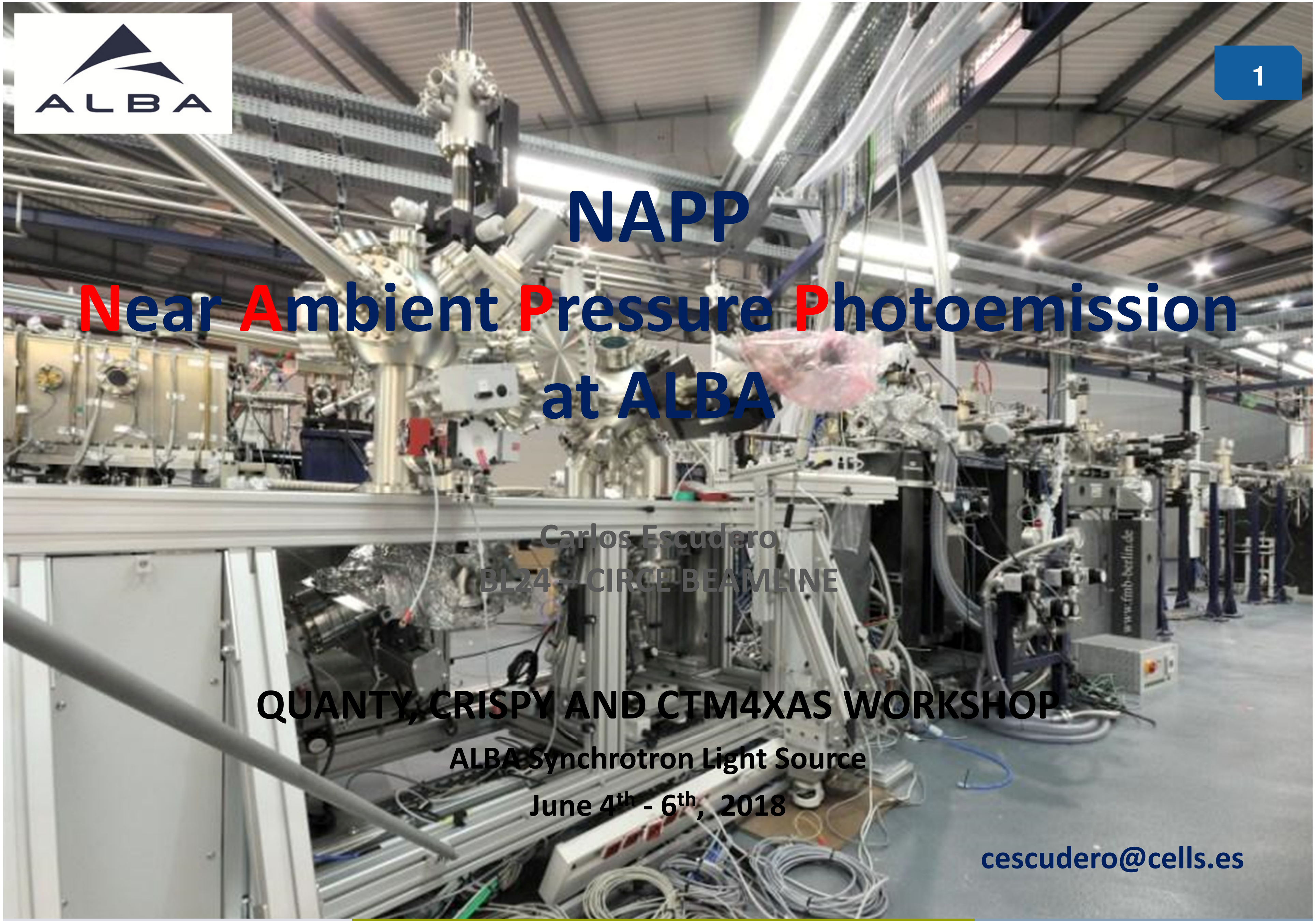


NAPP
Near Ambient Pressure Photoemission at ALBA

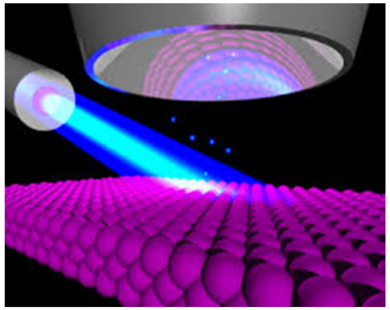
Carlos Escudero
BL24 – CIRCE BEAMLINE

QUANTY, CRISPY AND CTM4XAS WORKSHOP
ALBA Synchrotron Light Source
June 4th - 6th, 2018

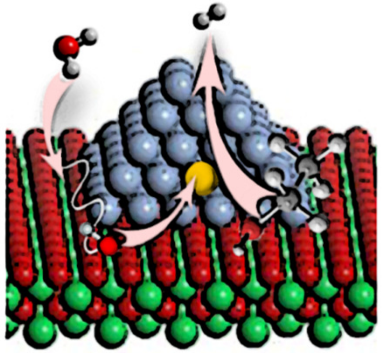
cescudero@cells.es

Outline

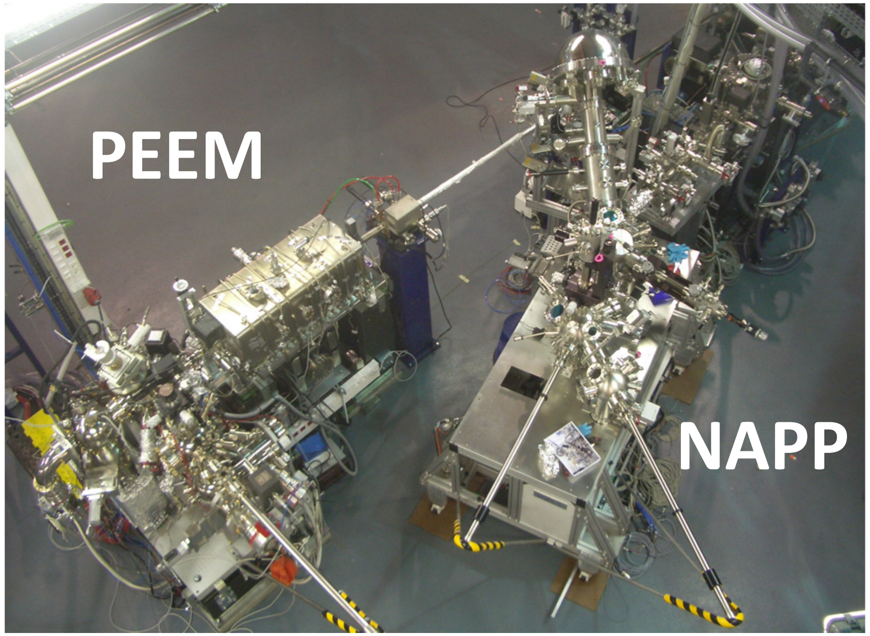
- **BL24- CIRCE: Near Ambient Pressure Photoemission (NAPP)**
  - NAPP at ALBA synchrotron, description and capabilities



- **NAPP, scientific applications**
  - Water adsorption
  - In situ studies of Electrochemical Promotion Of Catalysts
  - Surface rearrangement of bimetallic NPs in real catalysts
  - Soot oxidation studies with CeO_2

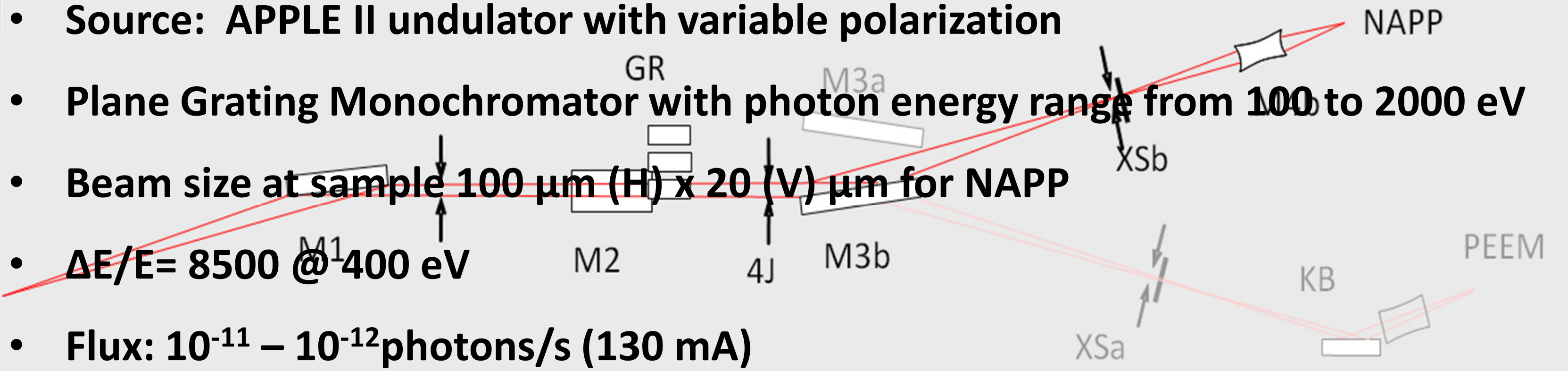


CIRCE - BL24 @ ALBA



PEEM: **P**hoto**E**mission **E**lectron **M**icroscopy

NAPP: **N**ear **A**mbient **P**ressure **P**hotoemission



- **Source: APPLE II undulator with variable polarization**
- **Plane Grating Monochromator with photon energy range from 100 to 2000 eV**
- **Beam size at sample 100 µm (H) x 20 (V) µm for NAPP**
- **$\Delta E/E$= 8500 @ 400 eV**
- **Flux: 10^{-11} – 10^{-12}photons/s (130 mA)**

NAPP, main capabilities

- XPS measurements under gas mixtures

  up to ≈ 20 mbar, with and without flow control

  Gas monitoring by RGA spectrometer

  Gases: O_2, CO, CO_2, H_2, Hydrocarbons, N_2, He
  Vapors: H_2O, MeOH, EtOH

- Peltier manipulator for sample cooling

  down to – 22.3°C (UHV) in 10 min
  down to – 13°C (1 mbar H_2O_v) in 10 min

- Sample heating by resistive heater or IR laser

  With button resistive heater up to 900°C in UHV) and 700°C (20 mbar N_2)

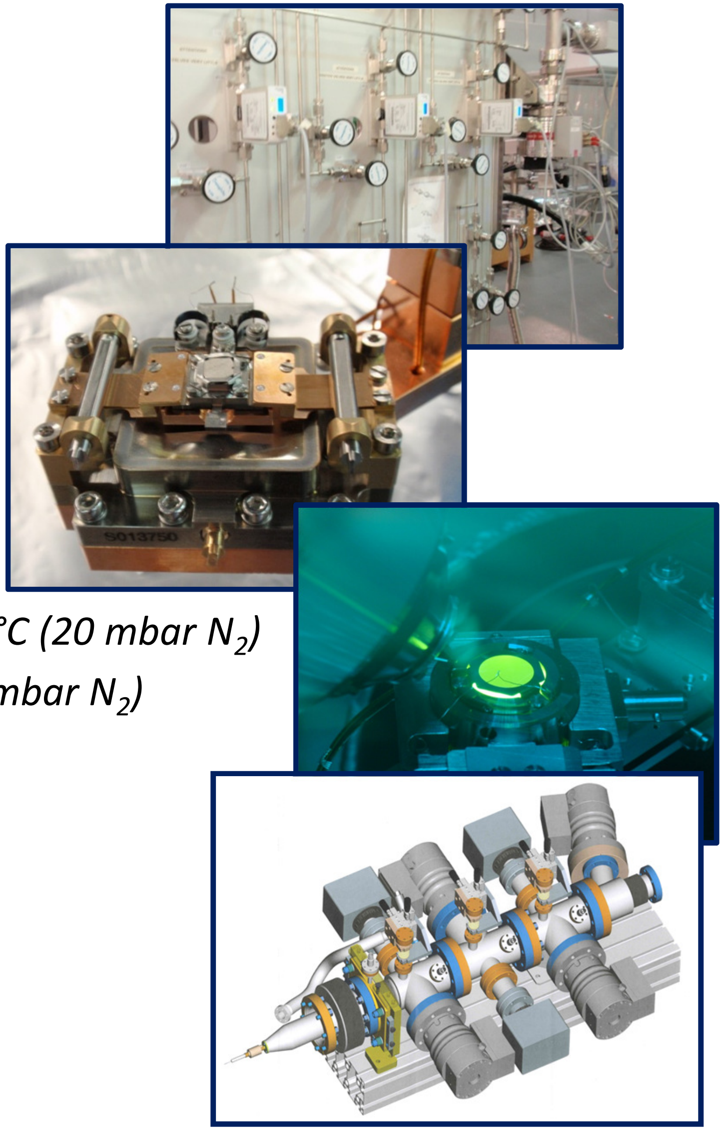
  With IR laser heater up to 1200°C in UHV) and 900°C (20 mbar N_2)

- UHV suitcase for sample transfer under vacuum

- Possibility of fully horizontal sample transfer

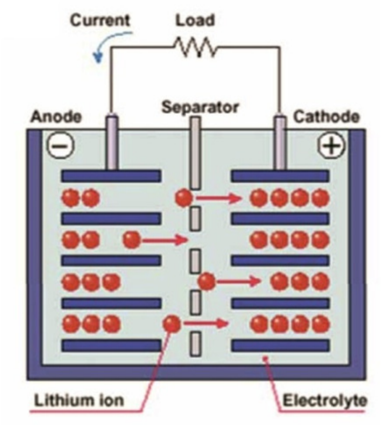
- PBE, photon beam entrance system

  differential pumping system, 10^9 P drop
  Adjustable apertures

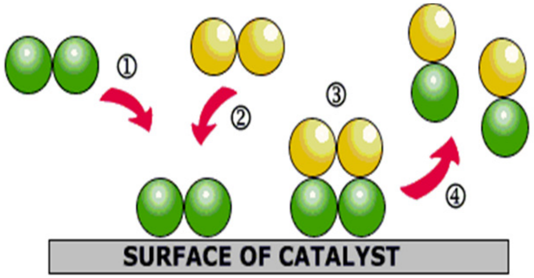


NAPP: scientific applications

Energy generation

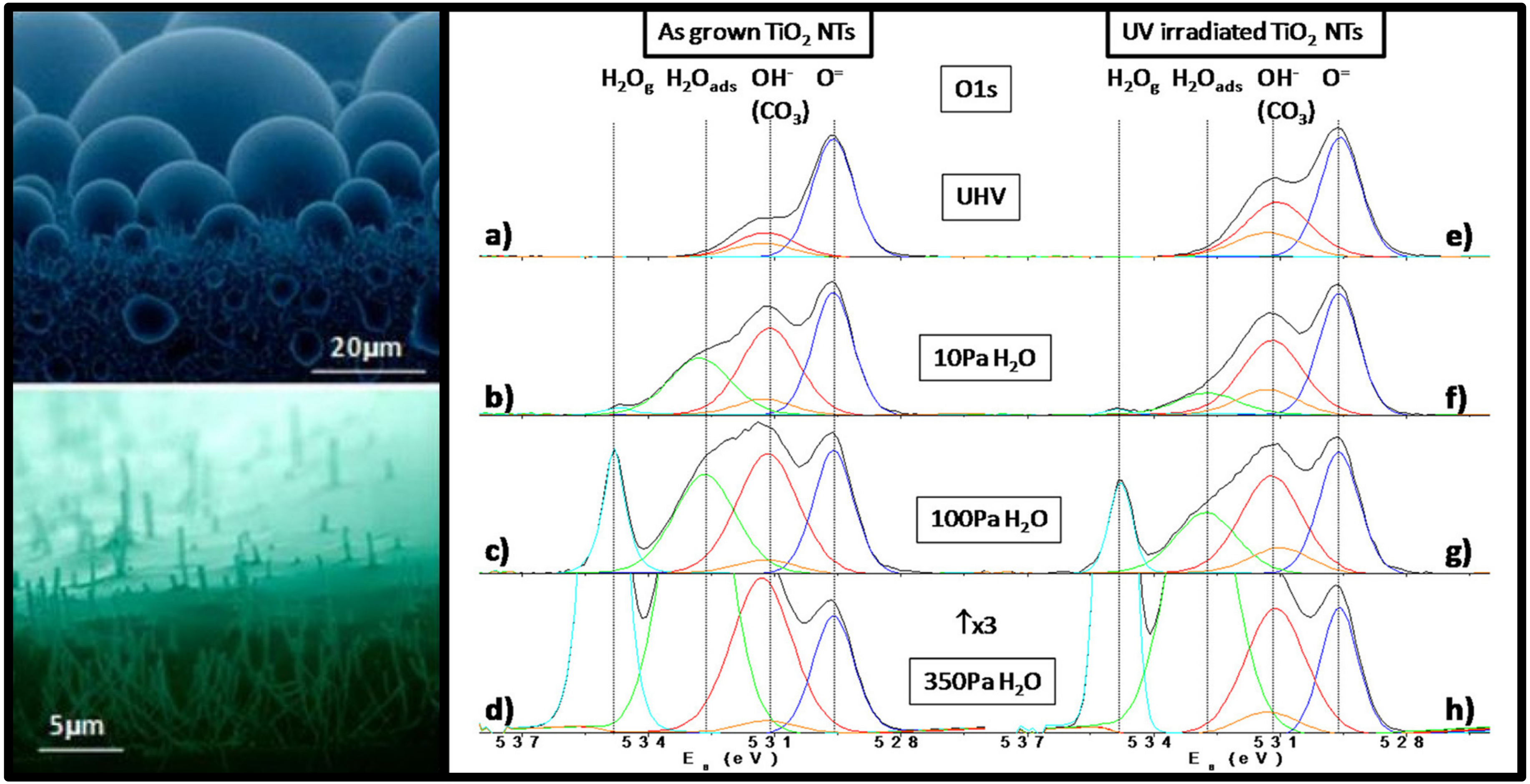


Heterogeneous Catalysis



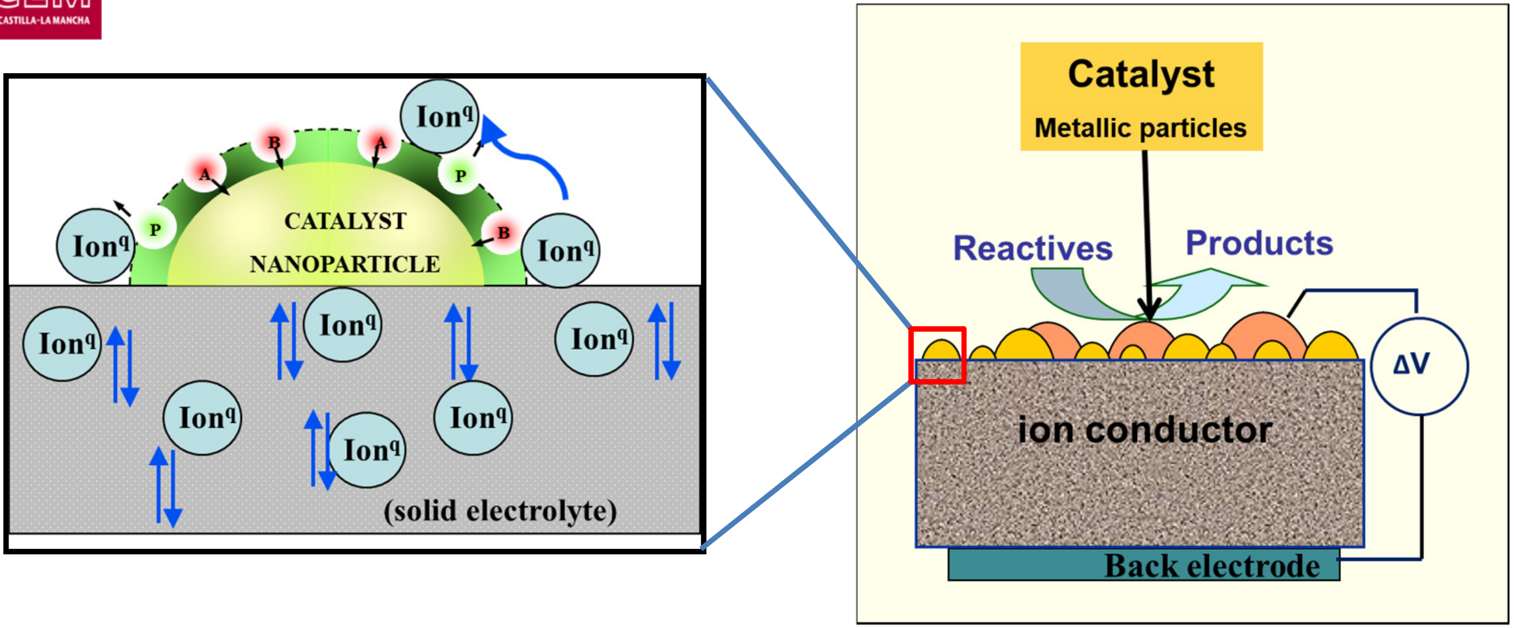
Environmental Science

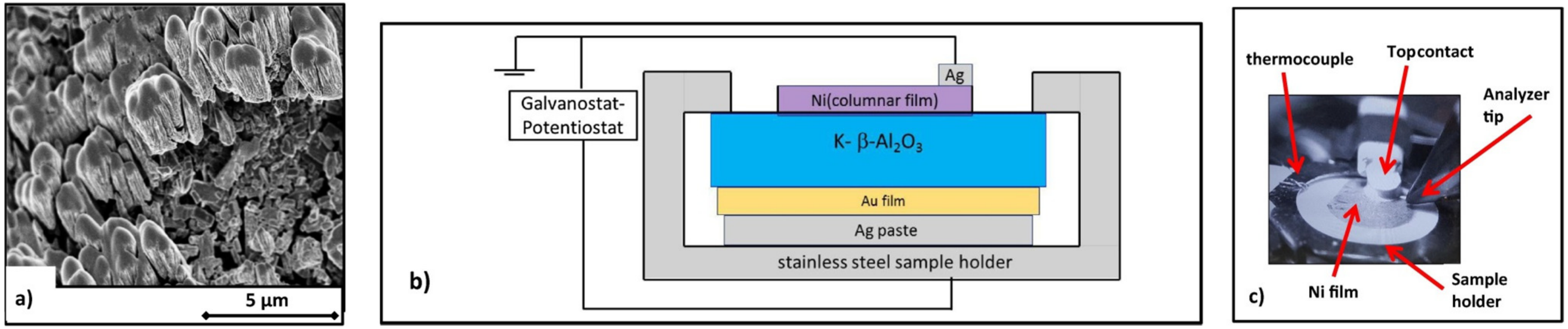
Water Condensation Mechanisms on Superhydrophobic and Superhydrophilic Titanium Dioxide Nanotubes



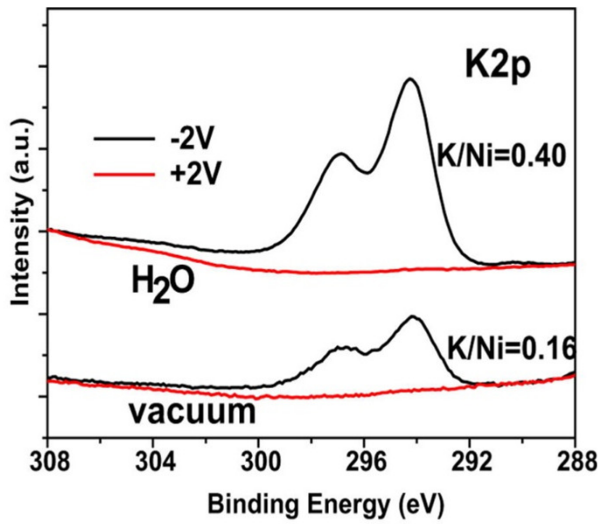
M. Macias-Montero et al., Langmuir 33, p.6449 (2017)

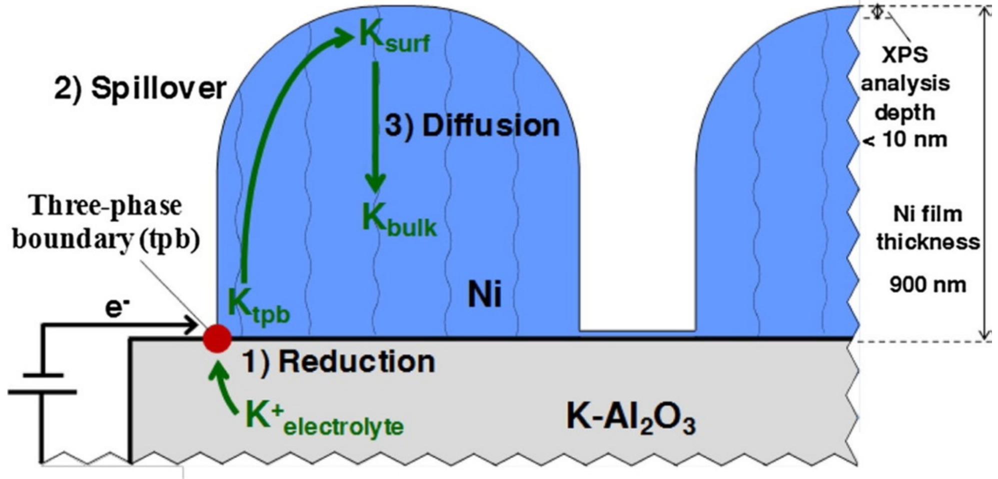
In situ monitoring of the phenomenon of Electrochemical Promotion Of Catalysis

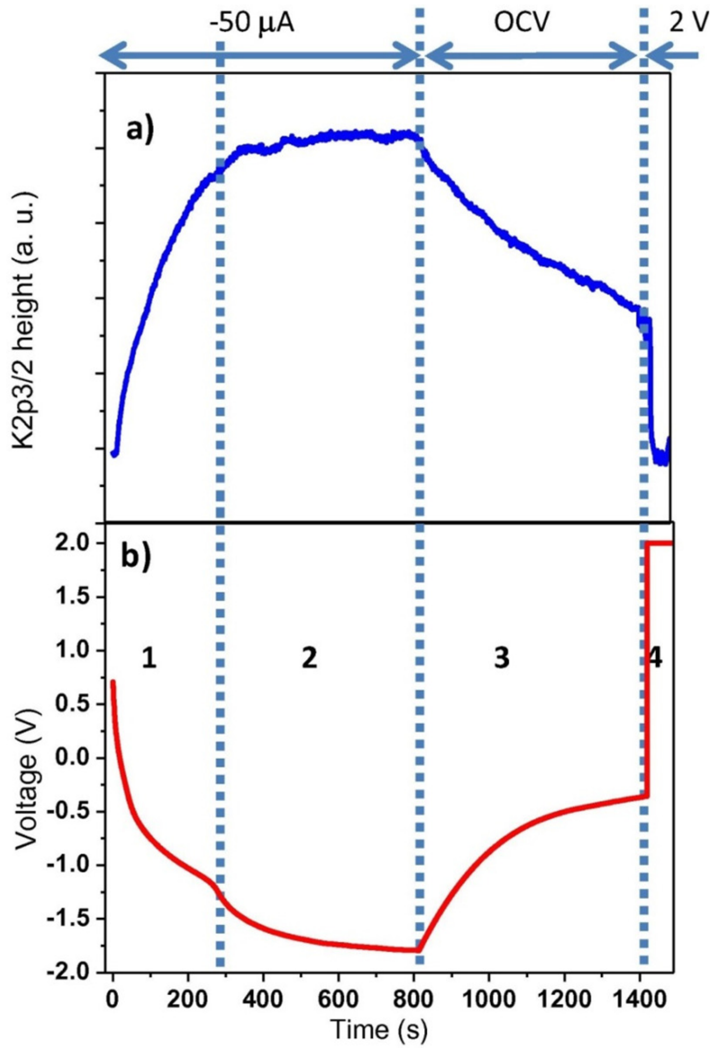




J.P.Espinós et. al., Journal of Catalysis 358 (2018) 27–34

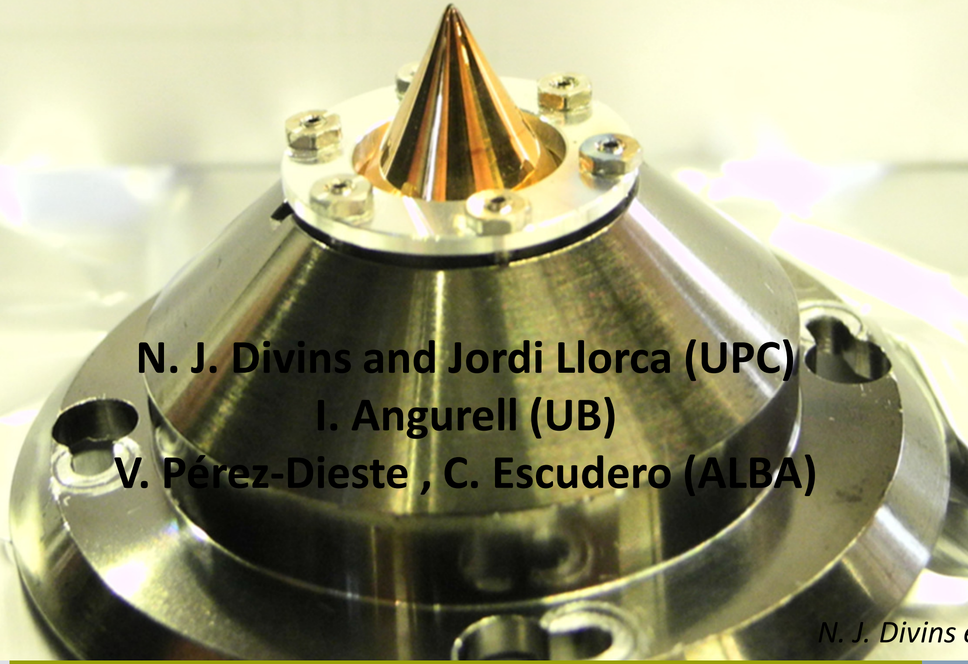






J.P.Espinós et. al., Journal of Catalysis 358 (2018) 27–34

Influence of the support on surface rearrangements of bimetallic nanoparticles in real catalysts



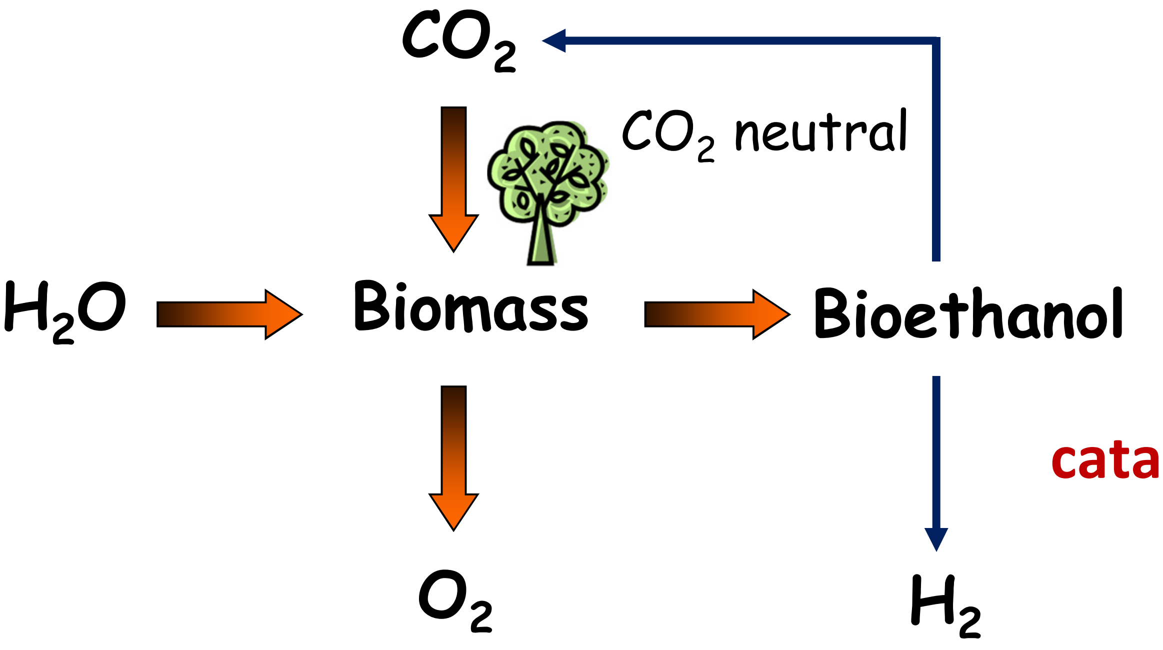
N. J. Divins and Jordi Llorca (UPC)
I. Angurell (UB)
V. Pérez-Dieste , C. Escudero (ALBA)

*N. J. Divins et al., **Science** 346, p.620 (2014)*

ESR – Ethanol Steam Reforming

$C_2H_5OH + 3\ H_2O \rightarrow 6\ H_2 + 2\ CO_2$ ΔH_R=347 kJ/mol

Bioethanol



CO_2

CO_2 neutral

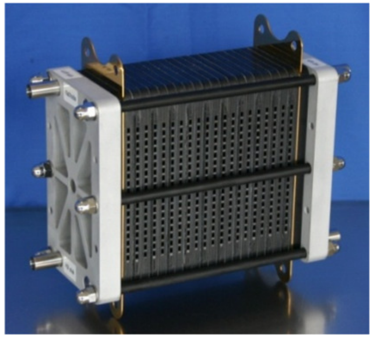
H_2O → Biomass → Bioethanol

O_2

H_2

catalyst

Fuel cell



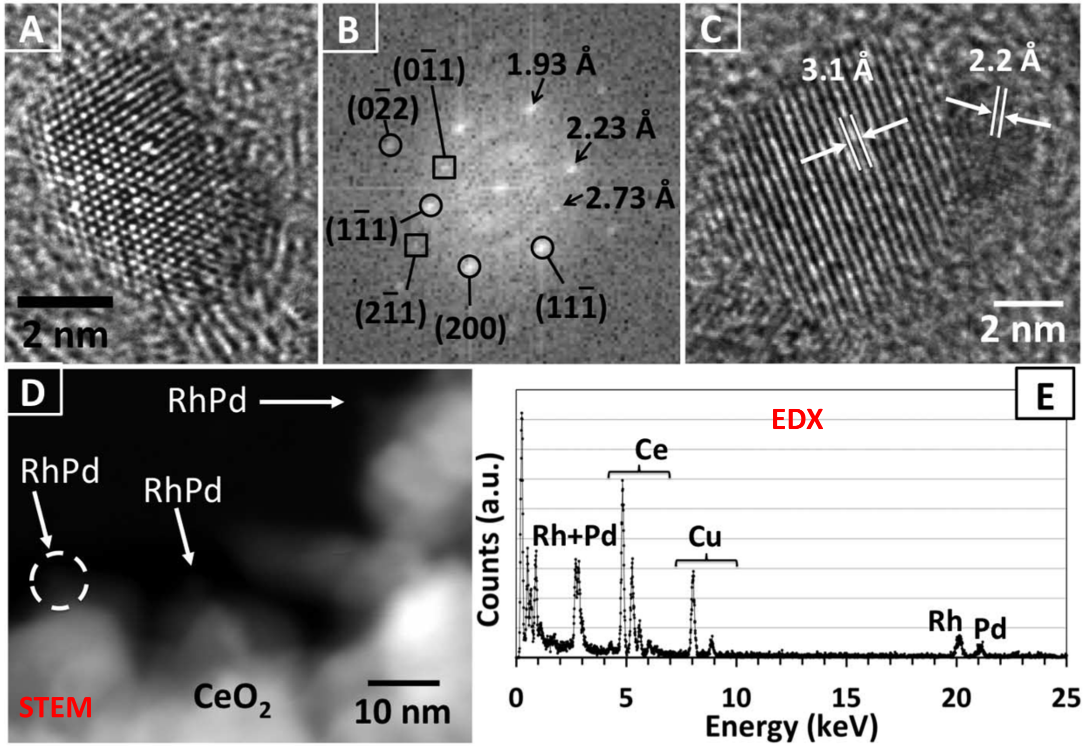
Which catalyst?

$Rh_{0.5}Pd_{0.5}$ Nanoparticles (NPs) for Ethanol Steam Reforming (ESR)

Why $Rh_{0.5}Pd_{0.5}$ NPs?

- Rh ***breaks*** C-C bond and sp^3 C-H bond
- Pd efficiently ***recombines*** H-H
- CeO_2 redox properties and oxygen storage capacity

HRTEM characterization

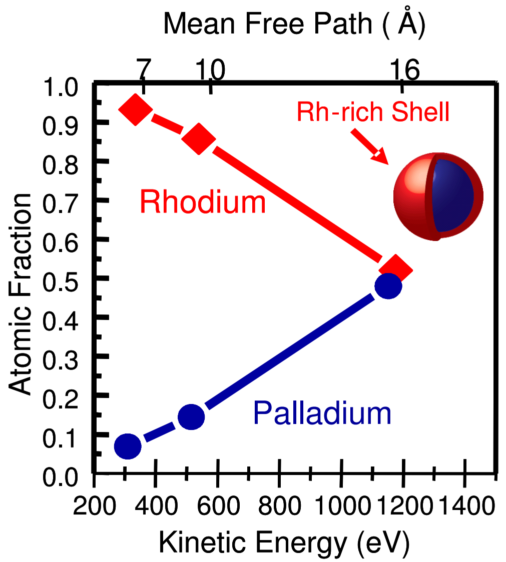


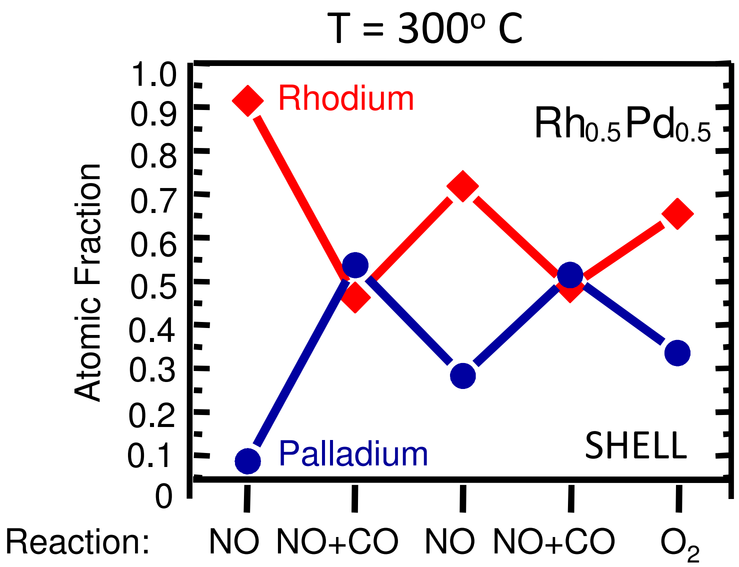
- Mean nanoparticle diameter = 4 ± 1 nm
- Rh and Pd are alloyed
- Atomic ration Rh/Pd=1

N. J. Divins et al., ***Science*** *346, p.620 (2014)*

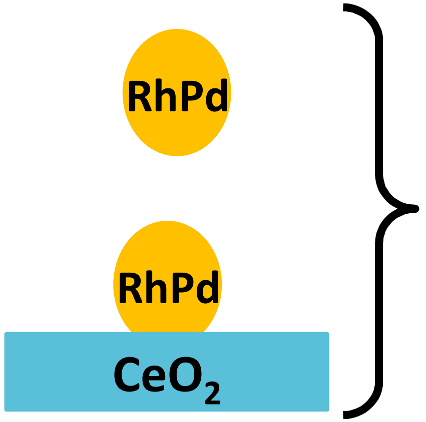
From previous experiments…

$Rh_{0.5}Pd_{0.5}$ NPs





How does CeO_2 influence the surface rearrangement of NPs in real catalysts?



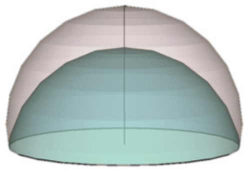
0.05 mbar

H_2 300°C

reaction 550°C

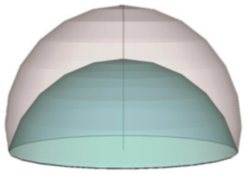
H_2 550°C

Outer shell



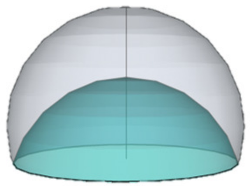
hv=670 eV

Intermediate layers



hv=875 eV

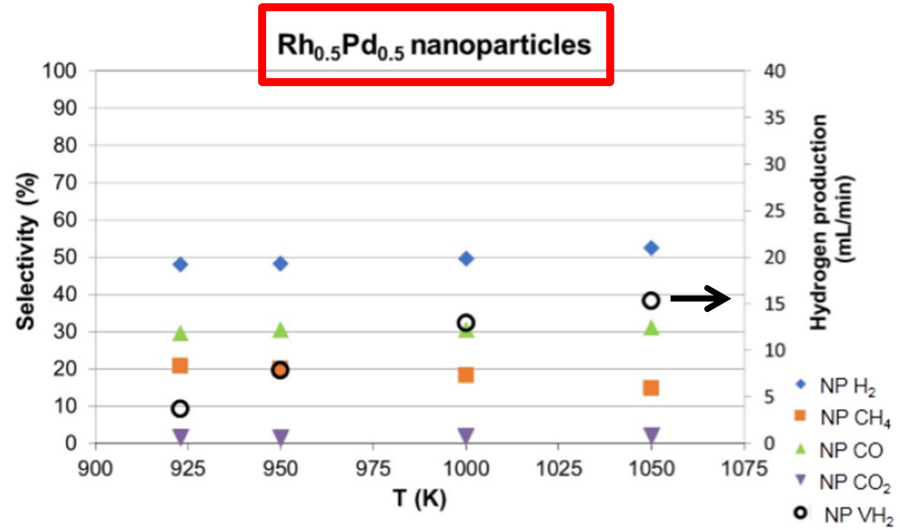
Core

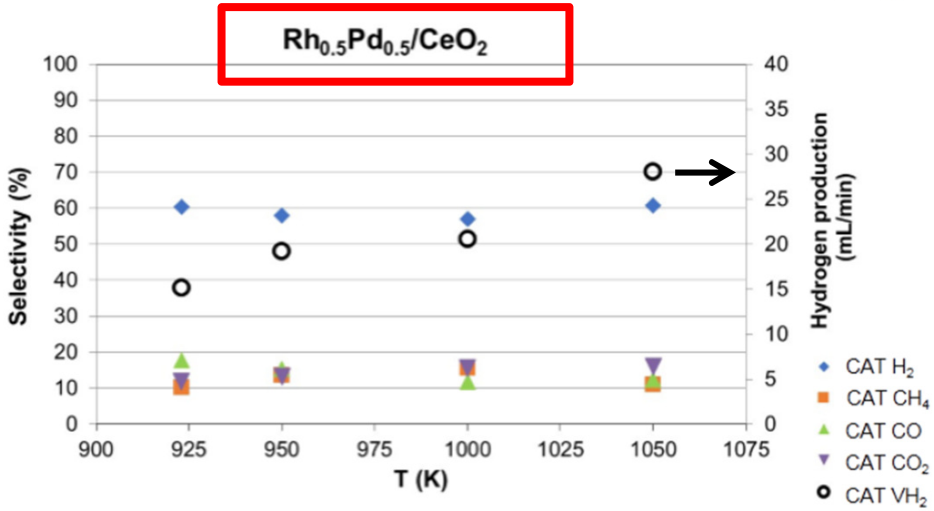


hv=1150 eV

F. Tao et al, Science. 322, 932 (2008)

Catalytic Performance Evaluation





H_2 production by $Rh_{0.5}Pd_{0.5}/CeO_2$ is twice than by model $Rh_{0.5}Pd_{0.5}$ NPs

(open black circles)

Less CO, less CH_4

ESR reaction steps with noble metals:

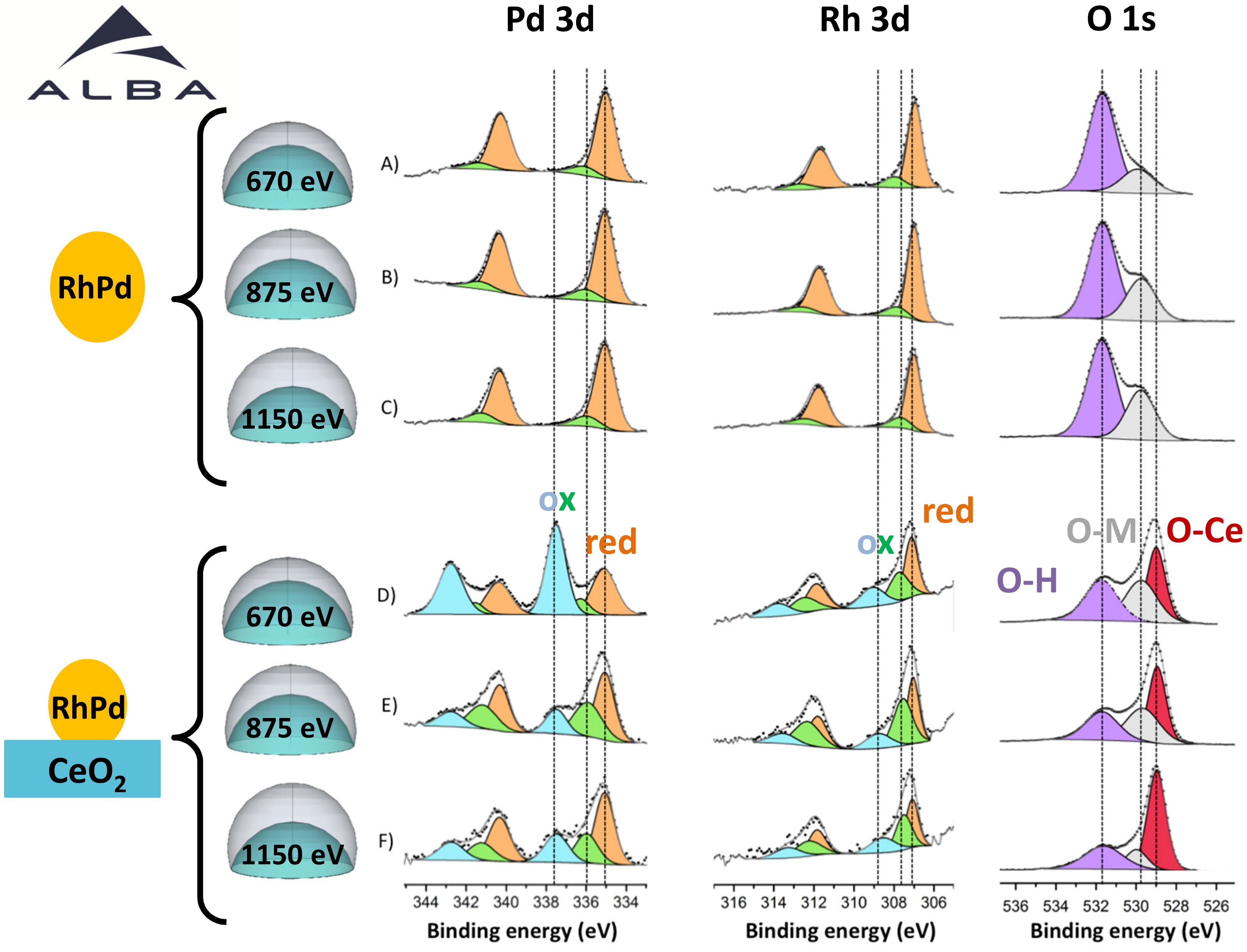
$C_2H_5OH \rightarrow H_2 + CO + CH_4$

$CO + H_2O \rightarrow H_2 + CO_2$

$CH_4 + H_2O \rightarrow 3\ H_2 + CO$

*N. J. Divins et al., **Science** 346, p.620 (2014)*

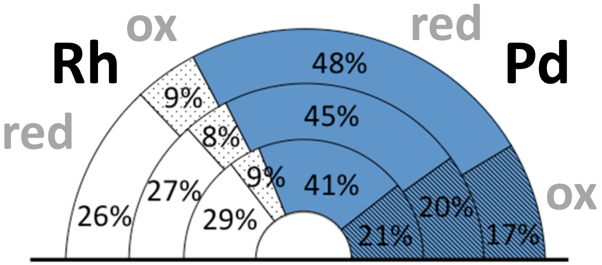
ESR conditions, 823K

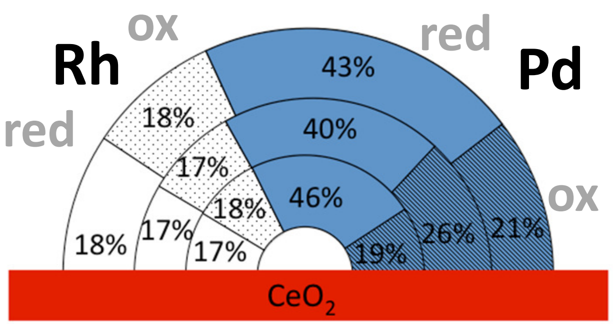


RhPd

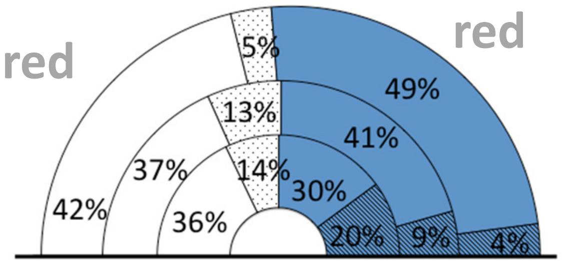
RhPd/CeO_2

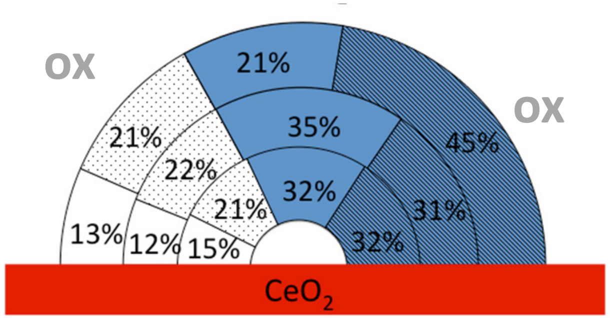
H_2 300°C



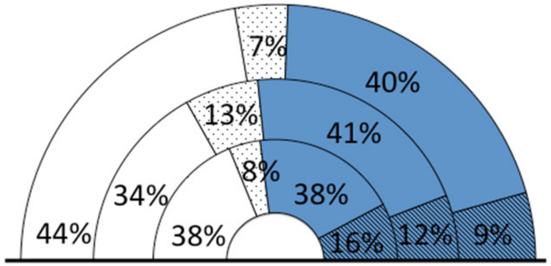


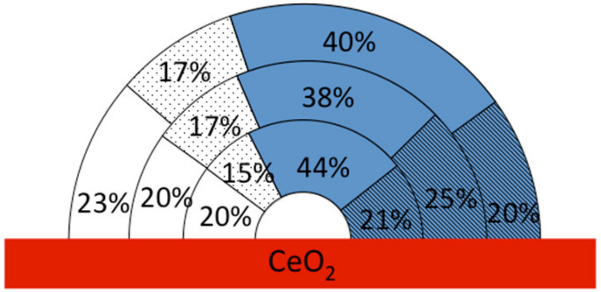
ESR reaction 550°C





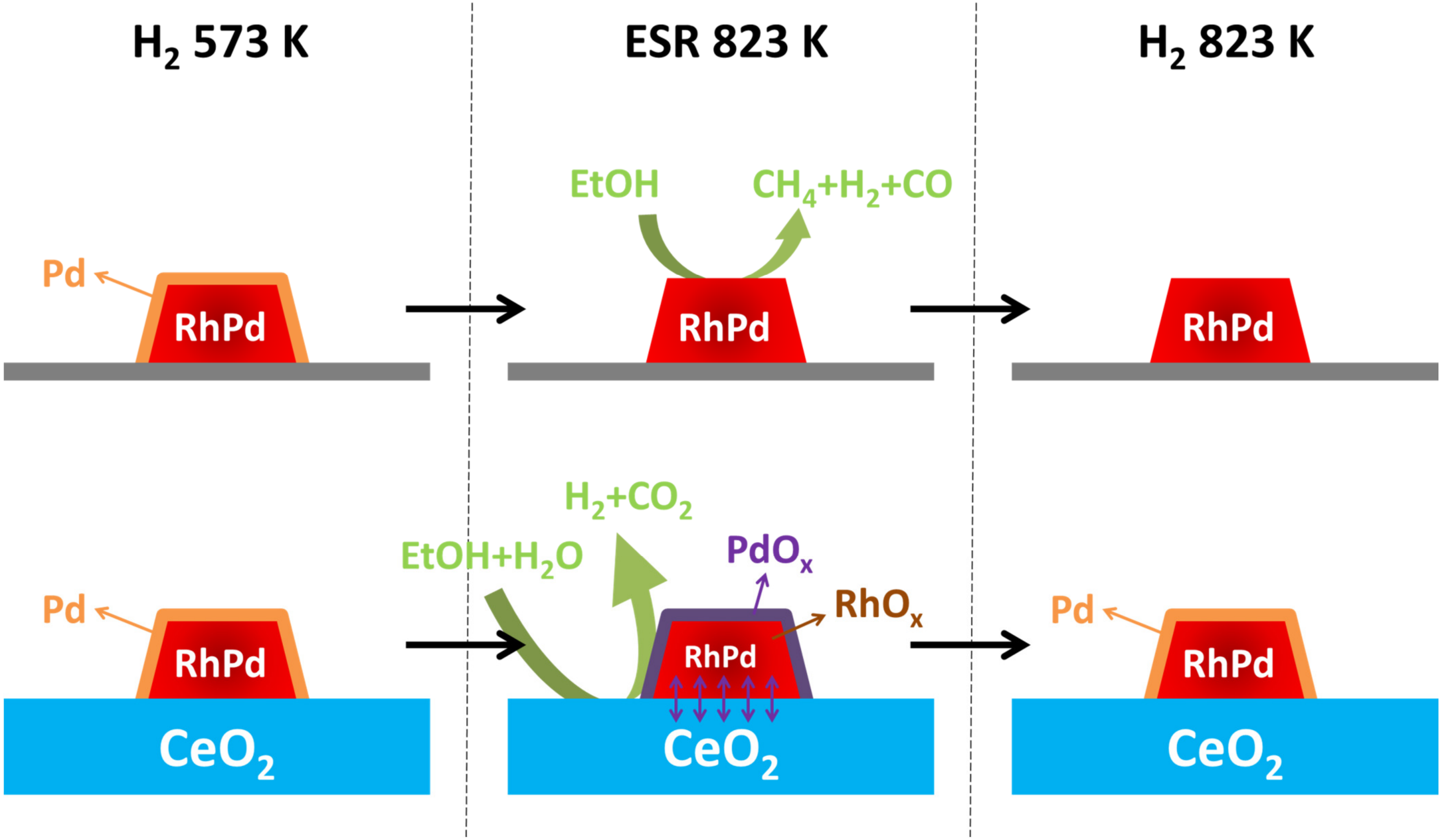
H_2 550°C



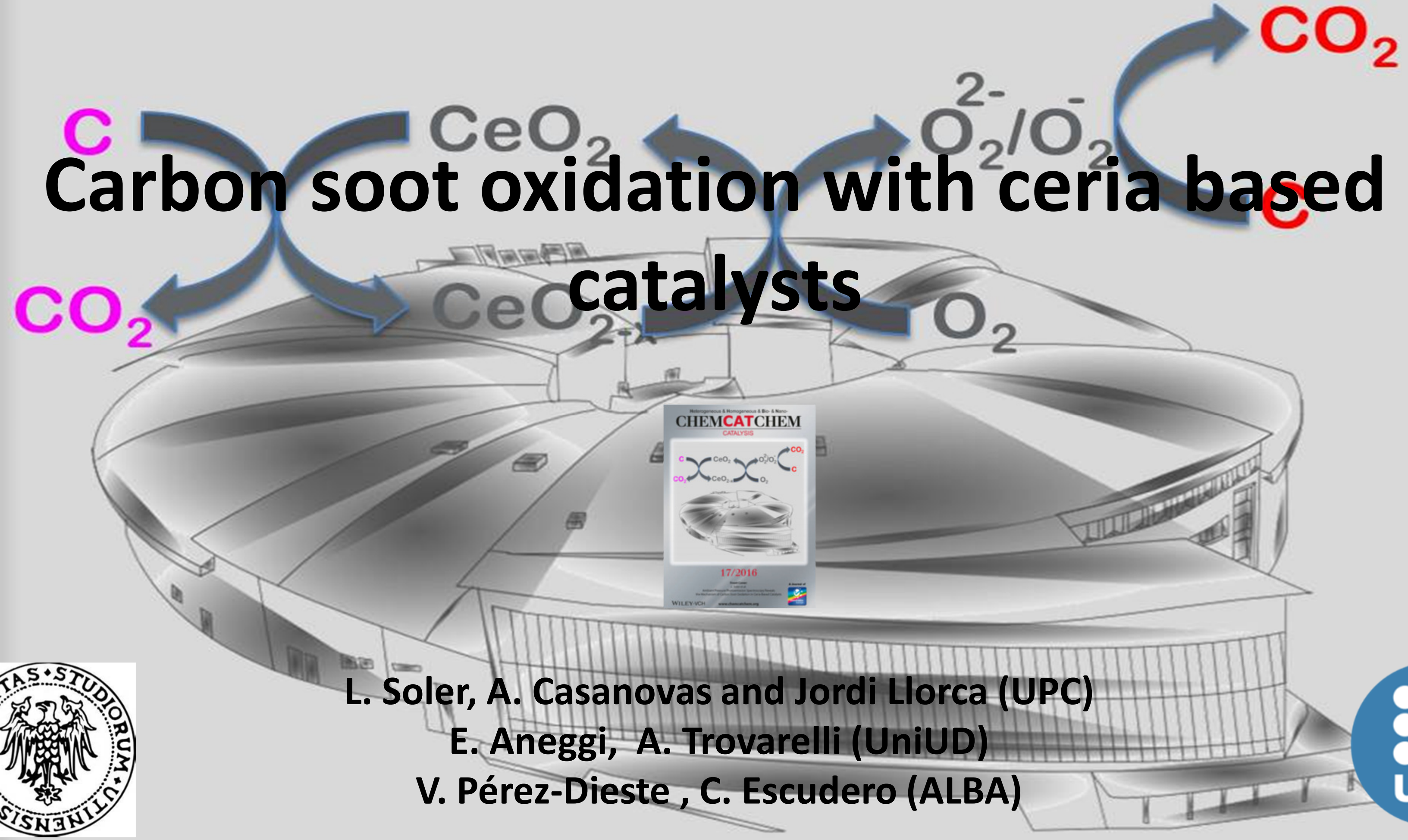


*N. J. Divins et al., **Science** 346, p.620 (2014)*

Model NPs vs real catalyst



N. J. Divins et al., **Science** 346, p.620 (2014)



Carbon soot oxidation with ceria based catalysts

L. Soler, A. Casanovas and Jordi Llorca (UPC)
E. Aneggi, A. Trovarelli (UniUD)
V. Pérez-Dieste , C. Escudero (ALBA)

L. Soler et al., ChemCatChem 8, p.2748 (2016)

Soot, a serious environmental and health concern

Soot combustion requires T > 600 °C, therefore catalysts are required to lower this T

CeO_2 based catalysts are among the most effective*

- Capacity to store and release oxygen
- Redox properties of the $Ce^{3+/4+}$ couple
- Structural integrity

*CeO_2 based catalysts are used in Three-Way Catalytic converters (TWC) for cars pollution control since mid 1980´s

*A. Bueno López, **Appl. Cat. B: Environmental** 146, p.1 (2014)*

Reaction mechanism

- Soot oxidation proceeds through a Mars-Van Krevelen mechanism

A. *Bueno López et al., **J Catal.** 230, p.237 (2005)*
B. *K. Harada et.al., **J. Phys. Chem. C** 118, p559 (2014)*

- The mechanism is also associated with the availability of adsorbed active oxygen species that spill over onto the soot surface

*A. Bueno López et al., **J Catal.** 230, p.237 (2005)*
*G. Mul et.al., **J. Catal.** 179, p258 (1998)*
*G. Preda et. al., **J. Phys. Chem. C** 115, p.5817 (2011)*
*J. Kullgren et. al., **J. Phys. Chem. Lett.** 4, p.604 (2013)*

- Formation of O_2^- and O_2^{2-} are suggested as precursor surface species responsible for soot oxidation

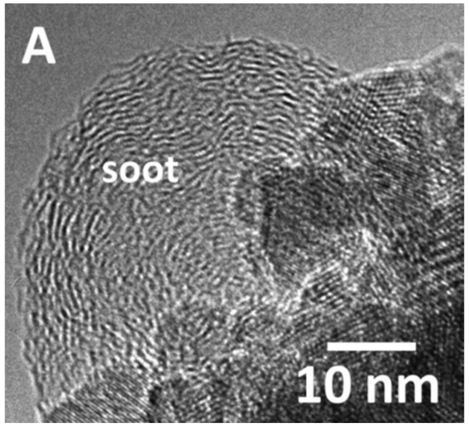
*J. Xuet. al., **Chem. Commun.** 46, p.1887 (2010)*
*J. Soria et. al., **J. Chem. Soc. Trans.** 91, p.1669 (1995)*
*V. Pushkarev et.al., **J. Phys. Chem. B** 108, p.5341 (2004)*
*E. Saab et. al., **Carbon** 45, p.561 (2007)*

NAPP experiments: CeO_2 soot vs bare CeO_2

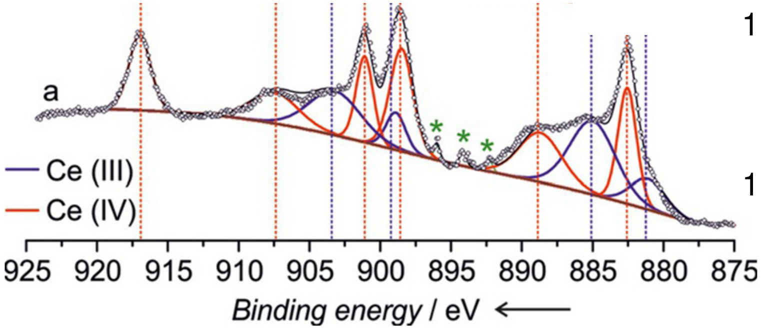
Ce 3d

CeO_2-soot

prepared by tight compact mode



Weight ratio catalyst-soot 20:1



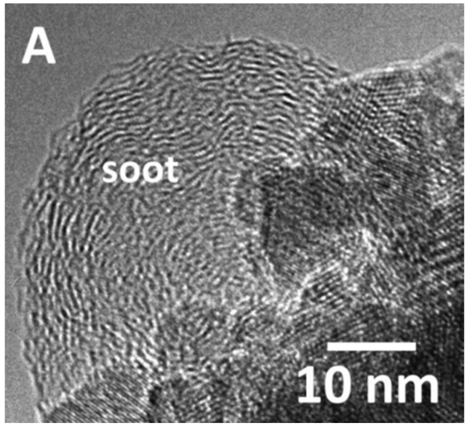
	C/Ce
CeO_2–soot 1 mbar O_2, 550 ˚C	2.9
⬆	
CeO_2–soot 1 mbar Ar, 550 ˚C	16.0
⬆	
CeO_2–soot 1 mbar Ar, 450 ˚C	24.4
Bare CeO_2 1 mbar Ar, 450 ˚C	

L. Soler et al., ***ChemCatChem*** *8, p.2748 (2016)*

CeO_2 soot vs bare CeO_2

CeO_2-soot

prepared by tight compact mode

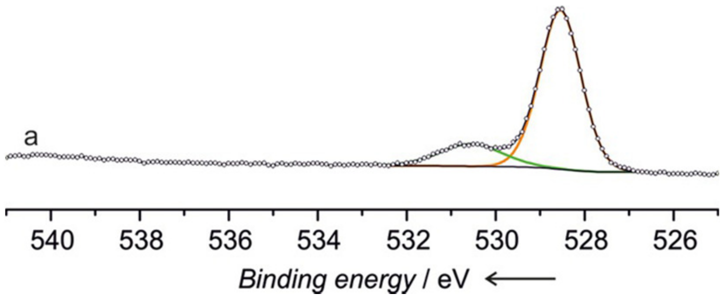


Weight ratio catalyst-soot 20:1

O 1s

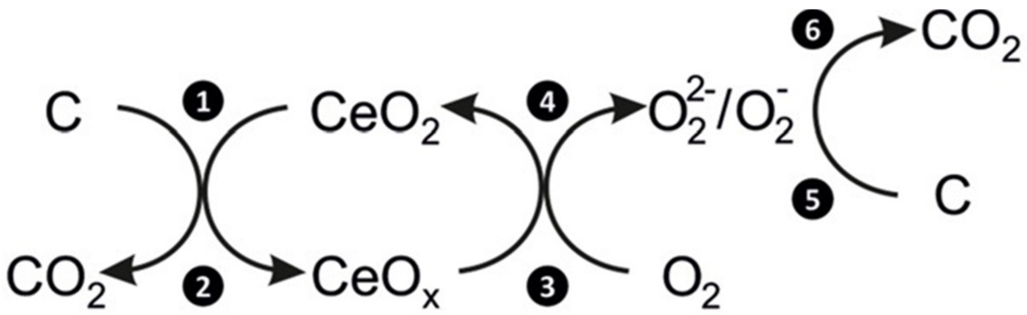
CeO_2–soot
1 mbar Ar, 550 ˚C

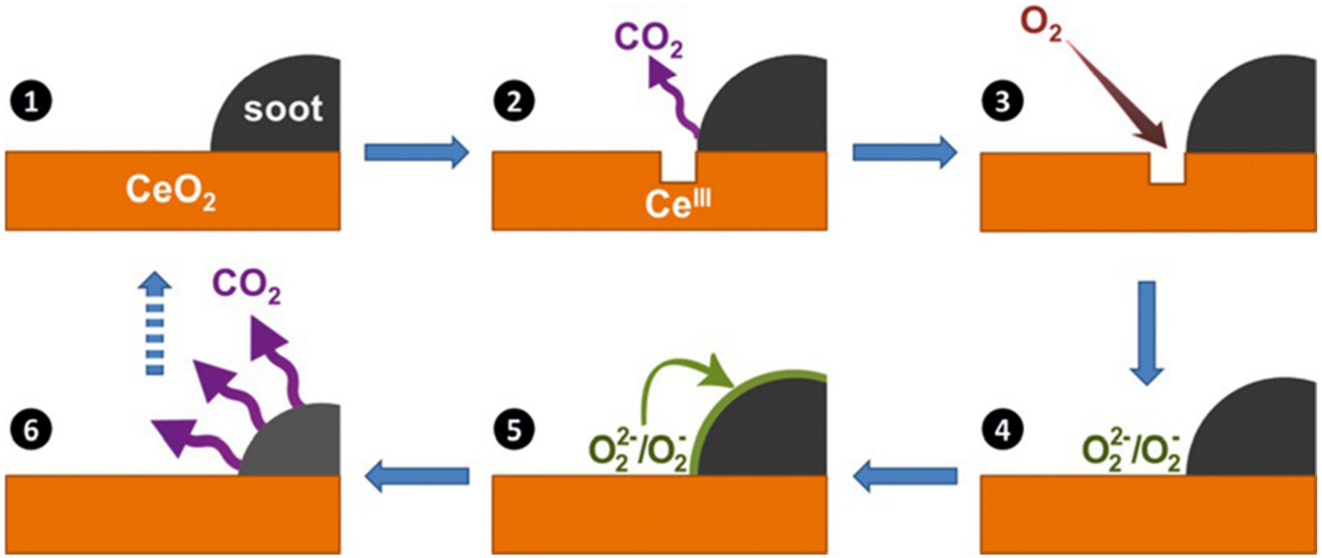
Bare CeO_2
1 mbar Ar, 450 ˚C



*L. Soler et al., **ChemCatChem** 8, p.2748 (2016)*

Scheme of the mechanism for soot oxidation over ceria-based catalysts





L. Soler et al., ***ChemCatChem*** *8, p.2748 (2016)*

Thanks to all ALBA staff

UCLM
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UNIVERSIDAD DE SEVILLA

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CONSEJO SUPERIOR DE INVESTIGACIONES CIENTÍFICAS

ICIQ

ICN2
Institut Català de Nanociència i Nanotecnologia

… And thank you for your attention!