

Why in situ observations in addition to other studies?

Which other in situ techniques associated?

...

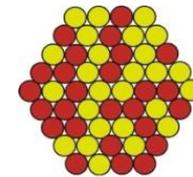
Optimize the properties (catalysis, optics..)

Control the synthesis and conditions of use
Understand the crystal growth and stability

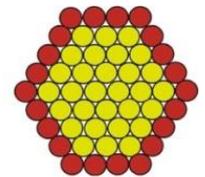
Morphology of Nanoalloys, Size
Crystal structure,
Chemical composition, Surface composition
During the growth

STABILITY in real conditions
(in solution, in gas, at varying temperature,
during chemical reactions...).

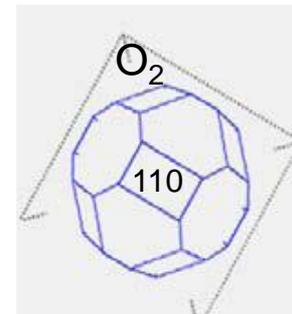
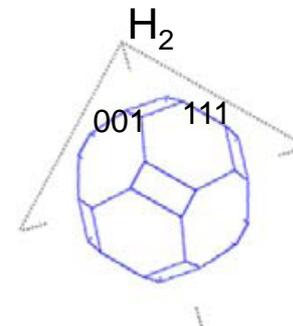
→ Ideas to improve the synthesis, indication of interest



Alloy



Core-Shell



For that,

→ **In situ TEM** (gas, liquid, varying temperature, with EDS, STEM HAADF, EELS) = powerful instrument

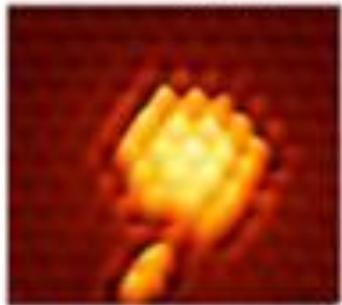
Local characterization at the atomic level with structural and chemical information

but artefacts due to irradiation

→ Association with **in situ spectroscopies (IR, XPS, SAXS measurements, AFM..)**

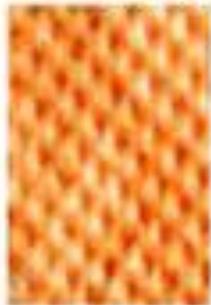
Statistical information from the sample, structure, chemistry, self organization

STM



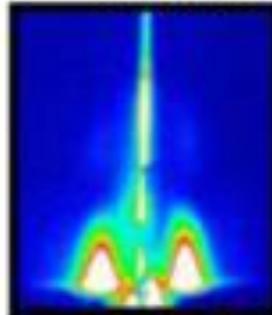
Pd27/MoS₂

AFM



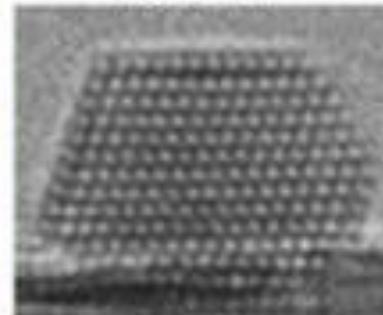
MgO(001)

GISAXS



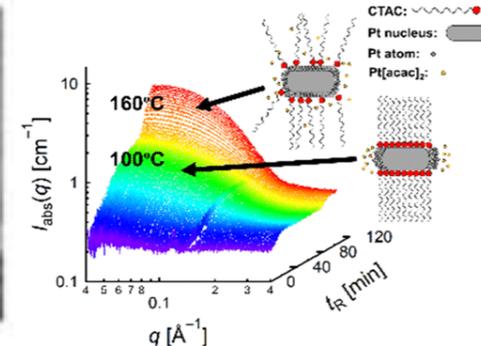
Pd/MgO

HRTEM



Au/MgO

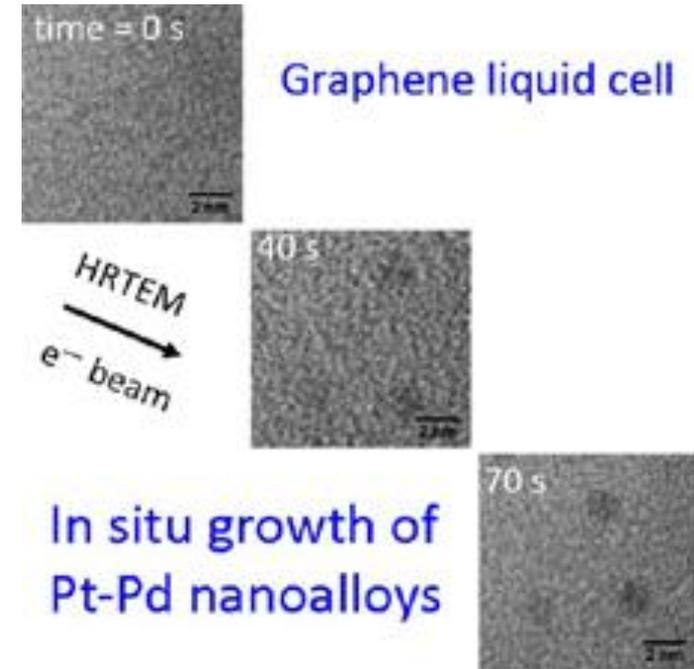
SAXS



« ETEM -ECELL for Nanomaterials in real conditions, reactivity, crystal growth,.. »

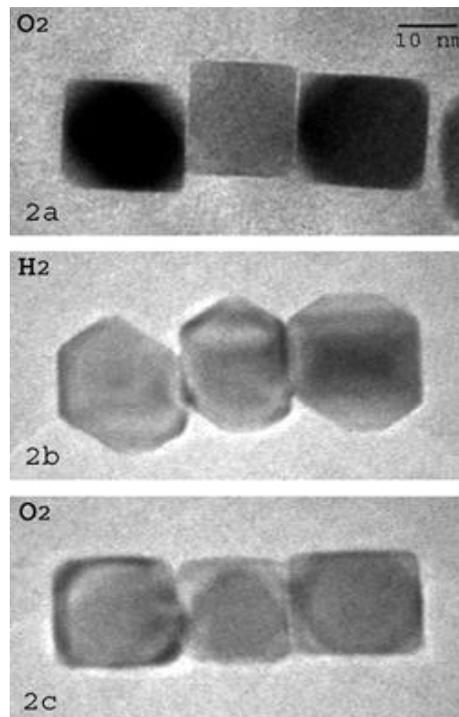
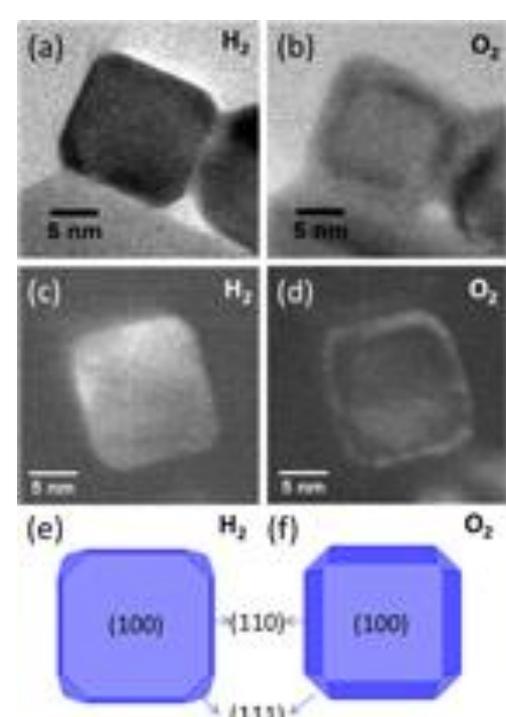
Growth mechanism of nano alloys in liquid
(Pt, Pt-Pd, Au, Au-Rh, Co-Ni ...)

Evolution of the structure and properties in gas
(Au-Pd, Au-Ag, Au-Rh, Pt-Pd, ...)



- Equilibrium shapes
- Adhesion energy with the substrate, interface metal/ oxide

* Reactivity of Pt-Pd and Au-Rh



Nanoalloys:

Correlation: Reactivity in gas, Structure, Chemical Structure, Simulations, ...

Au-Pd

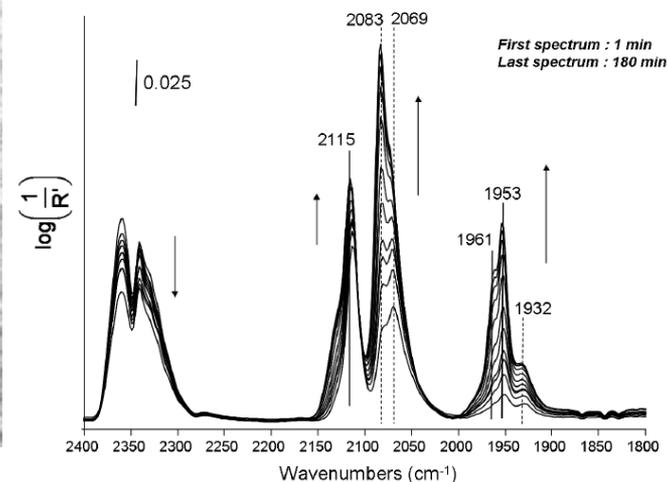
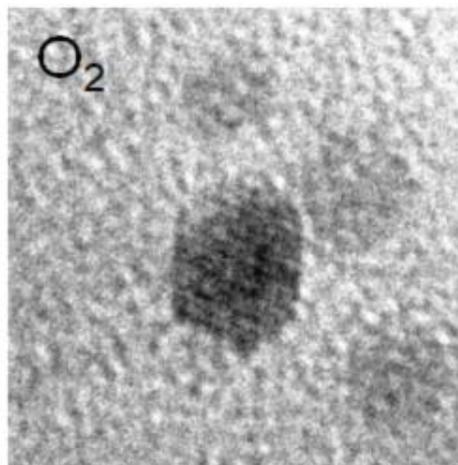
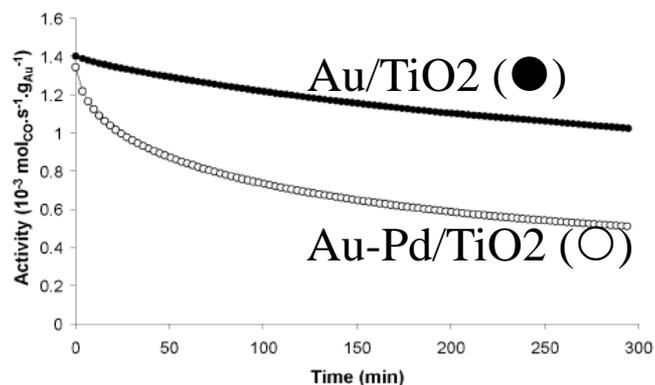
Au-Ag

Au-Rh

Pt-Pd

Au-Pd : Clusters for the oxidation of CO

In situ TEM – DRIFT - Reactivity



Laurent Delannoy, Suzanne Giorgio, Jean Gabriel Mattei, Claude R. Henry, Nadia El Kooli, Christophe Méthivier, Catherine Louis
Chem Cat Chem, 5 (2013) 2707

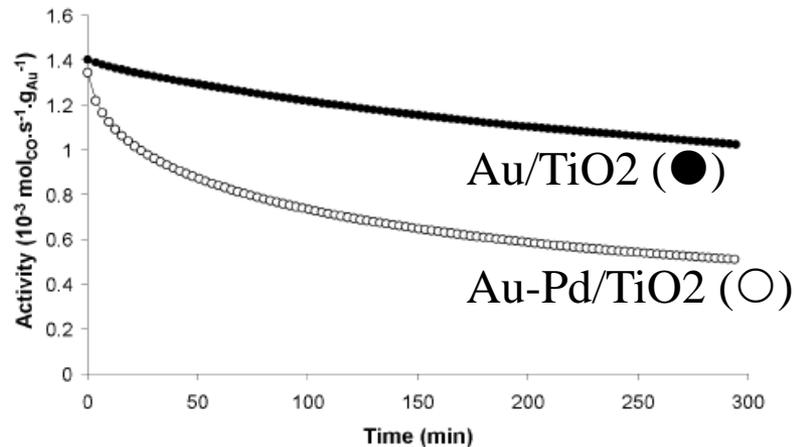
Au- Pd : Clusters for the oxidation of CO

$\text{Au}_{0.8}\text{-Pd}_{0.2}$

Homogeneous Disordered Structure , fcc

Even after strong irradiation

High rate of deactivation after the 1st reaction



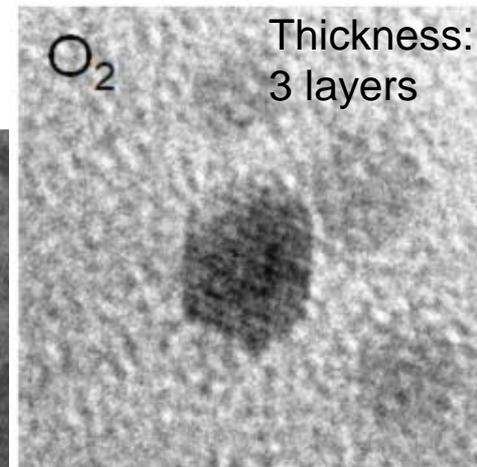
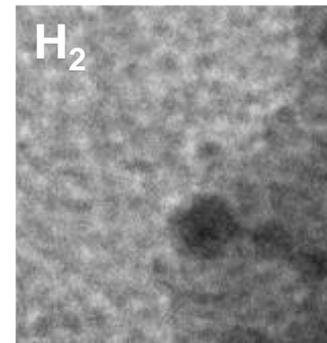
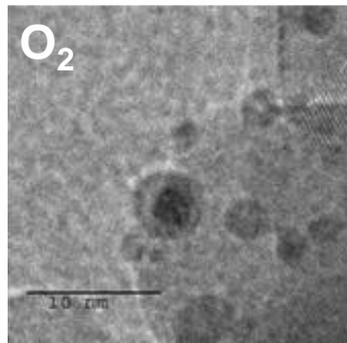
rather attributed to modification of the particle surface composition.

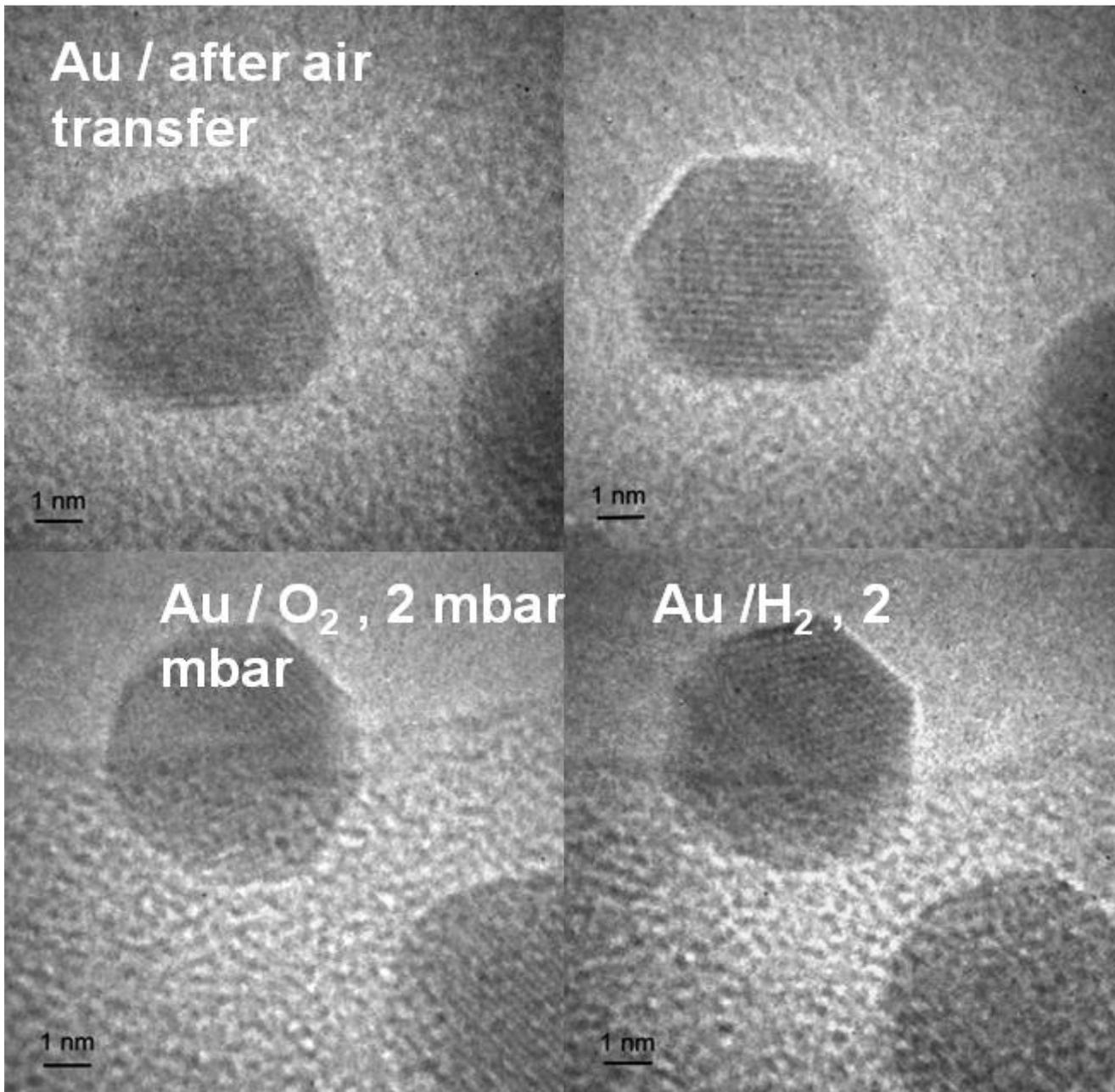
ETEM observations →

Segregations due to the adsorption of O₂

→ Core shell formation with O₂

- * metal segregation?
- * metal enrichment?
- * reaction product?





Au / after air transfer

1 nm

1 nm

Au / O₂ , 2 mbar

1 nm

Au /H₂ , 2 mbar

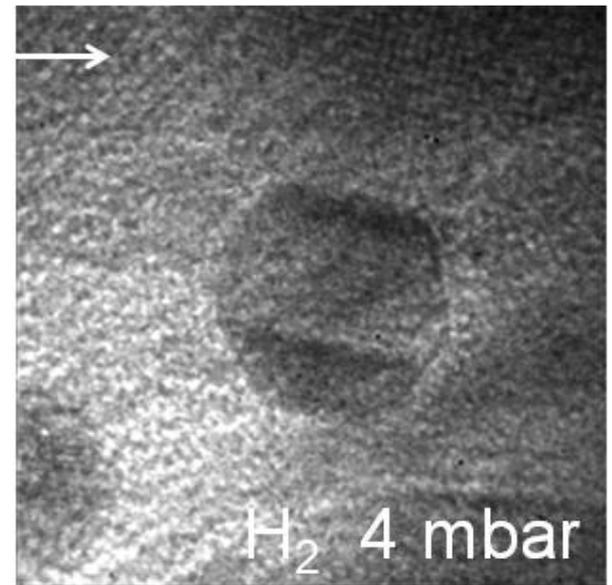
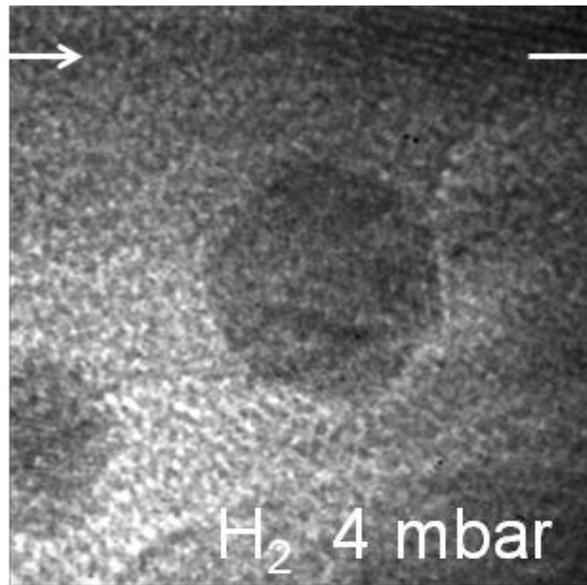
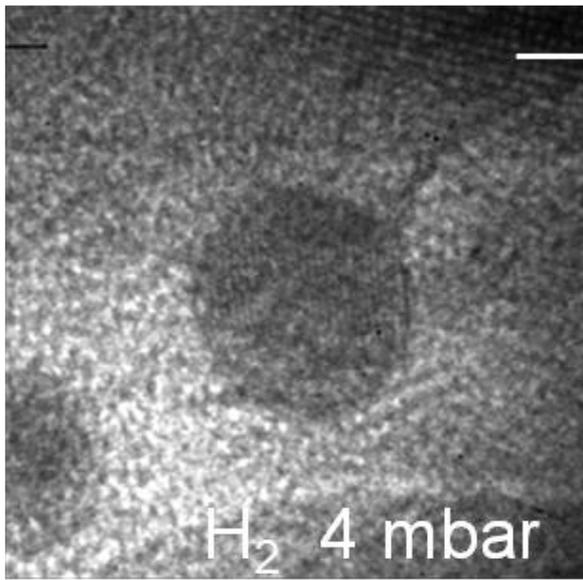
1 nm

Nothing on the surface

No shape

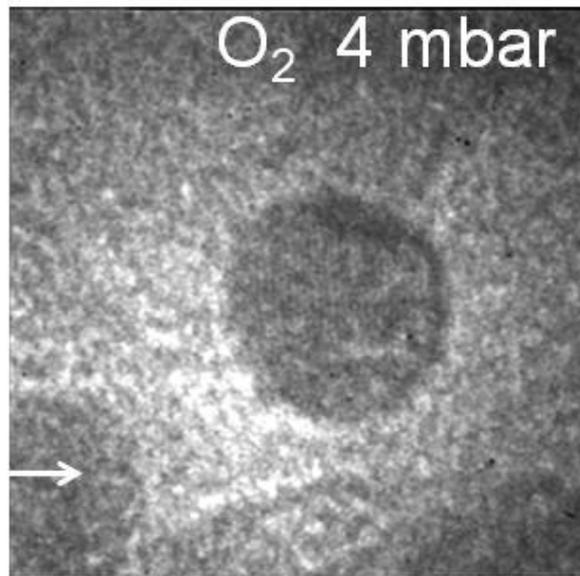
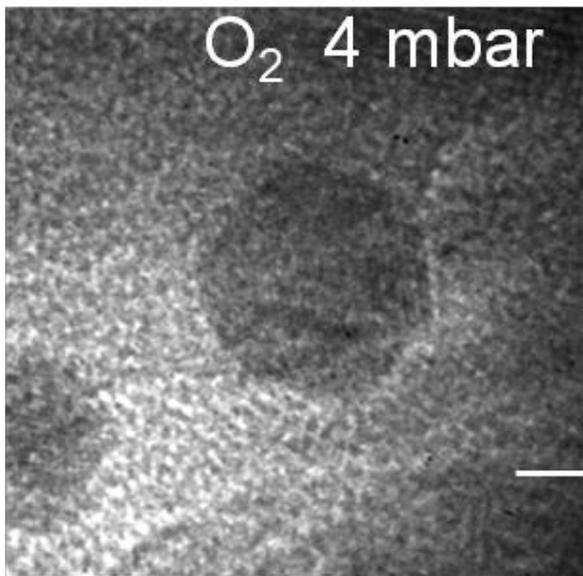
Facetting in H₂

Rounding in O₂



Circulation of H₂ => facetting,

Circulation of O₂ => rounding (more than in the case of Au / amorphous carbon)

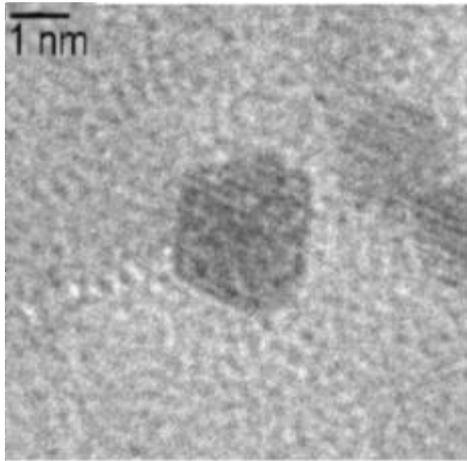


Same behaviour with a mixture CO + O₂ , rounding

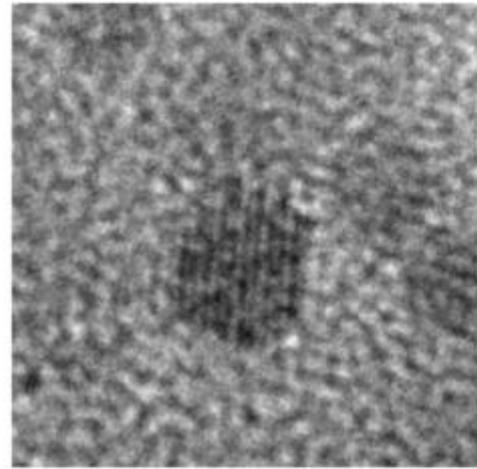
Nothing on the surface

Shell formation at the atomic scale (3 monolayers)

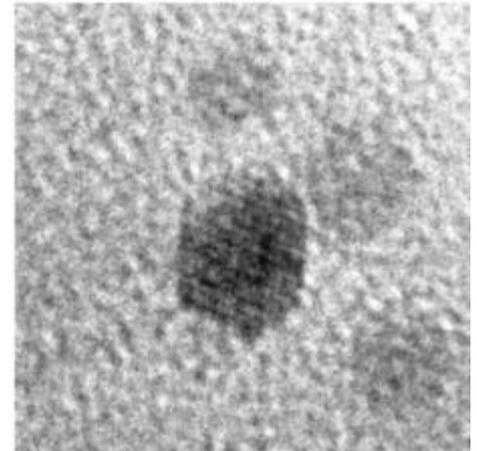
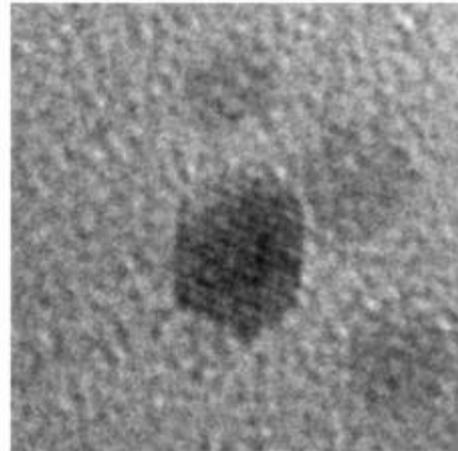
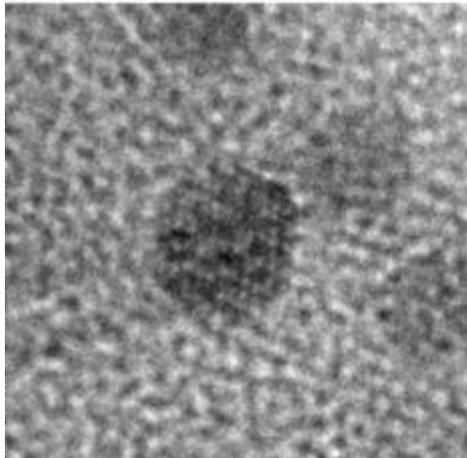
perfectly oriented / the core



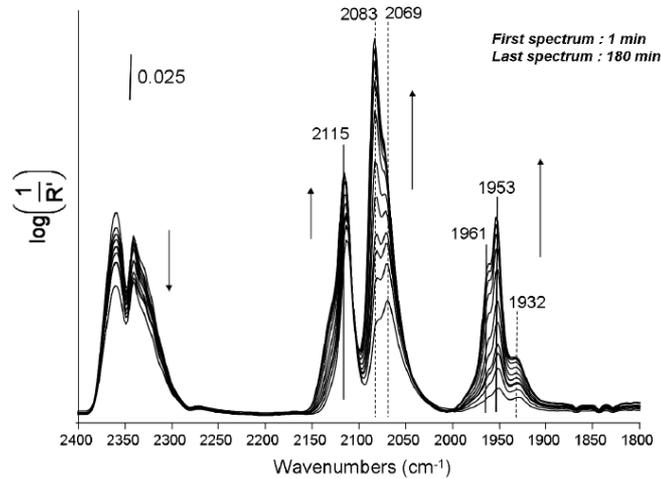
O₂



Au- |



DRIFT (contribution of CO adsorbed on Au or Pd)

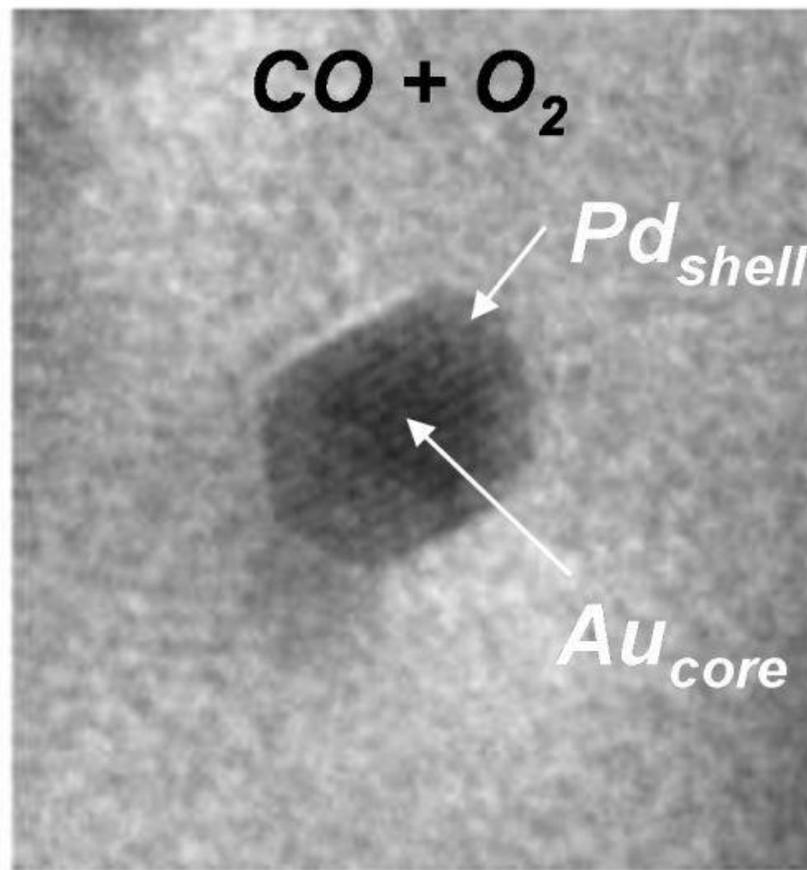
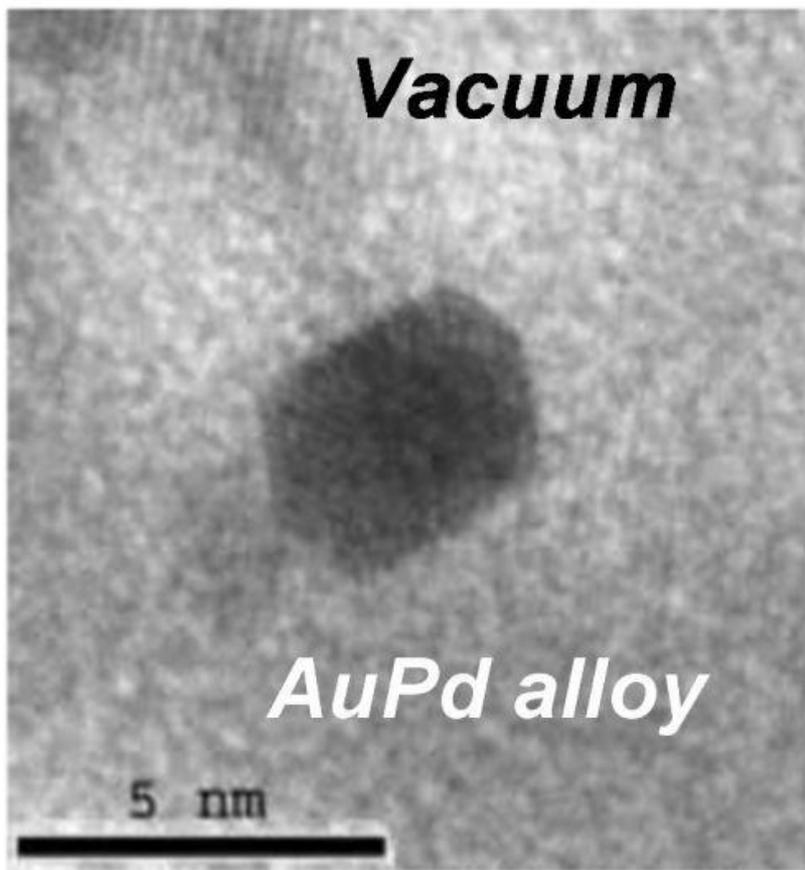


No contribution of CO adsorbed on Au

Higher contribution of CO adsorbed on Pd

→ Pd in the shell

DFT calculations → replacement of Au atoms by Pd preferentially at the edges and corners



Association between in situ TEM + DRIFT + reactivity

higher rate of deactivation in the first reaction stages observed for Au-Pd/TiO₂ compared to Au/TiO₂ could be related to the replacement of Au in low coordination sites (edges and corners) by Pd atoms.



TEM and DRIFTS => Segregations and Changes in the surface composition of isolated particles and from collections of Au-Pd NPs under CO/O₂

DFT calculations => Replacement of Au atoms by Pd preferentially at the edges and corners, under O₂.

Nanoalloys:

Morphology in gas, Reactivity, Interface/ substrate...

Au-Pd

Au-Ag

Au-Rh

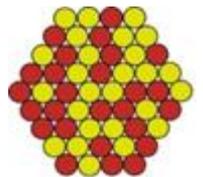
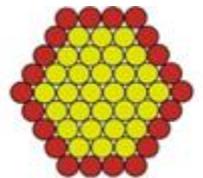
Pt-Pd

Pt must be saved!

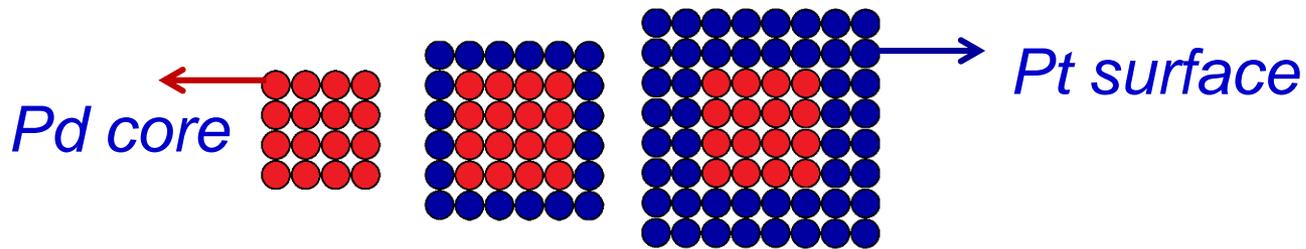
many Tons used every year! Not recycled

2 solutions:

- **keep Pt outside of another metal NPs**
- **enhance the activity of Pt by alloying with another metal**



Pt crystallized on Pd Nanocubes in solution



What is the most reactive thickness of Pt for the reaction of CO oxidation?

Association of

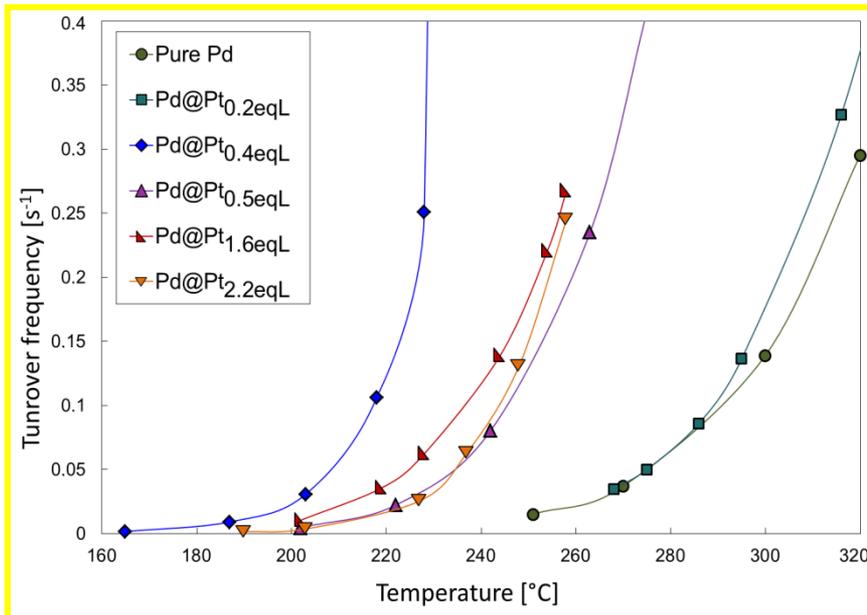
**E-TEM in liquid and gas
Gas Chromatography
Simulations**

De Clercq, Astrid; Olivier Margeat; Georges Sitja; Claude R Henry; Giorgio, Suzanne
J. Catal. (2016) 336 (2016) 33–40
Core-shell Pd–Pt nanocubes for the CO oxidation

CO oxidation by gas phase chromatography

Core-shell Pt@Pd nanocubes /SiO₂ with increasing equivalent atomic layers of Pt
(Reactivity for P_{O₂}/P_{CO}=1.5)

Best results for **0,4 equivalent layers of Pt** on the Pd nanocubes



Due to
the **shape?**
the **surface composition?**

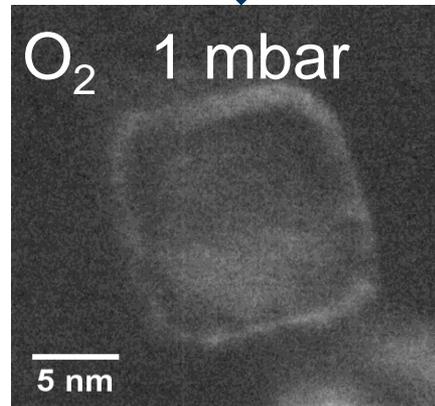
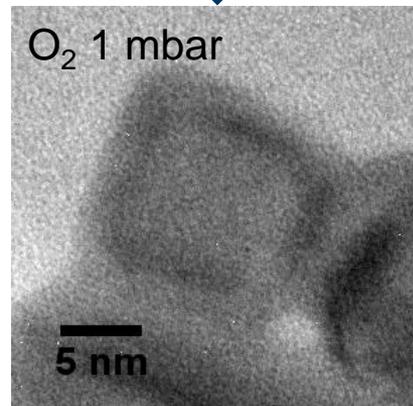
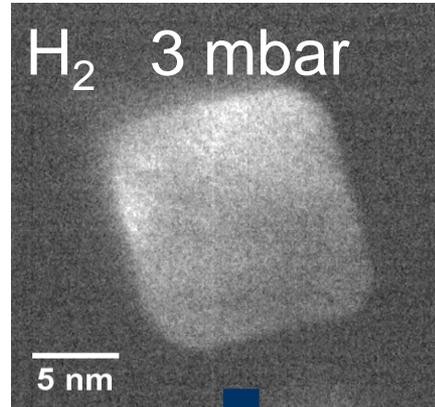
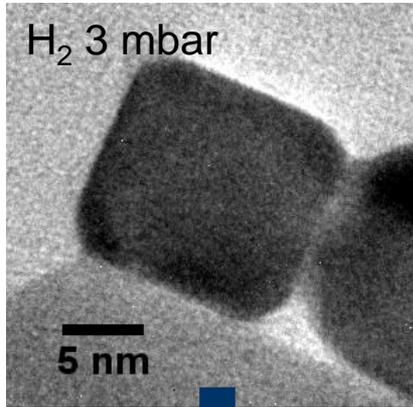
CO oxidation activities over the different samples

Higher amounts of Pt coverage do not improve any more the activity (TOF).

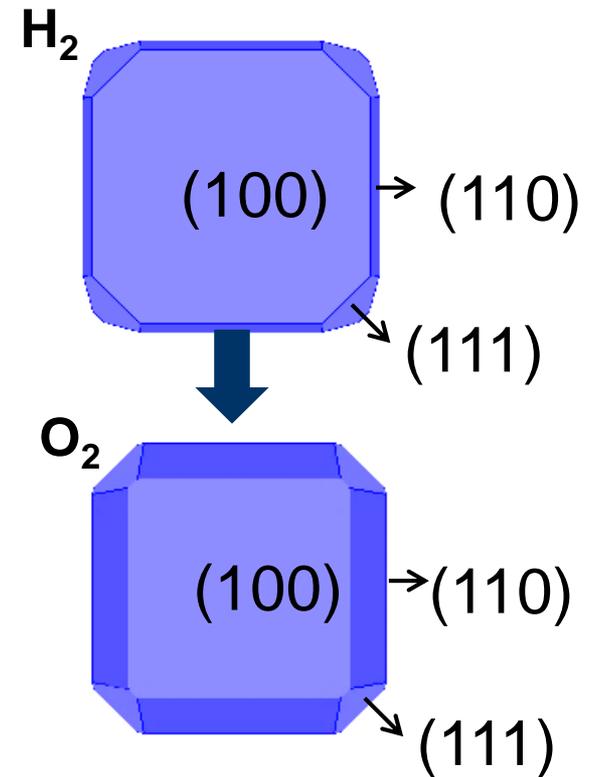
The TOF for Pd@Pt 0.5, 1.6 and 2.2 equivalent layers, even decreased with a factor 3 compared to the TOF for Pd@Pt_{0.4eqL}.

ETEM: nanocubes of pure Pd

- No change in H_2



Irradiation 10^4 A/m² at 300K

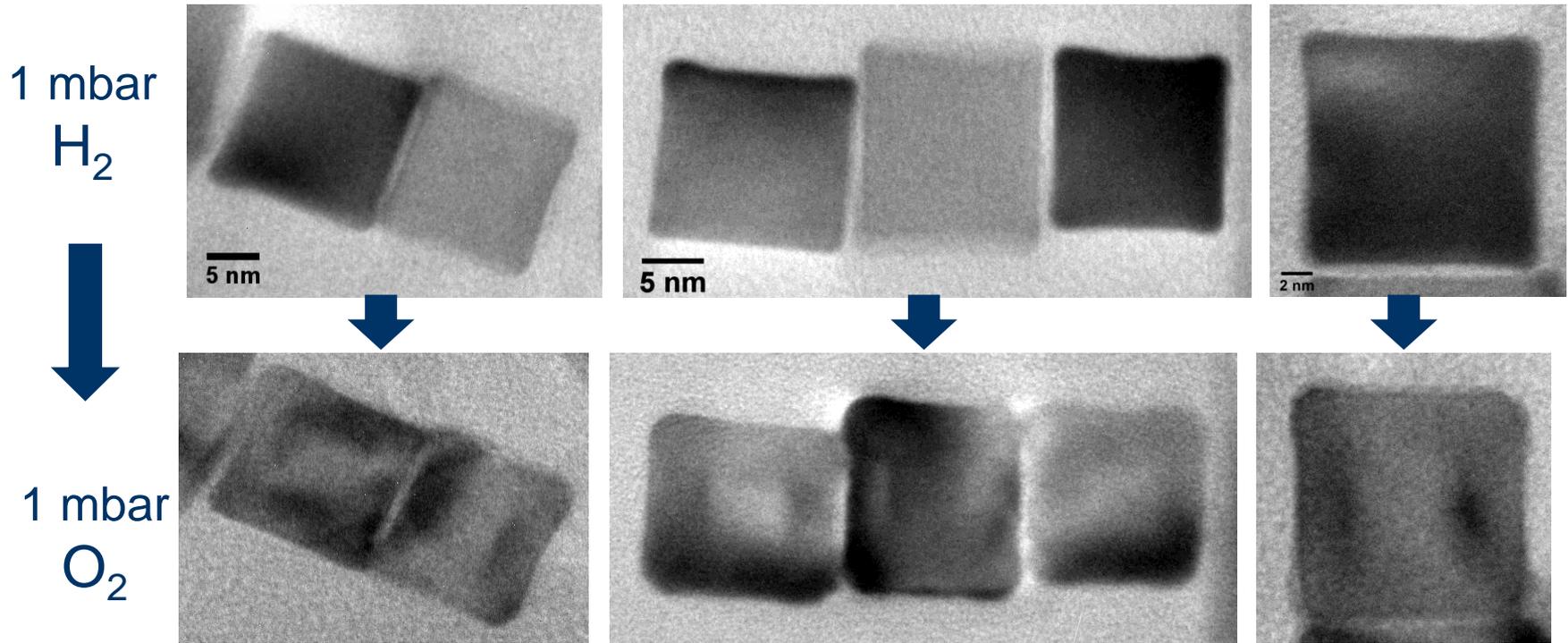


- Development of (110) facets under O_2 pressure,.

ETEM: nanocubes of Pd- Pt

De Clercq, Astrid; Olivier Margeat; Georges Sitja; Claude R Henry; Giorgio, Suzanne*
J. Catal. (2016) YJCAT11969

- Pd Nanocubes + 0.4 layers of Pt prepared in a reactor



- Rounding of the corners under O_2 pressure
- Formation (110) faces in O_2 (same behavior as pure Pd)

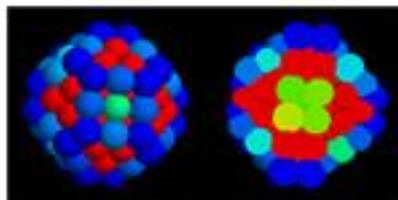
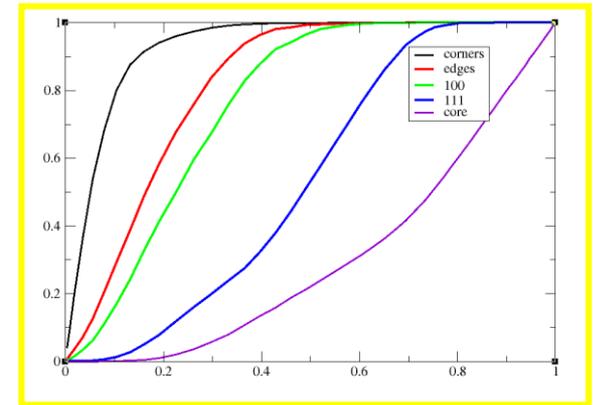
Theoretical calculations- Stable structure

- Monte carlo simulations based on a semi-empirical many body potential: to calculate thermodynamically stable configurations of a truncated octahedron of different sizes at 100-500K

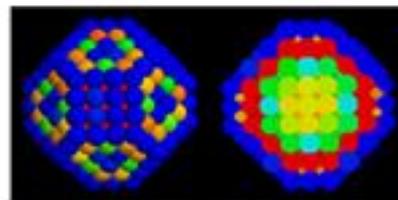
→ Pd at the surface

→ Pt in subsurface and core

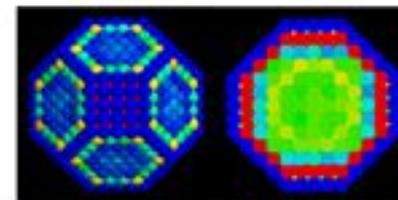
Example for 50-50% composition at 300K:



116 atoms, 1.4 nm



405 atoms, 2.2 nm



1289 atoms, 3.5 nm



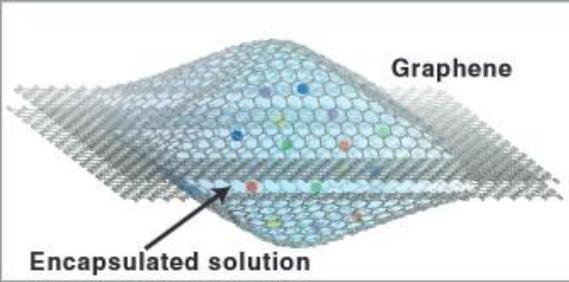
Pd

Pt

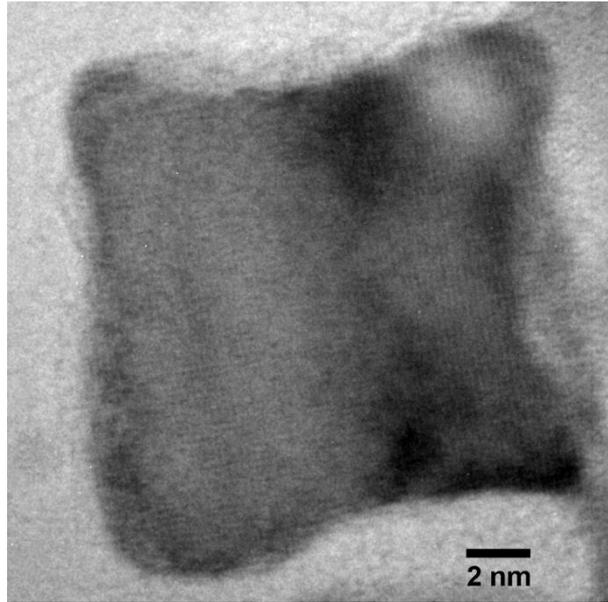
De Clercq, Astrid; Giorgio, Suzanne; Mottet, Christine*

Journal of Physics-Condensed Matter- 28, 6 (2016)

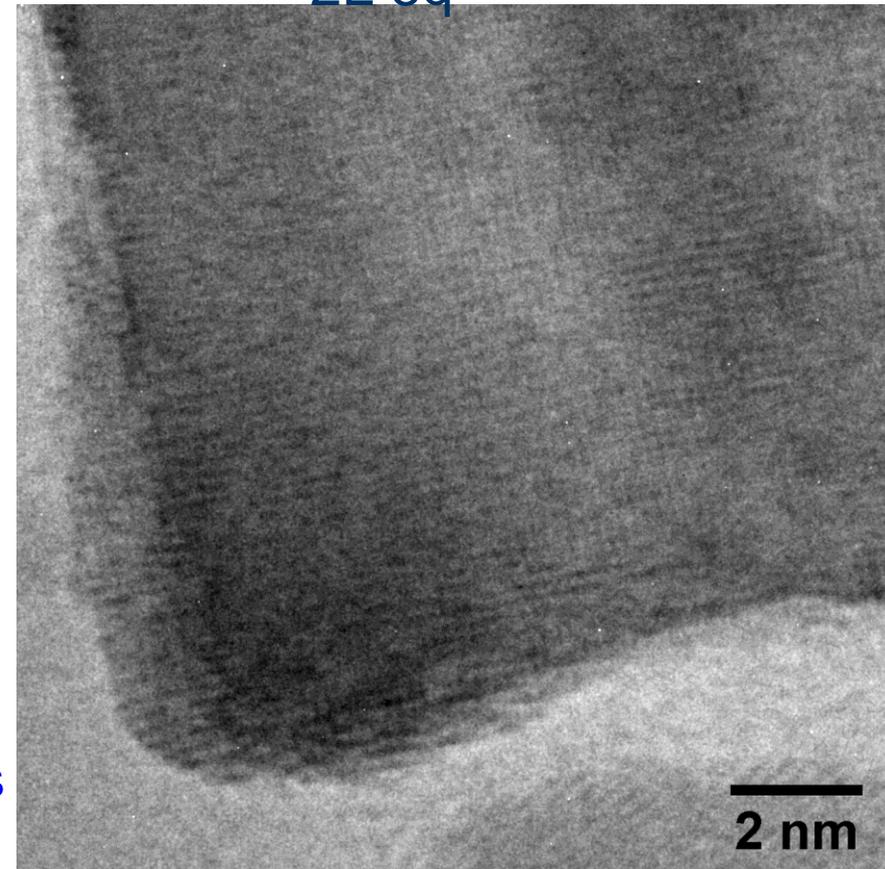
Pd surface and Pt subsurface segregation in Pt_{1-c}Pd_c nanoalloys



In situ growth of Pt shell on a Pd nanocube in a graphene oxide cell



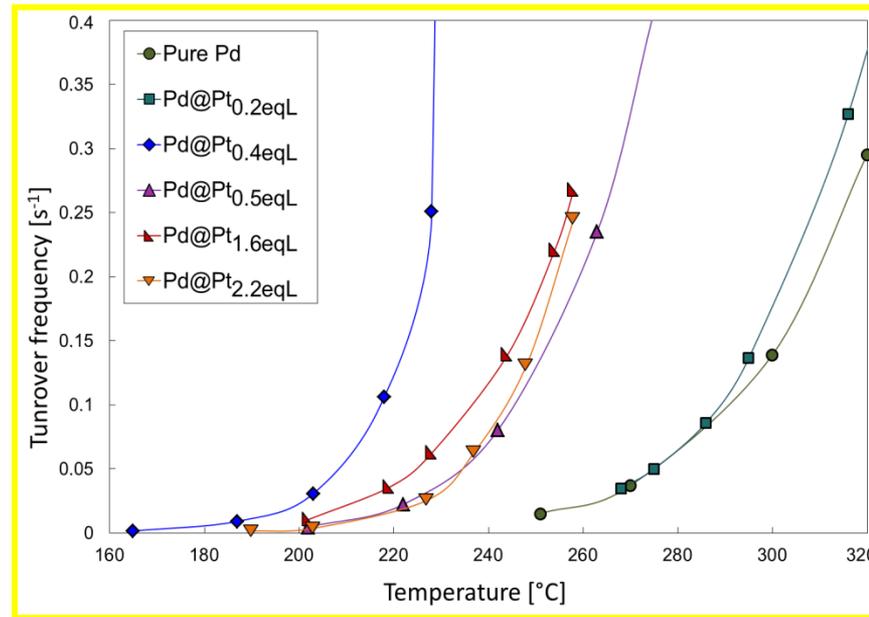
$\text{Pd}@\text{Pt}_{2\text{L eq}}$



Imperfect epitaxial Pt deposition:

- Most deposition as irregular corners
- Lattice deviations at the surface
- For higher amount of Pt more irregular deposition and defects

CO oxidation: Best results for 0,4 equivalent layers of Pt on the Pd nanocubes



Why?

- Modification of the electronic structure of the Pt atoms at the surface.
- Roughness, strain effects, compressive strain of the Pt shell due to the misfit between Pt and Pd lattices = moderate (1.3%)
- **Pt outside at the corners but below the surface at the center of the (100) faces.**

Nanoalloys:

Morphology in gas- Reactivity, Interface/ substrate...

Au-Pd

Au-Ag

Au-Rh

Pt-Pd

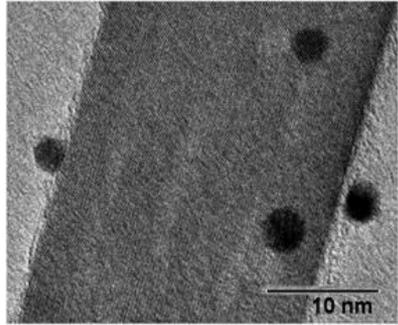
G. Berhault,¹ Z. Konuspayeva,¹ S. Giorgio,² T. Nguyen,¹ P. Afanasiev,¹ L. Piccolo¹,

J. Mater. Chem. A, 5, (2017), 17360

AuRh Supported on Rutile Nanorods: Structural Insight on the Growth of Nanoparticles and Performance

Au-Rh / TiO₂ nanocatalysts: growth and performance in hydrogenation

G. Berhault,¹ Z. Konuspayeva,¹ S. Giorgio,² T. Nguyen,¹ P. Afanasiev,¹ L. Piccolo¹,



Evolution of conversion rates as a function of reaction time for Au Rh/TiO₂ catalysts.

Alloys more active than pure Rh

(Rh in its metallic form in the alloy)

but single use

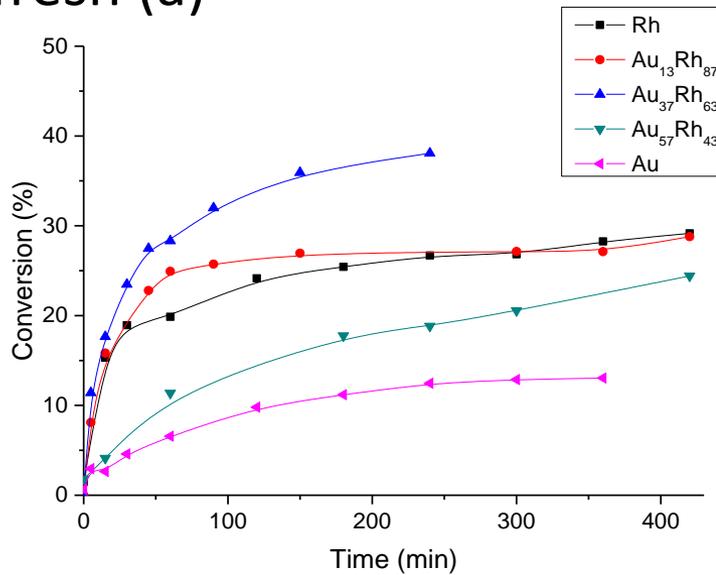
But the most active fresh catalysts is the worst if pre reduced (blue).

Question: what is the effect of H₂ ?

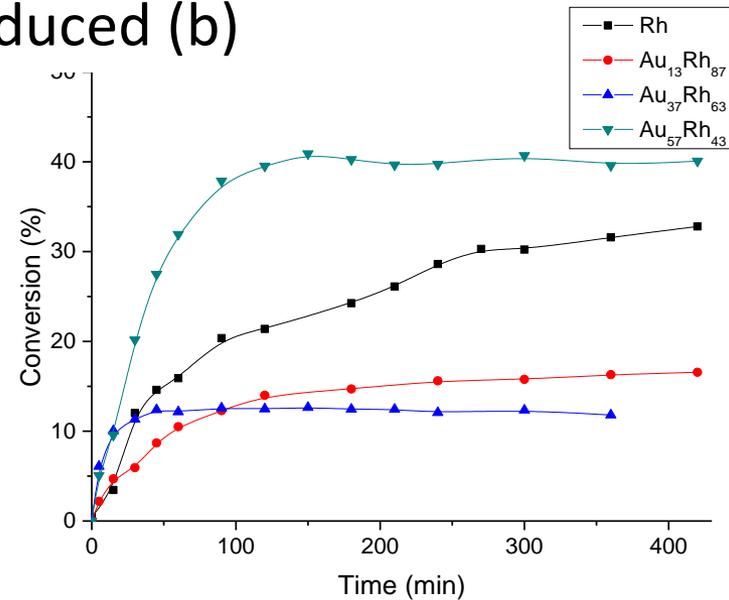
Poisoning, segregations, shape, size, structure?

Au-Rh/ TiO₂
nanorods

fresh (a)



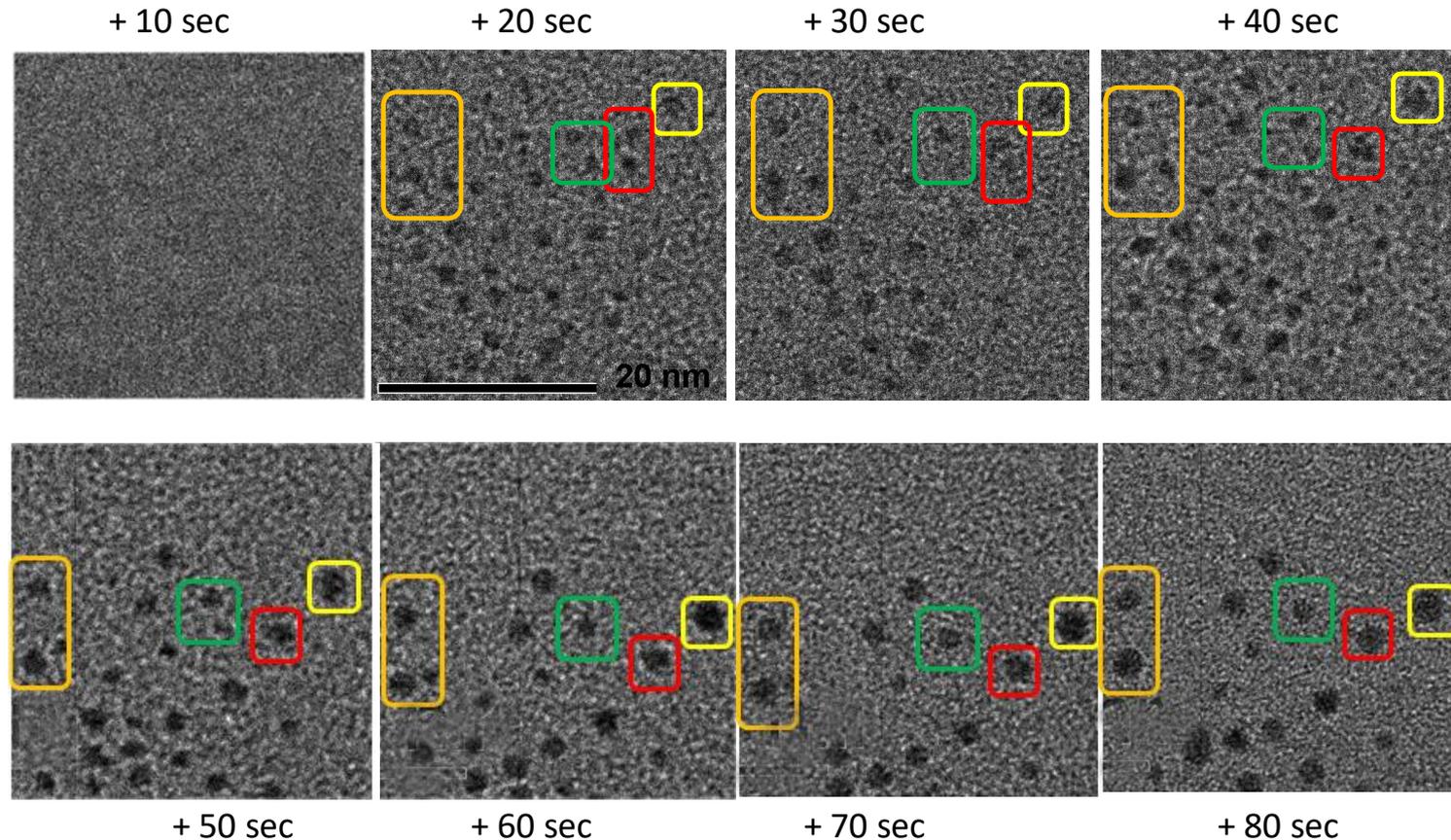
reduced (b)

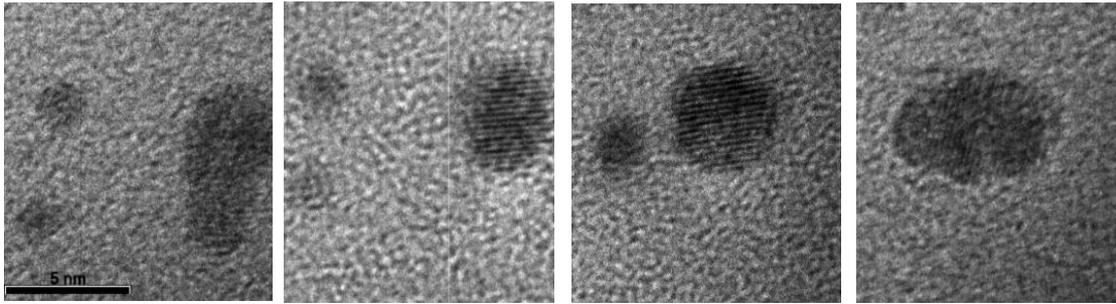


In situ TEM imaging of Au-Rh NPs during the growth in colloidal solution
In a selected area of a micro drop.

Au-Rh

In situ liquid TEM clearly shows simultaneously:
direct growth of individual NPs homogeneous in size ,
then coalescence

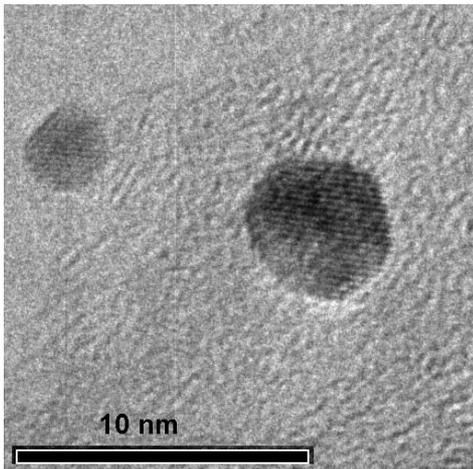




5 nm

Successive liquid TEM images showing the progressive coalescence of AuRh NPs in solution. The images were recorded with a time sequence of 10 s between them.

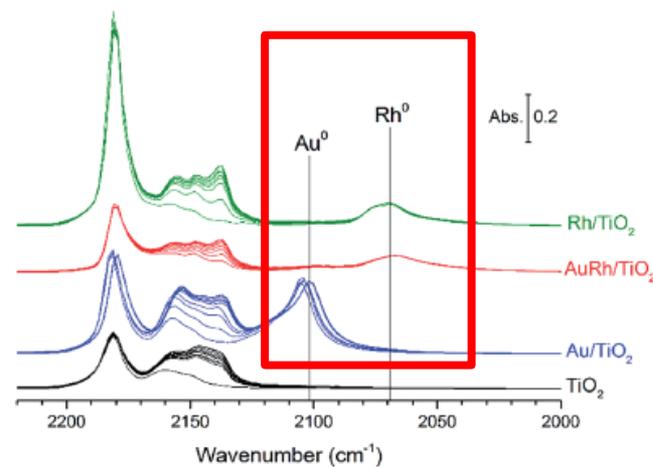
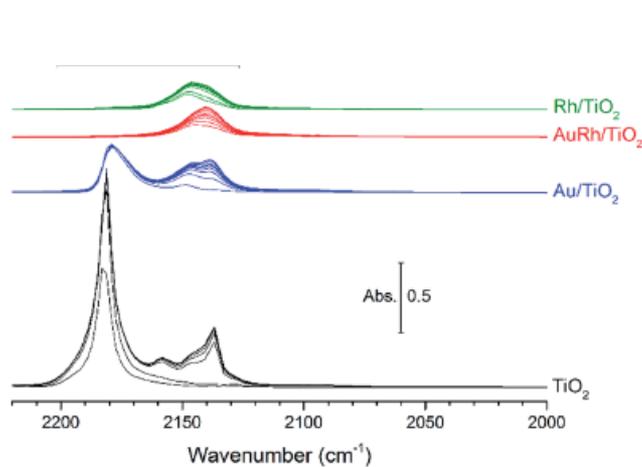
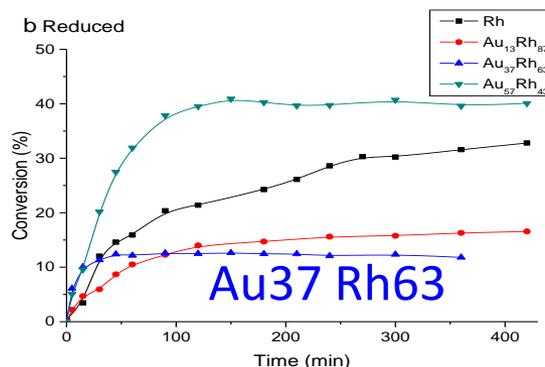
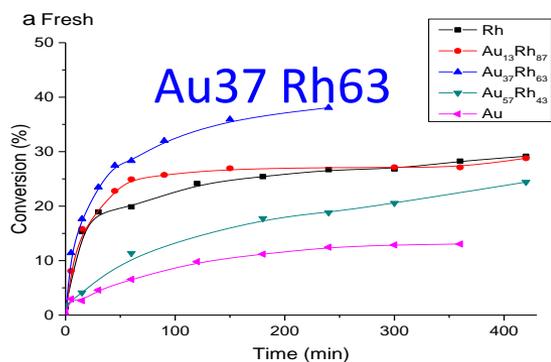
Au Rh in liquid- Coalescence during the growth



Facetted NP - Homogeneous structure

Surface composition?

Au37 Rh63: the best catalyst before reduction, but the worst after reduction!



In situ CO-FTIR spectroscopy results

CO– Au contribution : very small in the case of AuRh/TiO₂ << CO-Rh

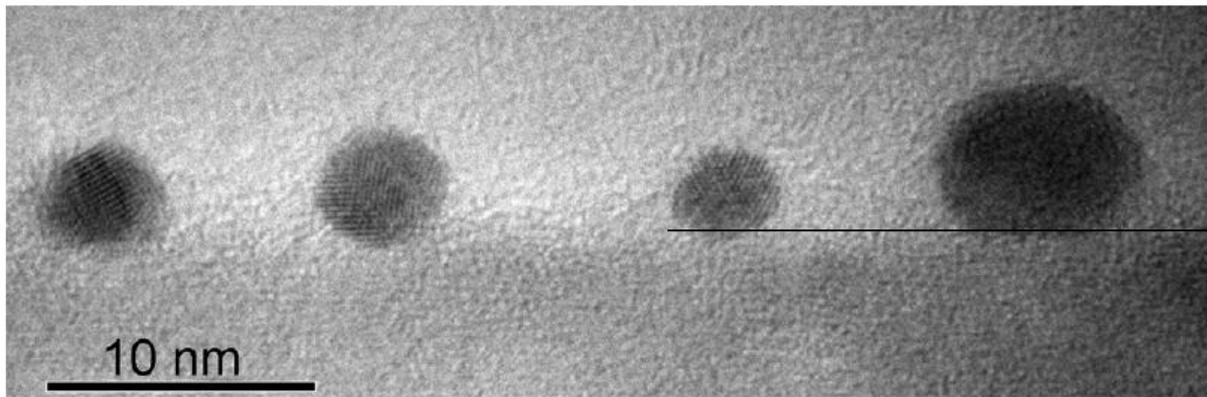
Rh may form a thin surface layer surrounding the nanoalloys

suggest formation of a Rh-rich shell over an Au core center for Au-Rh NPs.

Thickness? In situ observations in gas

Au-Rh nanoalloys /TiO₂

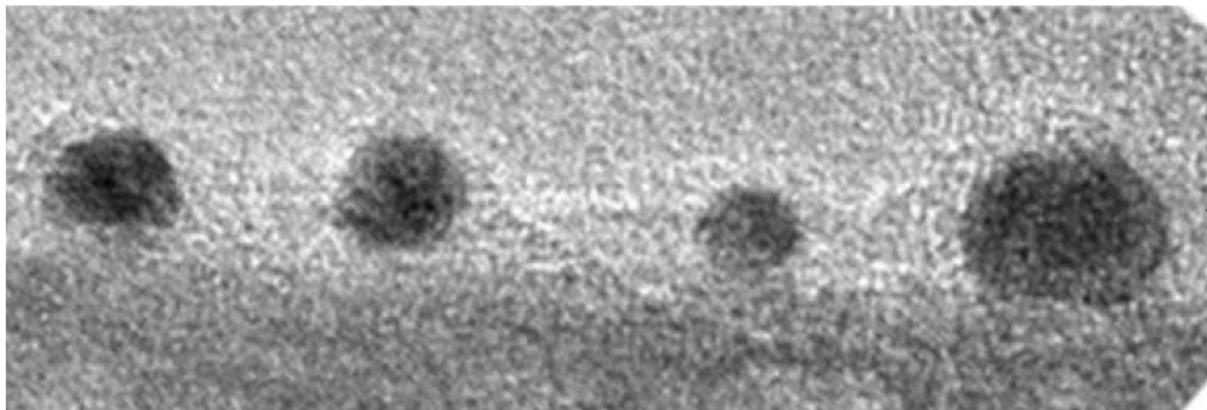
In situ ETEM imaging in pure gas



Interface

10 nm

4 clusters in profile view, in a flux of O₂ (1 mbar)



Shell thickness: 1 nm

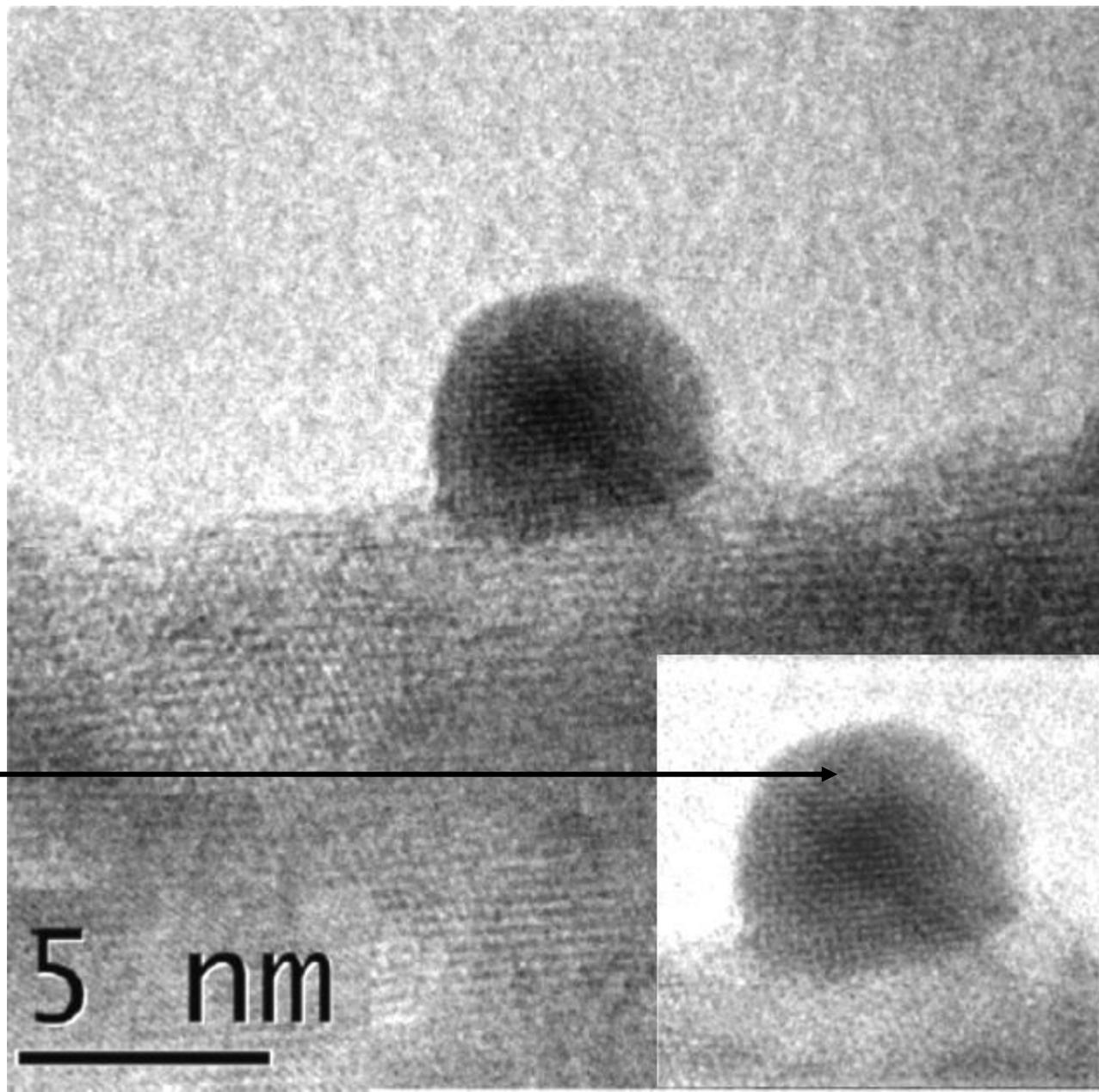
Same clusters in a flux of H₂, 1 mbar.

Core shell formation visible in the largest cluster

After annealing in H₂ at 400 °C-

Core shell structure still visible in the clusters > 5 nm
even after air transfer

Discontinuity at
the core/shell
interface



Why deactivation of Au-Rh after reduction?

In situ study of the growth by DLS and Liquid TEM

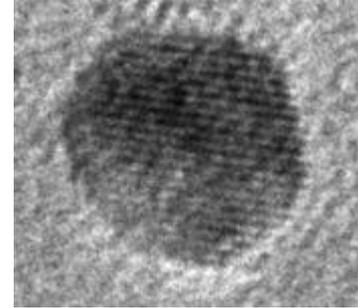
→ nucleation and growth by adsorption of the precursors then aggregation

→ nanoalloys with homogeneous disordered structure.

FTIR spectroscopy on CO molecules adsorbed on Au or Rh

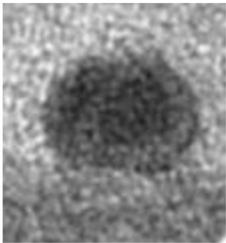
→ Both metals at the surface before reaction

→ Only Rh on the surface after hydrogenation



In situ TEM in gas

→ Core shell formation in a pressure of H₂



The reducing treatment at 350 °C enhances Rh segregation phenomena (Rh oxidized) and **limits the stabilization** effect of Au, so decreases the catalytic performances

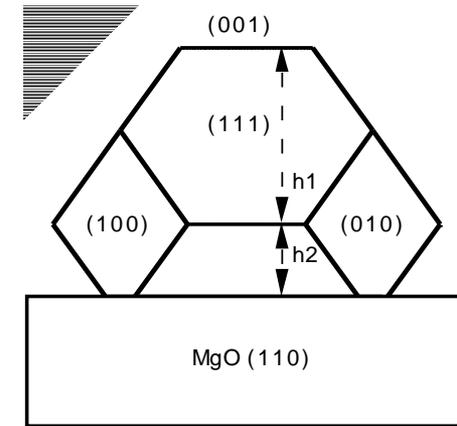
→ No solution to improve the system for catalysis!



Adhesion energy β : Pd / substrate,
determined from the 3D shape and the surface free energy

Wulff Kaishew: $\beta = \sigma_{100} \cdot (h_1 - h_2) / h_1$

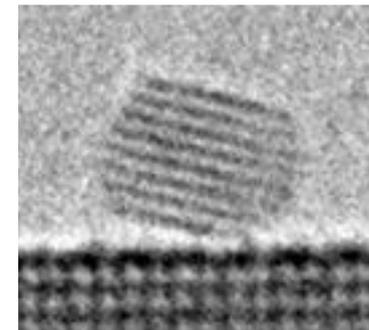
$\sigma_{100} = 1.7 \text{ J.m}^{-2}$ (single crystal)



Size	<5 nm	10- 15 nm	20- 30 nm
Adhesion energy	$\beta = 1.7 \text{ J.m}^{-2}$	1.05 J.m^{-2}	0.75 J.m^{-2}

β decreases

- when the particle size increases
- with the formation of defects at the interface and in a gas pressure of O_2 or $\text{O}_2 + \text{CO}$.



Oxido Reduction cycles of Au-Ag NPs (in pure H₂ and pure O₂)

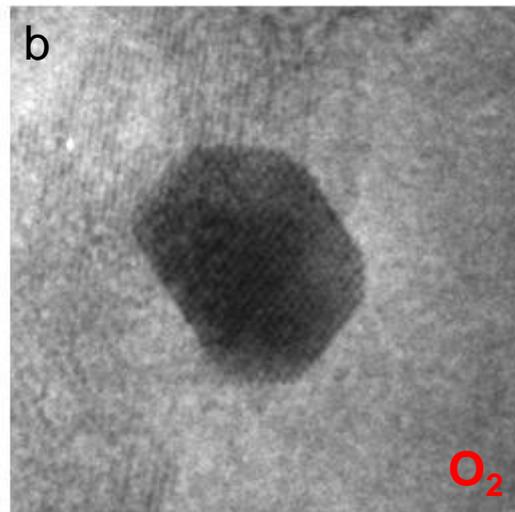
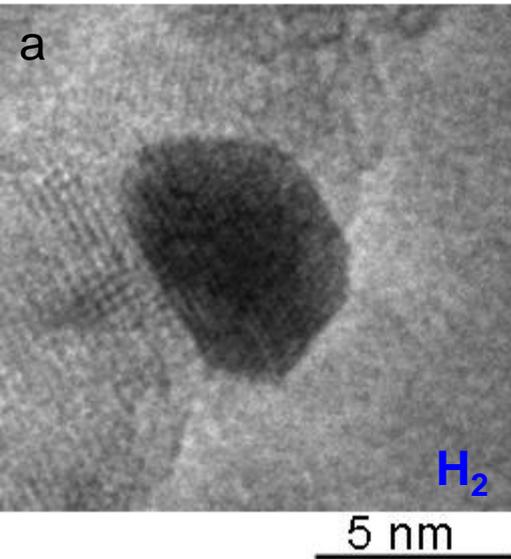
R. Zanella, C. Louis, S. Giorgio

Compared to Au-Cu NPs

A Nasserredine , J Nelayah, L. Delannoy

■ *nanoalloys AuAg*

Au- Ag / TiO₂ first stages (few seconds)

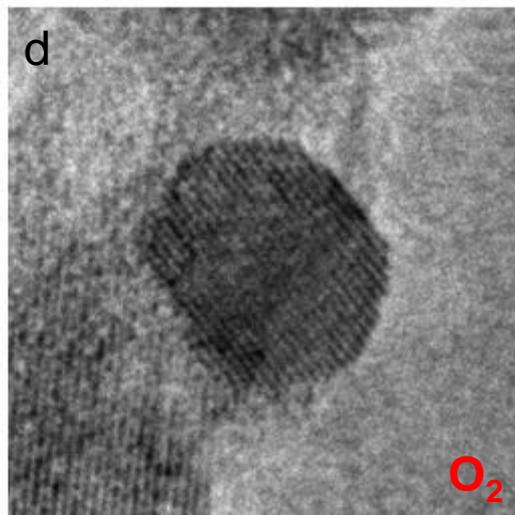
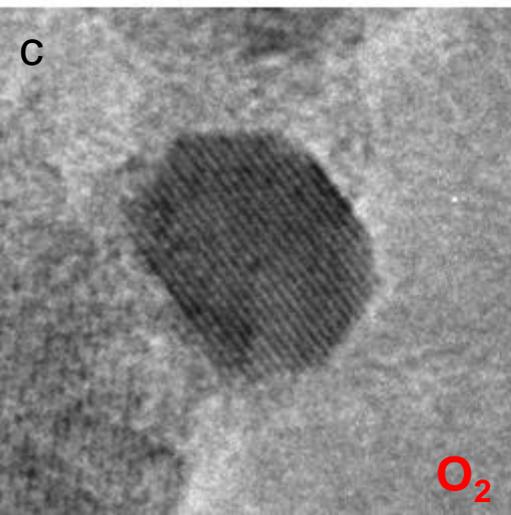


Adhesion energy

$$\beta = \sigma_{001} \cdot (h_{001} - h_s / h_{001})$$

During O₂ adsorption

β decreases



$$\beta_a = 0.50 \sigma_{001}$$

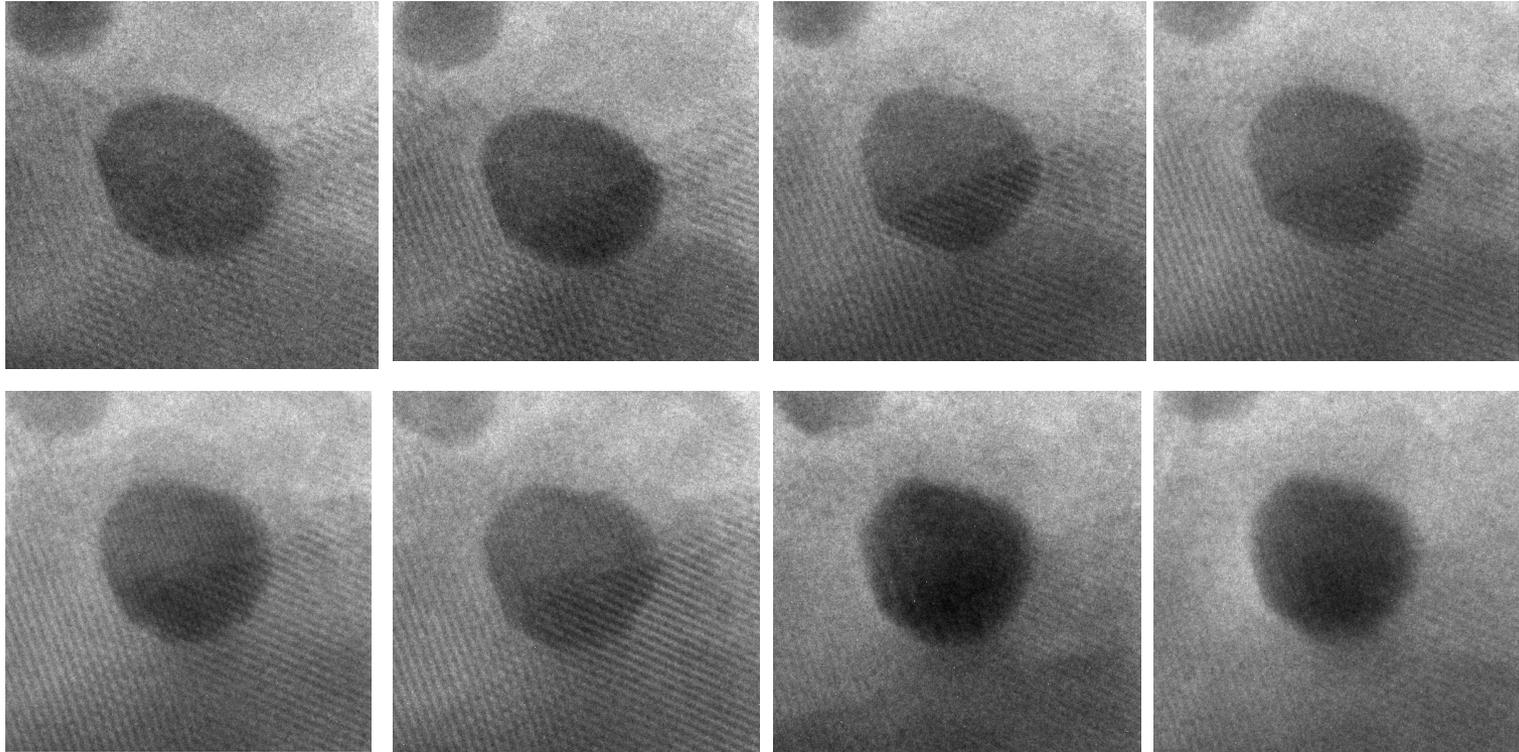
$$\beta_b = 0.43 \sigma_{001}$$

$$\beta_c = 0.28 \sigma_{001}$$

$$\beta_d = 0.07 \sigma_{001}$$

→ isotropic shape

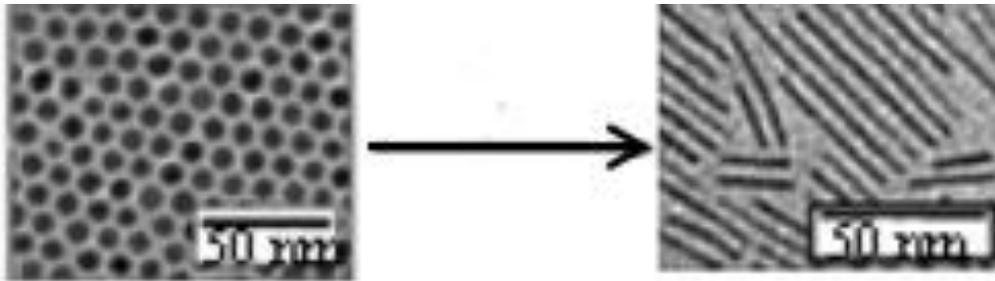
During 10 mn



No visible segregations- **Stability of the structure**

In situ Growth of Co and Co-Ni Nanoalloys in OAM

Arthur Moisset, Alexandre Sodreau, Anthony Vivien, Caroline Salzemann, Pascal Andreatza, Suzanne Giorgio, Marc Petit, Christophe Petit, NANOSCALE (2021)



Size and shape control during the growth

Evolution from Nanospheres to Nanorods with a smaller diameter

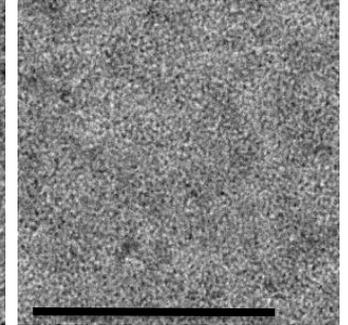
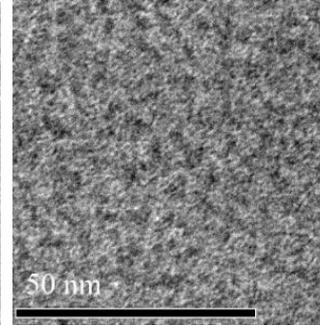
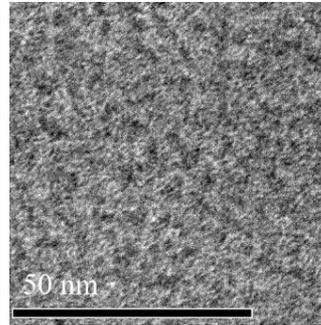
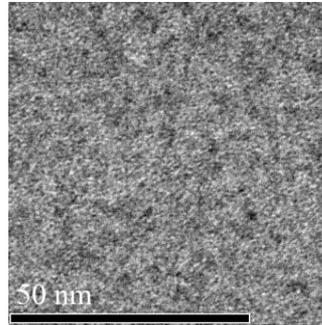
Why this evolution?

Which mechanism?

In situ study by SAXS and liquid TEM

Liquid TEM in graphene oxide

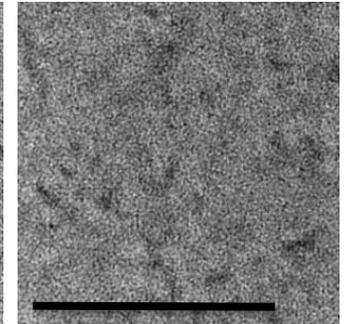
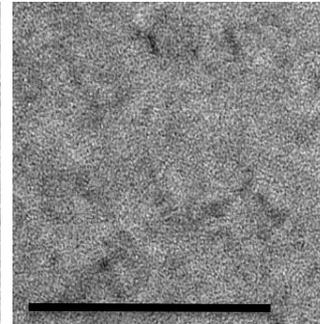
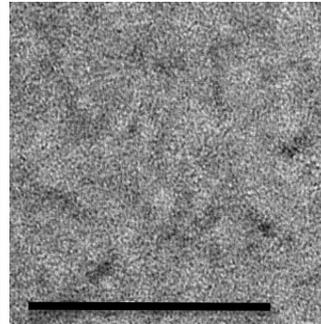
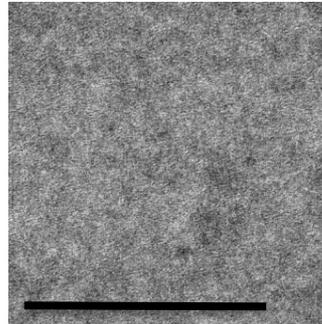
- Nucleation



- Growth

- Dissolution of Nanoparticles

- Alignment of small clusters along the OAM fibers



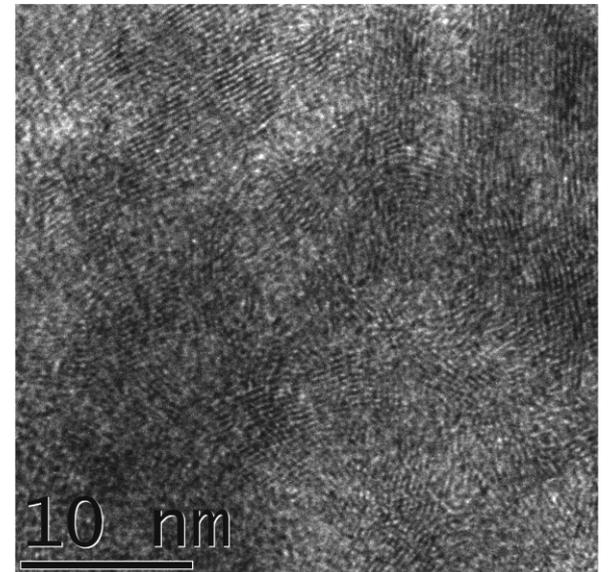
- Growth of Nanorods

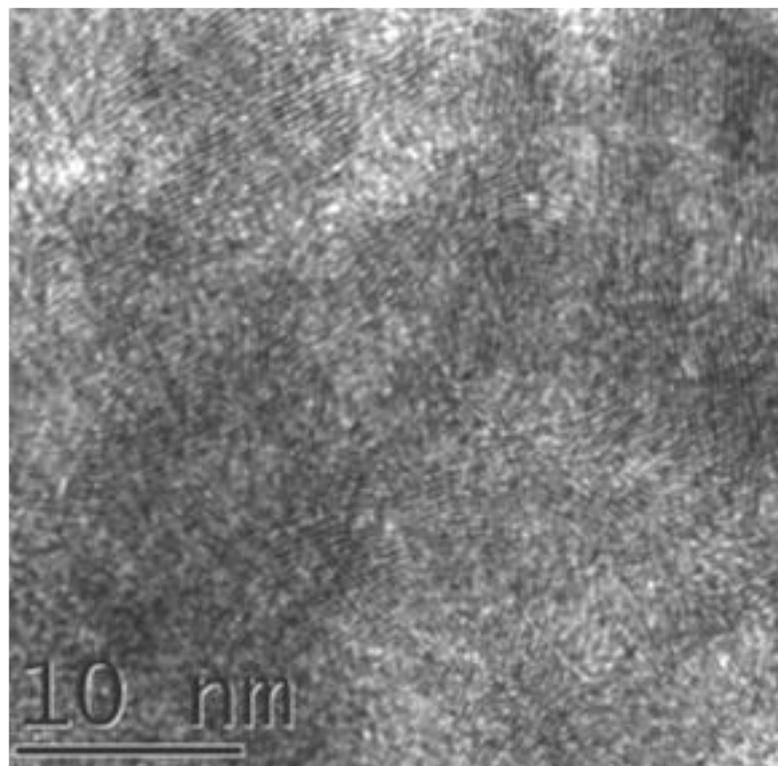
OAM fibers

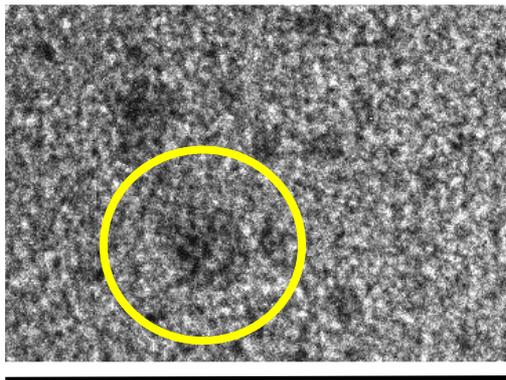
Pseudo in situ SAXS measurements

→ inter-lamellar distance of 5 nm

presence of texturing media of the OAM

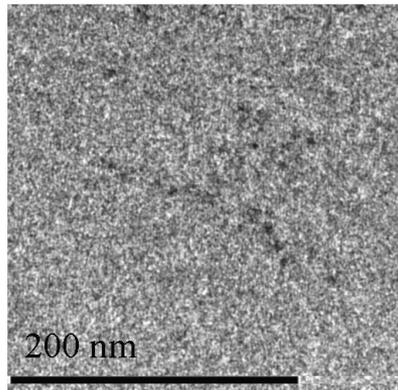




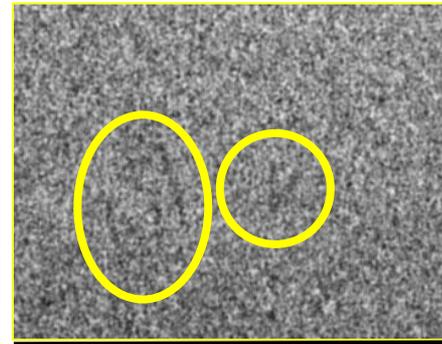


50 nm

1) Formation of Co NPs (4- 10 nm),

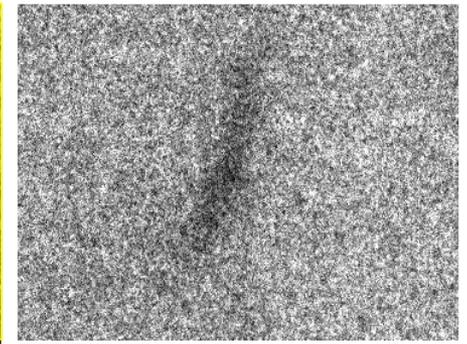


2) Dissolution of NPs



100 nm

3) Clusters
alignment OAM
OAM fibers



100 nm

4) Growth as
nanorods along
the OAM fibers

Pseudo in situ SAXS measurements

→ inter-lamellar distance of 5 nm presence of texturing media of the OAm

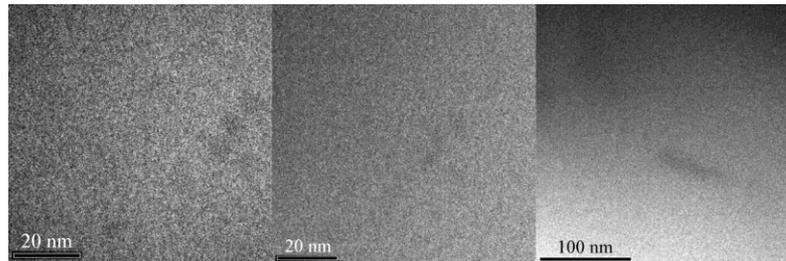
In situ observations in a liquid sample holder at varying temperature (Protochips)

Growth and Dissolution of nanospheres observed in a liquid sample holder, at increasing temperature in diluted OAM,

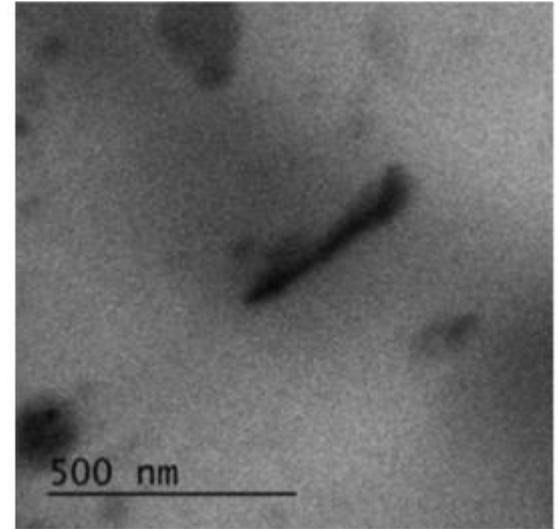
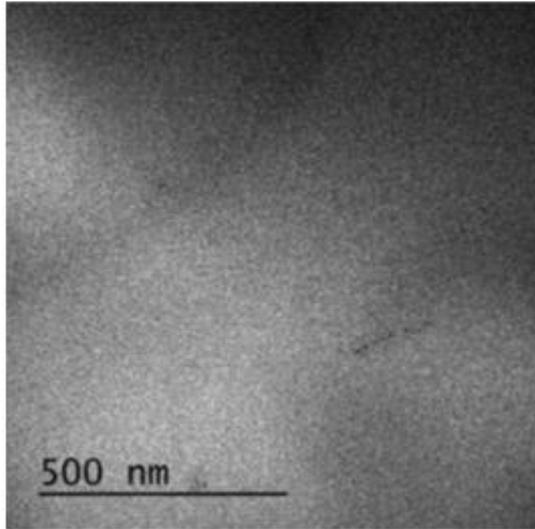
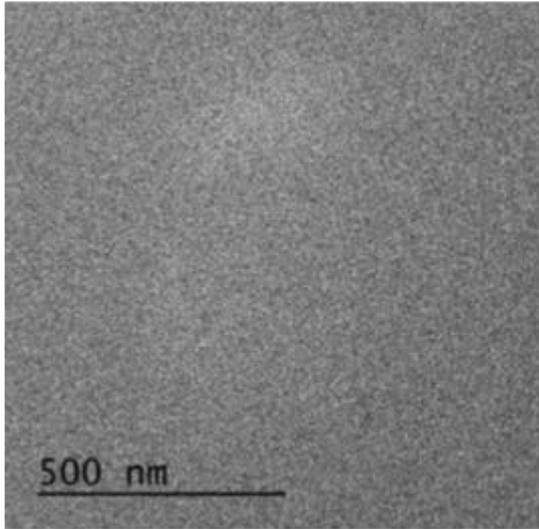
then

Re growth as nanorods.

until the production of H_2 which increases the pressure in the liquid cell.



Co-Ni

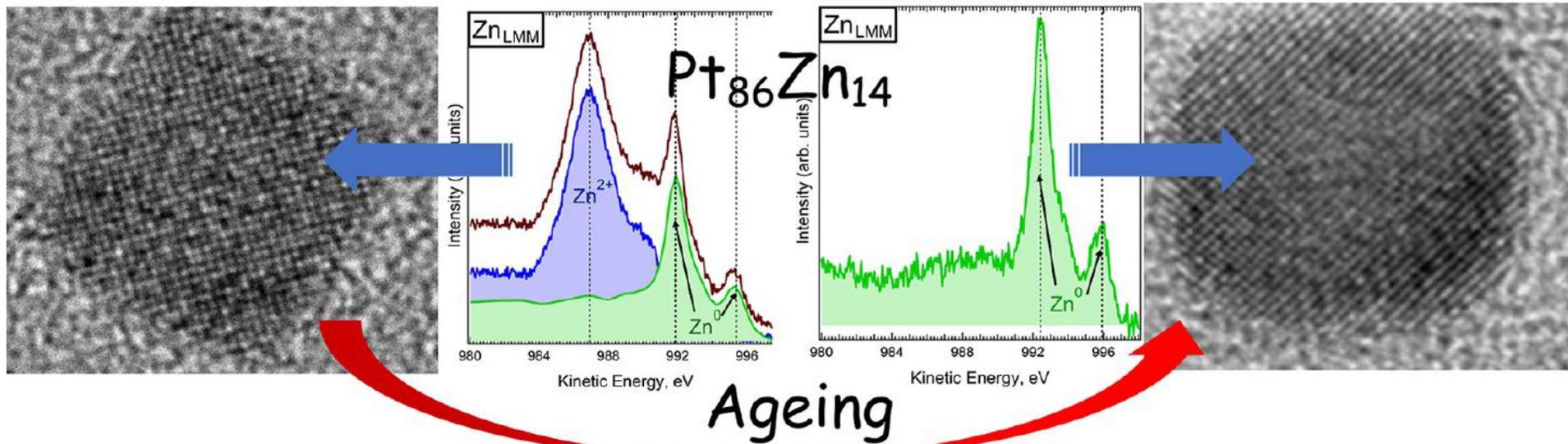


Alignment of
small grains //
OAM

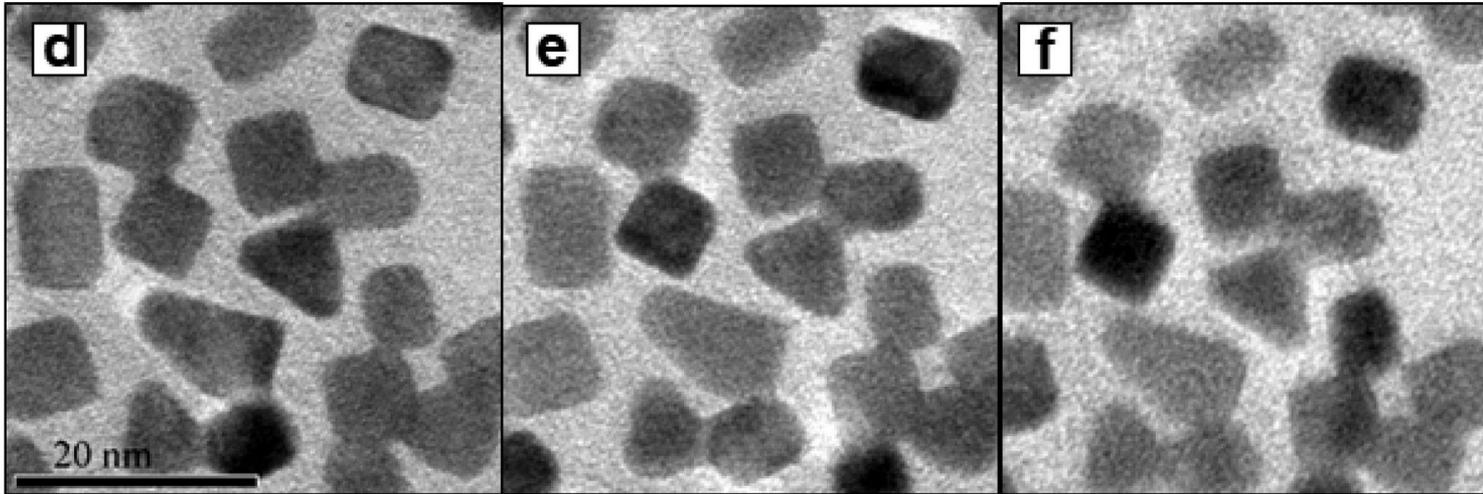
Segregations in the outer shell often observed in oxidizing or reducing conditions

Pt-Zn nanoalloys, for electrocatalytic reactions synthesized from Pt(acac)₂ and Zn(acac)₂ precursors in oleylamine

E-TEM + XPS + Auger spectroscopy → structural + chemical information



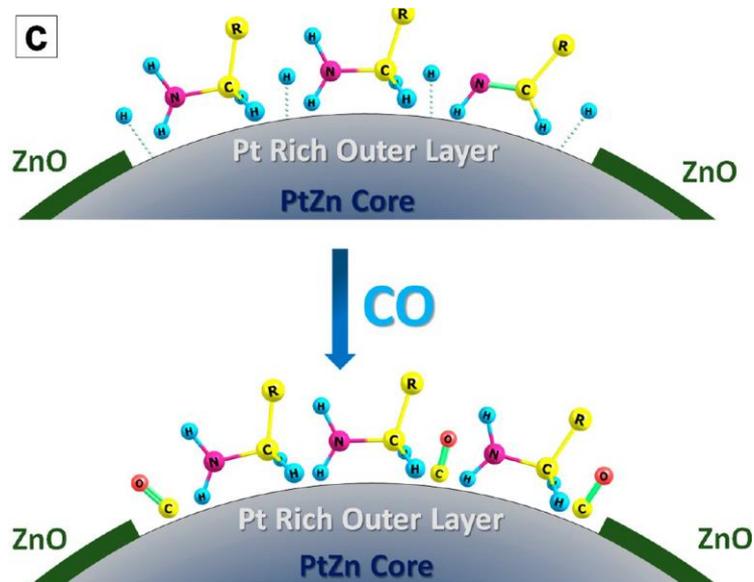
A. Zakhtser, A. Naitabdi, R. Benbalagh, F. Rochet, C. Salzemann, C. Petit and S. Giorgio
Chemical Evolution of Pt-Zn Nanoalloys Dressed in Oleylamine
ACS Nano (2021) DOI: 10.1021/acsnano.0c03366



E-TEM under O_2 (4 mbar) and controlled irradiation (beam current density of $13.5 A/cm^2$ on the sample)

→ gradient of concentration, compositional changes. But which ones?

XPS



Conclusion:

Interesting properties of materials related to the structure, chemical order....
In situ TEM gives ideas to improve the synthesis and conditions of use of nanoalloys.

Synthesis

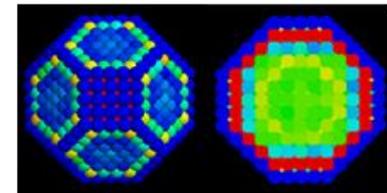
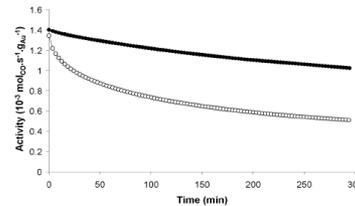
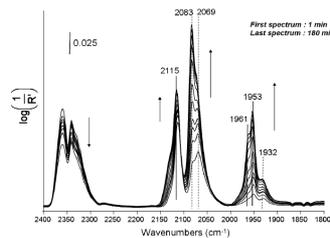
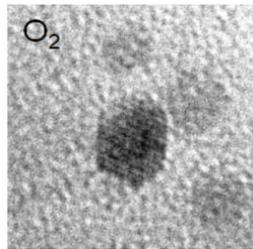
Necessary to control the nucleation and growth

- imaging in liquid TEM give information on the growth mechanism
- Ideas to improve the control of the nucleation and growth process?

Determine the Conditions of use

Unfortunately, sometimes unstable in gas or according to the temperature

- ETEM in gas give information about the behaviour during reaction
- Ideas to stabilize the structures?



1289 atoms, 3.5 nm

Associate many in situ techniques to follow the growth and to follow the evolution during the reactions in gas

(in situ XPS, SAXS, in situ IR, in situ AFM, reactivity, simulations...)