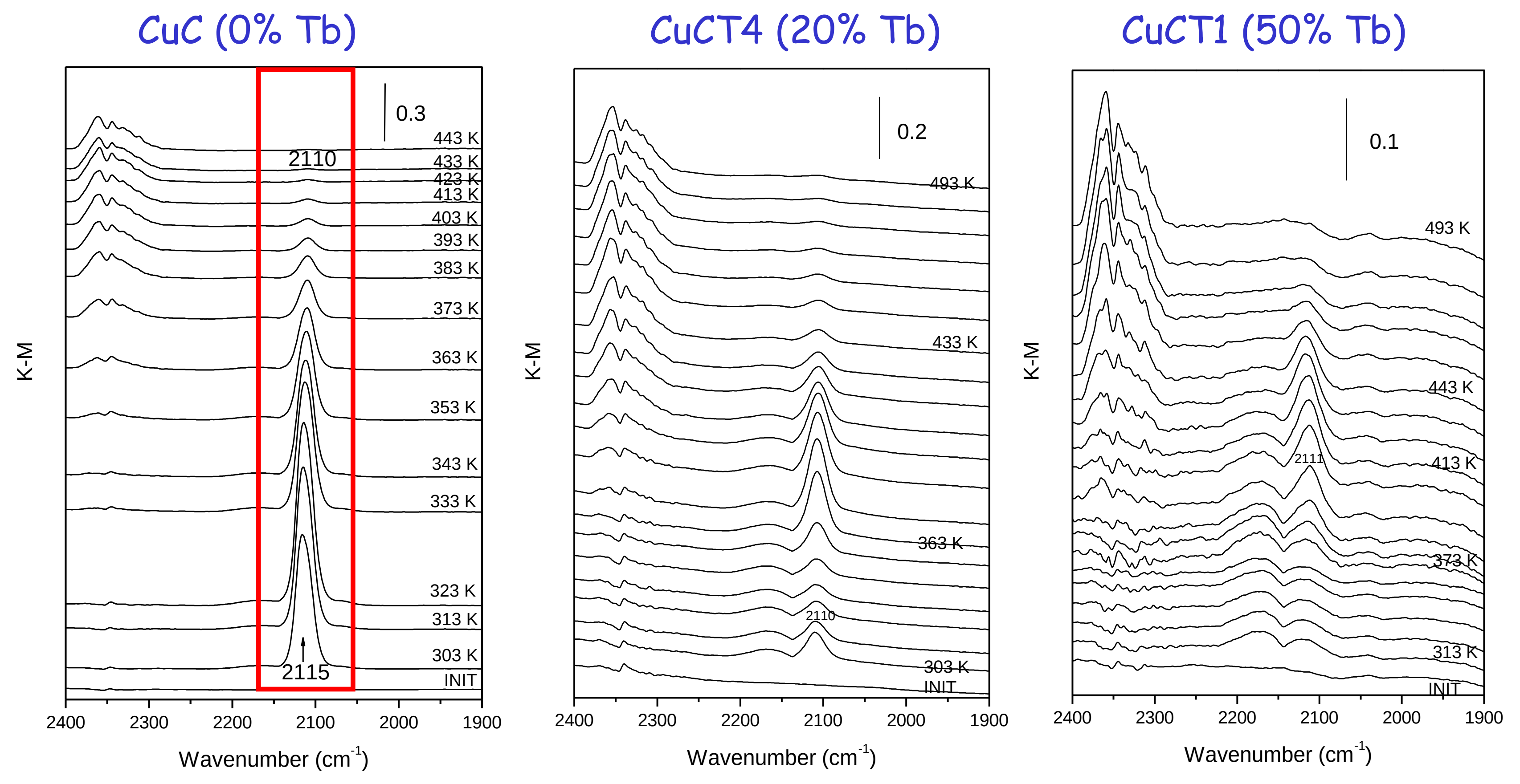
How work copper in CuC and CuCT catalysts during CO-TOX?

Operando – DRIFTS

Operando - XPS/XAES

Operando – DRIFTS analysis of CuC, CuCT4 and CuCT1

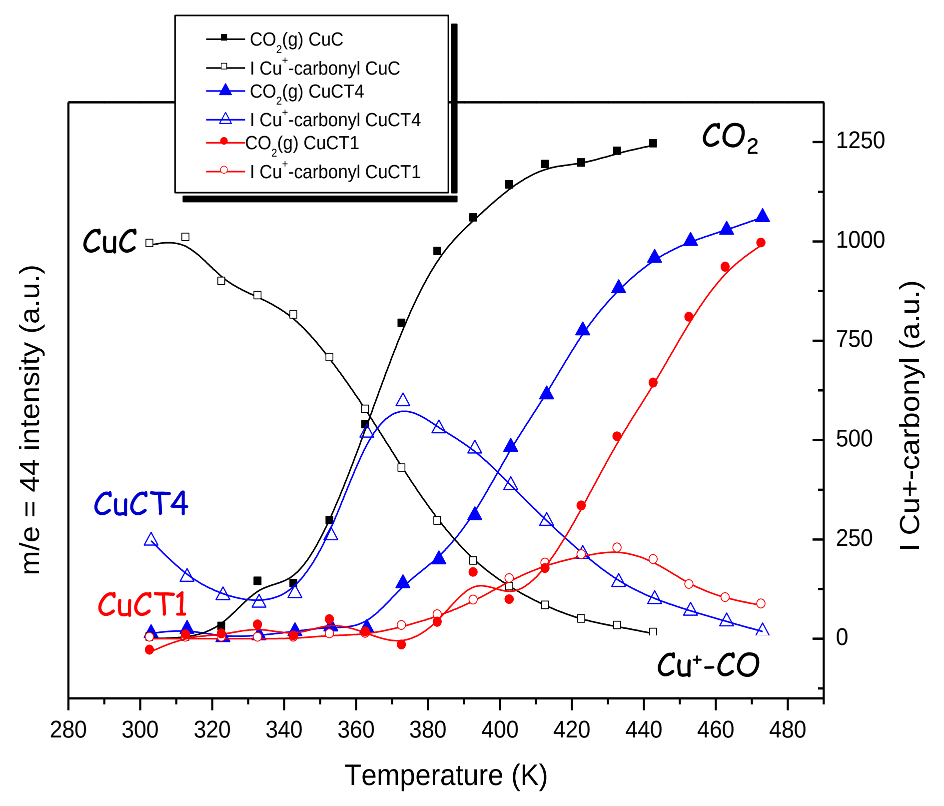
CO-TOX: 1% CO + 0.5% O_2



The amount of Cu^+-CO species, at 2110 cm^{-1} , decreases with increasing Tb content in the CeO_2 support indicating a lost of Cu^+ centers for CO

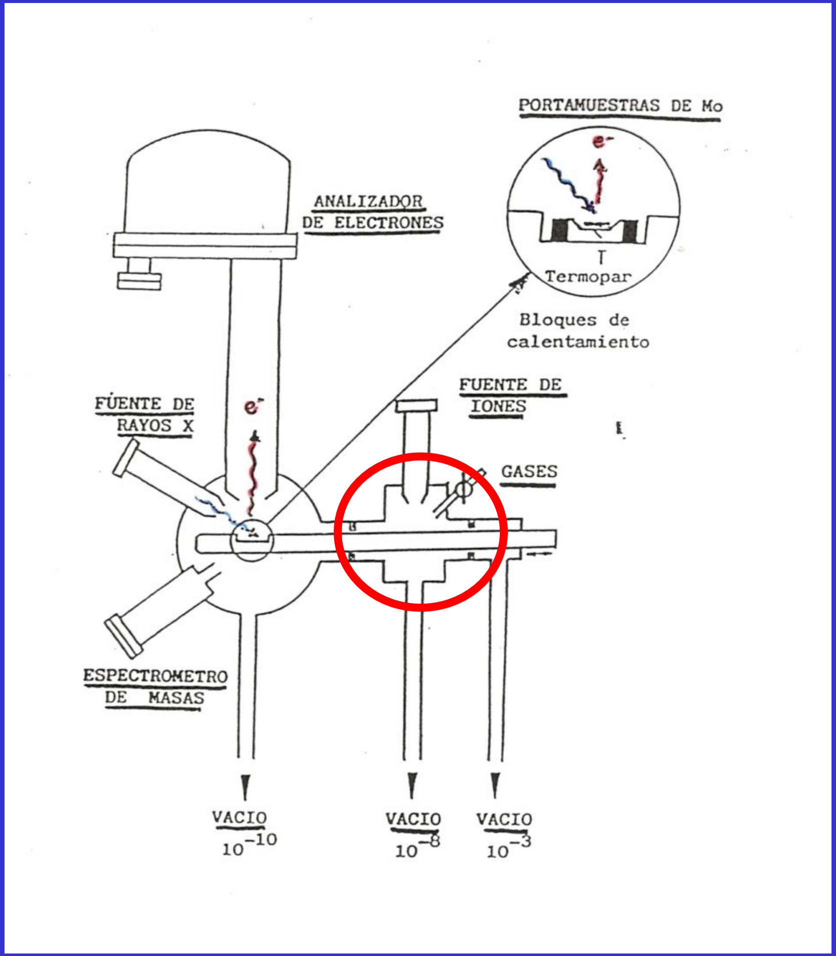
Operando - DRIFTS *vs.* Catalytic tests

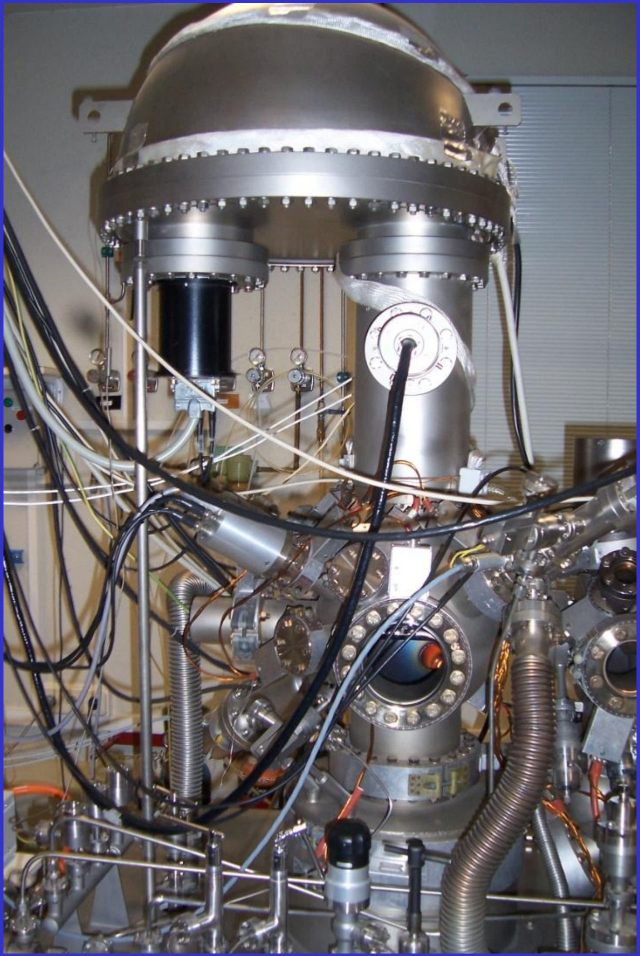
CO-TOX: 1% CO + 0.5% O_2



A. Martinez-Arias, Physical Chemistry and Chemical Physics, 14 (2012) 2144-2151

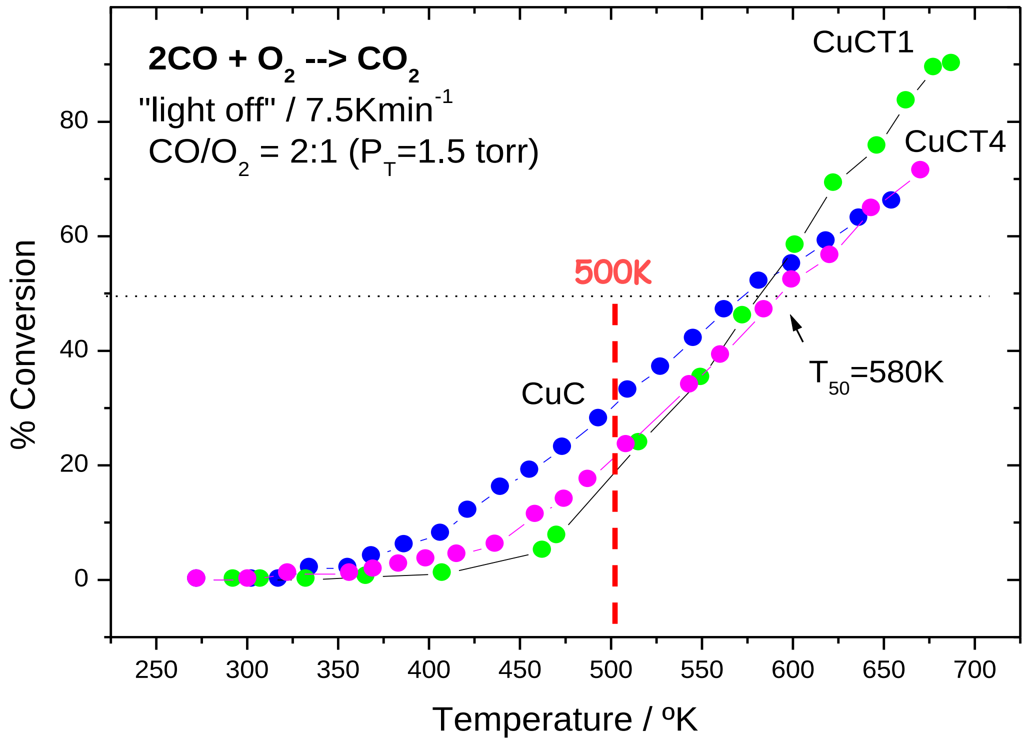
Operando - XPS/XAES





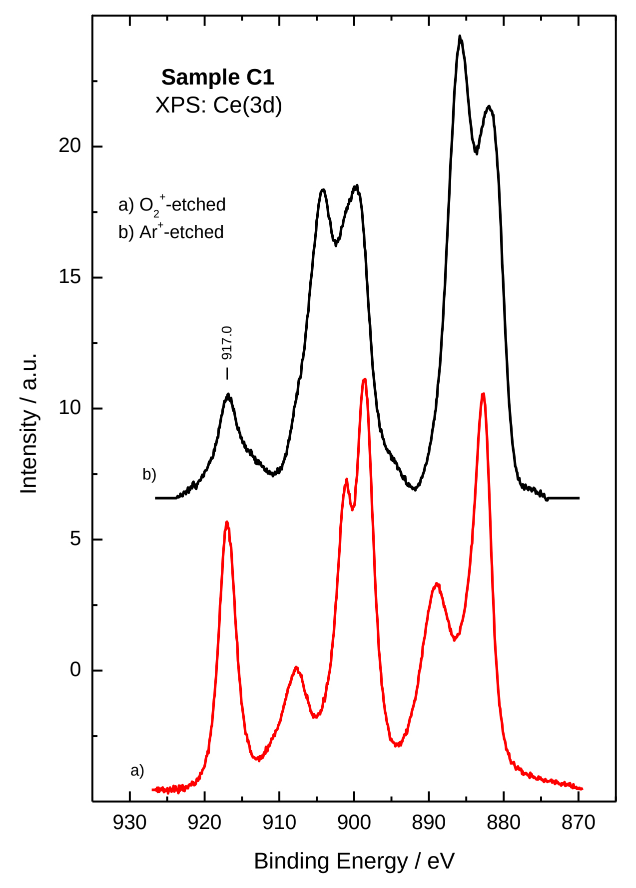
Main Chamber XPS, XAES and LEIS
Reaction Chamber: Gas manifold/MS, Ion-sputtering

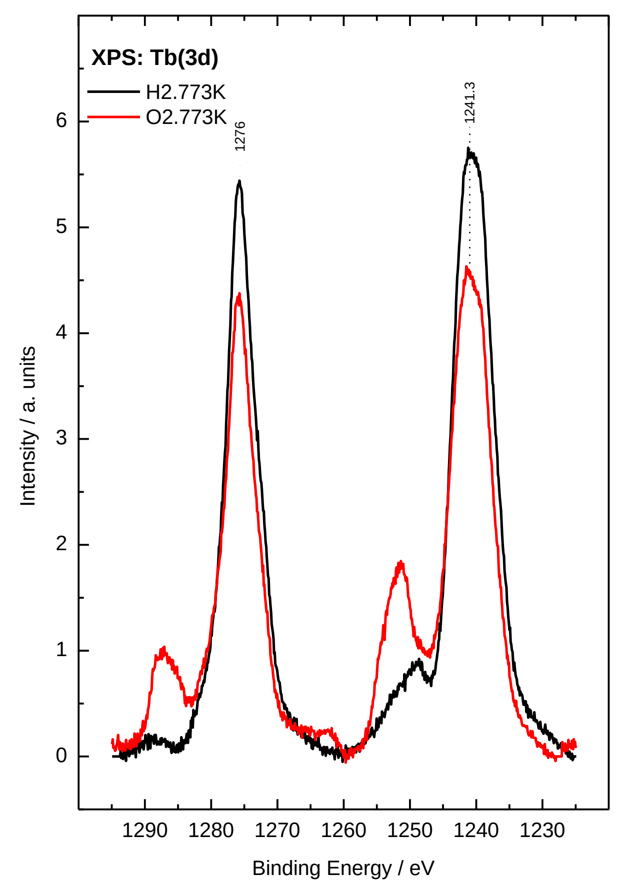
Operando - XPS/XAES



A. Martinez-Arias et al Phys. Chem Chem Phys 14 (2012) 2144-2151.

Factor Analisis: Ce(3d) and Tb(3d) in CuCT1

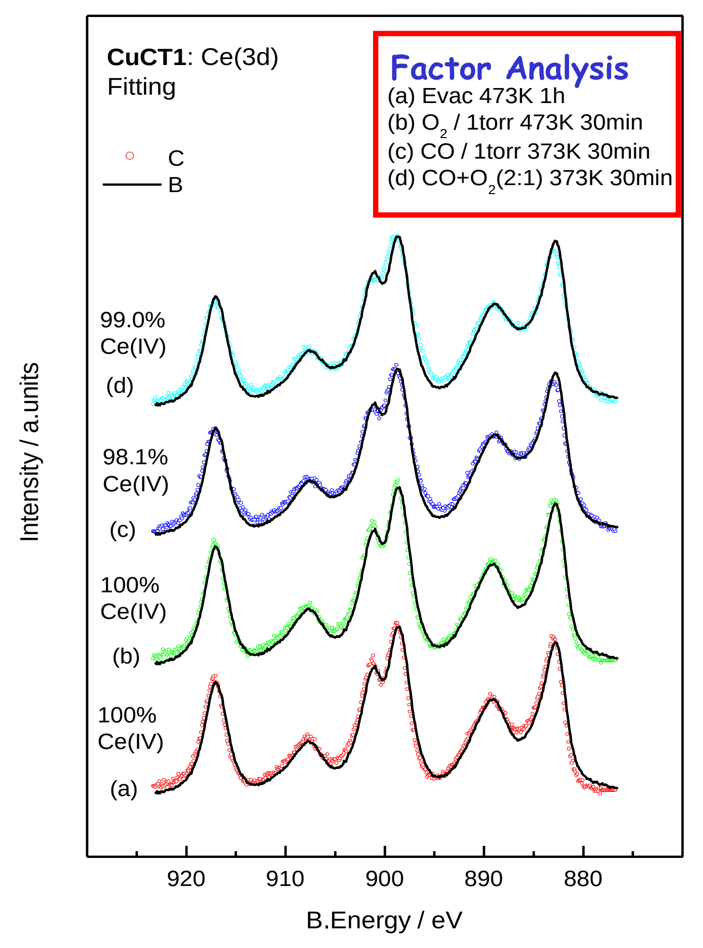


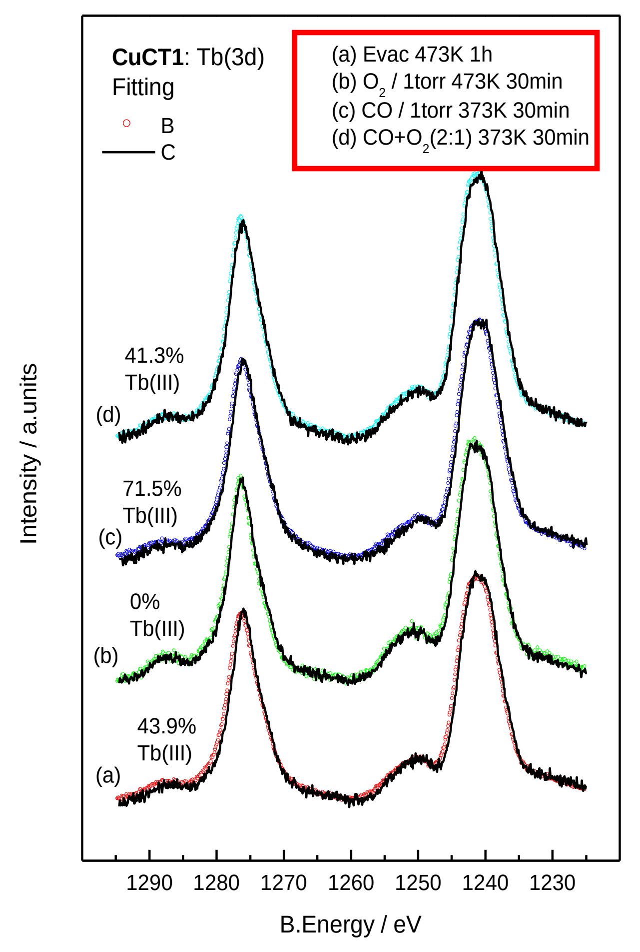


XPS: Ce(3d)
CeO_2 *vs.* Ce_2O_3

XPS: Tb(3d)
TbO_2 *vs.* Tb_2O_3

Operando-XPS: Ce(3d) and Tb(3d) in CuCT1





Operando-XPS was carried out under O_2 , CO and CO/O_2(2:1) and Ce(3d) and Tb(3d) spectra analysed by Factor Analysis

J.P. Holgado et al. Appl. Surf Sci. 161,301-315, 2000

Operando XPS of CuCT1 and CuC catalysts

Conclusions

1: copper dispersion, measured as Cu/(Ce+Tb) ratios, only sightly changes with the treatments and are similar to those observed in the CuC catalyst under similar conditions.

2: terbium dispersion, measured as Tb/(Ce+Tb), is not modified by the treatments and is similar to that observed in the CT1 support.

3: terbium oxidation state changes with the treatments (Tb^{3+}/Tb^{4+}). 43.6% of the terbium is as Tb^{3+} in the original calcined catalyst

4: cerium remains fully oxidized after all the treatments (100% Ce^{4+})

5: cerium and copper in CuC (reference) are more easily reduce than in CuCT1 and CuCT4 under reducing treatments (i.e. CO or H_2)

G. Munuera et al. CONCORDE Conference, "Catalytic Nano-Oxides Research and Development in Europe: Present and Future"
Sevilla (Spiain), 2006.

What happen to Copper in CuCT1 ?

CO/O_2 (2:1) reaction at 473K

Supports:

$Ce^{3+} + Tb^{4+} \rightarrow Ce^{4+} + Tb^{3+}$

Copper:

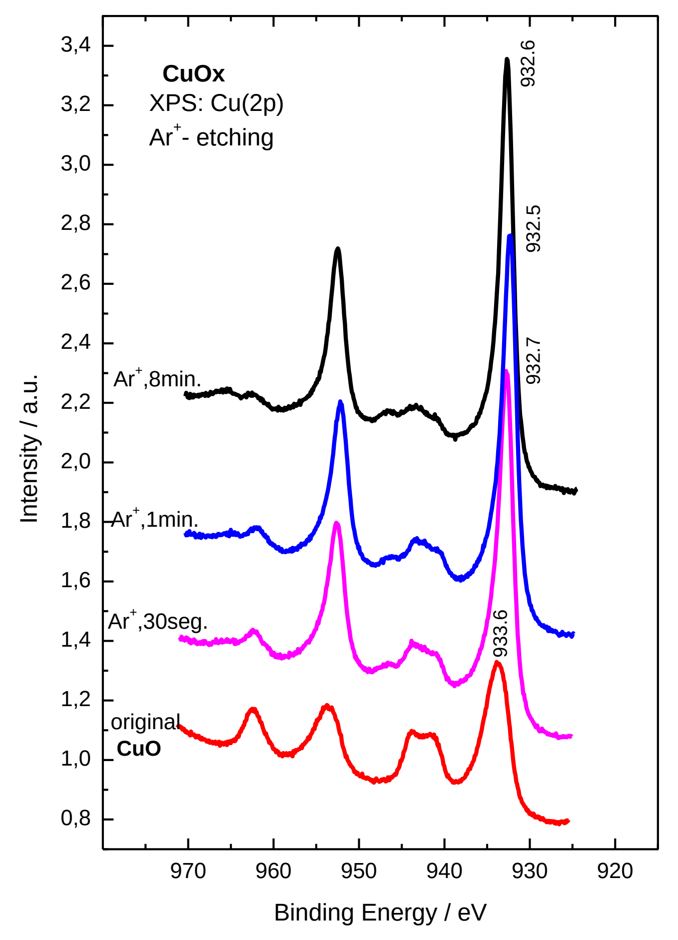
$Cu^{+} + Tb^{4+} \rightarrow Cu^{2+} + Tb^{3+}$

In priciple, Tb^{4+}/Tb^{3+} acts as a *"redox buffer"* against Cu^{2+}/Cu^{+} and Ce^{4+}/Ce^{3+} what explains the differences in reactivity observed in the three catalysts (CuC > CuCT4 >> CuCT1). This implies a strong electronic interaction through the interfase CuO-CeO_2 under CO-TOX *operando* conditions

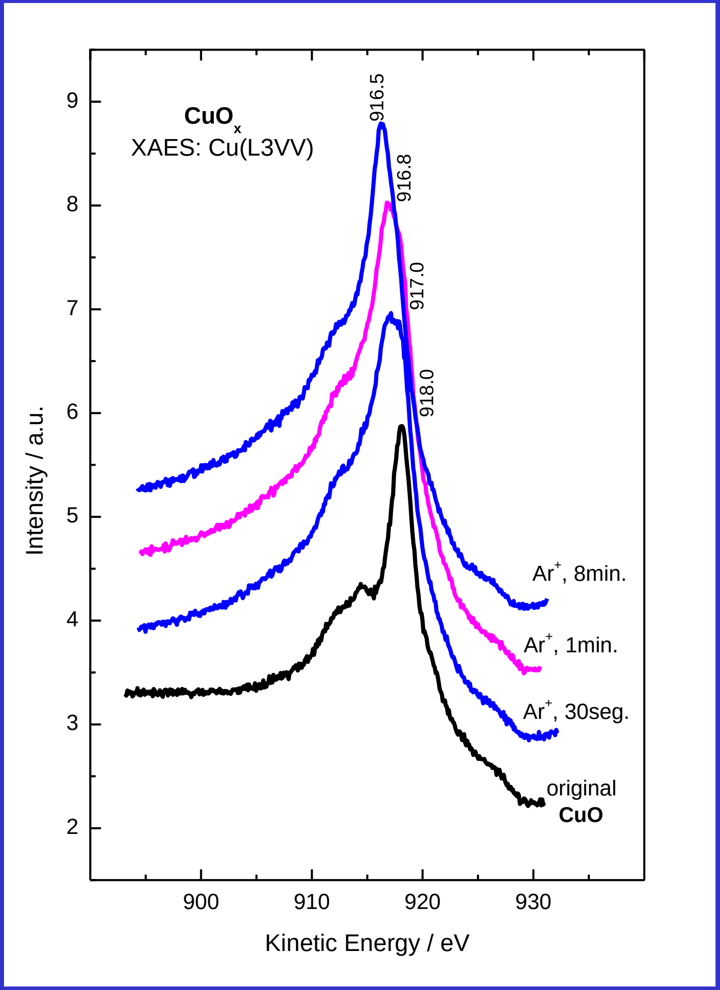
A . Martinez-Arias et al. Phys. Chem Chem. Phys, 14 (2012) 2144-2151

But, how is copper under *operando-XPS/XAES* conditions in CuO-CeO2 catalysts ?

Differential Ar^+-sputtering of CuO (bulk)



XPS: Cu(2p)

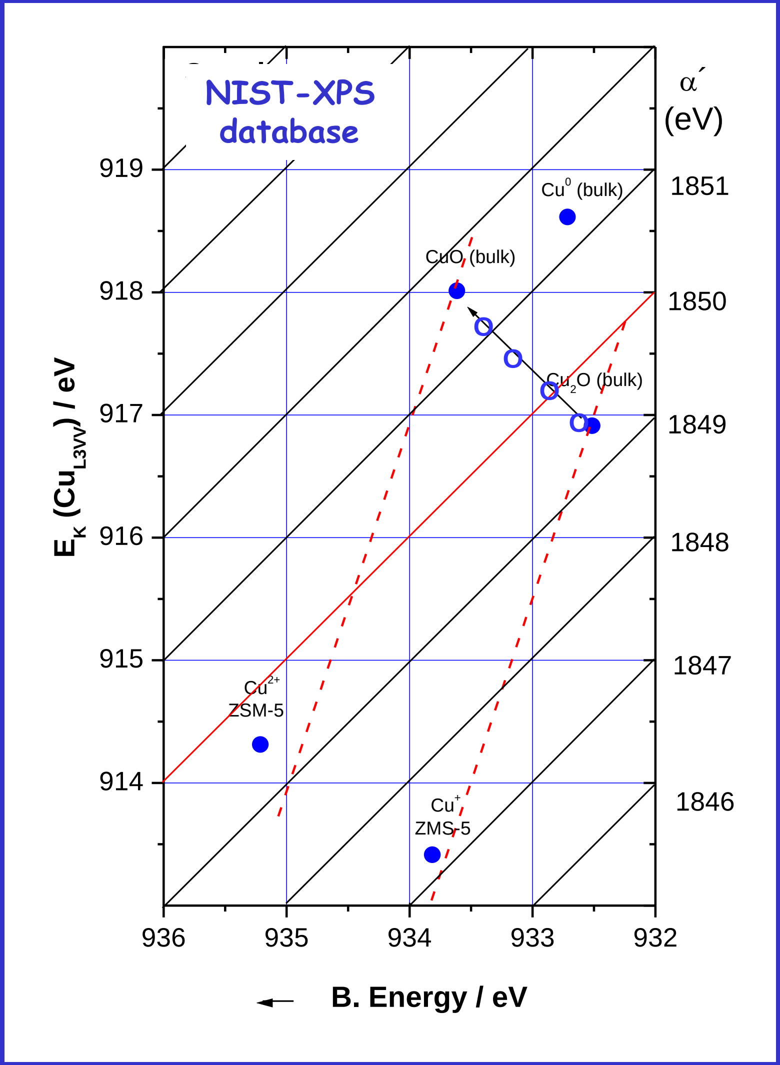


XAES: $Cu(L_3M_{45}M_{45}, {}^1G)$

Ar^+-sputtering: $CuO + Ar^+(3.5\ kV) \rightarrow Cu_2O + O(g)$

G. Munuera et al. CONCORDE Conference, "Catalytic Nano-Oxides Research and Development in Europe", Sevilla (Spain) 2006.

Wagner “chemical state plots” for copper



$E_{BE}(Cu2p)$ *vs.* $E_K(CuL_3VV)$

- Blue dots, bulk CuO, Cu_2O and Cu (foil) references and copper loaded ZSM-5 zeolites (W. Grünert et al.)

- *“slope -1”* full lines show the modified Auger parameter defined by Wagner as:

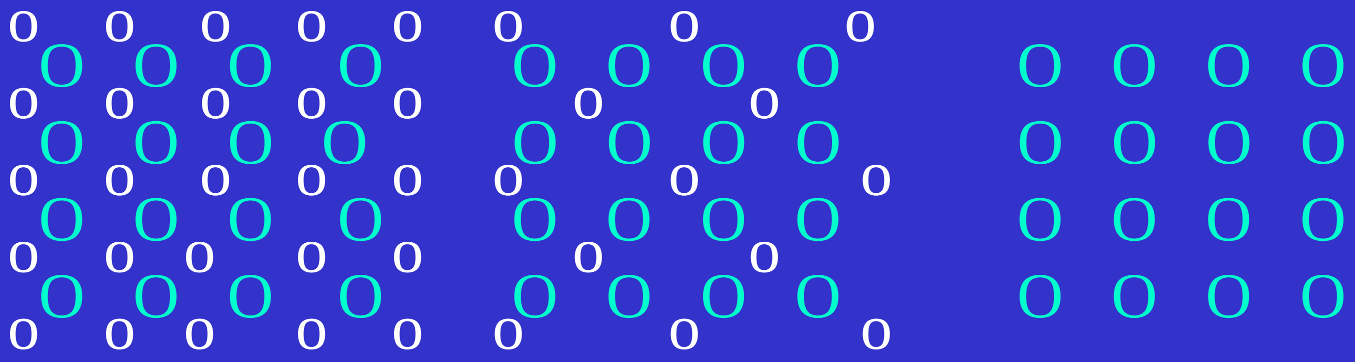
$$\boxed{\alpha' = E_{BE}(Cu2p) + E_K(CuL_3VV)}$$

α´ in eV (right scale) being related to the relaxation of the hole at the core-ionized copper atom (*“final state effects”*)

- *“slope -3”* red guide dash lines indicate similar “chemical states” to those of the respective references

C.D. Wagner Anal. Chem 44 (1972) 967
NIST X-ray Photoelectron Spectroscopy Database; http://srdata.nist.gov/xps/
W. Grünert et al. J. Phys. Chem. 98 (1994) 10832

Copper oxides: A metal "*stuffed*" with oxygen (cationic eutaxy)



CuO (Tenorite)　　Cu_2O (Cuprite)　　Cu (fcc)

The structure of the three *stable* copper oxides: cuprite (Cu_2O, cubic) tenorite (CuO, monoclinic) and paramelaconite (Cu_4O_3, tetragonal mixed valence) all have the same *fcc* array of Cu atoms with O atoms occupying tetrahedral interstices. The occupied tetrahedral are those needed to satisfy the linear two-fold coordination of Cu (I) and the planar four-fold coordination of Cu (II). This set of structures show an *fcc* eutaxy of cations, a concept first defined by O´Keeffe and Hyde.

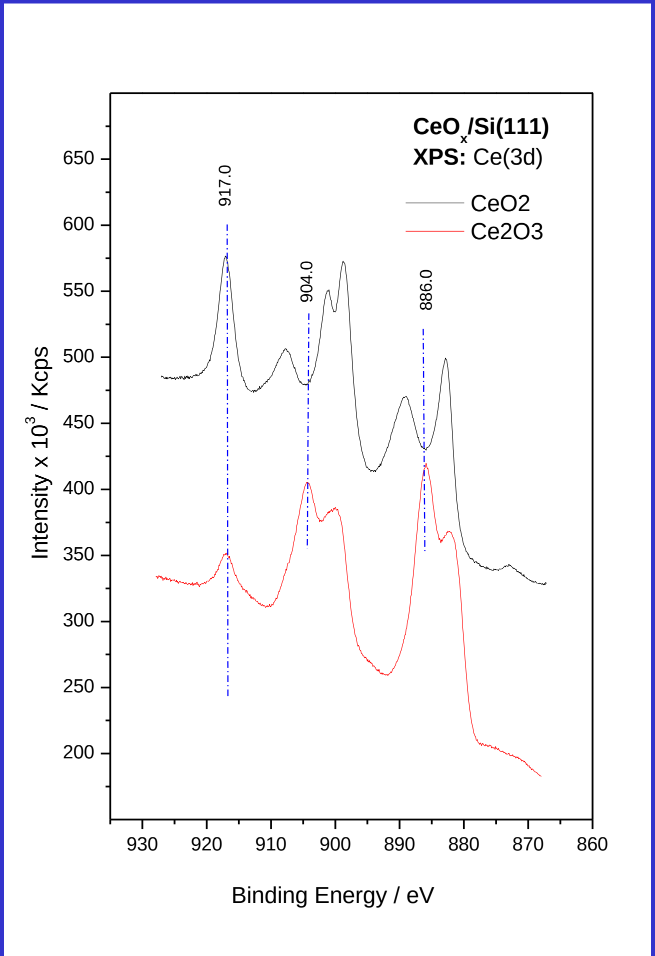
M. O´Keeffe and B.G.Hyde Structure and Bonding 61 (1985) 77-144
A. Vegas, Crystallography Reviews, 7 (2000) 189-283

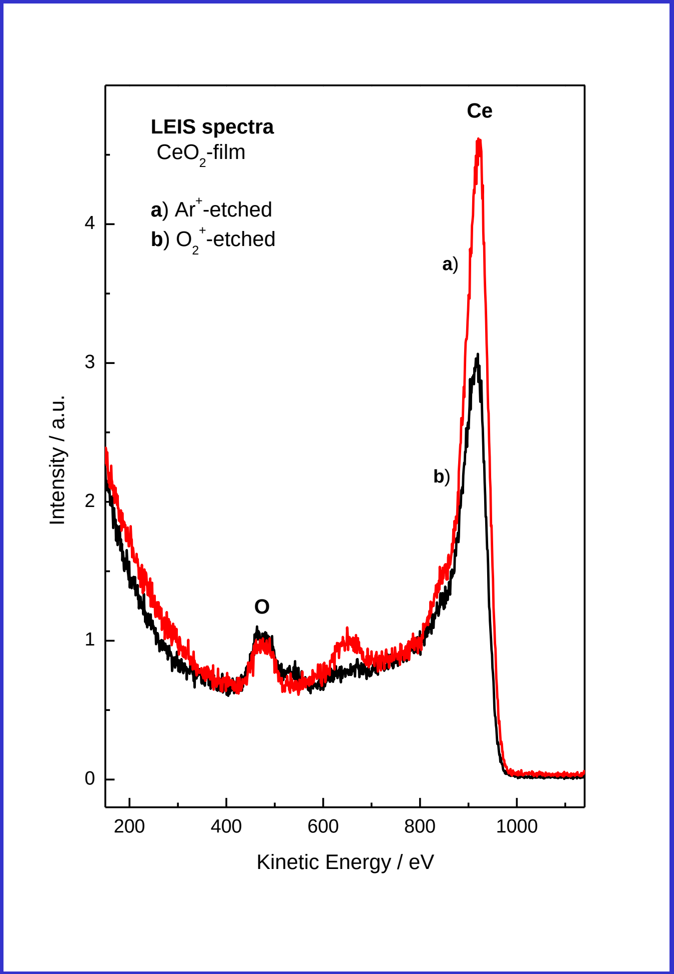
Looking into Copper: *Operando*-XPS/XAES

from $Cu_xO/CeO_2/Si(111)$ films

to Cu_xO/CeO_2 real catalysts

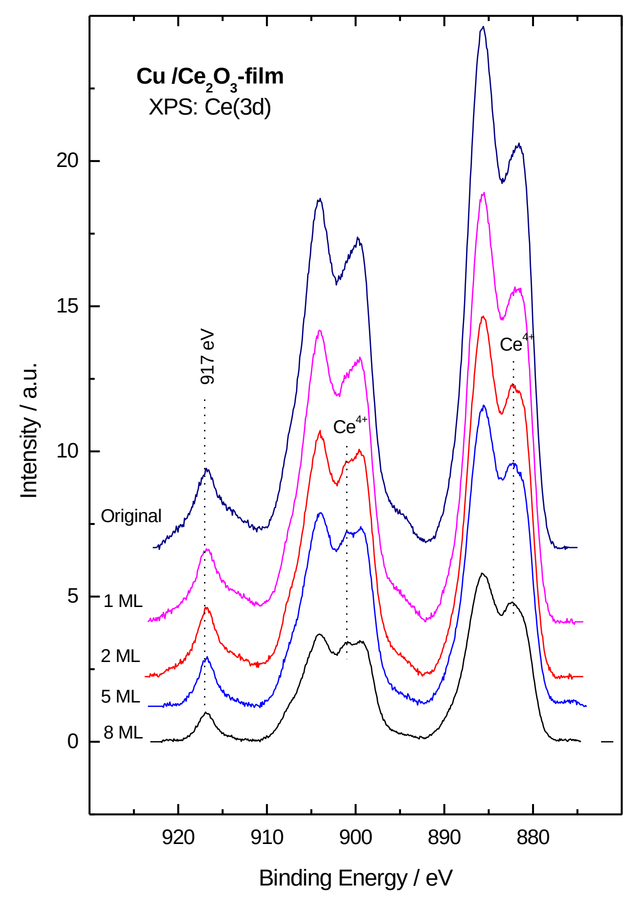
CeO_2/Si(111) vs. Ce_2O_3/Si(111) films

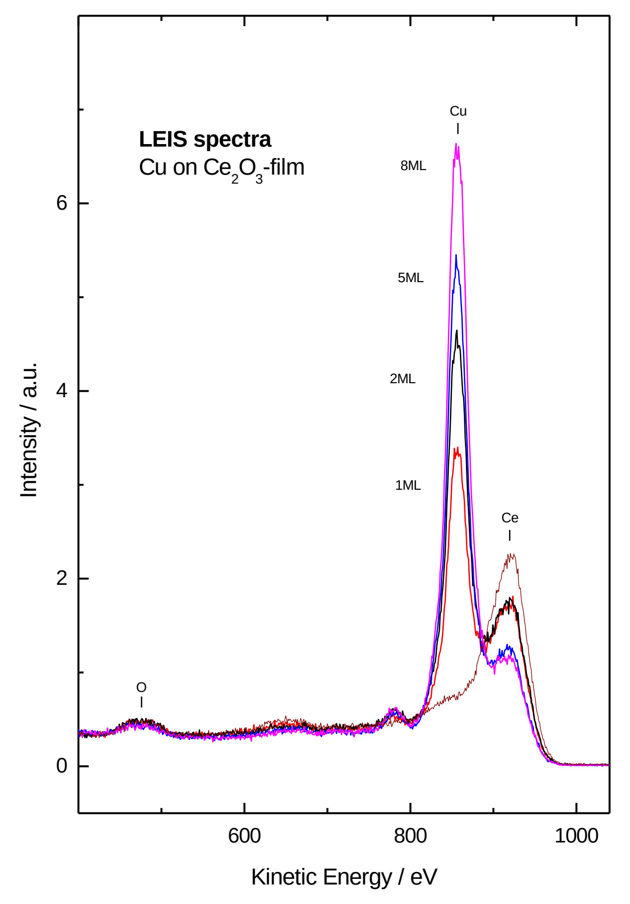




Low Energy Ions Scatering (LEIS/ISS) using He^+ (1KV) detects exclusively the atoms at the topmost layer of the surface

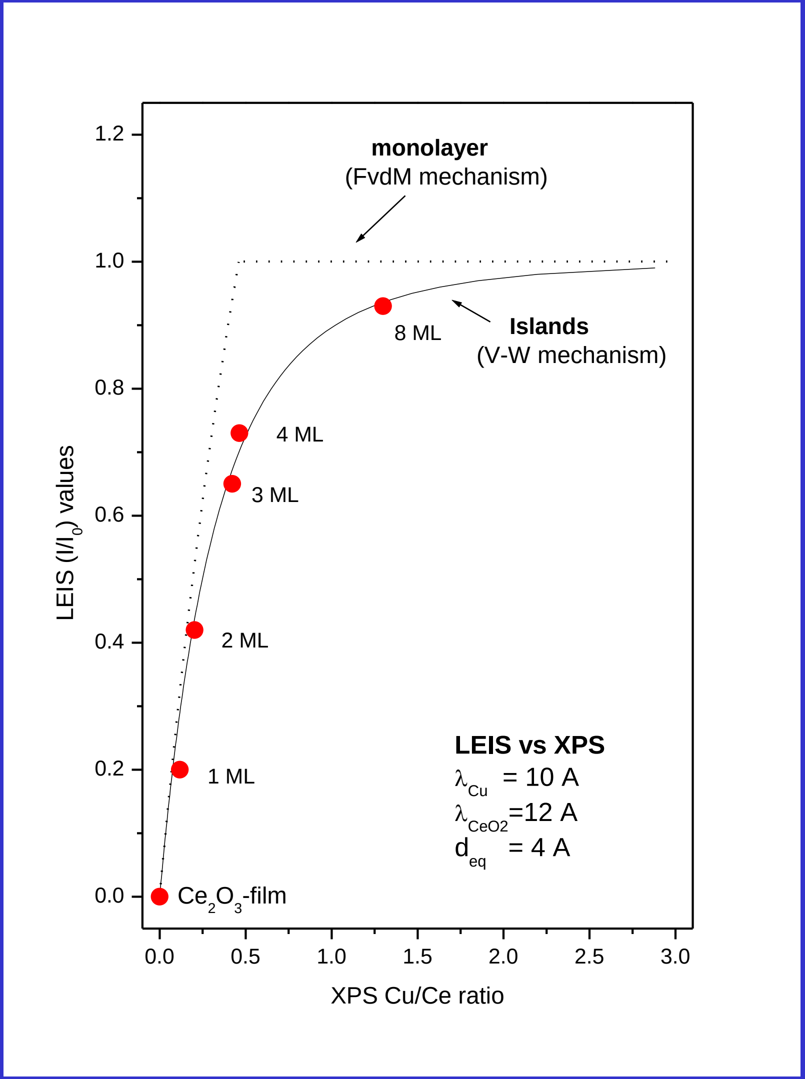
Study of Cu/Ce_2O_3/Si(111) films: Copper evaporation





Evaporation of copper (up to 8ML) on a highly reduced Ce_2O_3/Si(111) substrate followed by XPS (left) and LEIS (right) showing the progressive "*shadowing*" of the Ce_2O_3 sustract

Study of $Cu/Ce_2O_3/Si(111)$ films



Frank van der Merve "layer by layer" mechanism

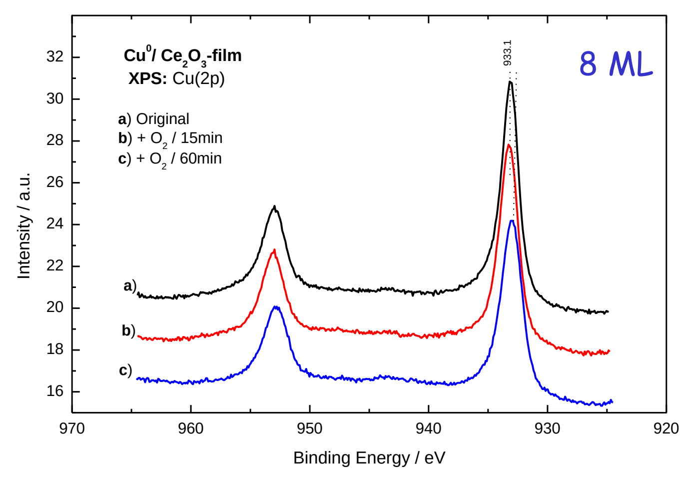
Volmer-Weber "Islands" mechanism

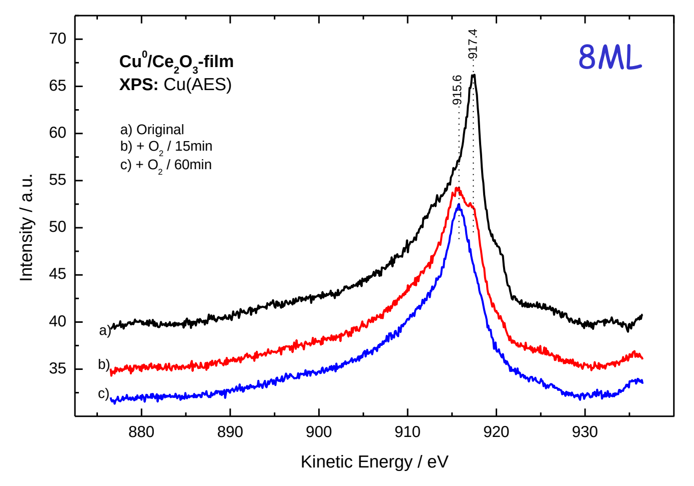
Stransi-Krastinov mechanism
"one layer + 3D islands"

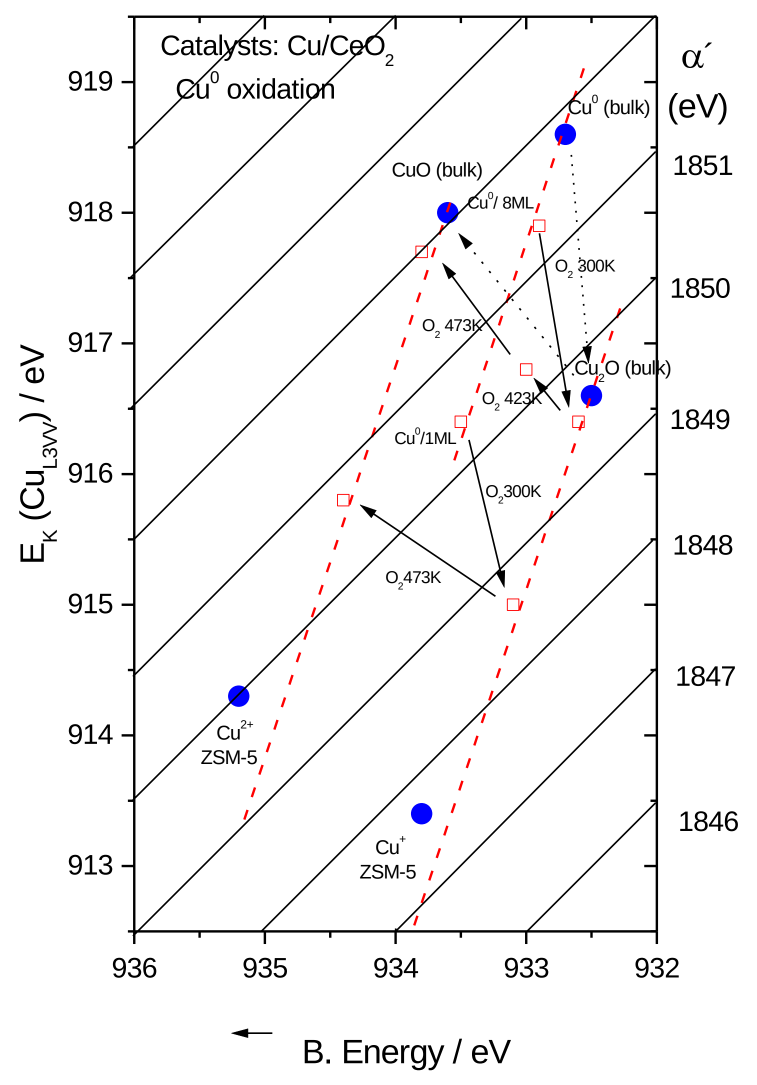
For metal deposited on oxidic supports the more general growing mode is the formation of "single layer islands" up to a coverage of 0.3-0.7 and then the formation of three-dimentional islands

V.M. Jimenez et al. Appl. Surf. Science 141 (1999) 186-192

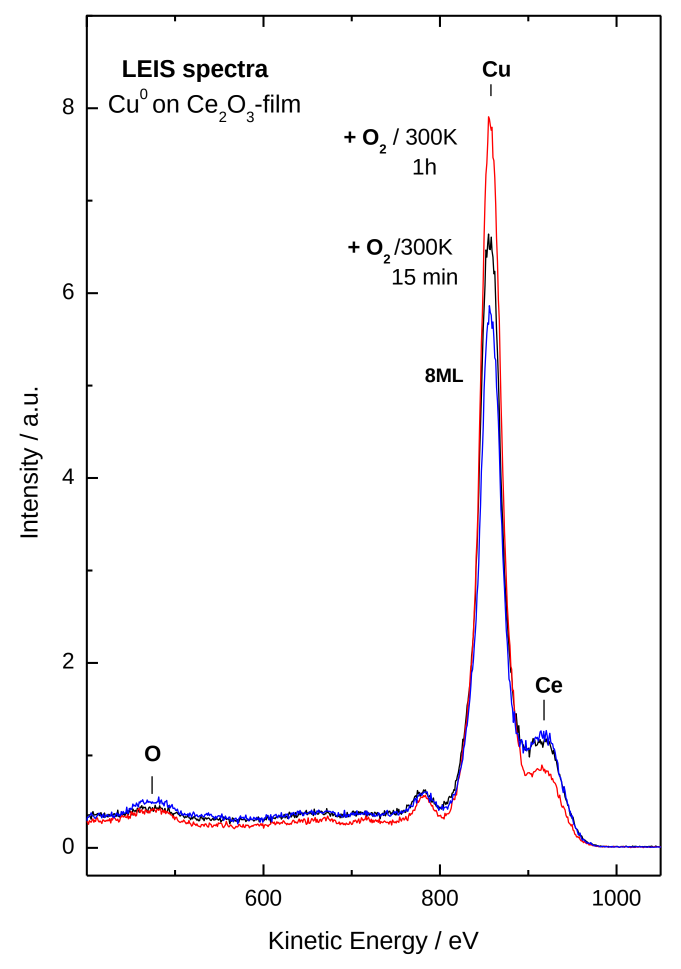
Oxidation of Cu/Ce$_2$O$_3$/Si(111) to CuO/CeO$_2$/Si(111)

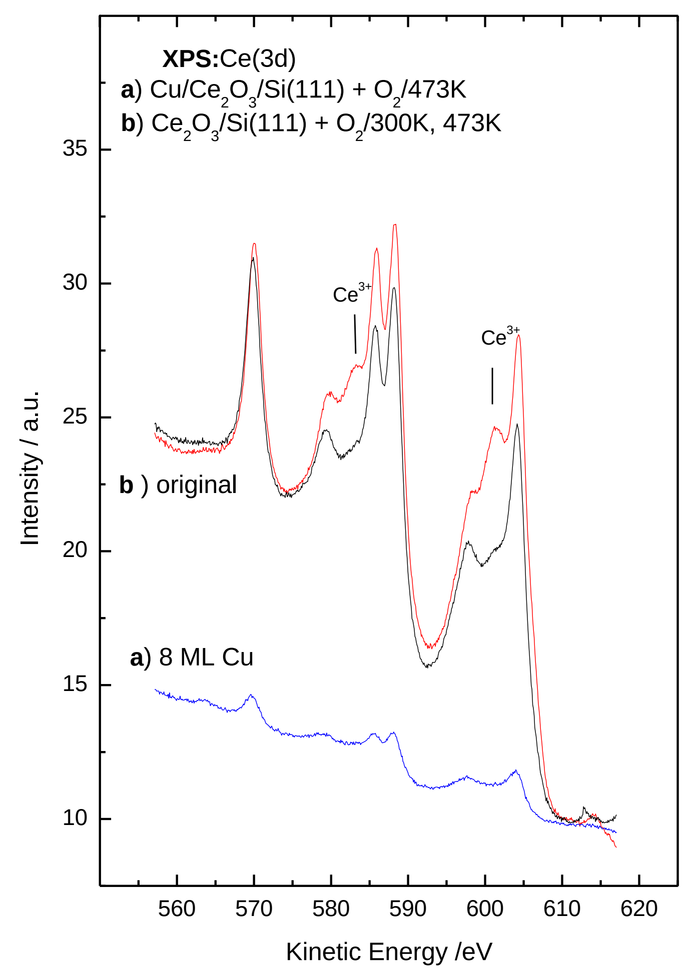






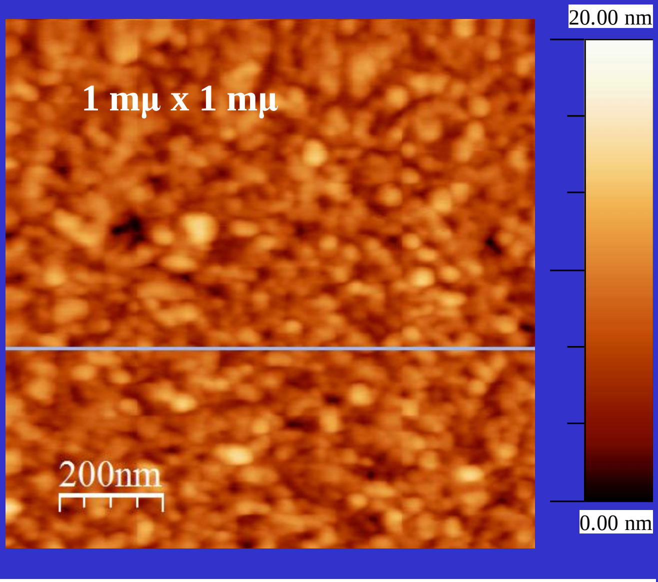
Oxidation of $Cu/Ce_2O_3/Si(111)$ to $CuO/CeO_2/Si(111)$

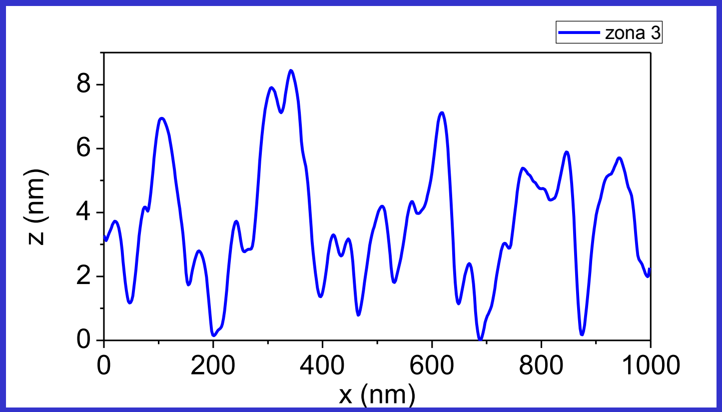




Holgado J.P. et al., Applied Surface Sci. 158 (2000) 164-171
B. Skårman et al., J. Catal. 181 (1999) 6-15

AFM study of CuO/CeO2/Si(111) films





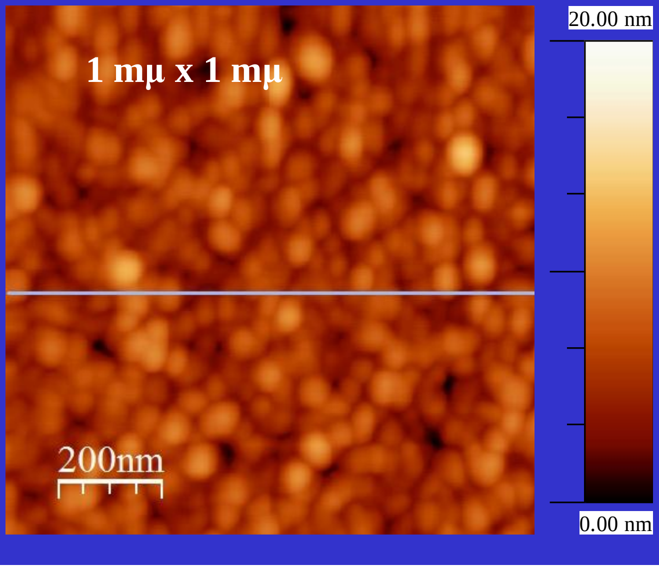
$CeO_2/Si(111)$

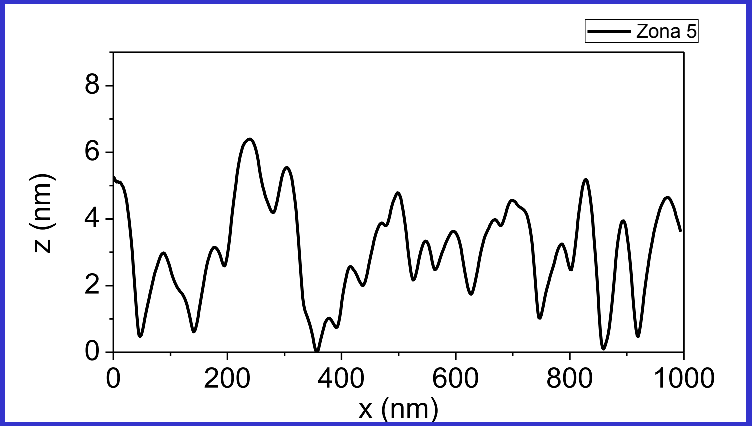
Av. Disc diam: 30 nm

RMS roughness: 2.0 nm

Peak to valley: 16.2 nm

Average hight: 7.2 nm





$Cu_xO/CeO_2/Si(111)$

Av.Disc diam.: 46 nm

RMS roughness: 1.8 nm

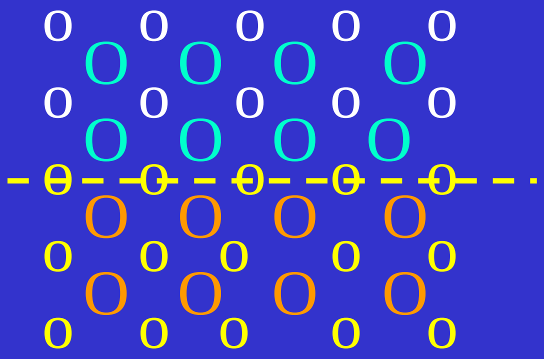
Peak to valley: 13.9 nm

Avarge hight: 5.6 nm

C. Munuera, ICMM-CSIC

Copper oxides - Ceria interfaces

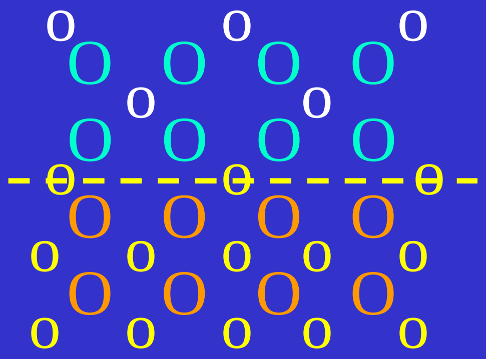
Tenorite



$CuO-CeO_2$

interface

Cuprite

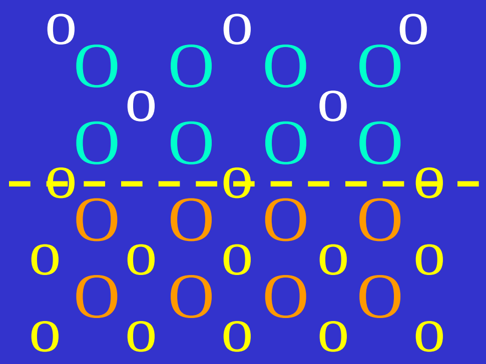


Cu_2O-CeO_2

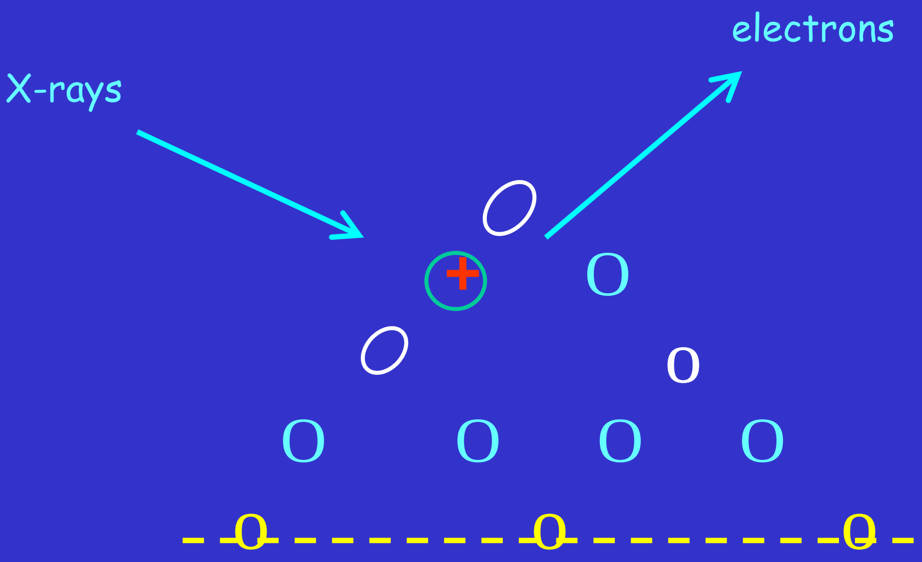
Since the cation lattice is essentialy maintained (cation eutaxy) appropiate cation lattice dimensions can be calculated. According to B. Skåman et al. a tensile strain is imposed to the copper oxides by ceria support which disminishes from 27% lattice mistfit for Cuprite to arround 8% for Tenorite. Misfit strain of this magnitude can only be maintained for a few monolayers of copper

B. Skårman et al. J. Catalysis, 181 (1999) 6-15

Cu_2O – CeO_2 interface: Extra-atomic relaxation (R^{ea})



Cu_2O-CeO_2



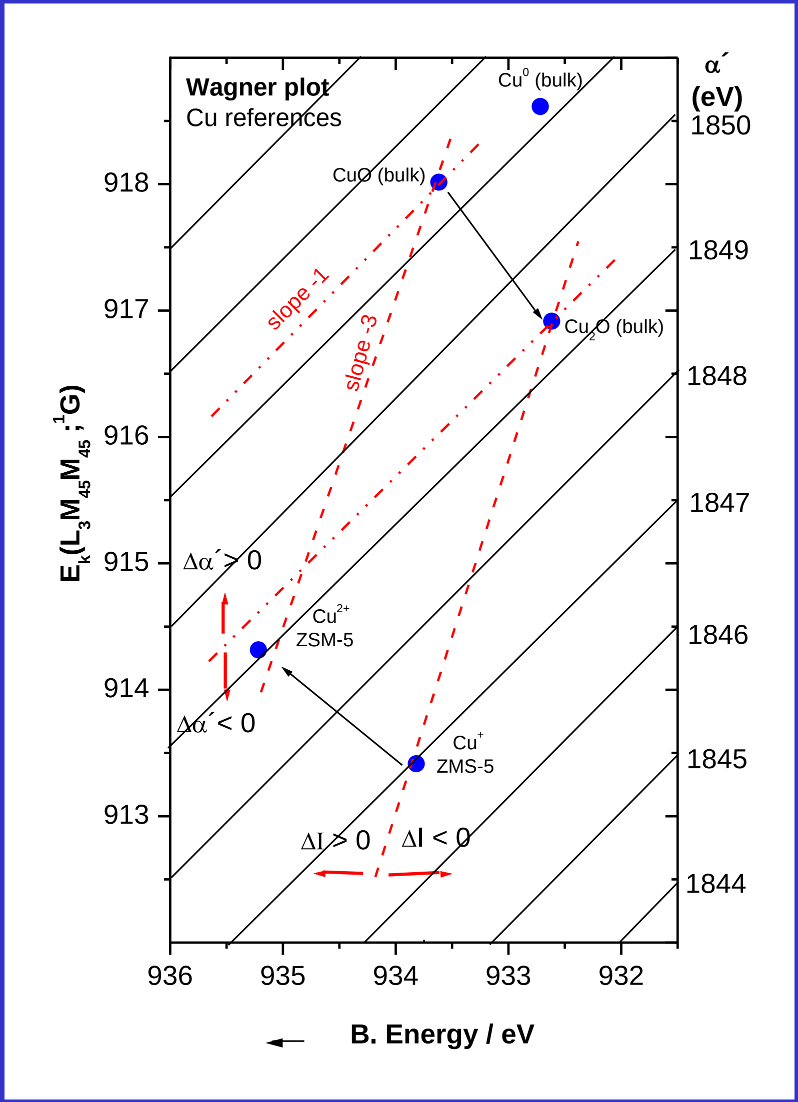
CeO_2

"final state effects"

The *hole* (+) left in the core-ionized copper polarizes the neighbour atoms. This "extra-atomic relaxation" process can be related to the Wagner modified Auger parameter shift ($\Delta\alpha' = 2\Delta R^{ea}$). To a good approximation, the electrostatic Moretti´s simple model shows that the Auger parameter shift is a function of the number, distance, electronic polarizability and local symmetry of the first neighbour ligands of the core-ionized copper atom calculated taking into account dipole-dipole interactions between them

G. Moretti Surf. Interf. Anal. 16 (1990) 159-162 ; *ibid* Journal Electron Spectroscopy 95 (1998) 95-144

Wagner "chemical state plots" for copper



$$\boxed{\alpha'_{Cu} = E_B(2p_{3/2}) + E_K(CuL_3M_{45}M_{45}\ ,\ ^1G)}$$

Moretti´s electrostatic model

$$\Delta\alpha' = (\alpha'_{Cu+ZSM5} - \alpha'_{Cu2O})$$

$$\Delta\alpha' = 2[\Delta R^{ia} + \Delta R^{ea}]$$

for a non-local screening:

$$\Delta\alpha' = 2\Delta R^{ea}$$

$$E_K = [const + 2(V_M + kq] -3E_B$$

$$I = [const + 2(V_M + kq]$$

$$\Delta I = 2\Delta(V_M + kq)$$

if ΔI = 0, same chemical state

C.D. Wagner Anal. Chem 44 (1972) 967; *ibid.Faraday Discuss. Chem. Soc. 60 (1975) 291*

T.D. Thomas, J. Electron Spectrosc. Relat. Phenom. 20 (1980) 117

G. Moretti, Surf. Interface Analysis, 17 (1991) 352-356

Calculated Δα´ values for Cu_2O on CeO_2 and ZSM5 zeolites using Moretti´s simple electrostatic model

Structure ($D_{\infty h}$)	$R_{Cu\text{-}O}$ (Å)	a_o (Å^3)	n_1	a_o (Å^3)	n_2	$2R^{ea}$ (eV)	Δα´ (eV)
Cu-O-Cu-O (Cu_2O, bulk)	1.85	3.3	2	----	----	7.18	0.0
Cu-O-Cu-O (Cu_2O cluster)	1.95	3.3	2	----	----	5.91	-1.27
Ce-O-Cu-O (CeO_2 interface)	1.95	3.3	1	2.7	1	5.43	- 1.75
Si-O-Cu-O (ZSM5 interface)	1.95	3.3	1	1.22	1	4.25	-2.93

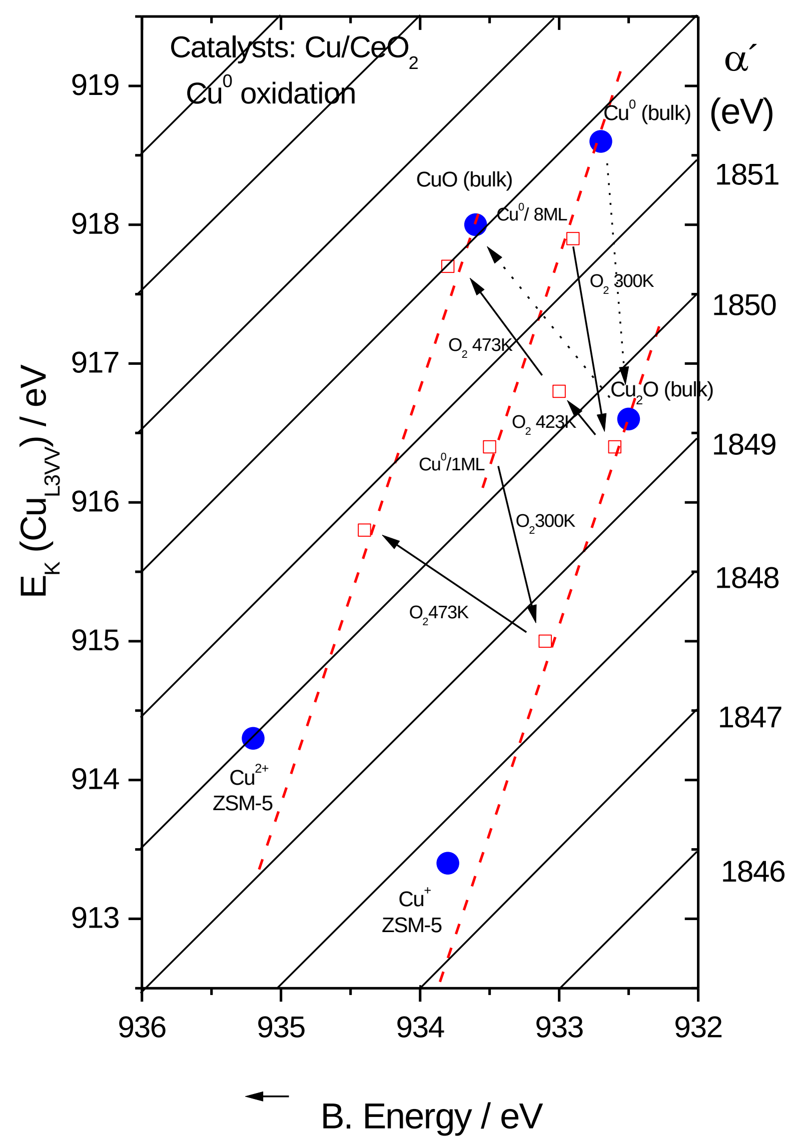
$2R^{ea}$ = $(\alpha'_{Cu^+(s)} - \alpha'_{Cu^+(g)})$; **Δα´** = $(\alpha'_{Cu^+(s)} - \alpha'_{Cu_2O/bulk})$; **$\alpha'_{Cu^+(g)}$** = 1838.4 eV

$$2R^{ea}\,(\text{eV}) = 14.4\, n a_o/R^4 (1 + D a_o/R^3)$$

a_o = polarizability of the ligands (Å^3)
n = number of nearneighbour
R = distance to the core-ionized atom (Å)
D = parameter taking into account the symmetry

G. Moretti et al.Surf. Interface Anal. 17 (1991) 352-356; *ibid.* Surf. Interface Anal. 31 (2001) 249-254

Study of $Cu_xO/Ce_2O_3/Si(111)$ films



Wagner Cu "chemical state plot"

$E_{BE}(Cu2p)$ *vs.* $E_K(Cu_{L3VV})$

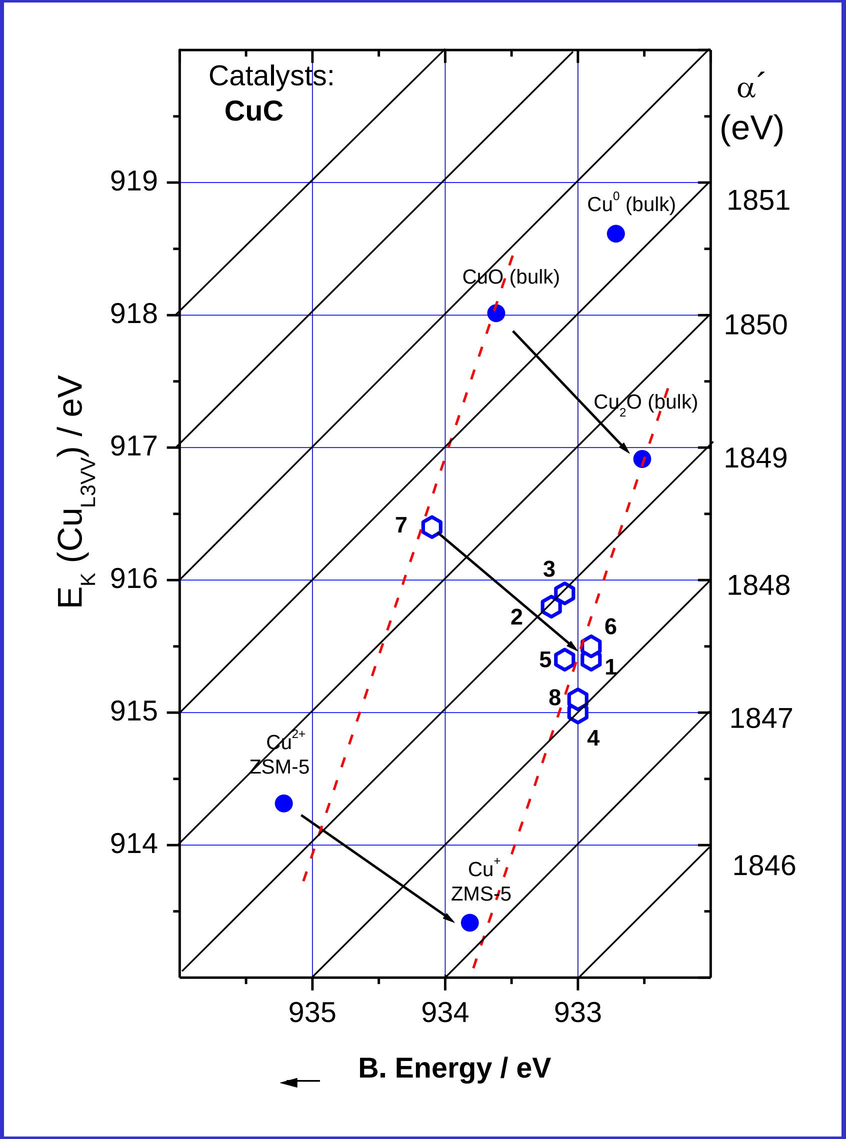
- XPS/XAES data of Copper in $Cu/Ce_2O_3/Si(111)$ model catalyst

- Evaporated copper experiments (1ML and 8ML) followed by *"in situ"* oxygen treatments from 300K to 473K

- *"slope -3"* red guide dashed lines indicate similar "chemical states" to those of the respective "bulk" references (e.g. Cu, Cu_2O and CuO)

Differences along the lines must be related with *size* and *interaction* of the copper clusters with the ceria (or ZSM5) supports

Operando- XPS/XAES of 1CuO/CeO$_2$ catalyst



Catalyst CuC: O$_2$, CO, H$_2$ and CO/H$_2$

Exp N°	Catalyst Treatments	Cu/Ce	O/(Ce+Cu)
1	evac 473K, 1h.	0.106	2,23
2	O$_2$/373K, 30 min	0.121	1.96
3	CO/573K, 15 min	0.100	2.13
4	H$_2$/ 473K, 15 min	0.109	2.08
5	CO + H2 (1:1) 473K, 15 min	0.092	2.06
6	CO + H2 (1:1) 473K, 15 min	0.095	1.97
7	O$_2$/573K, 30 min	0.106	1.92
8	CO + H2 (1:1) 473K, 15 min	0.090	1.99

Dispersion of copper remains almost unchanged for all the treatments even at temperatures higher than 473K without reduction to metallic copper

How is copper during CO-PROX ?

Preparation of new copper oxide-ceria catalysts

IMPREGNATION	
Catalyst name	Cu loading (wt. %)
$0.5CuO/CeO_2$	0.5
$1CuO/CeO_2$	1
$3CuO/CeO_2$	3
$5CuO/CeO_2$	5

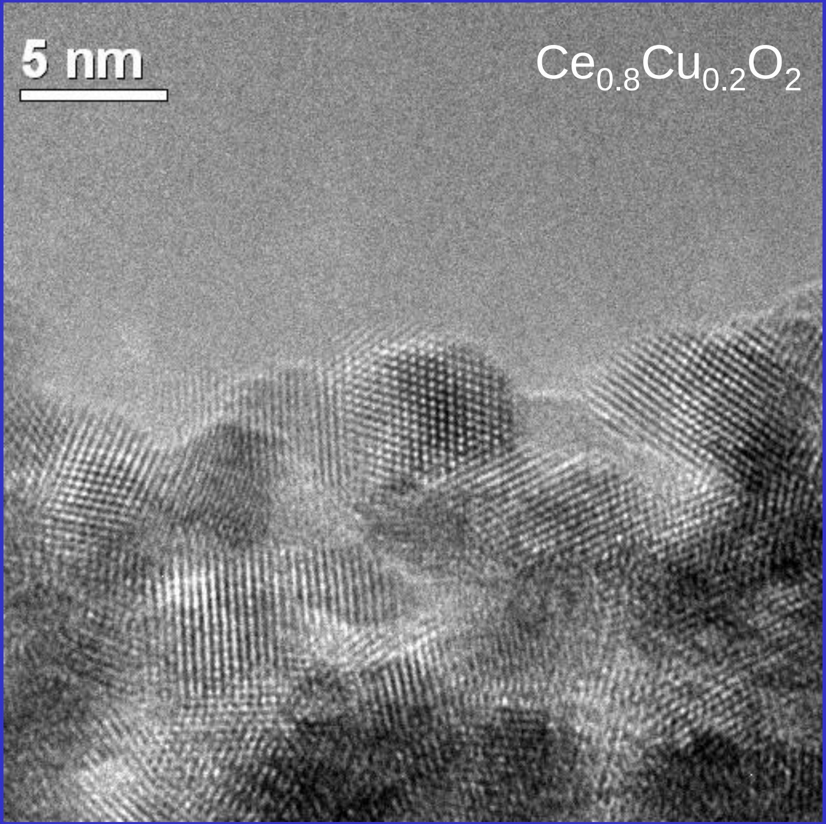
Prepared by impregnation of a CeO_2 support, obtained by microemulsion, with copper

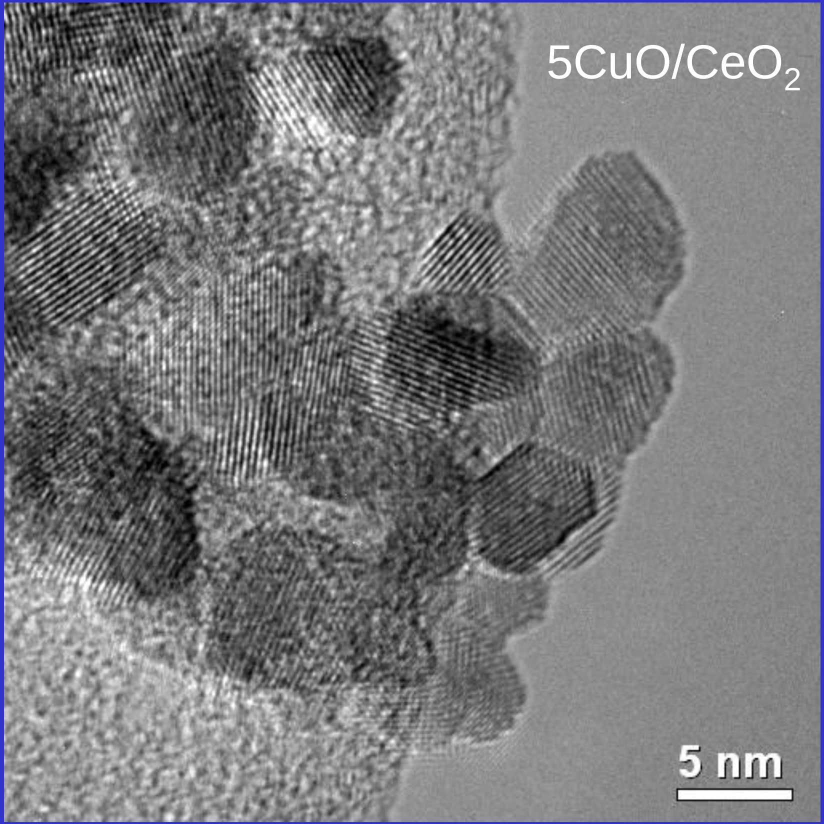
MICROEMULSION COPRECIPITATION	
Catalyst name	Ce:Cu atomic ratio
$Ce_{0.95}Cu_{0.05}O_2$	9.5:0.5
$Ce_{0.9}Cu_{0.1}O_2$	9:1
$Ce_{0.8}Cu_{0.2}O_2$	8:2

Prepared by coprecipitation of microemulsions of copper and ceria

D. Gamarra et al. J. Phys Chem. C 111 (2007) 11026

CuO/CeO_2 catalysts: Structural characterization

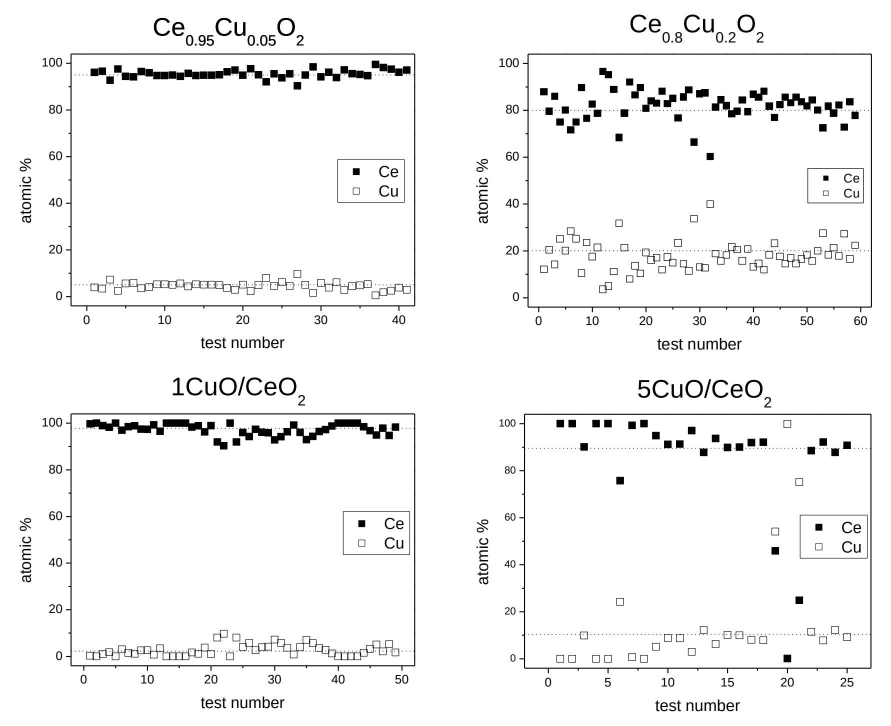




D. Gamarra et al. J. Phys Chem. C 111 (2007) 11026

CuO/CeO_2 catalysts. Structural characterization

XEDS-STEM

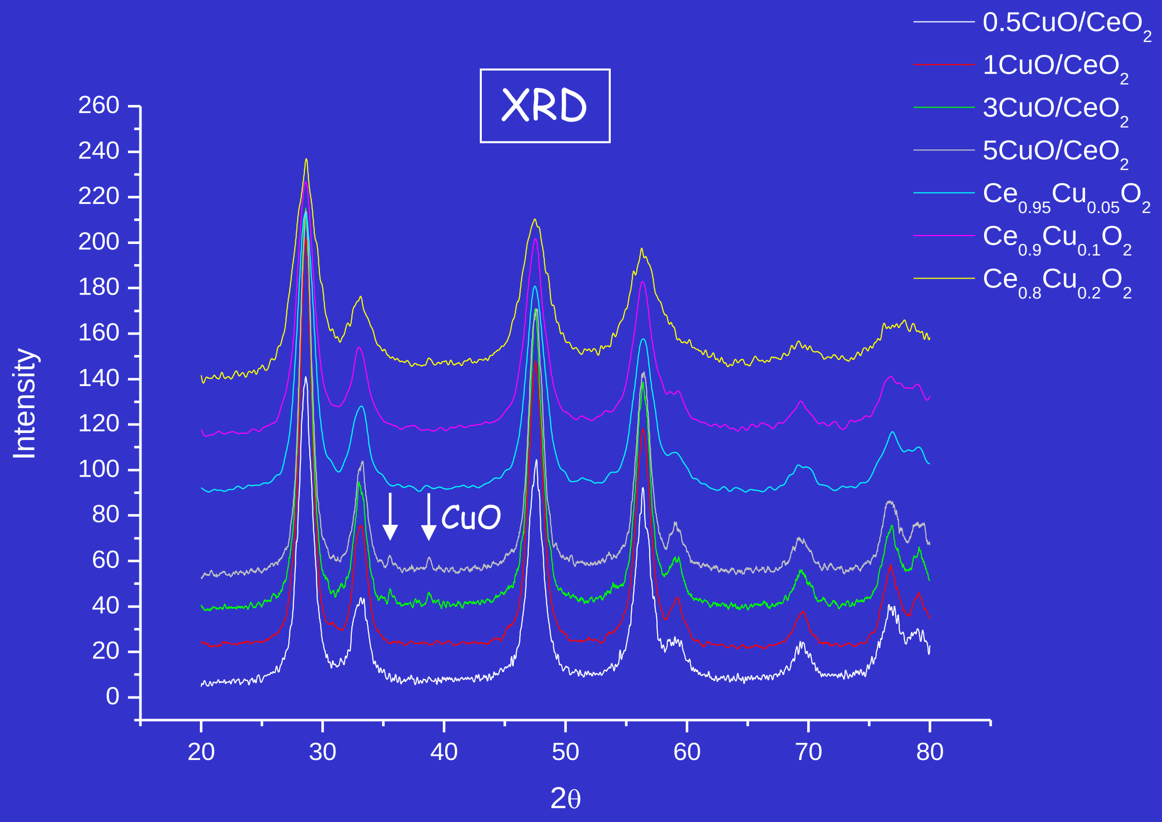


X-ray Energy Dispersive Spectra

D. Gamarra et al. J. Phys Chem. C 111 (2007) 11026

CuO-CeO2 catalysts: Textural/structural characterization

Catalyst	**S_{BET}/m^2g^{-1}**
$0.5CuO/CeO_2$	115.9
$1CuO/CeO_2$	106.5
$3CuO/CeO_2$	106.0
$5CuO/CeO_2$	100.8
$Ce_{0.95}Cu_{0.05}O_2$	129.6
$Ce_{0.9}Cu_{0.1}O_2$	135.8
$Ce_{0.8}Cu_{0.2}O_2$	151.0



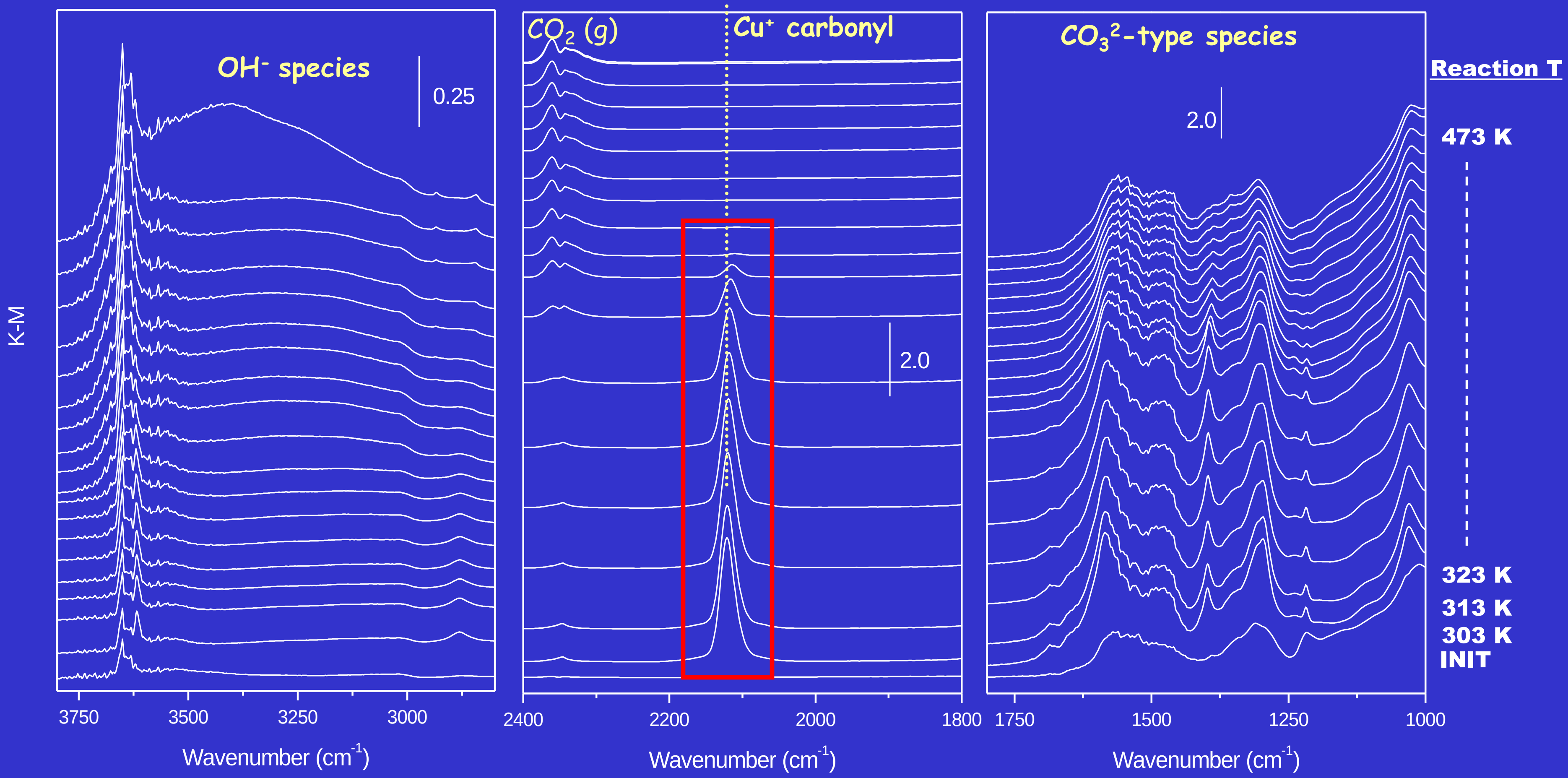
XRD results for $Ce_{1-x}Cu_xO_2$ at room temperature

Sample	Lattice constant, a (Å)	Microstrain (a.u.)
CeO_2	5.400	0.85
$Ce_{0.95}Cu_{0.05}O_2$	5.401	1.14
$Ce_{0.9}Cu_{0.1}O_2$	5.401	1.24
$Ce_{0.8}Cu_{0.2}O_2$	5.406	1.85

D. Gamarra et al. J. Phys Chem. C 111 (2007) 11026

Cu_xO-CeO_2 catalysts: *Operando*-DRIFTS analysis

CO-PROX: 1% CO + 1.25% O_2 + 50% H_2 over 1CuO/CeO_2



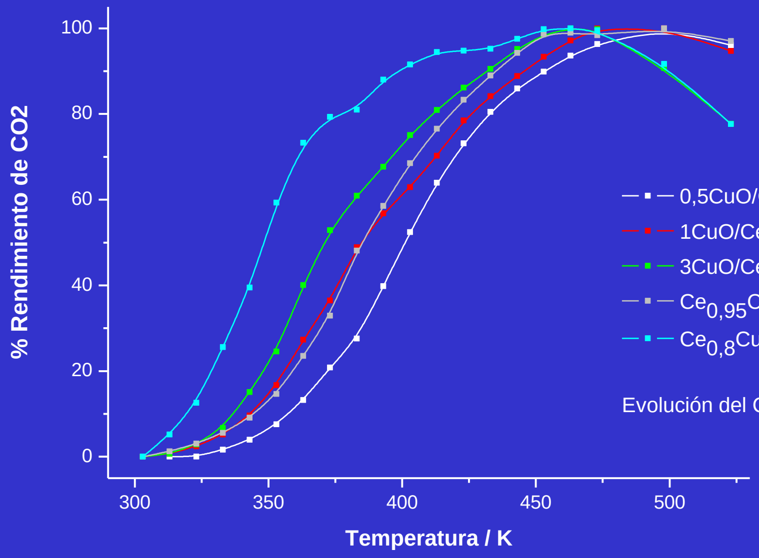
Difuse Reflectance Infrared Fourier Transformed Spectroscopy

D. Gamarra et al. J. Phys Chem. C 111 (2007) 11026 and J. Am. Chem. Soc. 129 (2007) 12064

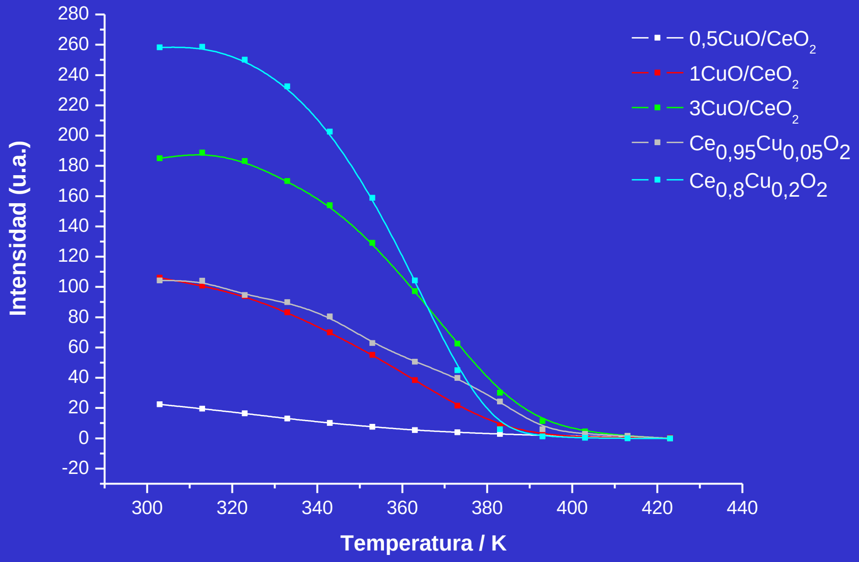
CuO/CeO$_2$ catalysts: *Operando*-DRIFTS analysis

CO-PROX: under 1% CO + 1.25% O_2 + 50% H_2

QMS DATA for m/e = 44



Cu$^+$ carbonyl intensity

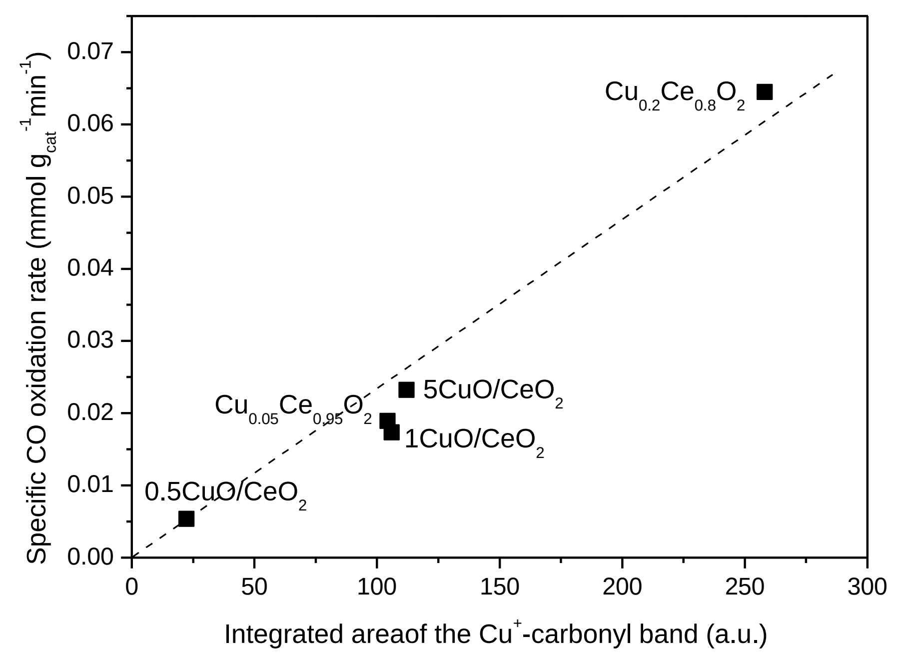


A correlation exist between the capacity to form Cu$^+$-CO of each catalysts and its activity for CO oxidation

D. Gamarra et al. J. Phys Chem. C 111 (2007) 11026 and J. Am. Chem. Soc. 129 (2007) 12064

CuO-CeO2 catalysts. *Operando*-DRIFTS analysis

CO-PROX: under 1% CO + 1.25% O_2 + 50% H_2

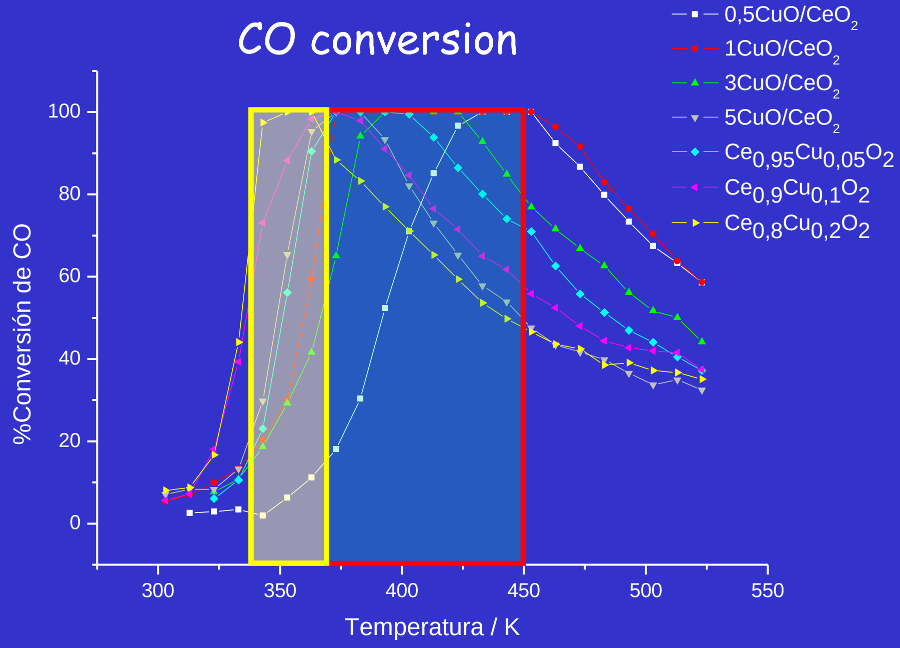


CO oxidation activity correlates with the intensity of Cu^+ carbonyls formed under reaction conditions; this, along with consideration that such carbonyls reflect interfacial copper oxide reduction, indicates that such activity is basically related to the interfacial redox activity

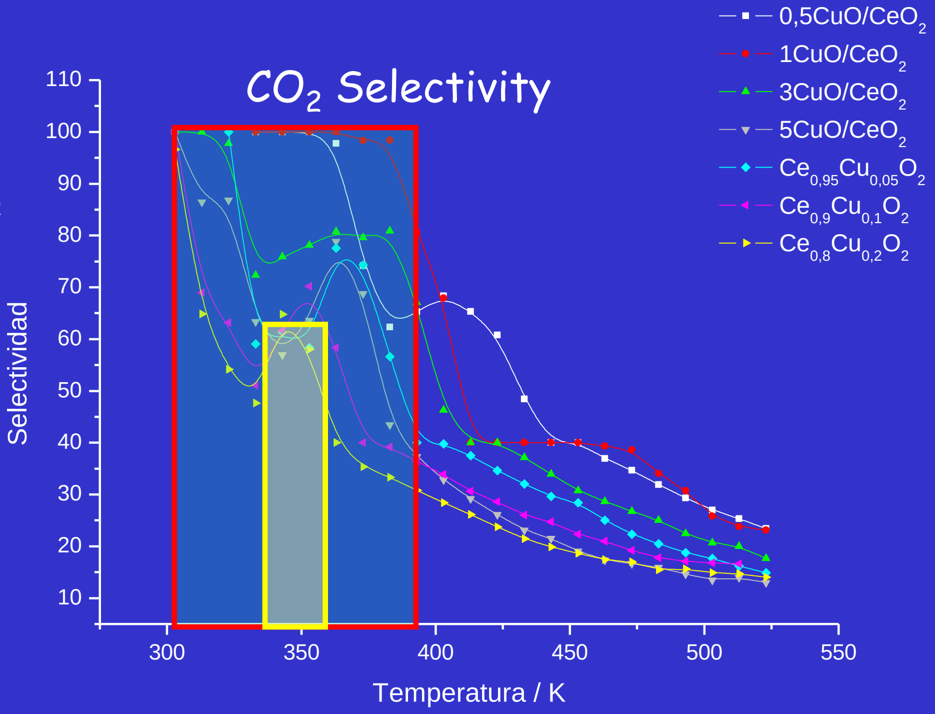
D. Gamarra et al. J. Am. Chem. Soc. 129 (2007) 12064

Cu_xO/CeO_2 catalysts: Catalytic activity

CO-PROX: under 1% CO + 1.25% O_2 + 50% H_2



CO conversion



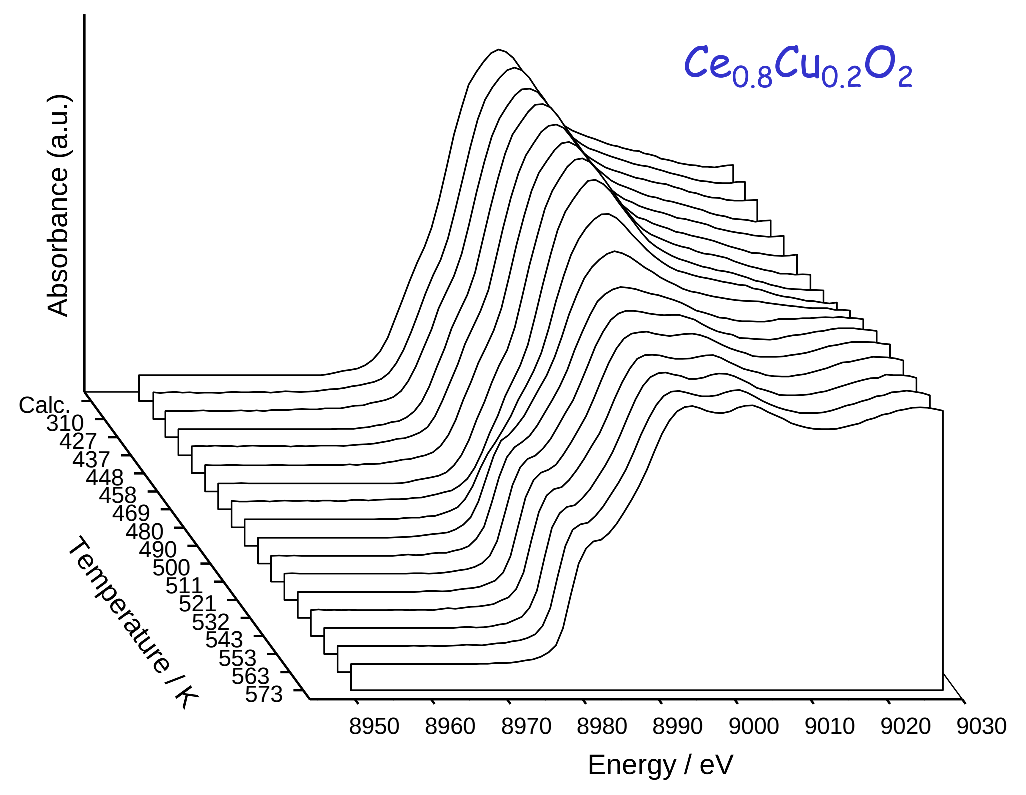
CO_2 Selectivity

The window for CO conversion of catalysts prepared by Cu/Ce coprecipitation are active for CO oxidation at lower temperatures but with a much lower CO_2-selectivity while those prepared by impregnation shows much wider windows for both with a coincidence of ca 50-60 K

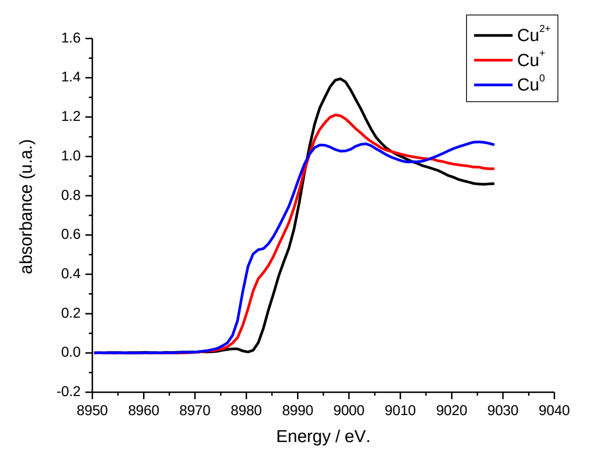
D. Gamarra et al. J. Phys Chem. C 111 (2007) 11026

CuO-CeO2 catalysts: *Operando*-XANES Cu-K edge

CO-PROX: under 1% CO + 1.25% O_2 + 50% H_2



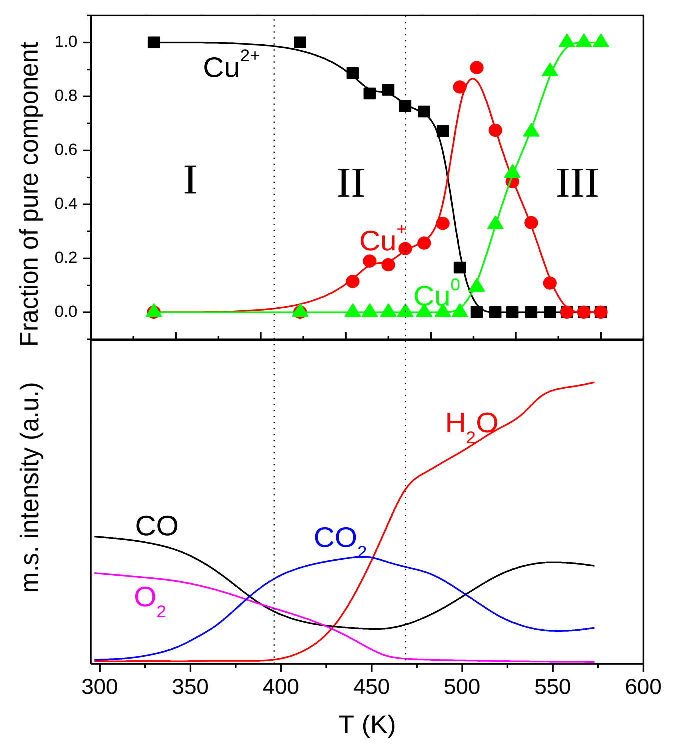
Components detected



D. Gamarra et al. J. Am. Chem. Soc. 129 (2007) 12064

CuO-CeO2 catalysts: *Operando*-XANES Cu-K edge

CO-PROX: under 1% CO + 1.25% O_2 + 50% H_2 on $Ce_{0.8}Cu_{0.2}O_2$

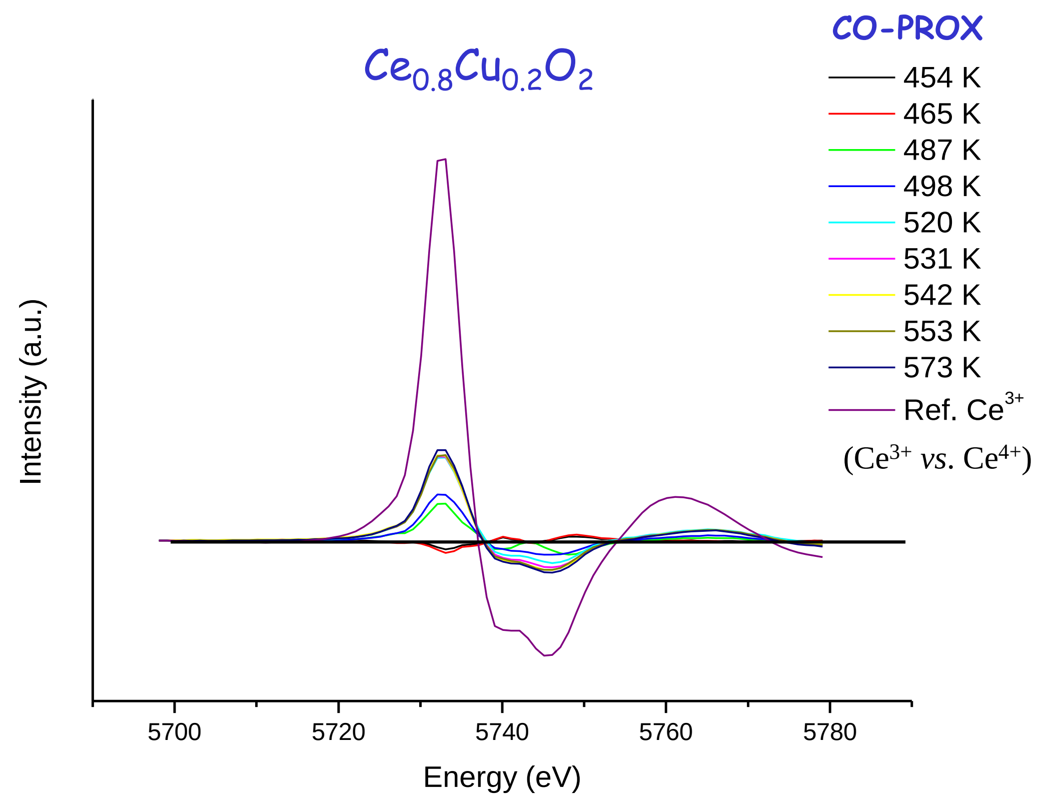


H_2 oxidation apparently proceeds when the copper reduction is extended from interfacial positions to the rest of the copper oxide clusters. This along with consideration that CO oxidation appears related to interfacial copper oxide sites suggests that the CO-PROX activity could be modulated upon changing the structural characteristics of the dispersed copper oxide component and its interface with the support

D. Gamarra et al. J. Am. Chem. Soc. 129 (2007) 12064

CuO-CeO2 catalysts. *Operando*-XANES Ce L_{III}-edge (difference spectra)

CO-PROX: under 1% CO + 1.25% O_2 + 50% H_2

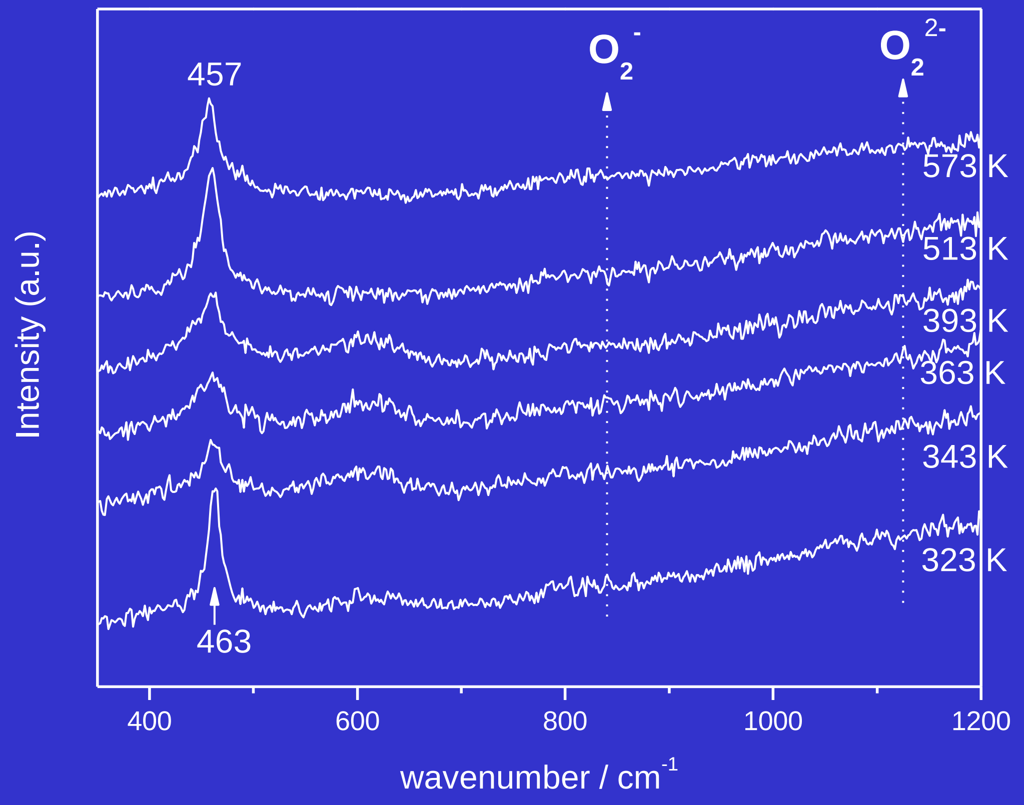


During the CO-PROX reaction some Ce^{3+} is seen also by XPS

D. Gamarra et al. J. Am. Chem. Soc. 129 (2007) 12064

Active oxygen species in CuO-CeO_2. *Operando*-Raman

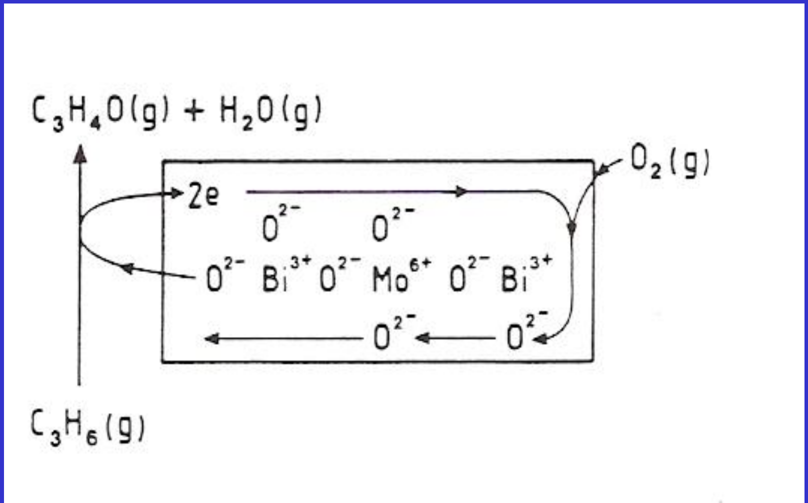
CO-PROX: under 1% CO + 1.25% O_2 + 50% H_2 on $Ce_{0.8}Cu_{0.2}O_2$



oxidation mechanism using lattice O^{2-} of CeO_2 ?

D. Gamarra et al. J. Am. Chem. Soc. 129 (2007) 12064

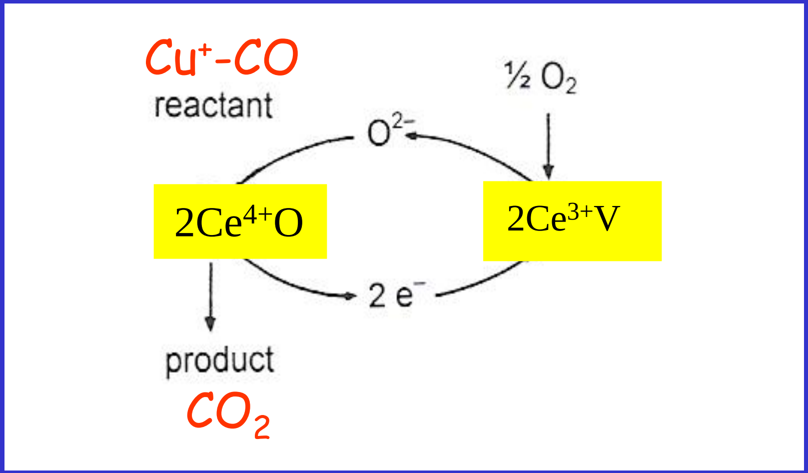
Mars-van Krevelen Mechanism for oxidation



Sacrificial mechanism

Some metal oxides that possess perovskite, fluorita or pyrochlore structures are prone to release their structural oxygen to an incoming reactant - such as hydrocarbons or carbon monoxide - and subsequently make good the loss by assimilating oxygen from the gas phase

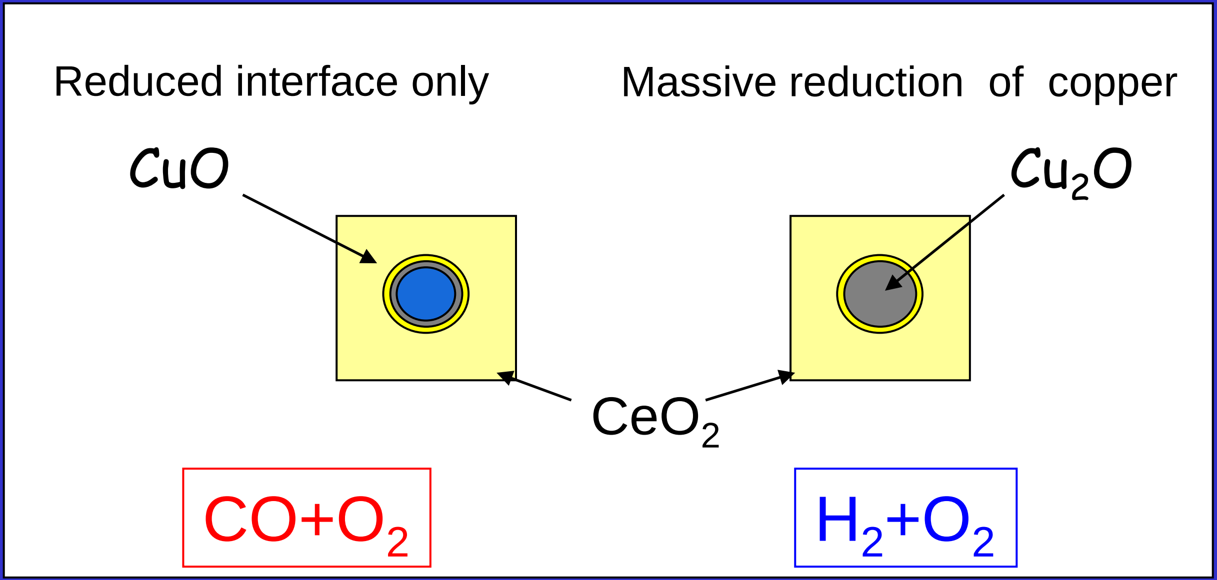
Reduced $2Ce^{3+}V$ centers at the CeO_2, probably nearby the Cu_xO particles, were also detected during CO axidation in *operando*-XPS/XAES experiments



P. Mars, P. van Krevelen Chem.Eng. Sci. Suppl.. 1954,3.41

In summary

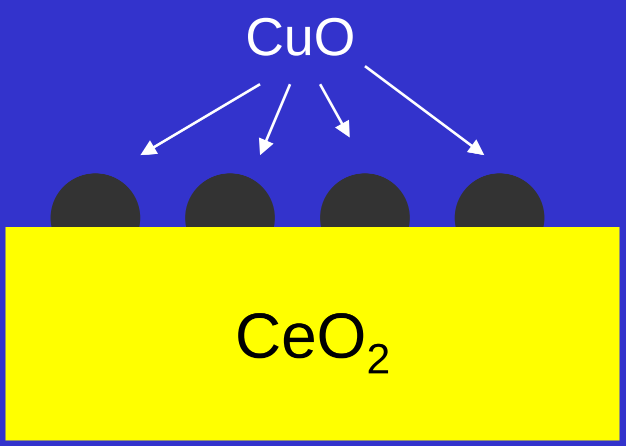
- Both CO and H_2 oxidation activities are enhanced by Cu_xO dispersion.
- CO oxidation is related to formation of interfacial sites in Cu_xO particles.
- H_2 oxidation is related to formation of reduced sites on top of Cu_xO particles.



- These hypotheses open the possibility to control the CO-PROX activity by acting separately on the Cu_xO/CeO_2 interfaces and the CuO particles.

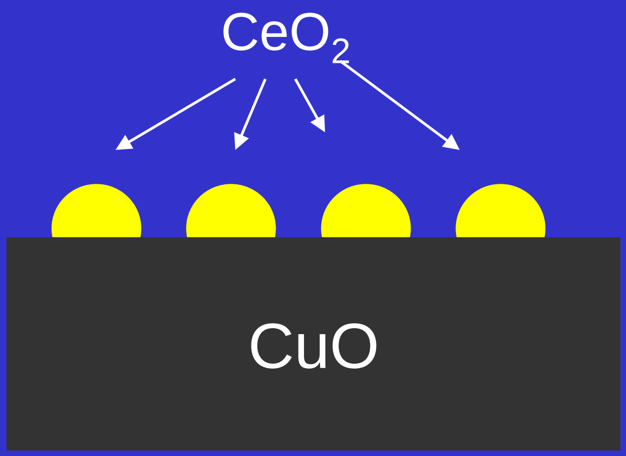
Optimization of CuO/CeO_2 catalysts: inverse systems

Classic configuration



CuO/CeO_2

Inverse configuration



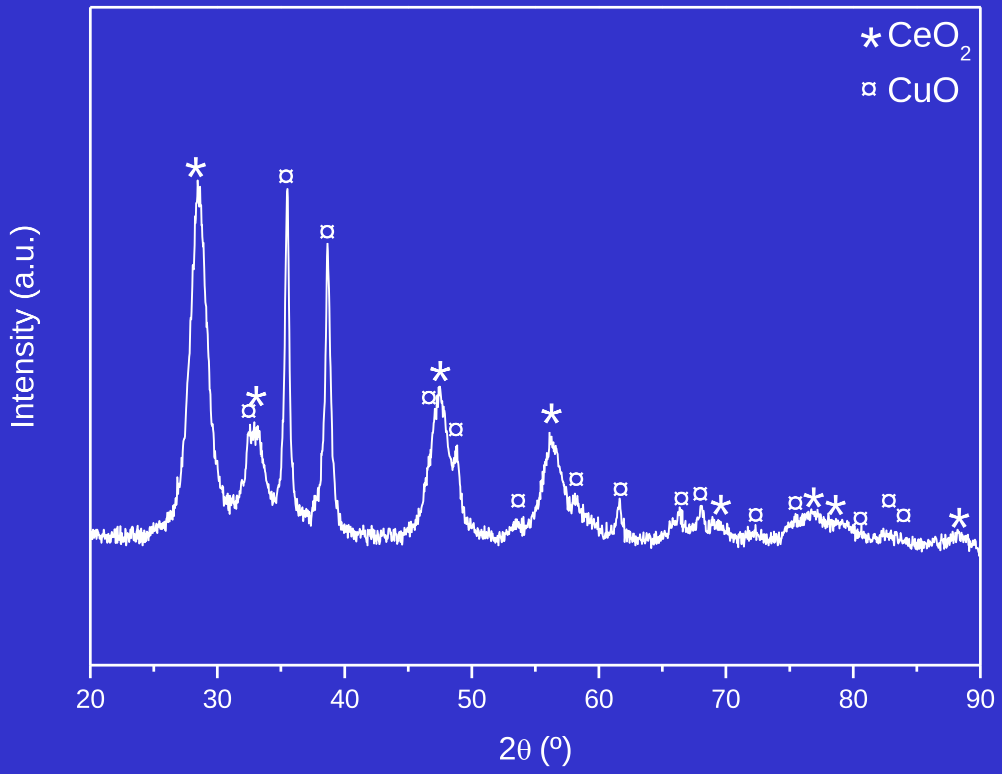
CeO_2/CuO

Why ?

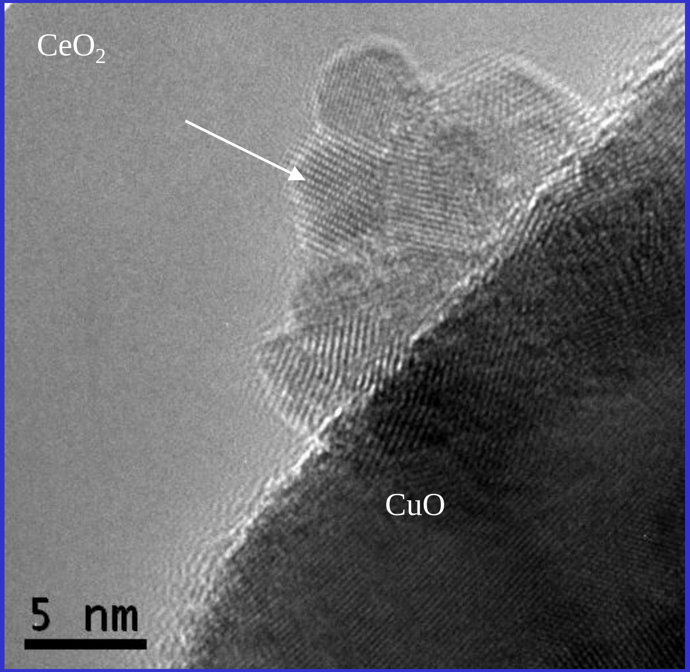
A. Hornés et al. J. Am. Chem. Soc. 132 (2010) 34

Inverse CeO_2/CuO. Structural and morphological characterization

XRD



HREM

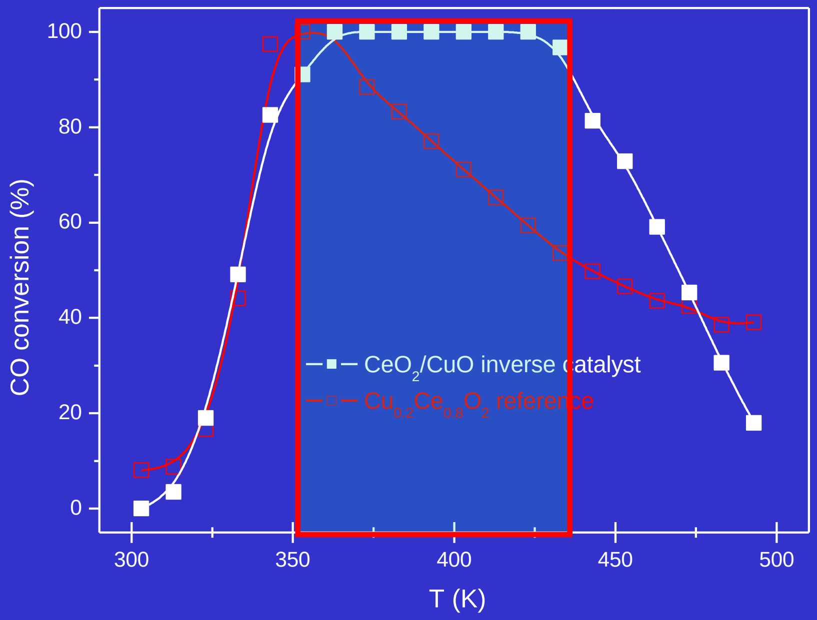


A. Hornés et al. J. Am. Chem. Soc. 132 (2010) 34

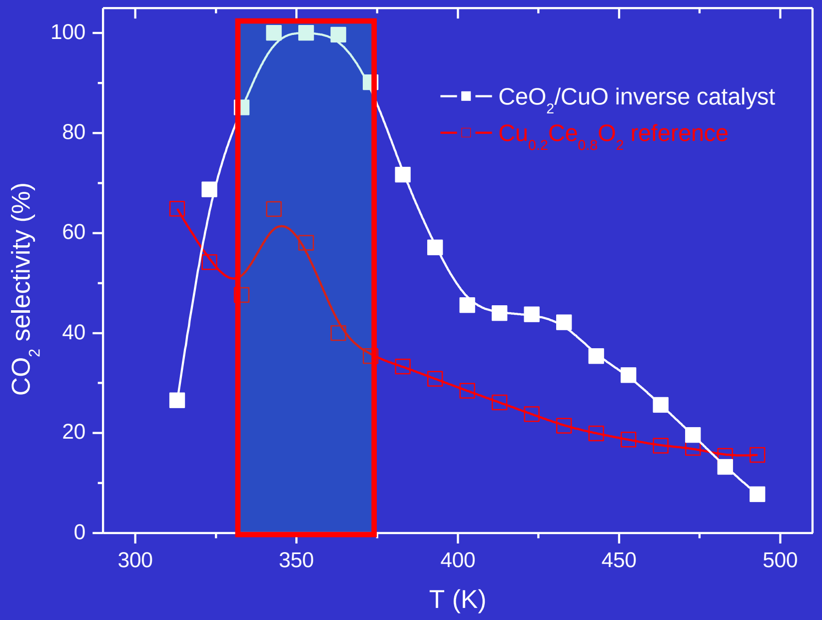
Inverse CeO_2/Cu_xO. Catalytic activity

CO-PROX: under 1% CO + 1.25% O_2 + 50% H_2

CO conversion



CO_2 selectivity

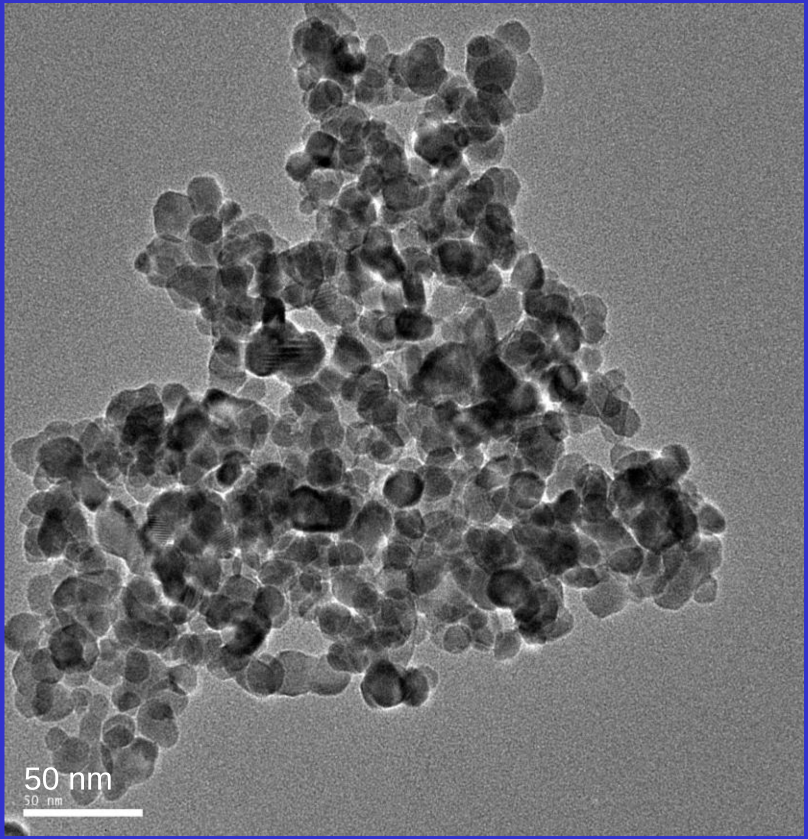


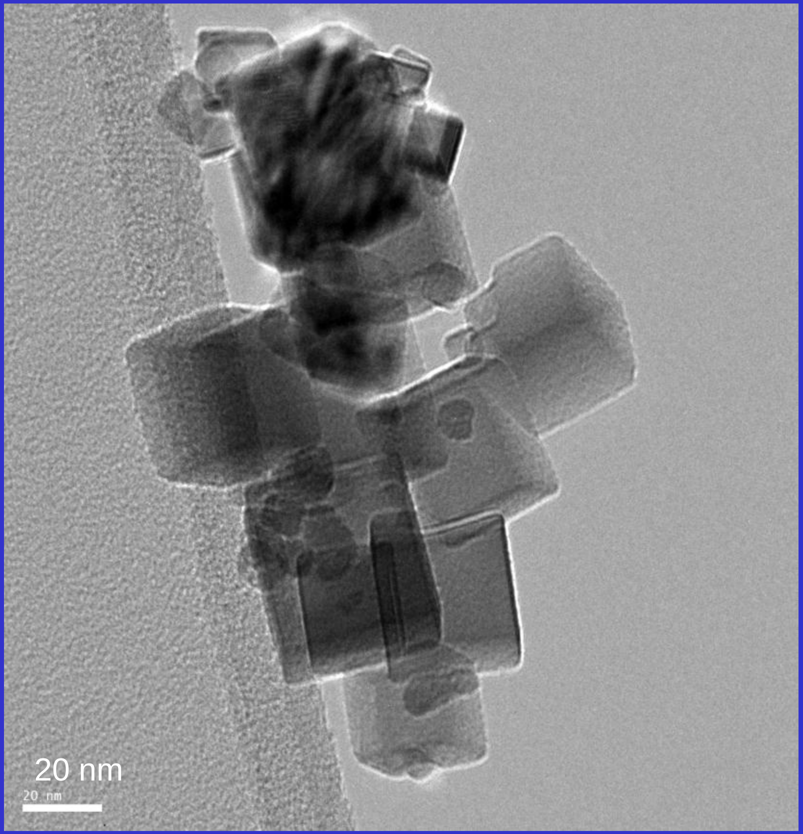
CO Conversion: $CO + \frac{1}{2}O_2 \rightarrow CO_2$

CO_2 Selectivity: $CO \rightarrow CO_2 >> H_2 \rightarrow H_2O$

A. Hornés et al. J. Am. Chem. Soc. 132 (2010) 34

Or … why not change the CuO-CeO2 interfaces ?





CuO/CeO_2-NP

CeO_2 (111)

CuO/CeO_2-NC

CeO_2(100)

General features of Cu_xO/CeO_2 catalysts for CO-PROX and related processes

- In general terms, a correlation between redox and catalytic properties is observed, suggesting the existence of redox-type mechanisms in which both the copper oxide and the support components are involved.

- Their high catalytic activity for CO oxidation (either with or without H_2) seems to be due to the existence of strong synergetic CuO-support interactions.

- Such interaction appears to facilitate copper oxide reduction which help to activate the reactants. Stabilization of reduced states of copper by such interaction has been observed under *operando* conditions.

- The physicochemical properties of Cu_xO/CeO_2 interfaces strongly depend on the nature or type of both the copper oxide and the support entities.

Who is who?

- Daniel Gamarra (ICP-CSIC)
- Aitor Hornés (ICP-CSIC)
- Ana B. Hungría (ICP-CSIC, Univ. Cádiz)
- Parthasarathi Bera (ICP-CSIC)
- Antonio López Cámara (ICP-CSIC)
- Laura Barrio (BNL- USA, ICP-CSIC)
- Marcos Fernández-García (ICP-CSIC)
- José A. Rodríguez (BNL -USA)
- Arturo Martínez-Arias (ICP-CSIC)
- J. Carlos Conesa (ICP-CSIC)
- Javier Soria (ICP-CSIC)
- Guillermo Munuera (Univ. Sevilla, ICMS)
- Jonathan C. Hanson (BNL - USA)

MINISTERIO
DE EDUCACION
Y CIENCIA

Comunidad de Madrid
La Suma de Todos

Looking into Copper in CO-PROX Catalysts:
A Multitechnique Approach

" Although *concepts* and *ideas* occupy a central place in the grand sweep of our understanding of the nature of the world arround us, it is a mistake to imagine that they play a greater role than *tools* and *techniques* in achieving scientific progress. "

Prof. Sir John Meuring Thomas

Opening lecture (Turning Points in Catalysis)
First European Congress on Catalysis (EUROPACAT-1, Montpellier 1993)
Angew. Chem. Intern. Ed. Engl. 1994, 33, 913-937

Some Highlights in Heterogeneous Catalysis

1990-2000

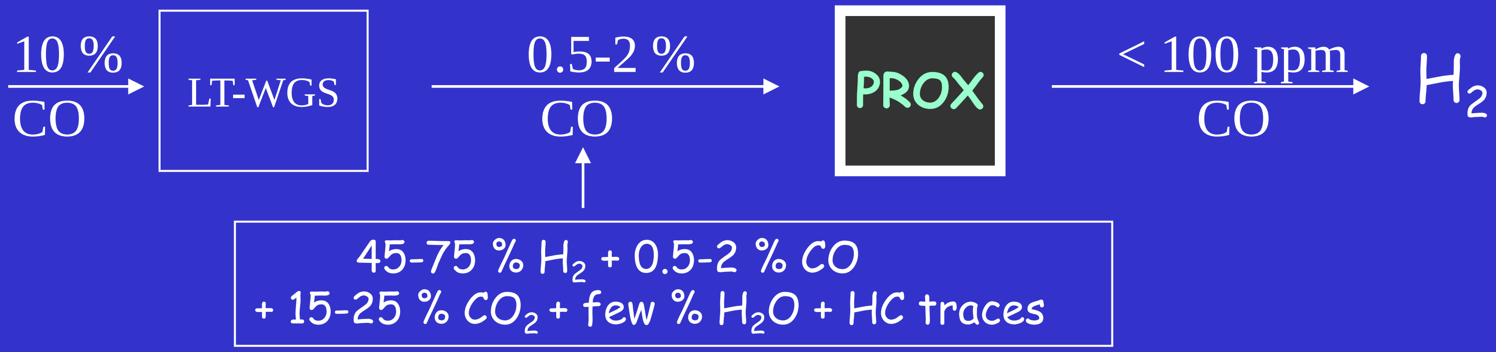
M/CeO_2 (M = Pt, Rh) for *TWC car catalysts*

$Rh\text{-}Pt/Ce_{1-x}Zr_xO_2/\gamma\text{-}Al_2O_3\text{-}La_2O_3$

2000-2012

CuO/CeO_2 catalysts for CO oxidation
(TOX and CO-PROX)

Catalytic Preferential Oxidation of CO



10 %

CO

LT-WGS

0.5-2 %

CO

PROX

< 100 ppm

CO

H_2

45-75 % H_2 + 0.5-2 % CO
+ 15-25 % CO_2 + few % H_2O + HC traces

Requirements for CO-PROX catalysts

$$\boxed{\text{CO-PROX: } CO + H_2 + (O_2) = CO_2 + H_2}$$

- High reactivity for CO oxidation
- Low reactivity for H_2 oxidation

} CO_2-Selectivity

- High resistence to poisoning by CO_2 and H_2O

Active sites in CuO-CeO$_2$ catalysts: Kinetic analysis

$$\boxed{\begin{aligned} -r_{CO} &= 3.4\times10^{10}\exp\left(\frac{\text{-94.4 kJ/mol}}{RT}\right) \\ &\times p_{CO}^{0.91} p_{CO_2}^{-0.37} p_{H_2O}^{-0.62} \text{ mol/kg/s} \end{aligned}}$$

$$\boxed{\begin{aligned} -r_{H_2} &= 6.1\times10^{13}\exp\left(\frac{\text{-142 kJ/mol}}{RT}\right) \\ &\times p_{H_2} p_{CO_2}^{-0.48} p_{H_2O}^{-0.69} \text{ mol/kg/s} \end{aligned}}$$

H.C. Lee, D.H. Kim. Catal. Today 132 (2008) 109

$Cu_xO/(Ce,M)O_y$ catalysts: General characteristics

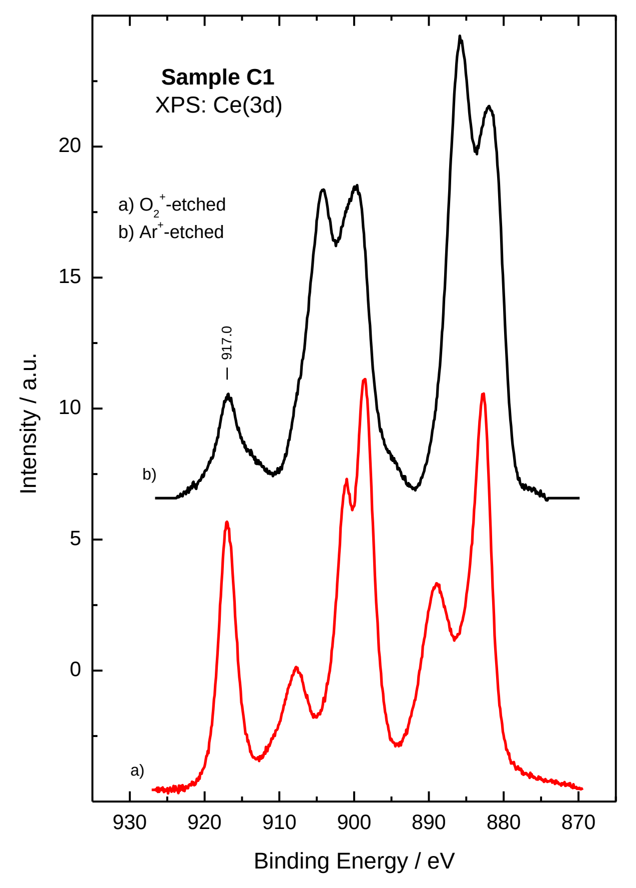
Catalyst	Support employed and Ce/M atomic ratios[a]		Copper loading (wt. %)	S_{BET} (m^2g^{-1})	Structural properties: phases detected and crystal size[b]	
CuO/CeO_2	CeO_2	----	1	92	Fluorite CeO_2	≈ 8 nm
CuO/CT1 (50% Tb)	Ce-Tb mixed oxide	Ce/Tb = 1.10	1	95	Fluorite Ce-Tb mixed oxide	≈ 6 nm
CuO/CT4 (20% Tb)	Ce-Tb mixed oxide	Ce/Tb = 3.93	1	104	Fluorite Ce-Tb mixed oxide	≈ 7 nm

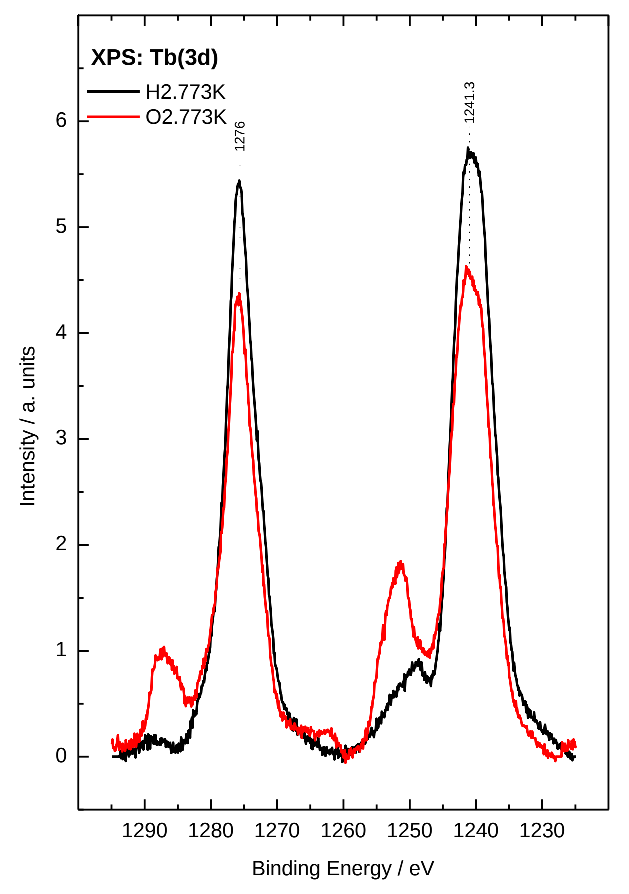
[a] ICP-AES values. [b] Based on XRD, HRTEM and Raman

The copper catalysts (1% w/w Cu) were prepared on supports contaning 20% and 50% of Tb to examine posible electronic interactions of the modified support with the Cu_xO active phase of the catalysts during CO-TOX

A. Martínez-Arias et al. J. Power Sources 151 (2005) 32

Factor Analisis: Ce(3d) and Tb(3d) in CuCT1

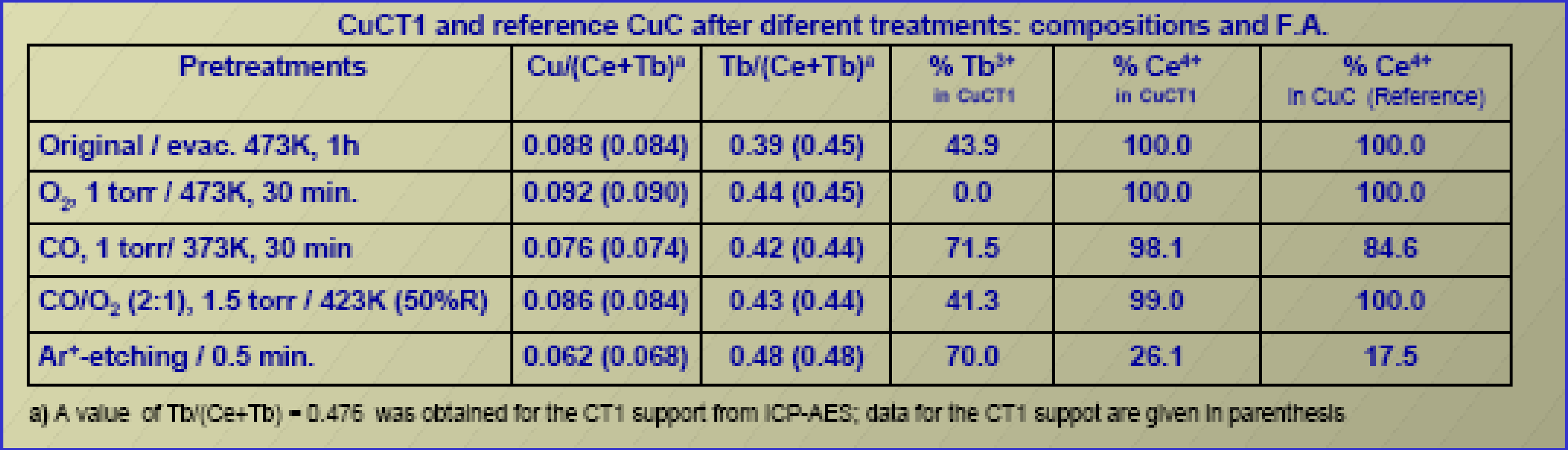




XPS: Ce(3d)
CeO_2 *vs.* Ce_2O_3

XPS: Tb(3d)
TbO_2 *vs.* Tb_2O_3

Operando-XPS of CuCT1 and CuC catalysts



CuCT1 and reference CuC after diferent treatments: compositions and F.A.

Pretreatments	Cu/(Ce+Tb)[a]	Tb/(Ce+Tb)[a]	% Tb^{3+} in CuCT1	% Ce^{4+} in CuCT1	% Ce^{4+} in CuC (Reference)
Original / evac. 473K, 1h	0.088 (0.084)	0.39 (0.45)	43.9	100.0	100.0
O_2, 1 torr / 473K, 30 min.	0.092 (0.090)	0.44 (0.45)	0.0	100.0	100.0
CO, 1 torr/ 373K, 30 min	0.076 (0.074)	0.42 (0.44)	71.5	98.1	84.6
CO/O_2 (2:1), 1.5 torr / 423K (50%R)	0.086 (0.084)	0.43 (0.44)	41.3	99.0	100.0
Ar^+-etching / 0.5 min.	0.062 (0.068)	0.48 (0.48)	70.0	26.1	17.5

a) A value of Tb/(Ce+Tb) = 0.476 was obtained for the CT1 support from ICP-AES; data for the CT1 suppot are given in parenthesis

Column 1: copper dispersion only sightly changes after the treatments and is similar to that observed in the CuC catalyst, given in parenthesis.

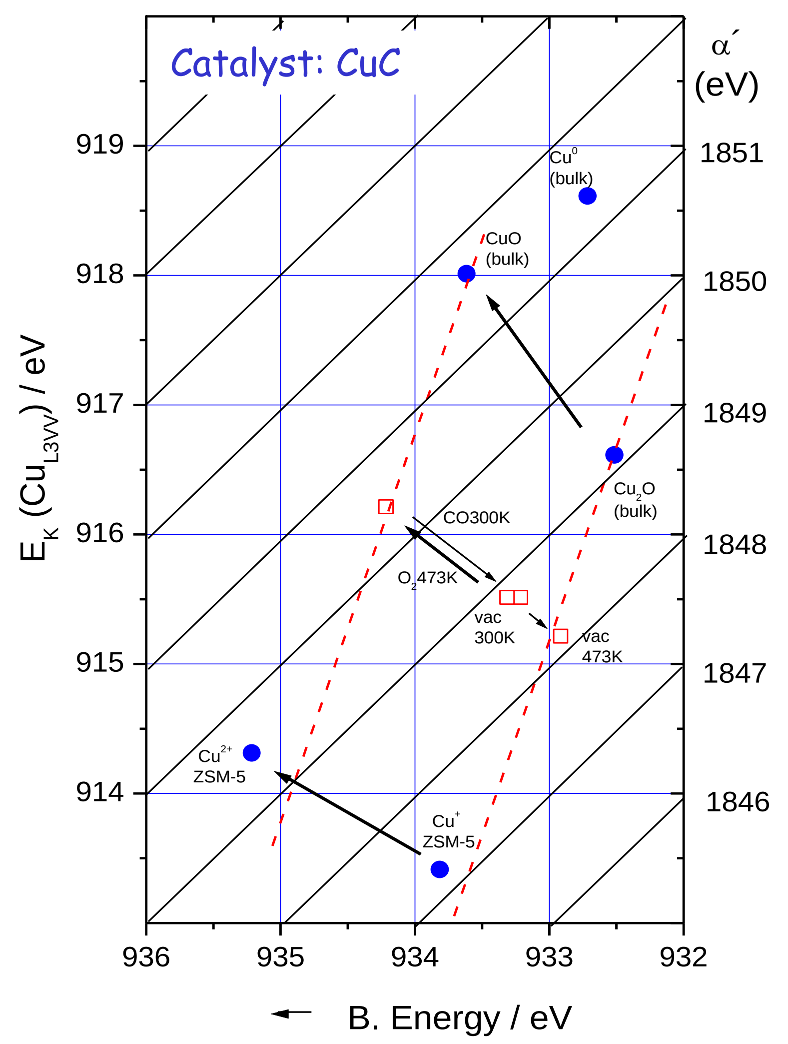
Column 2: terbium dispersion is not modified by the treatments and is similar to that observed in the CT1 support, given in parenthesis.

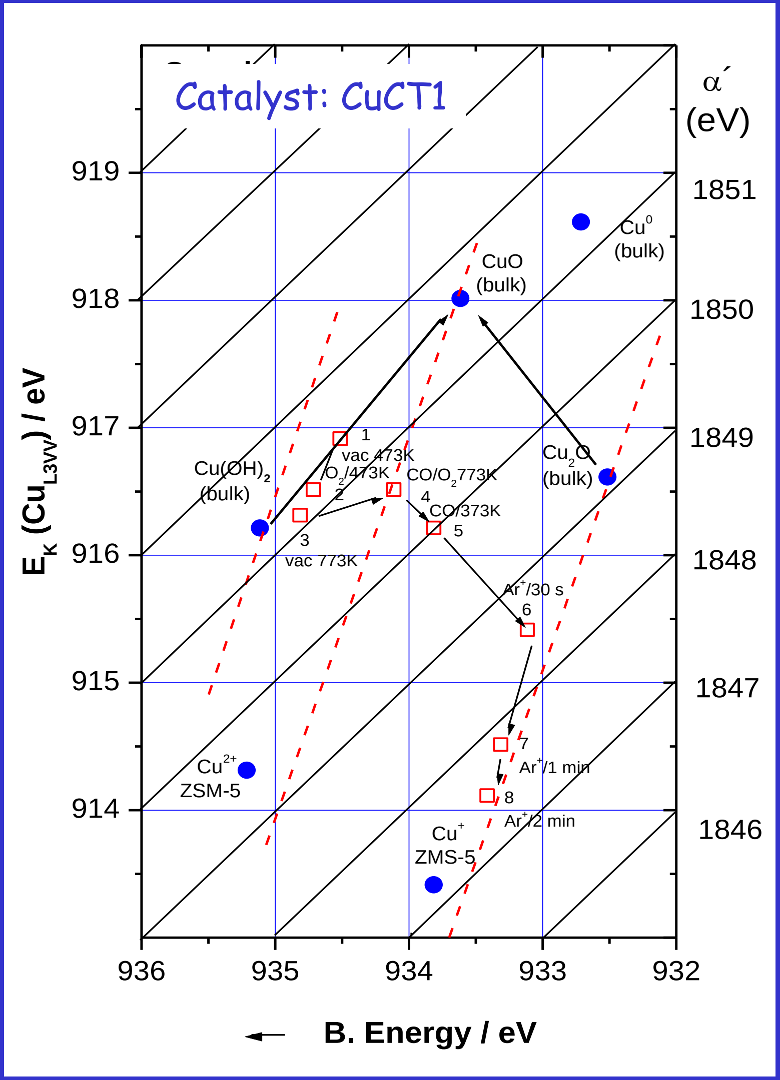
Column 3: terbium oxidation state changes with the treatments (Tb^{3+}/Tb^{4+})
Column 4: cerium remains fully oxidized after all the treatments (Ce^{4+})

Column 5: cerium in CuC (reference) is more reducible than in CuCT1 under reducing treatments (i.e. CO or Ar^+-etching)

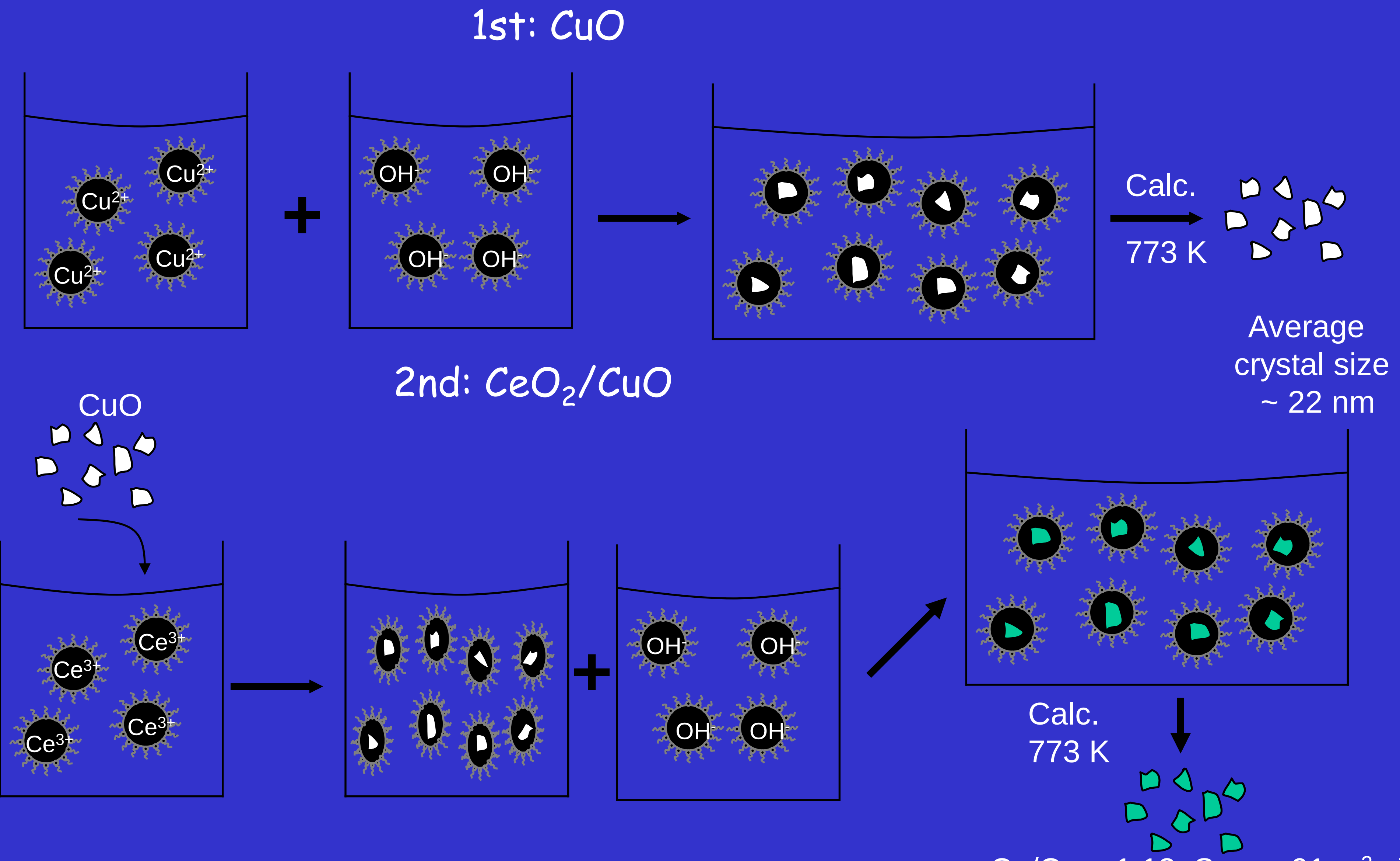
G. Munuera et al. CONCORDE Conference, "Catalytic Nano-Oxides Research and Development in Europe", Sevilla (Spain) 2006.

Wagner "chemical state plots" of copper for CuC and CuCT1





Inverse CeO_2/CuO Preparation



1st: CuO

Calc.
773 K

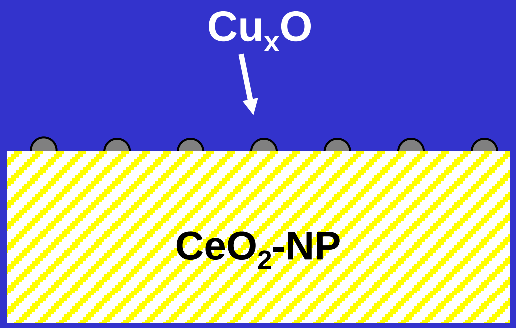
Average
crystal size
~ 22 nm

2nd: CeO_2/CuO

Calc.
773 K

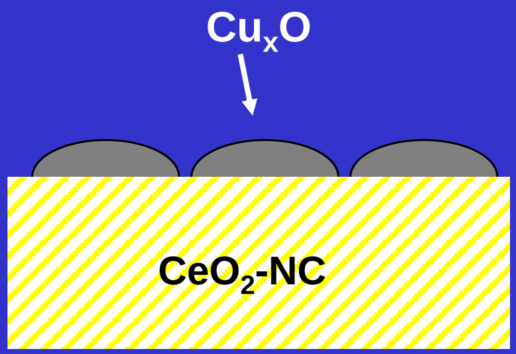
Cu/Ce = 1.13; S_{BET} = 91 m^2g^{-1}

A. Hornés et al. J. Am. Chem. Soc. 132 (2010) 34



Cu_xO

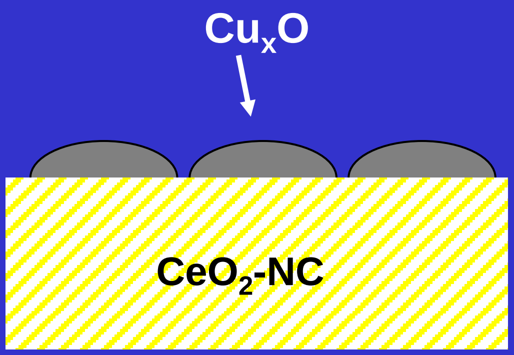
CeO_2-NP

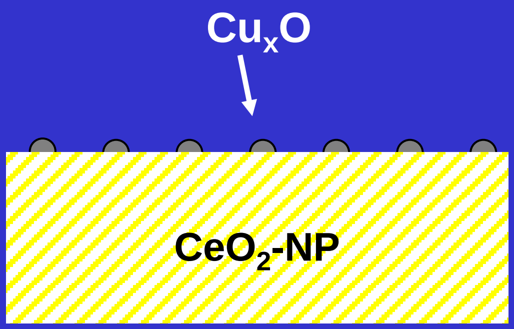


Cu_xO

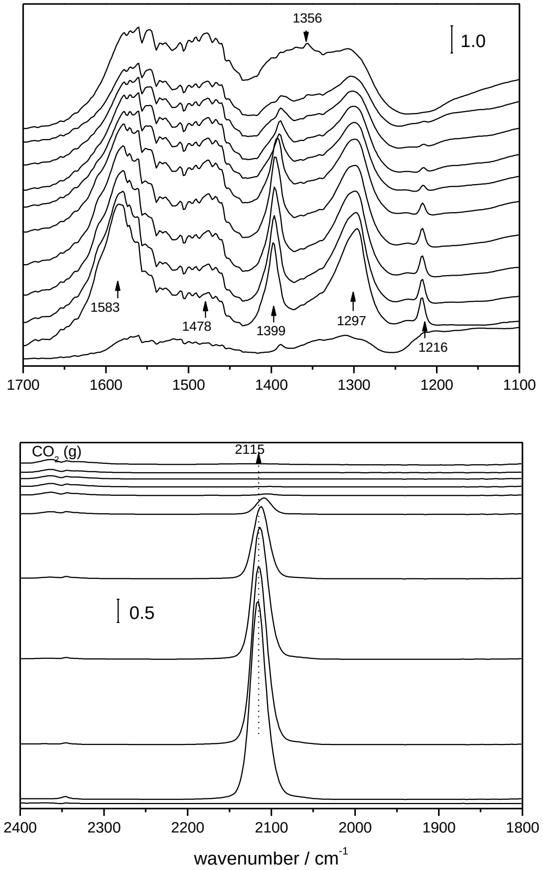
CeO_2-NC

Sample	Crystal size (nm)	Lattice parameter a (Å)	Microstrain ($\Delta d/d$)	F_{2g} frequency (cm^{-1})	F_{2g} FWHM (cm^{-1})	S_{BET} (m^2g^{-1})
CeO_2-NC	46	5.406	0.0001	464	15.5	20
CeO_2-NP	7	5.410	0.0019	462	23.3	130
Cu/CeO_2-NC	42	5.404	0.0002	463	15.5	14
Cu/CeO_2-NP	7	5.410	0.0025	460	28.2	115

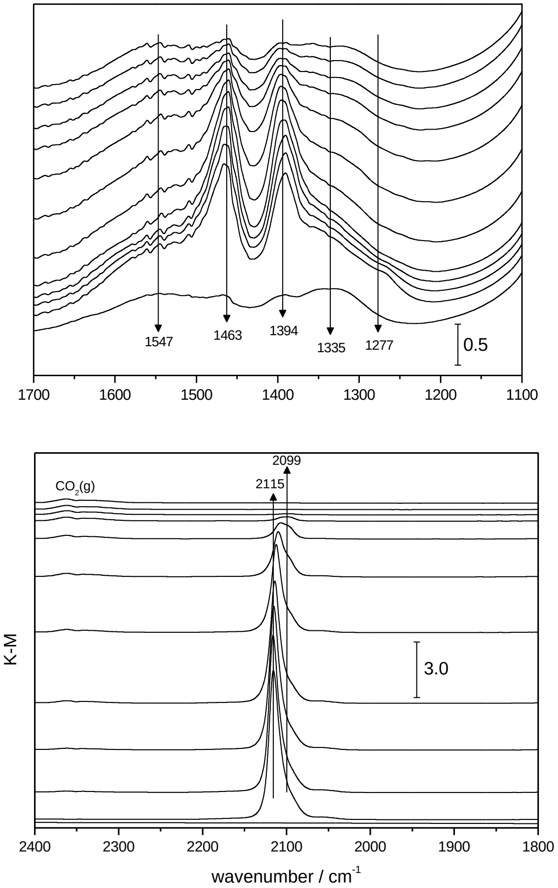




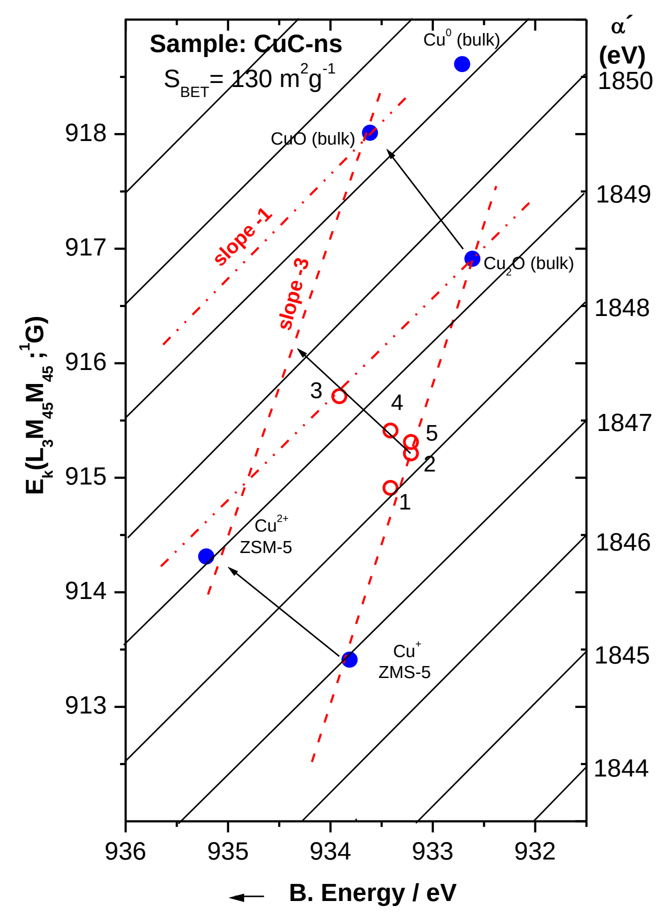
Cu/CeO_2-NP

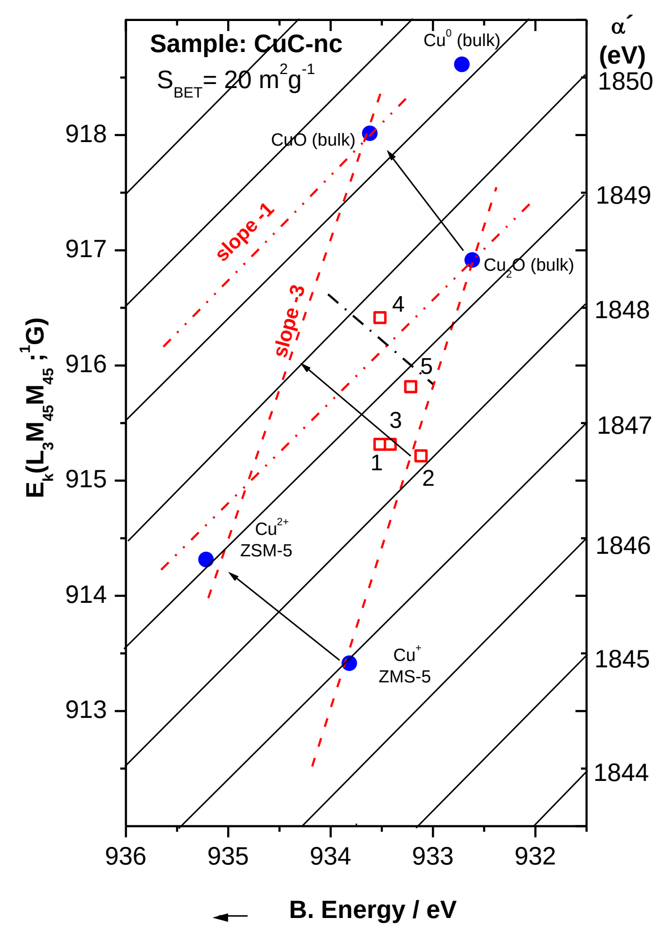


Cu/CeO_2-NC



Operando-XPS/XAES CO-TOX and CO-PROX reactions: CuC-NP and CuC-NC catalysts



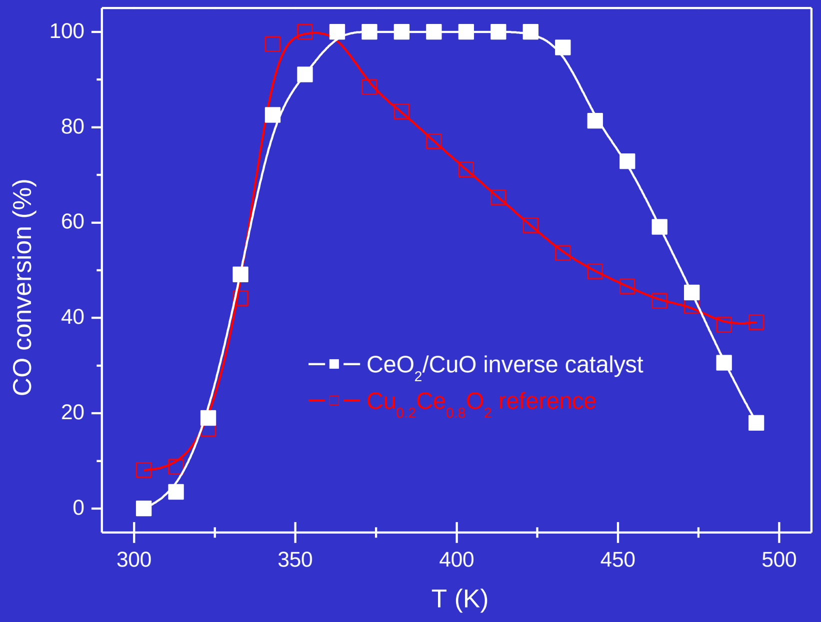


Treatments/473K: (1) evac. ; (2) red CO ; (3) CO-TOX ; (4) CO-PROX; (5) red H_2

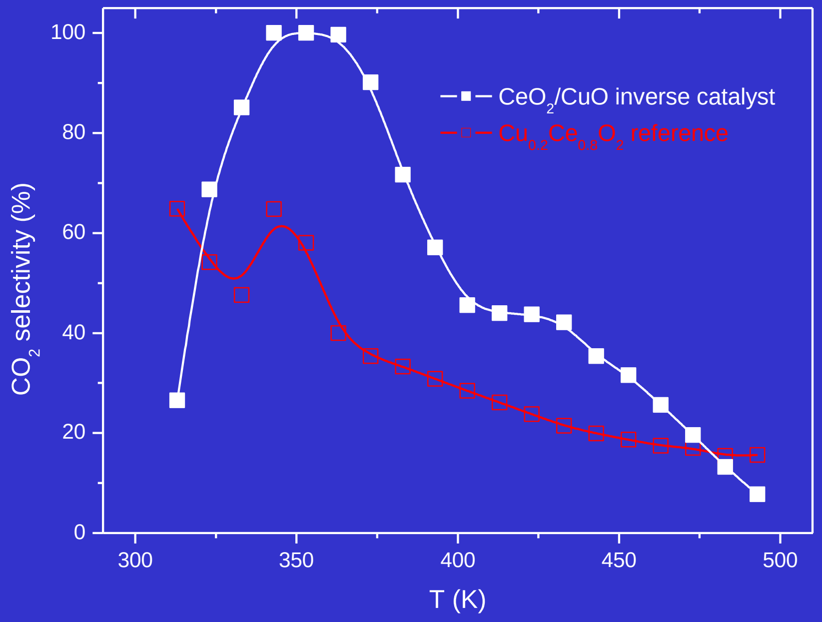
Catalytic conversion vs. selectivity in CuO-CeO$_2$ catalysts

CO-PROX: under 1% CO + 1.25% O_2 + 50% H_2

CO-conversion



CO$_2$-selectivity

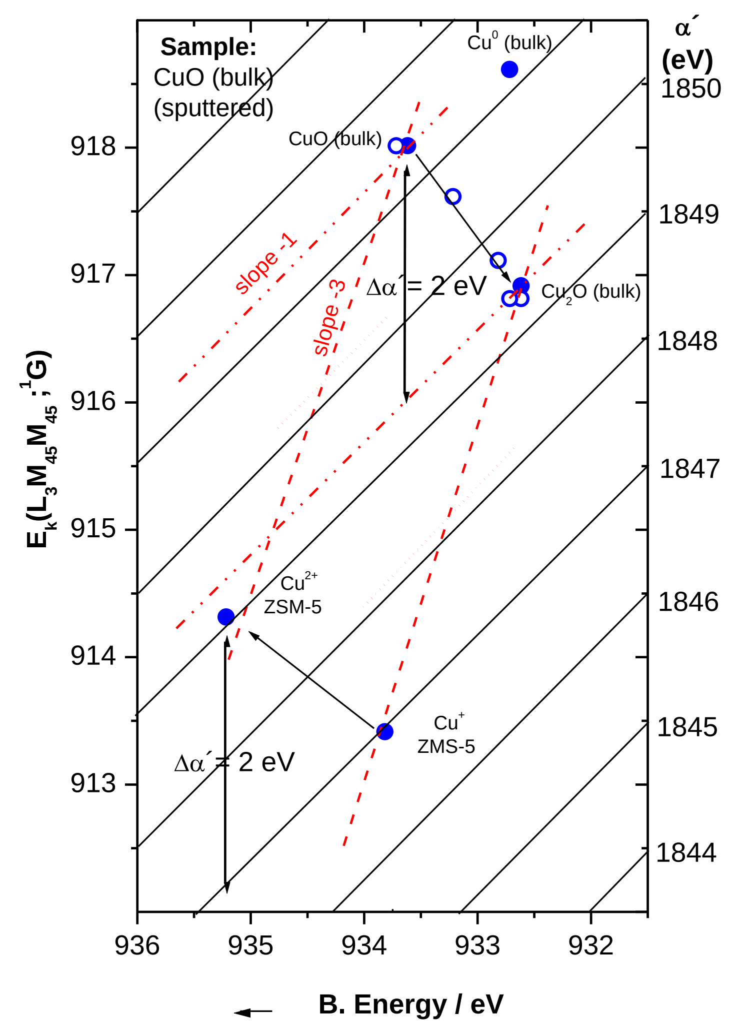


CO-Conversion: $CO + \frac{1}{2}O_2 \rightarrow CO_2$

CO$_2$-Selectivity: $CO \rightarrow CO_2 \gg H_2 \rightarrow H_2O$

A. Hornés et al. J. Am. Chem. Soc. 132 (2010) 34

Wagner “chemical state plot” for copper



W. Grünert et al. J. Phys. Chem., 1994, 98, 10832

E_{BE}(Cu2p) *vs.* E_K(CuL_3VV)

- XPS/XAES data of copper in Ar+-etched bulk CuO (Tenorite)
- Differential sputtering of CuO produce reduced Cu_xO surfaces
- “*slope -3*” red dash lines indicate similar “*chemical states*” to those of the respective references
- Thus, the copper loaded in ZSM-5 zeolites prepared by W. Grünert et al. have the same “*chemical states*” as CuO and Cu$_2$O
- Differences are in the modified Auger parameter (Δα´ ≈ 2.4 eV) which are related to those “*final state effects*”

Looking into Copper in CO-PROX Catalysts:
A Multitechnique Approach

“ Although *concepts* and *ideas* occupy a central place in the grand expansion of our understanding of the nature of the world around us, it is a mistake to imagine that they play a greater role than *tools* and *techniques* in achieving scientific progress.”

“Aunque *ideas y conceptos* ocupan un lugar central en la expansión del conocimiento de la naturaleza del mundo que nos rodea, es un error imaginar que juegan un papel mayor que las *herramientas* y las *técnicas* en el progreso científico”

John Meuring Thomas

Opening lecture (Turning Points in Catalysis)
First European Congress on Catalysis (EUROPACAT-1, Montpellier 1993)
Angew. Chem. Intern. Ed. Engl. 1994, 33, 913-937