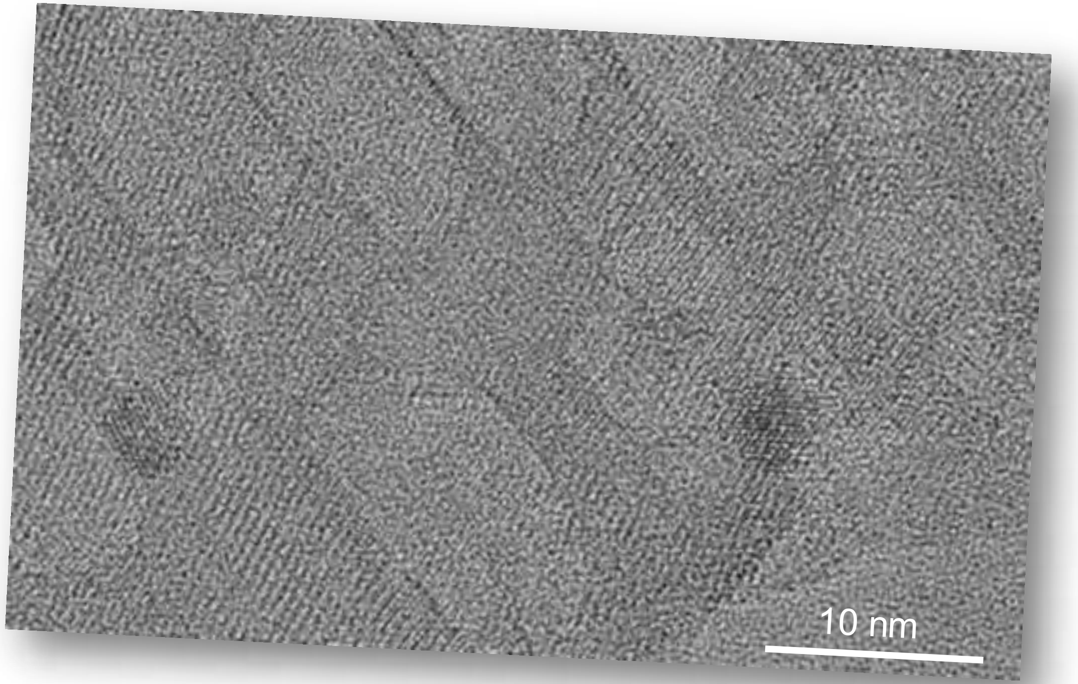
# Why don't we follow the **calcination** and **reduction** stages of **Pd nanocatalysts** supported on alumina in situ directly in an **Environmental Transmission Electron Microscope**?


UNIVERSITÉ DE LYON

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ifP Energies nouvelles

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[2]IFP Energies Nouvelles, Rond-point de l'échangeur de Solaize, BP 3, 69360 Solaize, France

# OUTLINE

- **Environmental Transmission Electron Microscopy: a rapid introduction**

*In situ TEM under gas and in temperature: towards Operando nanocharacterization*

- **Preparation of Pd nanocatalysts supported on $\delta$-$Al_2O_3$**

*Calcination and reduction stages in situ directly in ETEM*

- **Conclusion and Perspectives: Environmental Tomography**

*Follow the evolution of Nanoparticles in real time in 3D in the context of catalysis*

# Beyond High Vacuum: Environmental TEM…

## • Environmental EM: a technical issue

**High Vacuum**
≈ $10^{-6} – 10^{-11}$ mbar

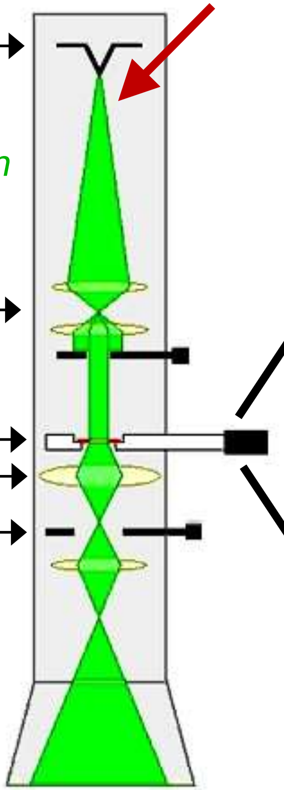
Electron gun

*Electron beam*

Condenser lenses

**Object** (thin)
Objective lens
Aperture(s)

Viewing chamber (screen)



**Straining experiments**
Tensile, shear, fatigue, Nano-indentation/ compression

**Temperature experiments**
Heating / cooling

**Other**
Biasing / lighting…

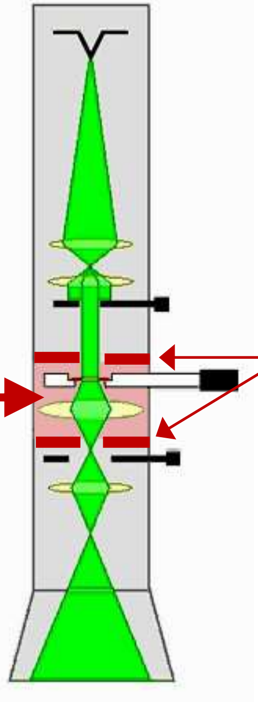
http://insight.stanford.edu

Ladislaus Lazlo MARTON

(a) a pair of electron transparent 'windows' can be placed above and below the specimen to seal it, and its gas atmosphere, from the column;
(b) alternatively a pair of small apertures can be placed above and below the specimen. Gas leakage into the column is then limited to that which escapes via the apertures.

L. MARTON_*Bull. Acad. Roy. Belg. Cl. Sci.* **21** (1935) 553-564

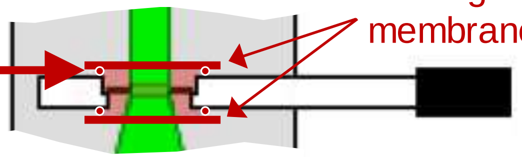
### 1. Dedicated ETEM (Environmental TEM)



Fixed apertures

**GAS** / liquid
**Partial Pressure**
(≈ < a few mbars)

### 2. Ecell (Environmental *closed* Cell)



Sealing membranes

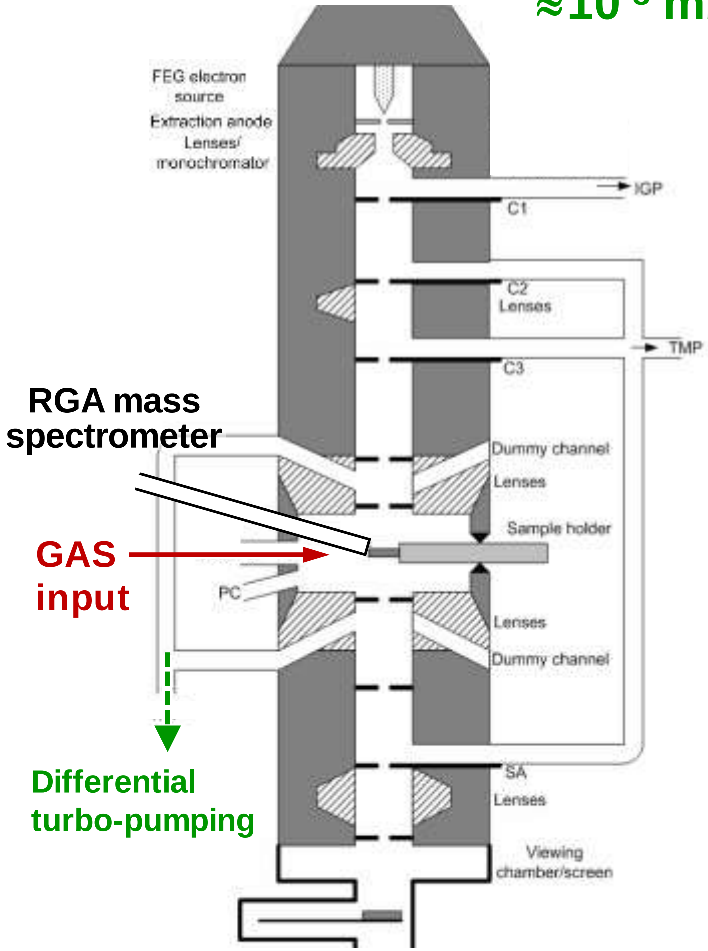
**GAS / LIQUID Pressure**
(≈ < a few bars)

# Beyond High Vacuum: Environmental TEM…

Aberration-corrected FEI TITAN ETEM, 80-300 kV
at Univ. Lyon, F


http://www.clym.fr/Ly-EtTEM_examples/Ly-EtTEM_examples.html

**Controlled pressure range:**
**≈$10^{-8}$ mbar – ≈20 mbar**




*Equipped with:*

- EDX SDD analyzer
- **G**atan **I**maging **F**ilter
- Tomographic holder
- Pico-indenter
- Fast 16 Mp CMOS camera Oneview™


25 fps in 4K
100 fps in 2K

- MEMS-based ($SiN_x$ chip) *heating holder*

1100°C

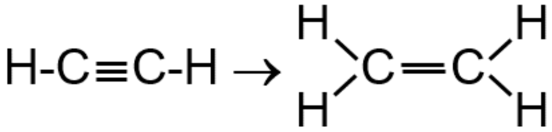
# Preparation of Pd nanocatalysts supported on δ-$Al_2O_3$

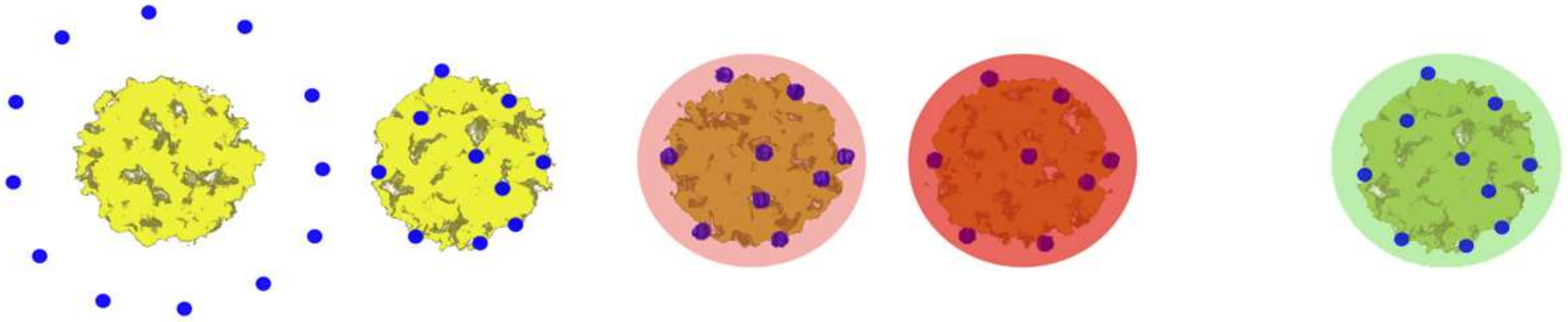
- **Background** ***(selective hydrogenation in petrochemistry)***

Ex.: C2 cut

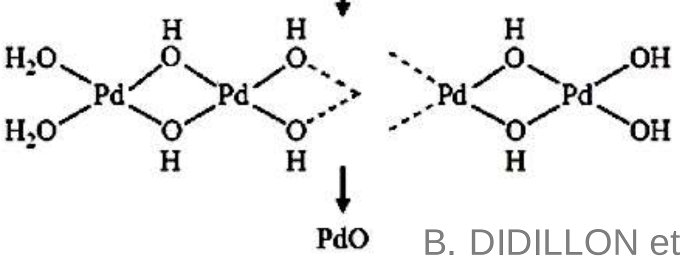
*Looking for…* **ethylen**

*Impurity…* **acetylen**



SHAPING the support → Impregnation with the active phase → drying → Calcination → **PdO on $Al_2O_3$** → Reduction → **Pd on $Al_2O_3$**




**Air ≈ 120°C**

**Air ≈ 450°C**

**$H_2$ ≈ 150°C**

Experiments in the microscope

S. KONETI et al., *Microsc. Microanal.* **22** 5 (2016) 58

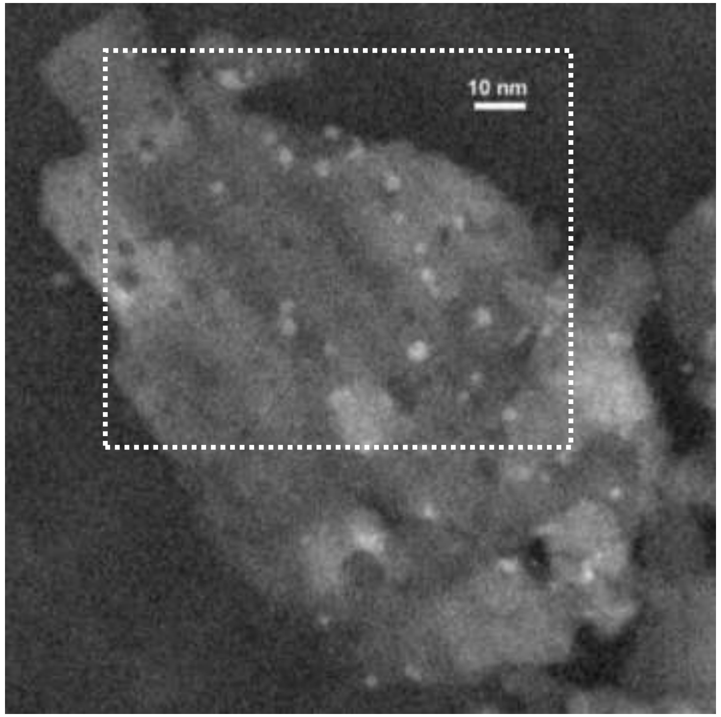
B. DIDILLON et al., 41-54 in *Studies in Surface Science and Catalysis* **118** (1998)

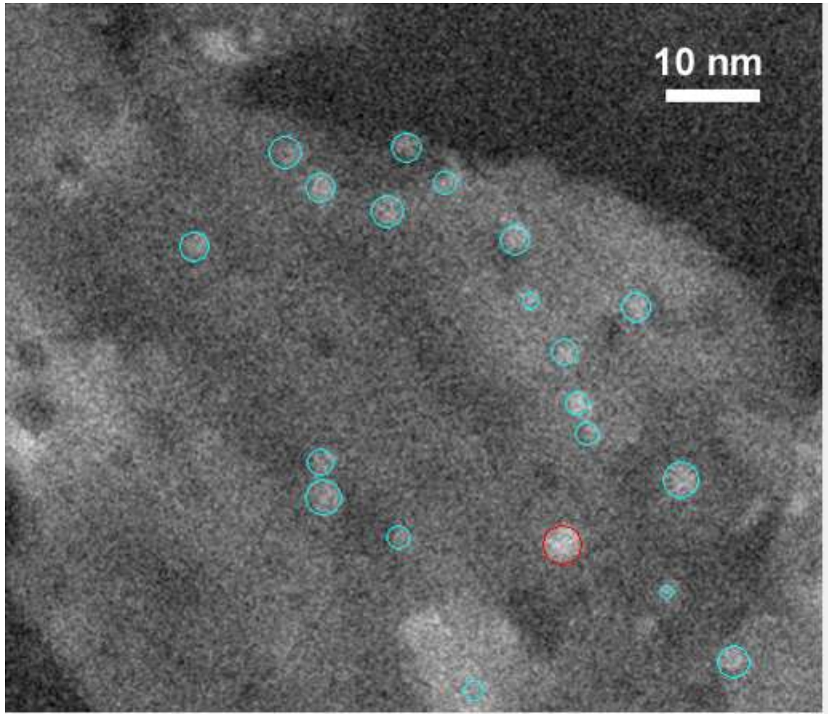
M. RAMOS-FERNANDEZ ET AL., *Oil & Gas Science and Technology – Rev. IFP*, **62** 1 (2007) 101-113

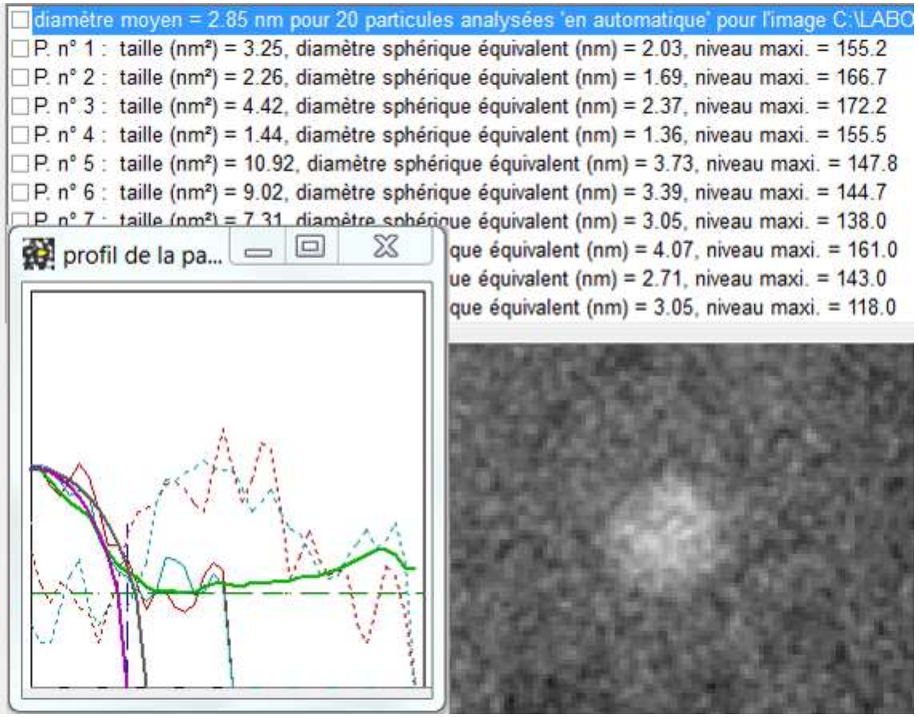
- **Objective 1**

## Size of NPs: comparison in situ ETEM vs. Conventional ‘ex situ’ measurements

*Identify growth process (Ostwald Ripening / coalescence)*



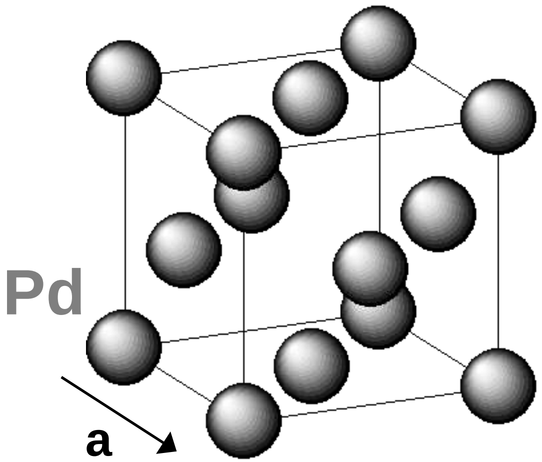



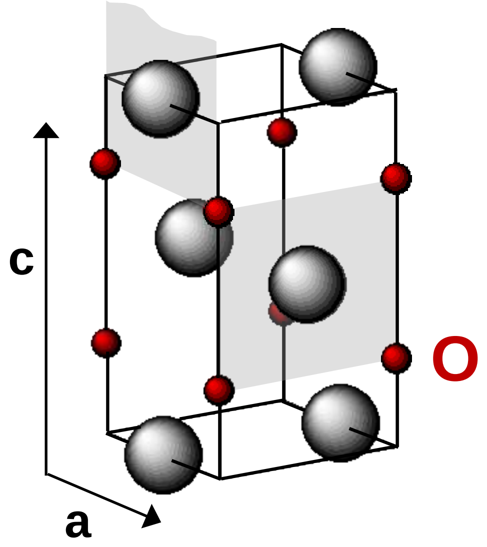

⇨ **STEM-(HA)ADF images, ImageJ™ and home-made softwares**

- **Objective 2**

**Confirm the nature and crystallography of NPs at each stage of the preparation**

**Pd**, fcc Fm-3m
a = 0.39 nm

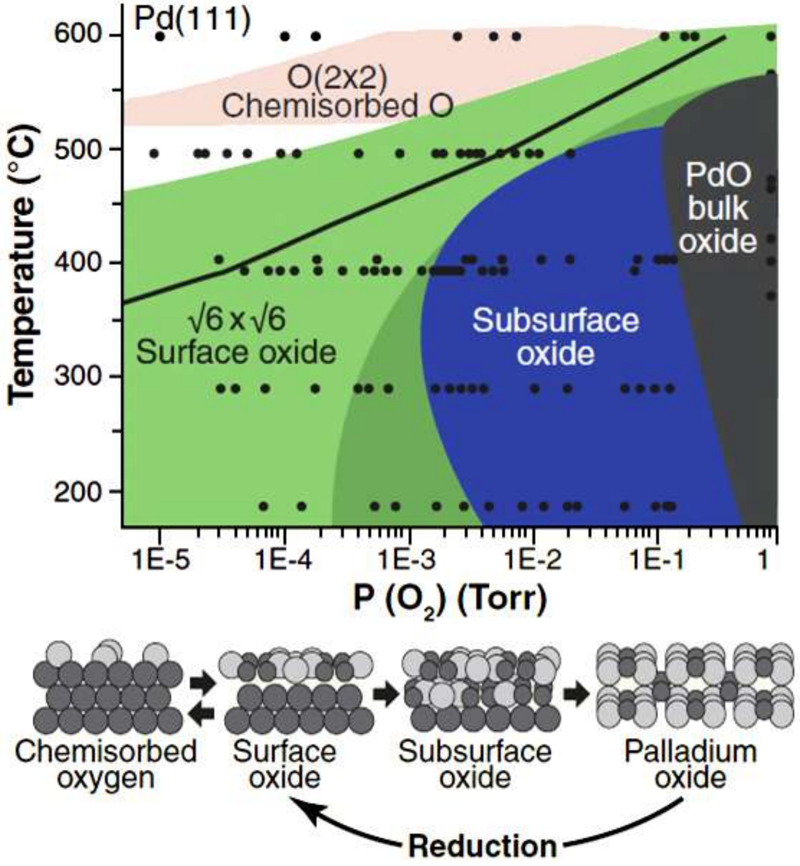



**PdO**, tetragonal P42/mmc
a = 0.302, c = 0.531 nm

J. WASER et al., *Acta Cryst.* **6** (1953) 661

G. KETTELER et al., *J. Am. Chem. Soc.*, **127** 51 (2015) 18269

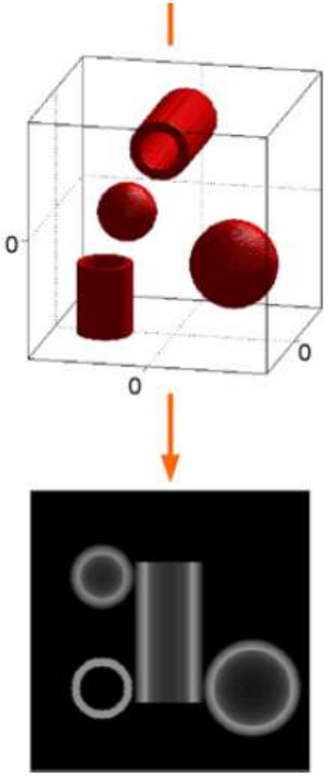


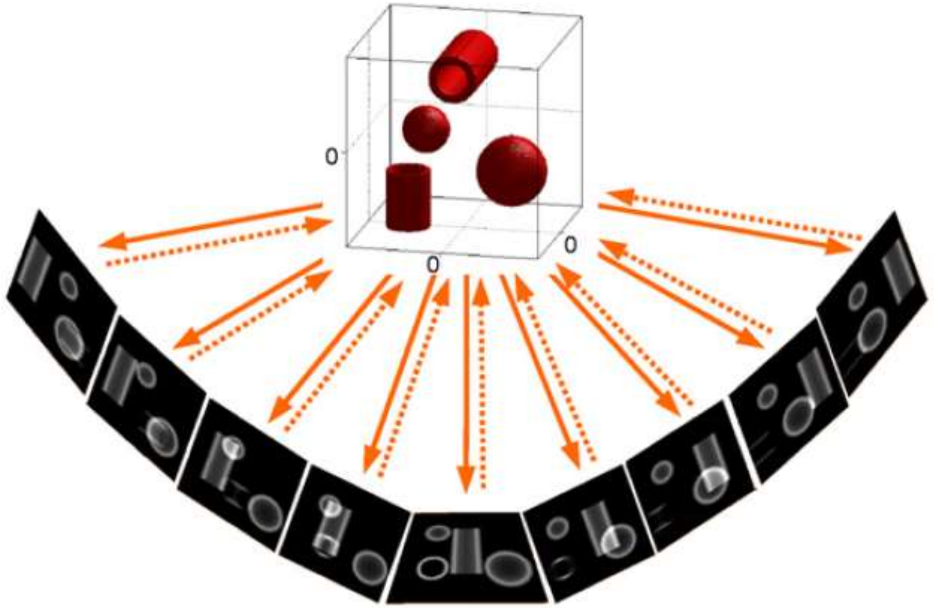
# Preparation of Pd nanocatalysts supported on δ-$Al_2O_3$

- **Objective 3**

## Attemps for *in situ* 3D characterization

*Fast acquisition of 'tilt series' to freeze a microstructure evolving under gas and T°*





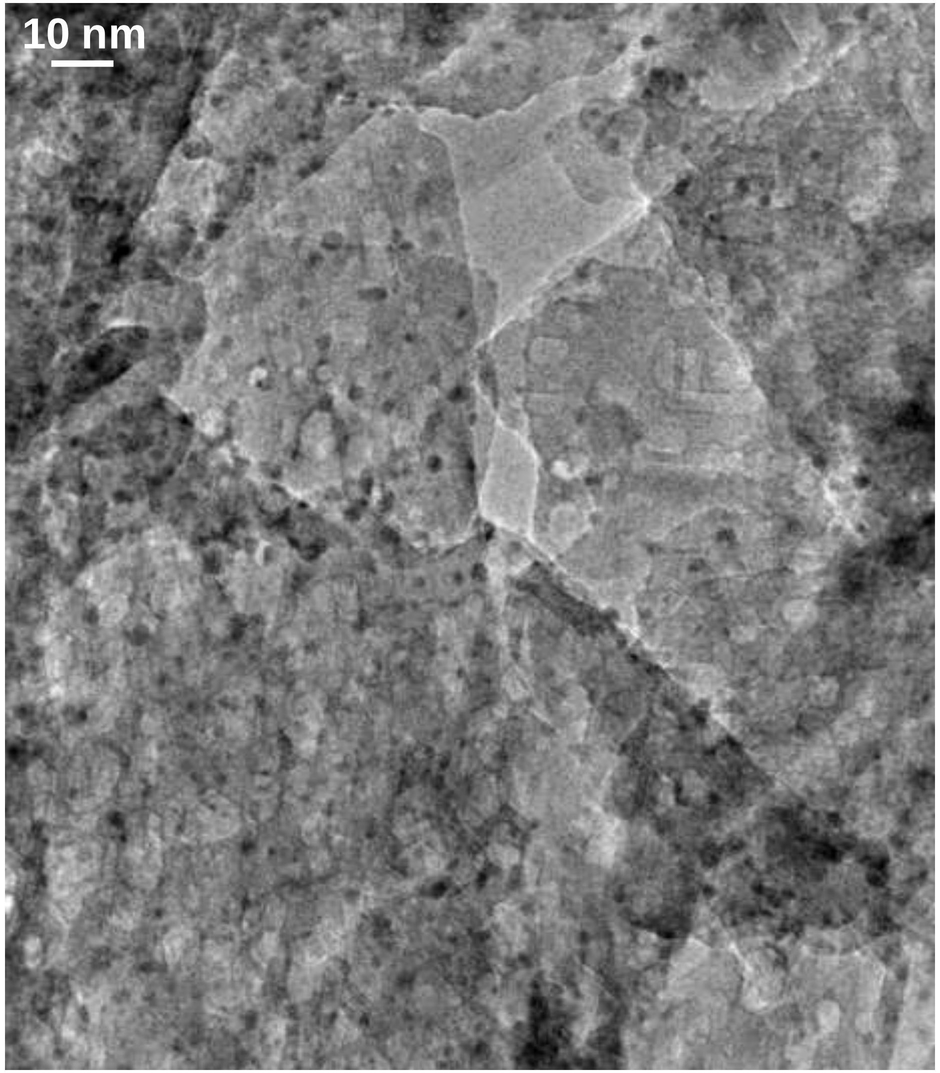
M. BARCENA, A.J. KOSTER, *Seminars in Cell & Developmental Biology*, **20** (2009) 920-930

"It is tempting to contemplate whether soon we might be able to image in 3D relevant processes in catalysis, such as the sintering of supported metal nanoparticles under near to realistic reaction conditions, or the evolution of catalysts during synthesis."

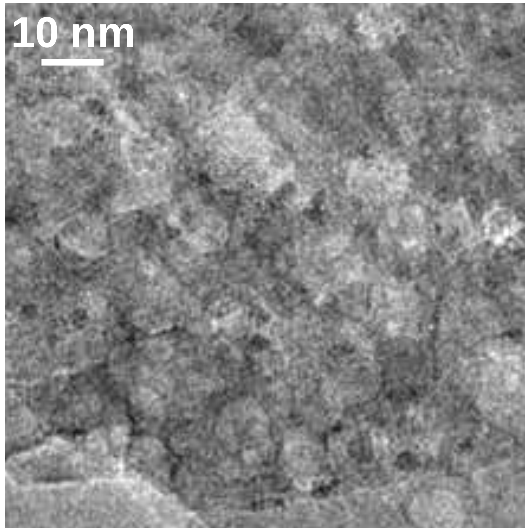
J. ZECEVIC et al., *Current Opinion in Solid State and Materials Science* **17** (2013) 115

# Size of NPs: in situ ETEM vs. 'ex situ' TEM

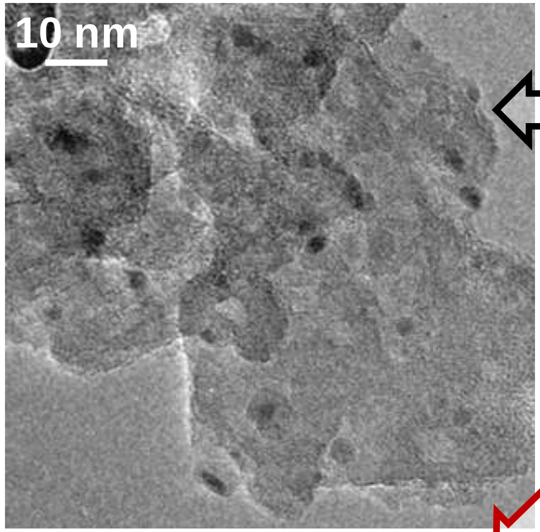
Impregnated state




Dried in air, 2 hrs 150°C

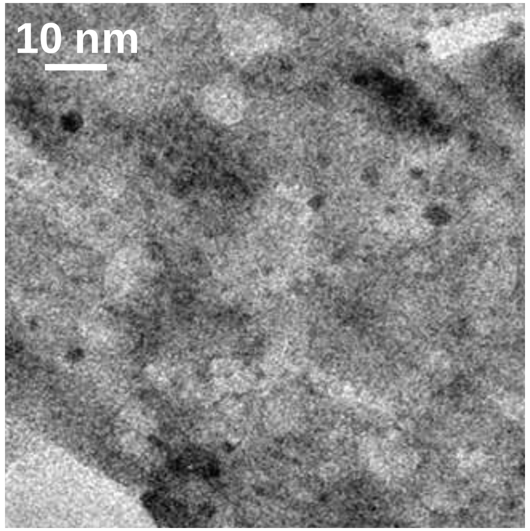



Calcined in air, 2 hrs 450°C

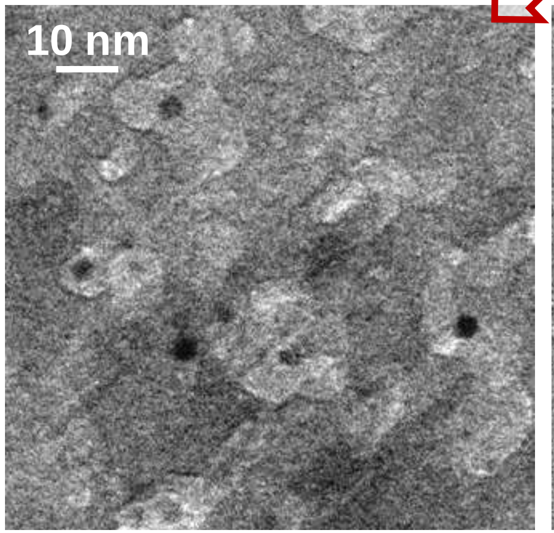



*BF, TEM* from EX-SITU treatments

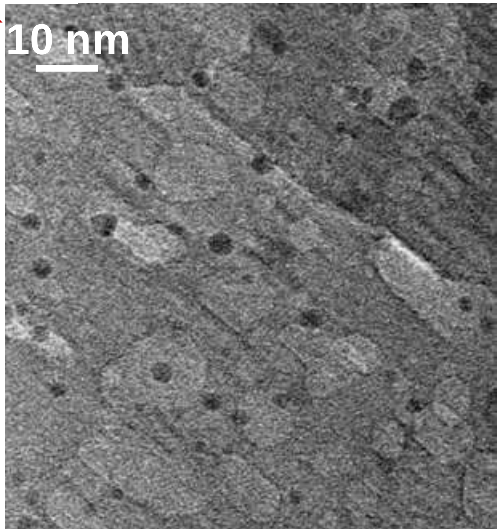
IN-SITU environmental *BF, ETEM* treatments




Heated in 1.6 mbar air, 2 hrs 150°C



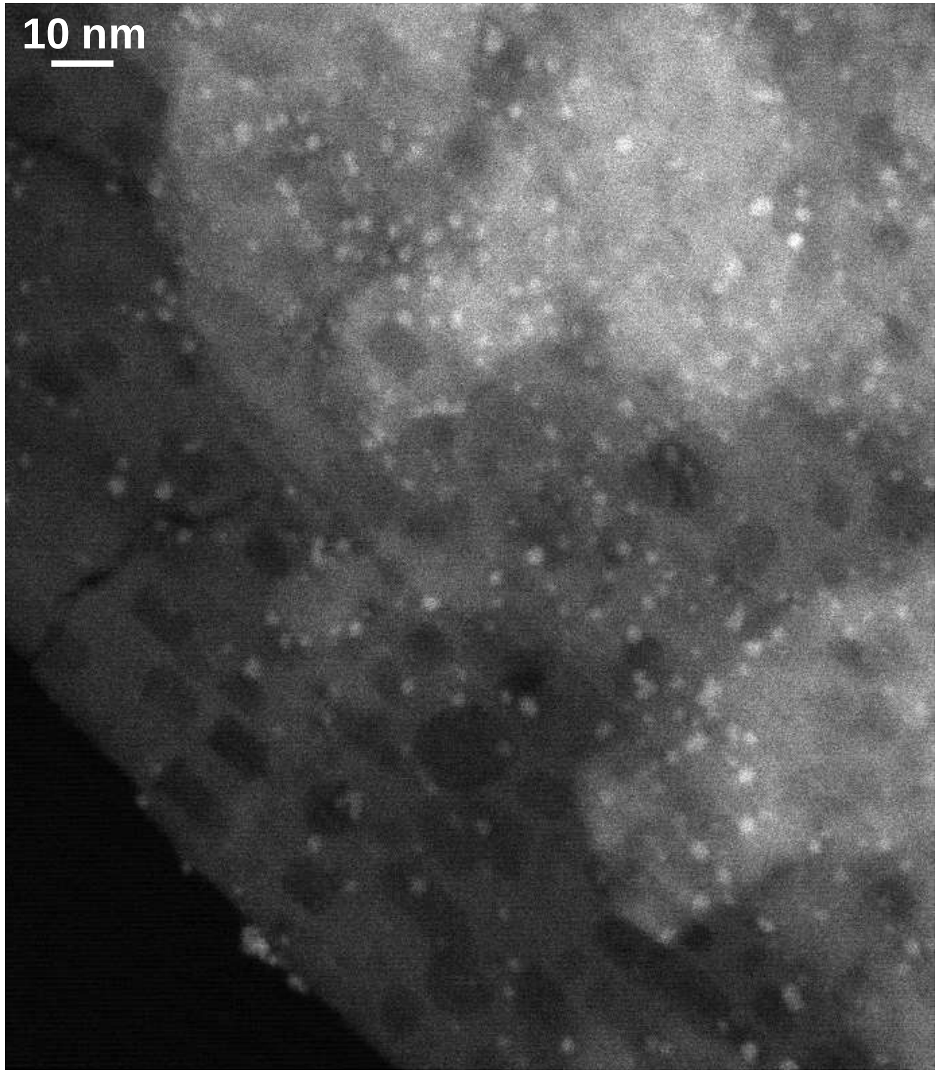

Heated in 1.6 mbar air, 2 hrs 450°C




Reduced in 10 mbar $H_2$, 2 hrs 150°C

# Size of NPs: in situ ETEM vs. 'ex situ' TEM

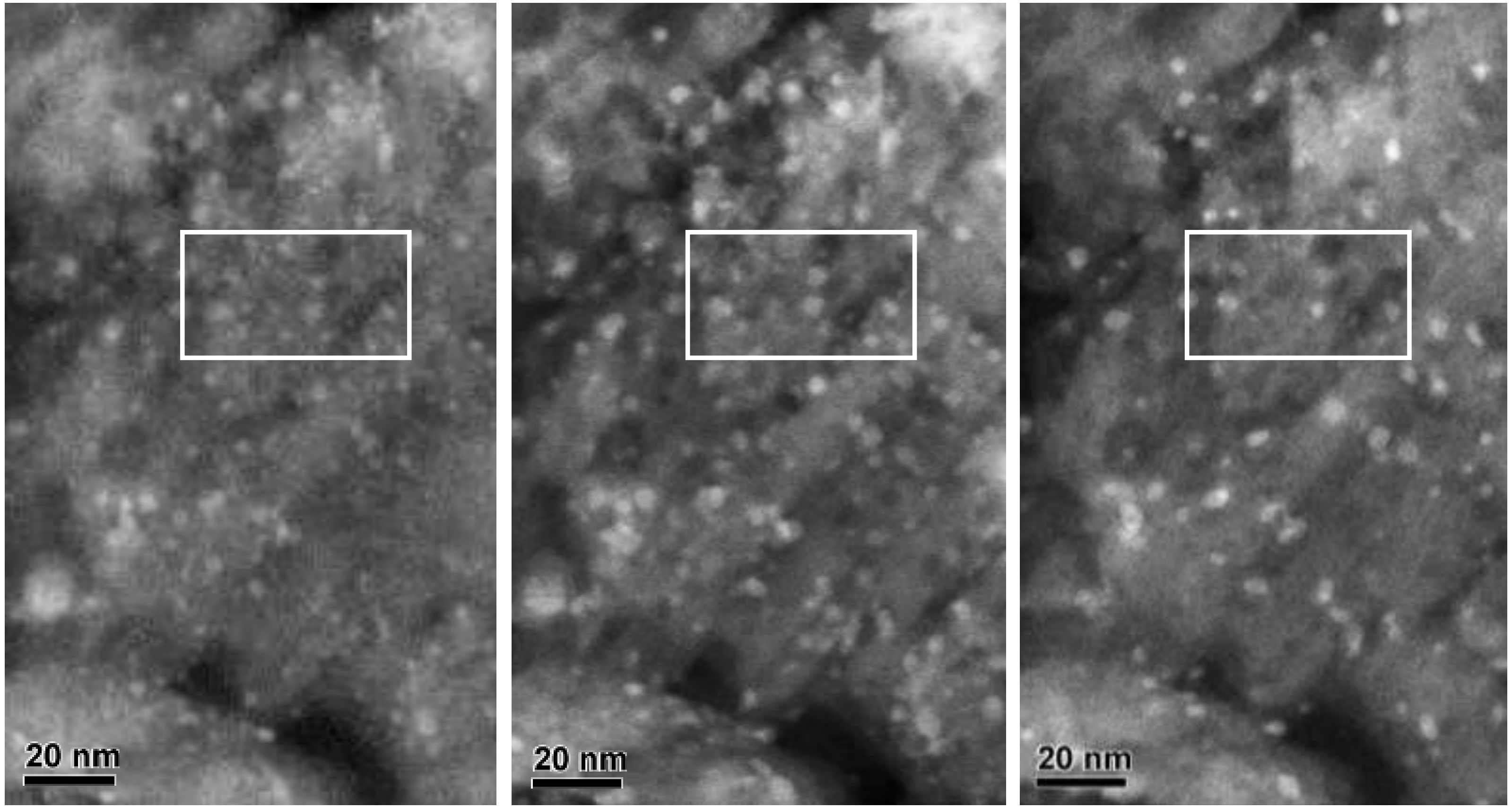
**Impregnated state**




**IN-SITU environmental *ADF-STEM, ETEM***

*Identical location*

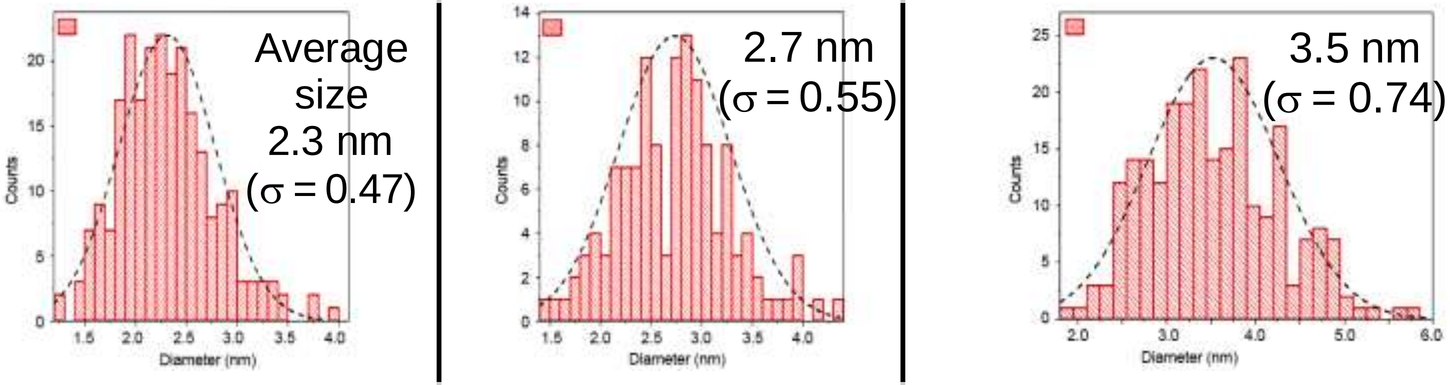
| Heated in 11.8 mbar $O_2$, 2 hrs 200°C | Heated in 11.8 mbar air, 2 hrs 450°C | Reduced in 11 mbar $H_2$, 2 hrs *200°C* |
|---|---|---|



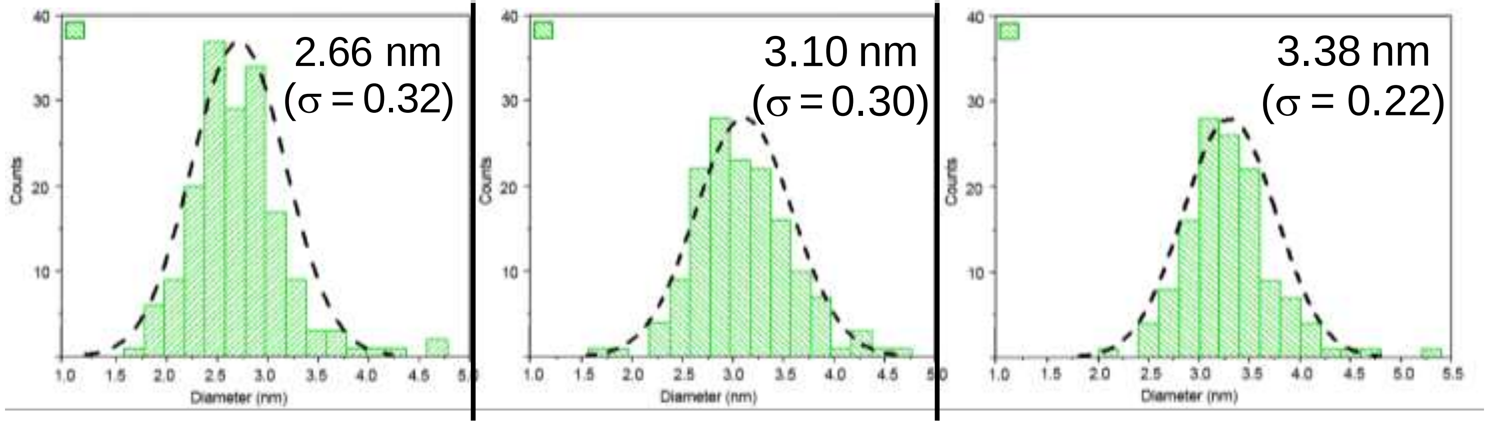
# Size of NPs: in situ ETEM vs. 'ex situ' TEM

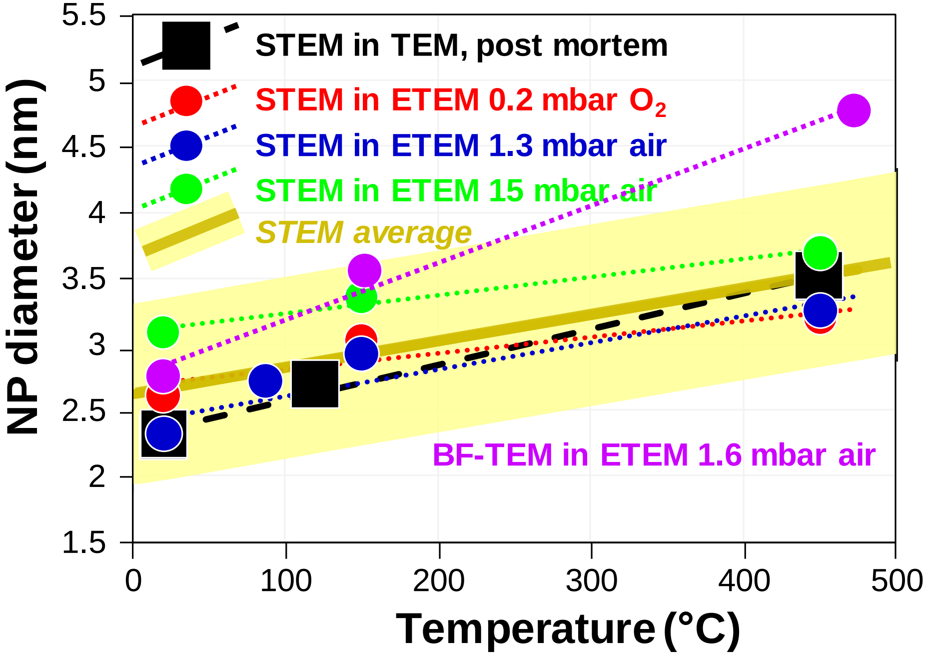
| **Impregnated** | **Dried** (120-150°C) | **Calcined** (425-450°C) |
|---|---|---|

***High Vacuum STEM, post mortem experiments***




***Environmental STEM, in situ experiments***




**Final average sizes (nm):**

| Impregnated | Dried | Calcined |
|---|---|---|
| **2.57** ± 0.5 | **3.0** ± 0.5 | **3.41** ± 0.5 |

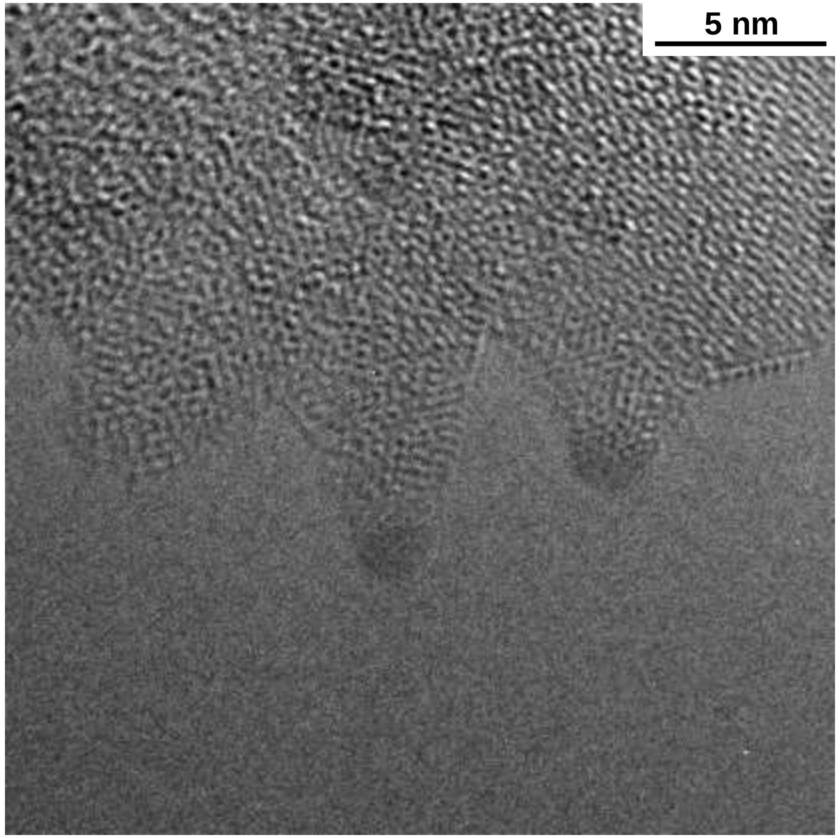
# Size of NPs: in situ ETEM vs. 'ex situ' TEM

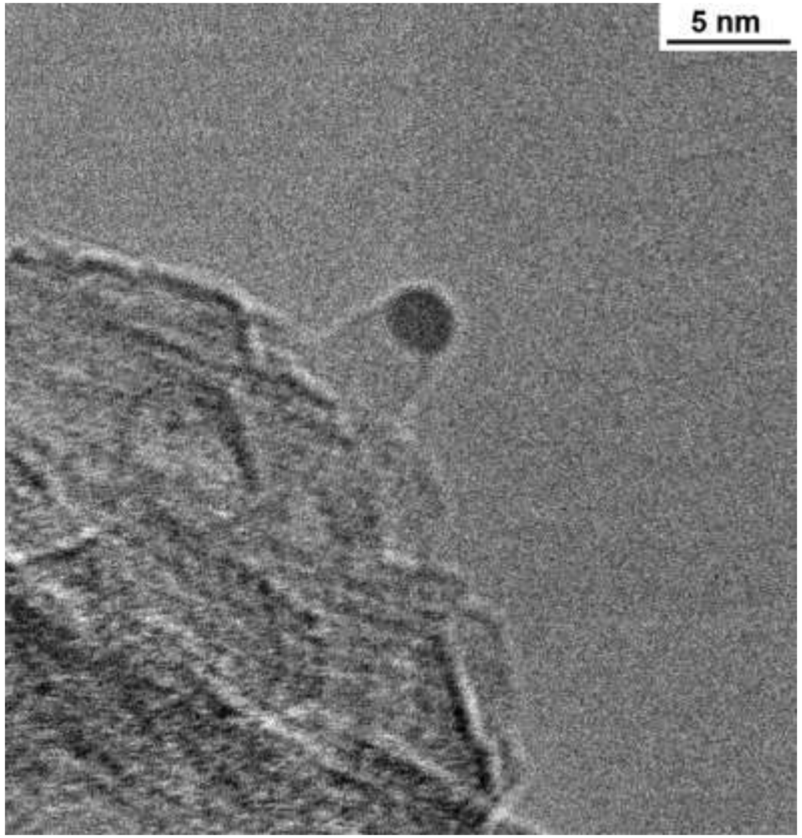
- **Dangers of *high mag* TEM: irradiation effects**

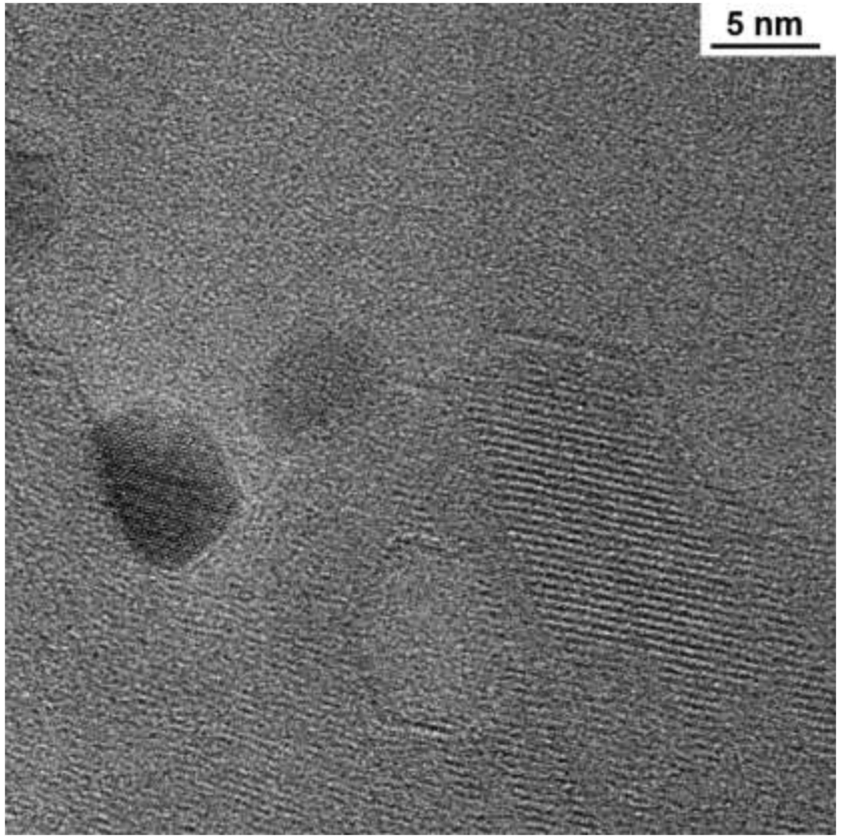
M. RAMOS-FERNANDEZ et al., *Oil & Gas Science and Technology*, **62** 1 (2007) 101

**Impregnated state,**
20°C, High Vacuum

***in situ* calcination,** 475°C, 1.6 mbar Air

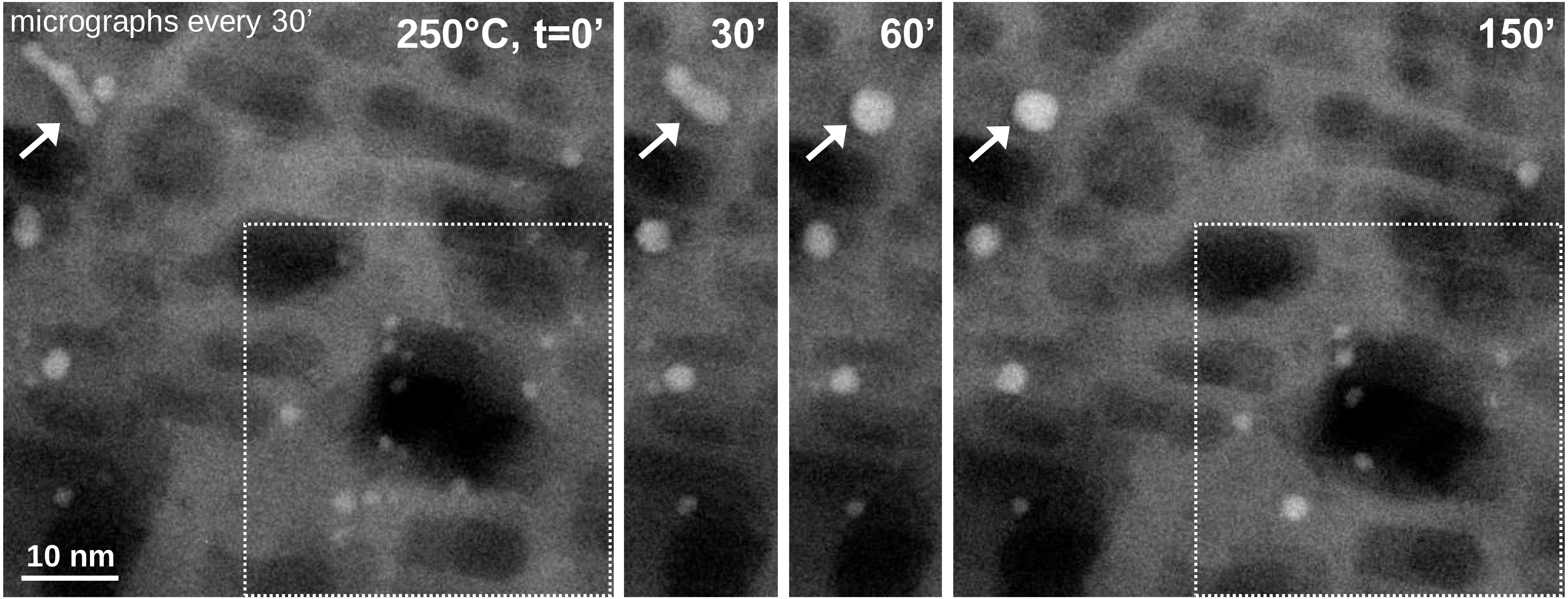


# Tracking the evolution of NPs (2D STEM)

- ‘Low Temperature’, 250°C under $O_2$: same area followed over 2 ½ h., *BEAM OFF*

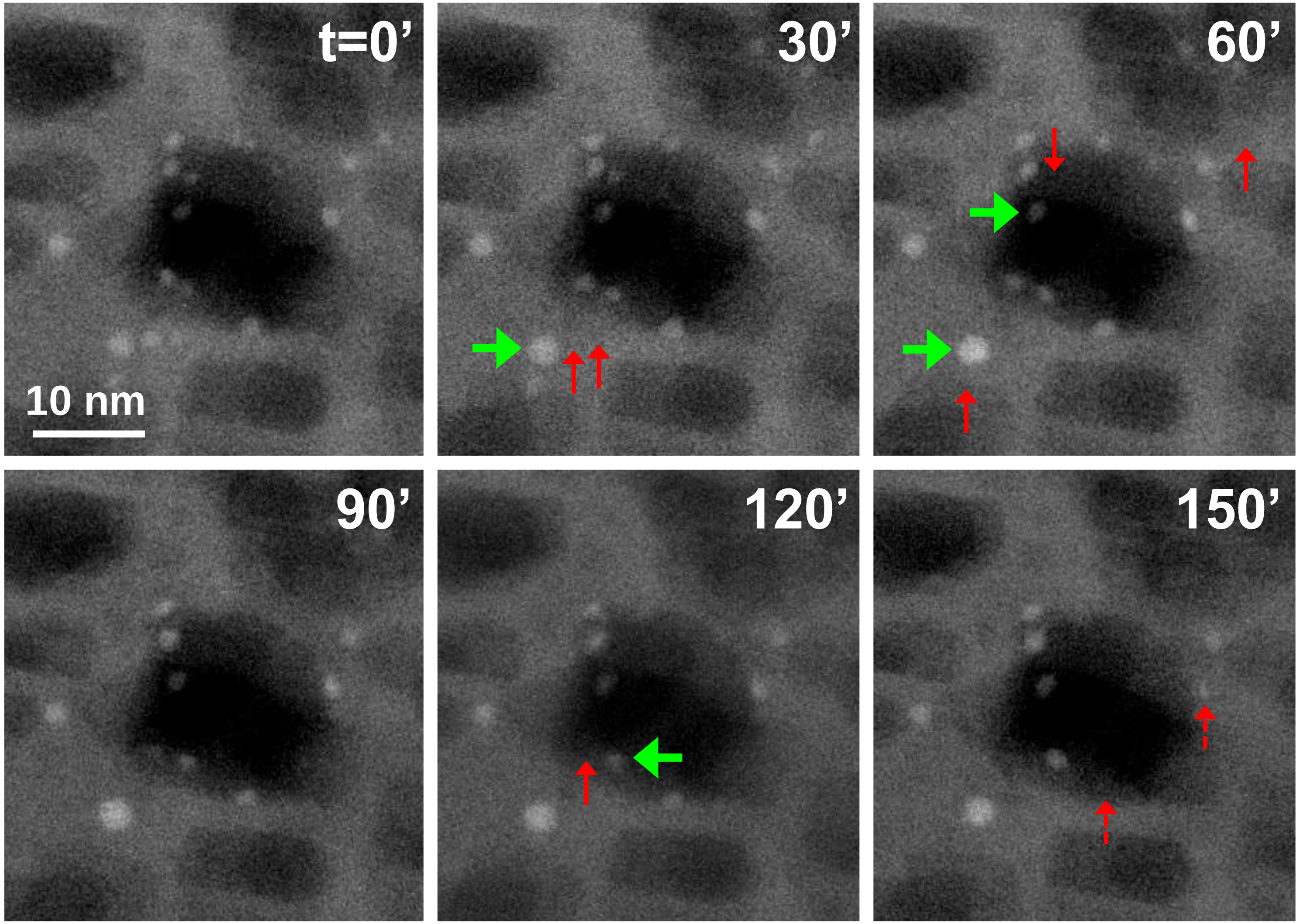



⇨ **LITTLE MOBILITY of NPs: occasional COALESCENCE when NPs are VERY CLOSE one to each other**

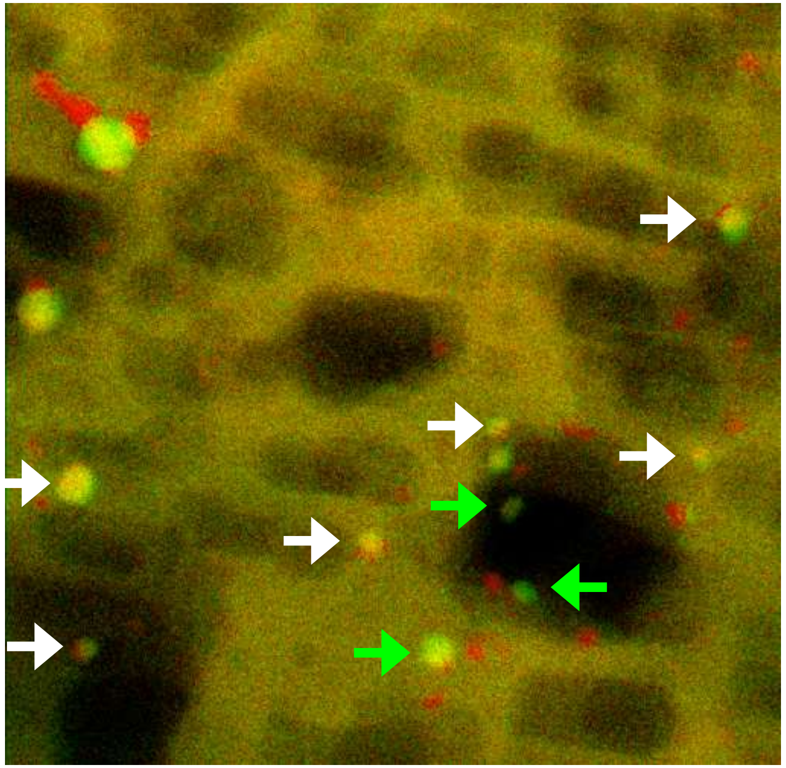
# Tracking the evolution of NPs (2D STEM)

Disappear

Grow




Pd NPs at t=0’ Pd NPs at t=150’

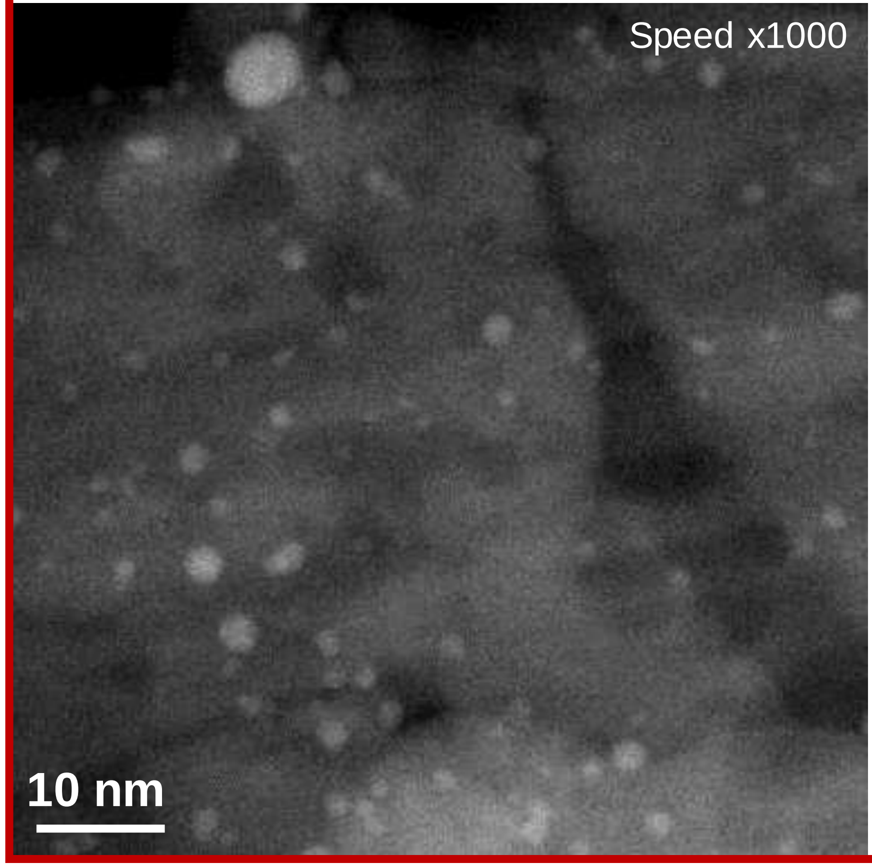


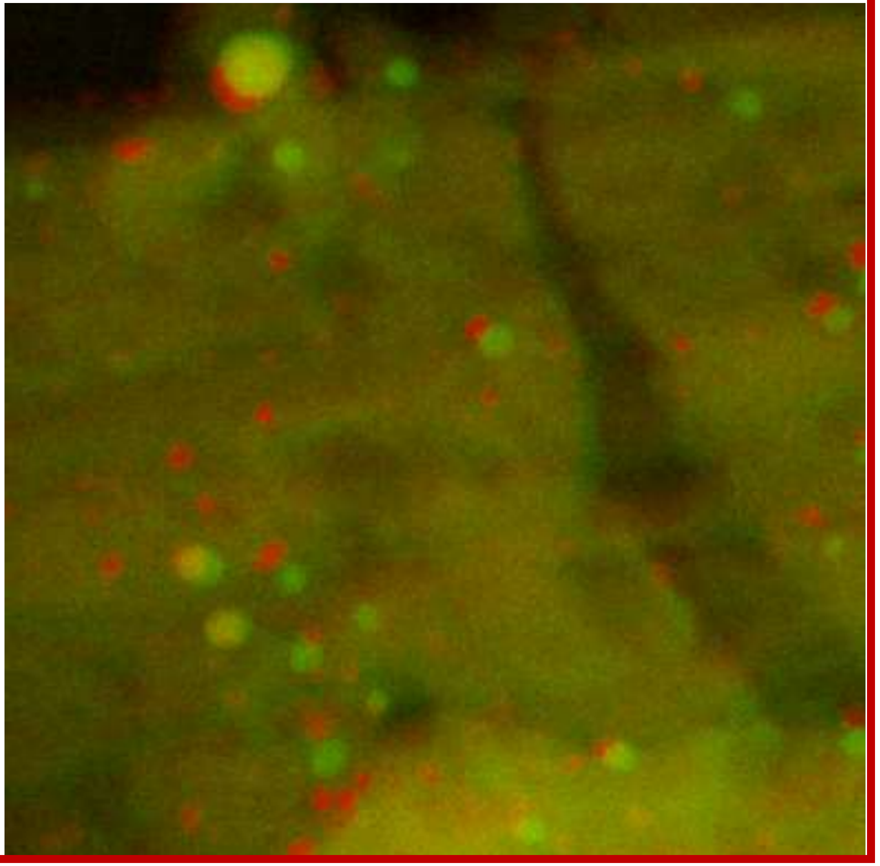
DISAPPEARANCE of *SMALL* NPs at the expenses of *LARGER* IMMOBILE ones: Ostwald Ripening growth

# Tracking the evolution of NPs (2D STEM)

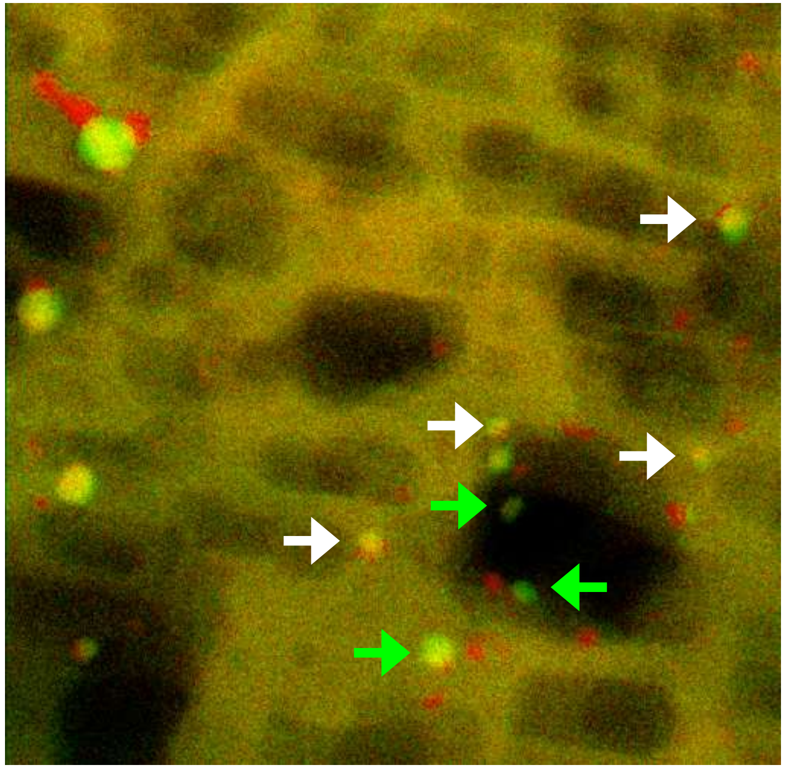
- **Warning: irradiation effects** (don't be too much demanding…)

**Same experiment over 150' but micrographs every 2'**



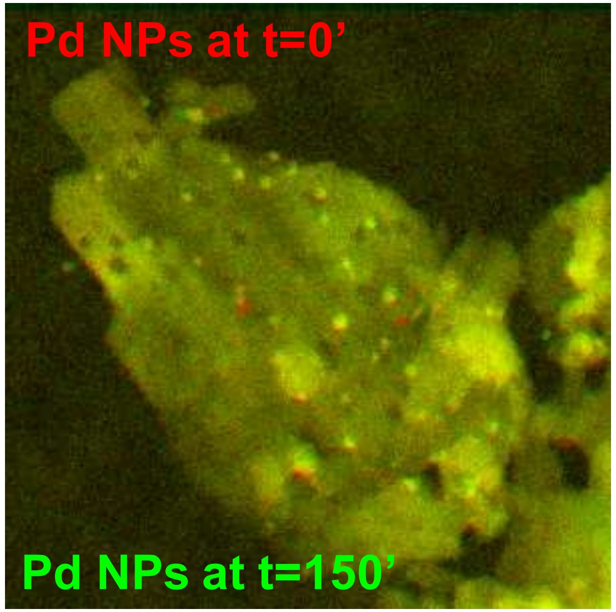
**Pd NPs at t=0'** **Pd NPs at t=150'**



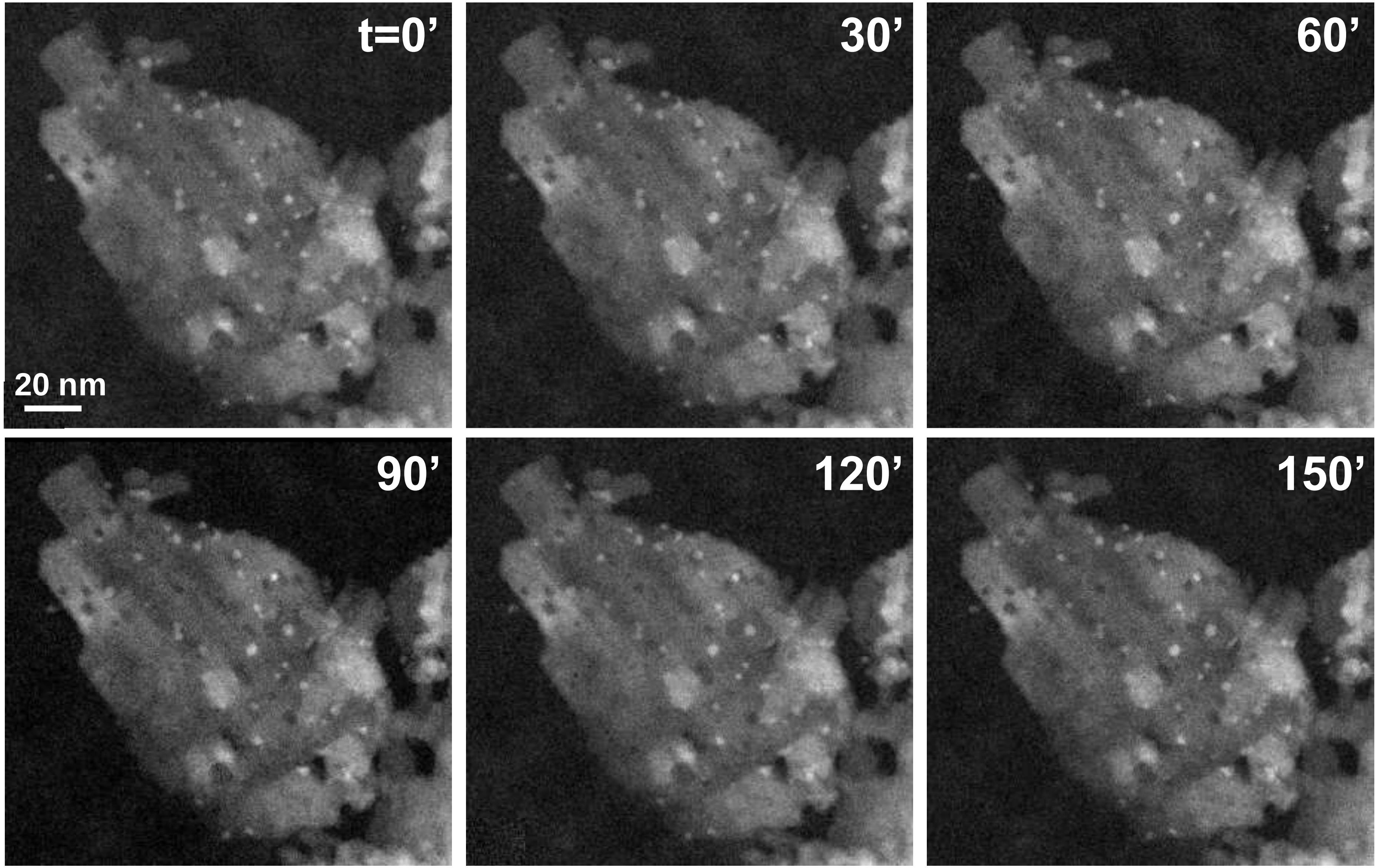
⇨ **IRRADIATION-induced MOBILITY of NPs during prolonged exposure to the electron probe *(even in STEM)***

# Tracking the evolution of NPs (2D STEM)

- **Calcination Temperature: 450°C, 10 mbar $O_2$**



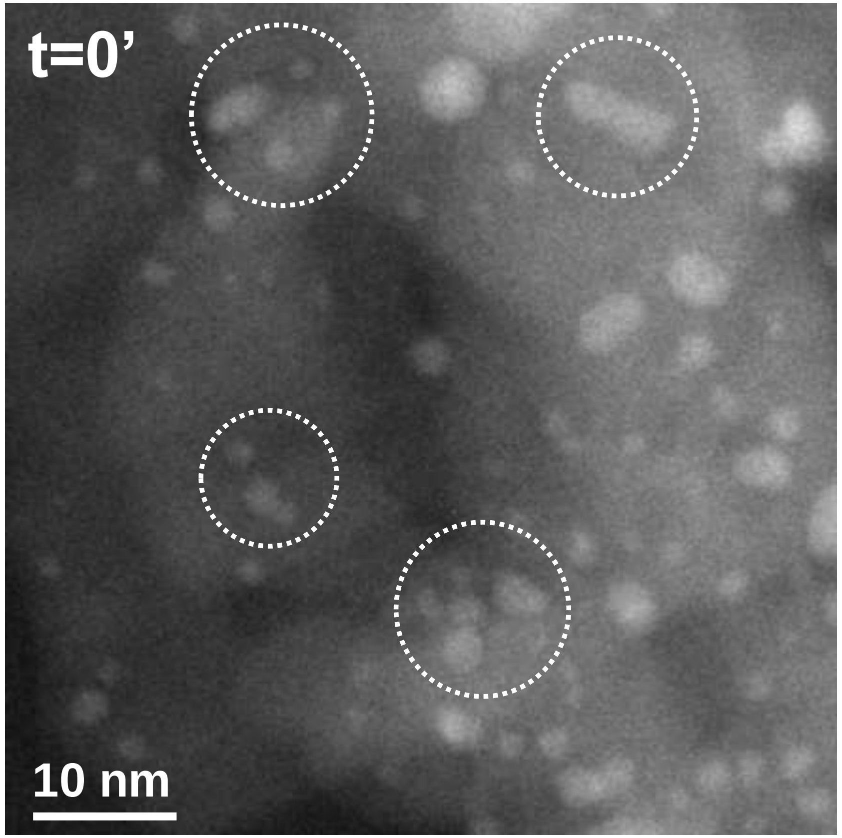

⇨ **NO MOBILITY (slight increase of size): no significant coalescence**

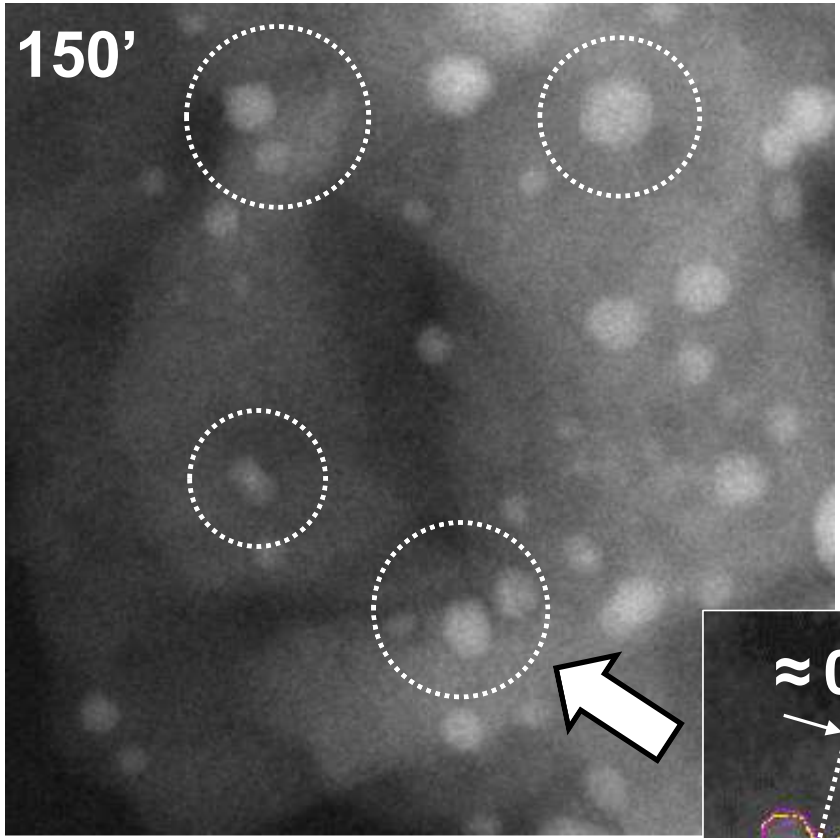


# Tracking the evolution of NPs (2D STEM)

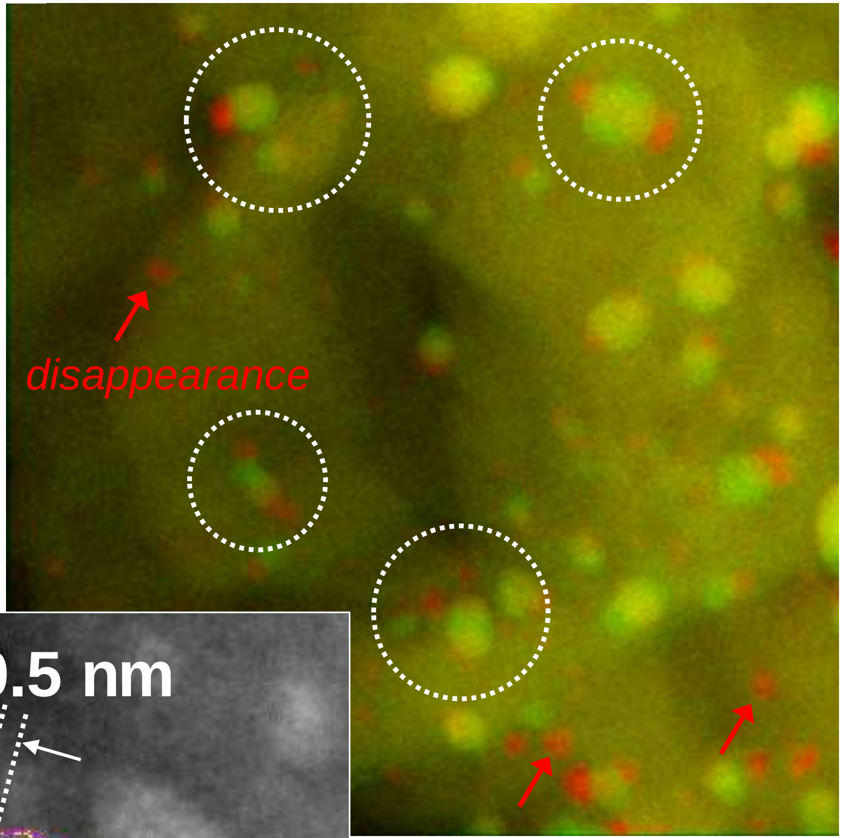
- **Confirmation of coalescence *only* when NPs are *very* close one to each other**

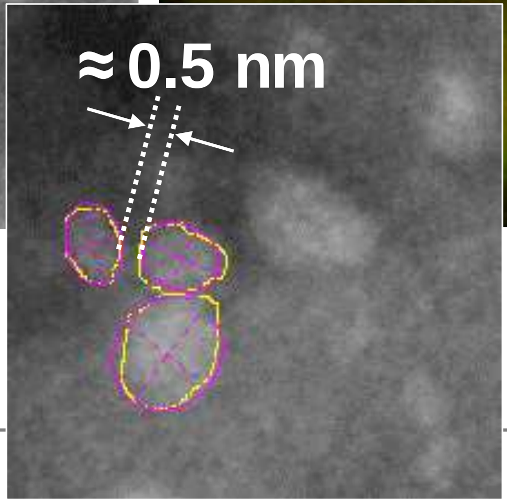
(other area) **experiment over 150’, micrographs every 30’**




**Pd NPs at t=0’** **Pd NPs at t=150’**



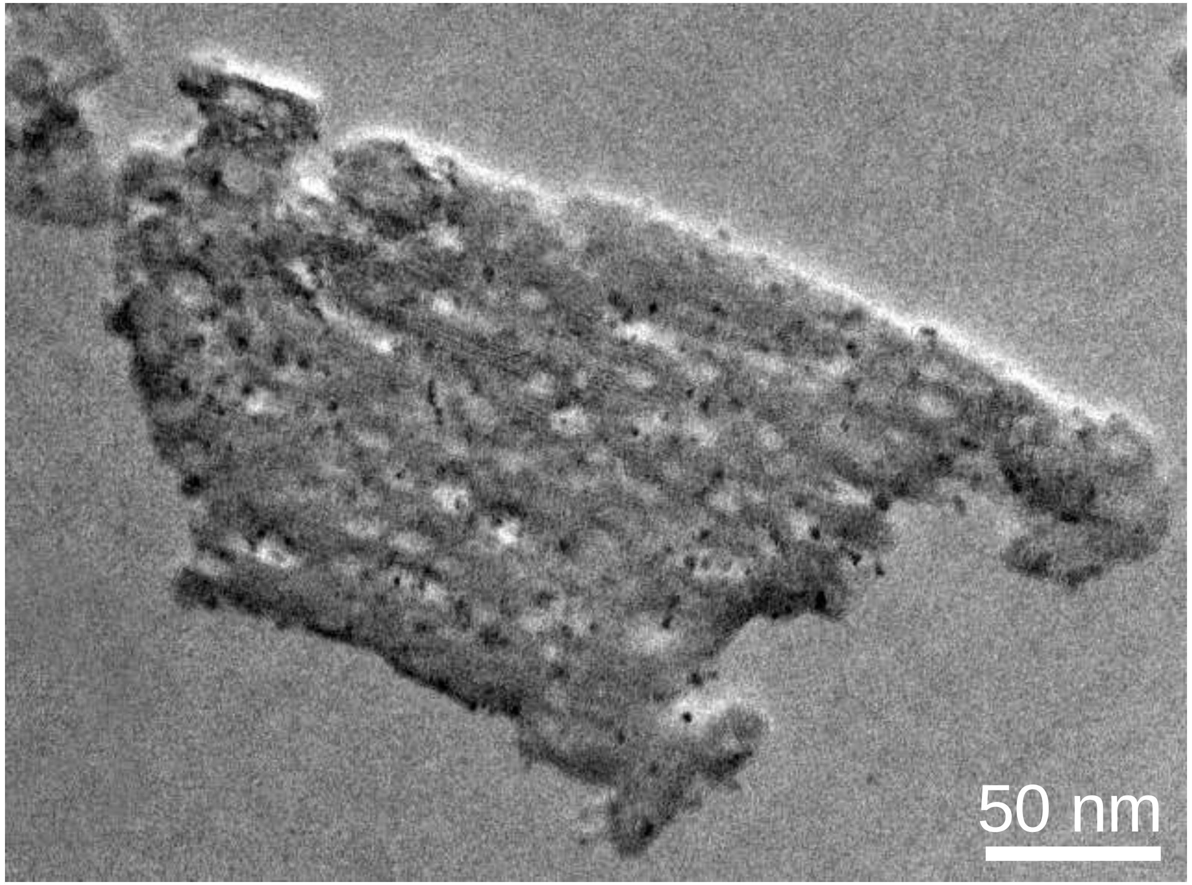

⇨ **Coalescence only when NPs are *almost* in contact**

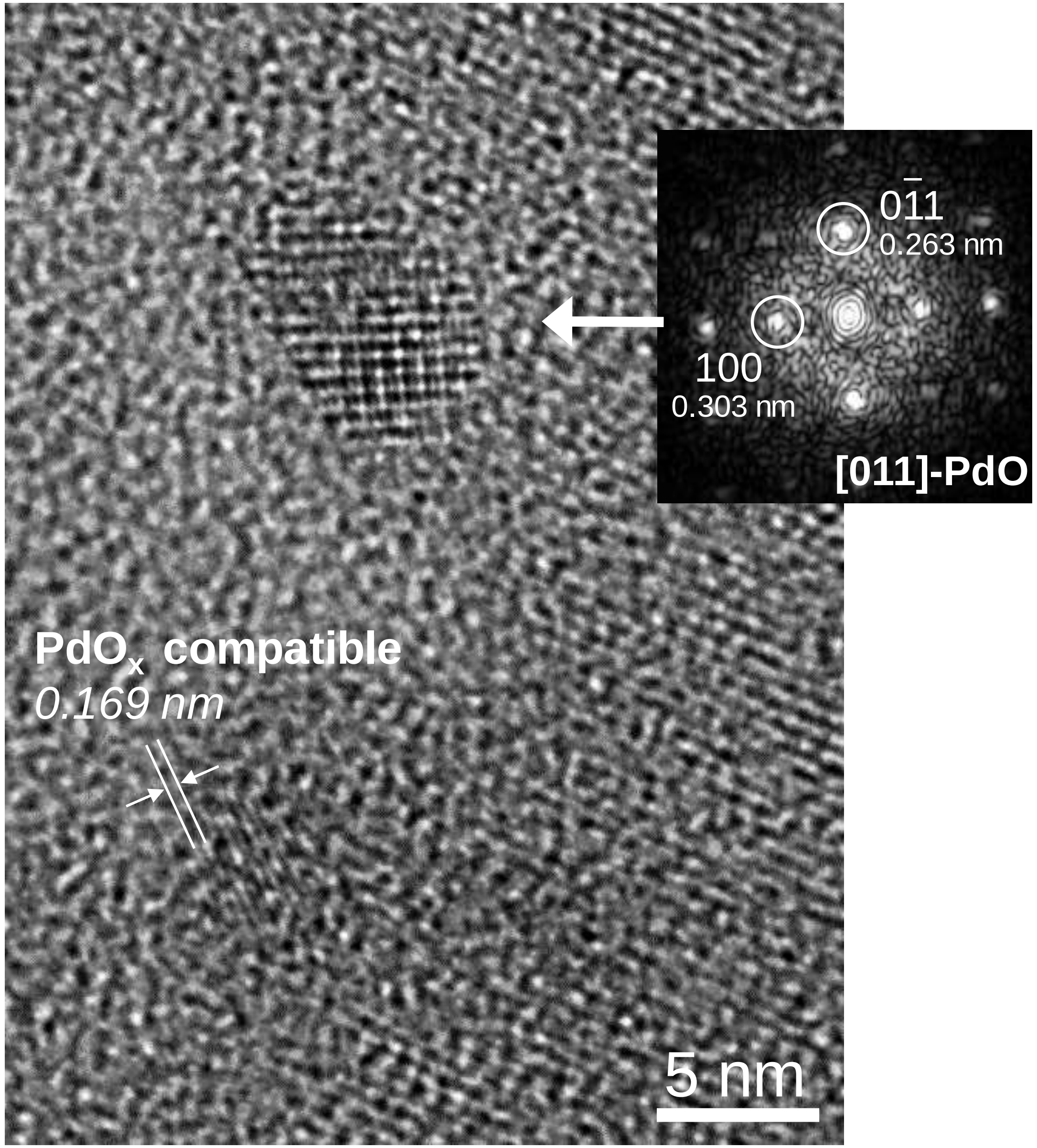
# Nature and Crystallography of Pd-based NPs

- **Initial (Impregnated) state**

**collodial PdO expected**

B. DIDILLON et al., pp. 41-54 in ‘Studies in Surface Science & Catalysis’ **118** (1998)

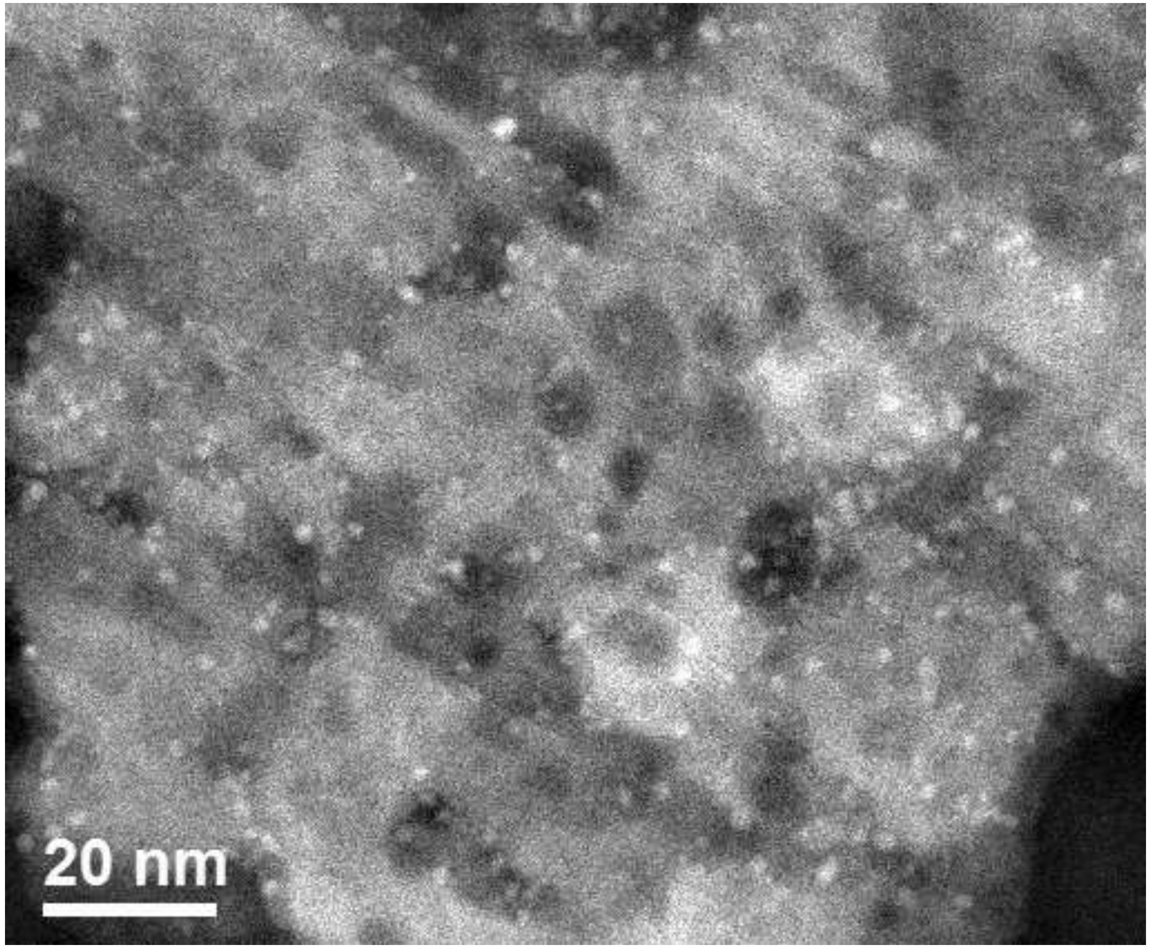


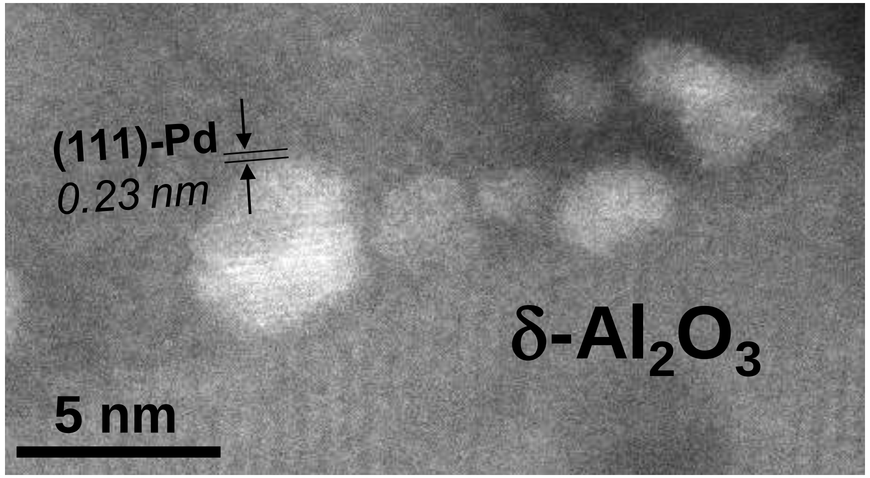



# Nature and Crystallography of Pd-based NPs

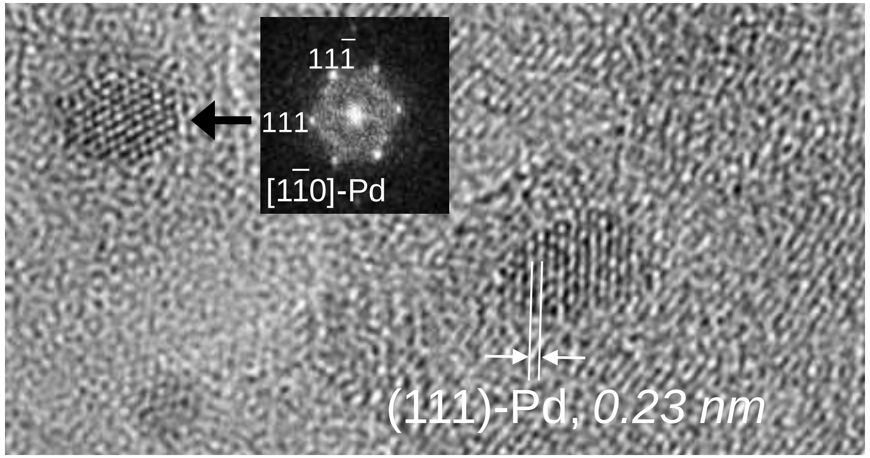
- **Initial (Impregnated) state**

**colloidal PdO expected BUT presence of fcc Pd NPs** *(post mortem, High Vacuum)*




*STEM-(HA)ADF*




*BF TEM*

# Nature and Crystallography of Pd-based NPs

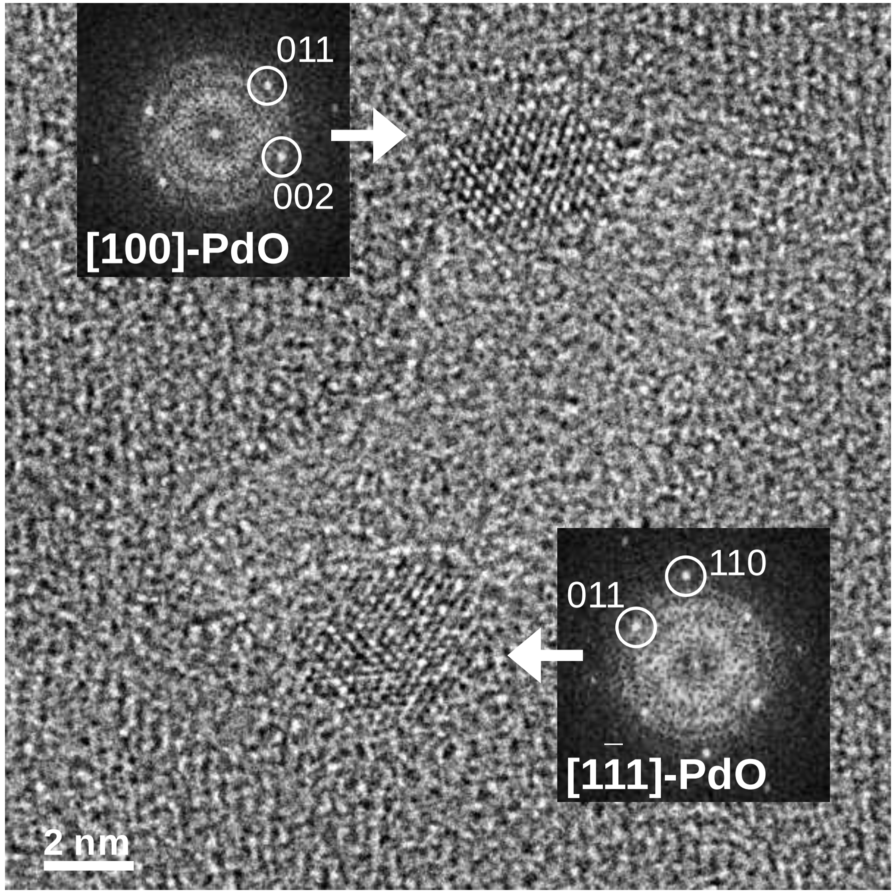
- **Calcined state (after 2 h. under AIR *or* $O_2$ at 450°C)**

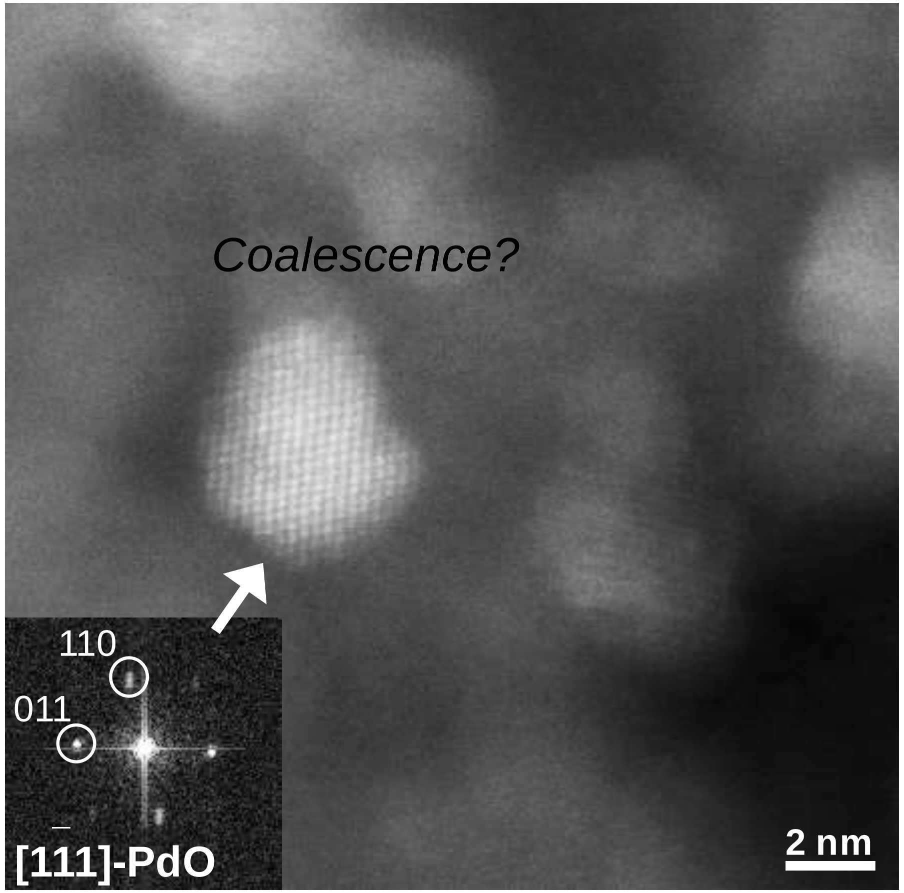
***Mainly*** **$PdO_x$**

**In situ calcination in ETEM, 2h 450°C, $O_2$ 10 mbar**

**20°C after calcination in ETEM, 2h 450°C, $O_2$ 10 mbar**

*BF TEM*



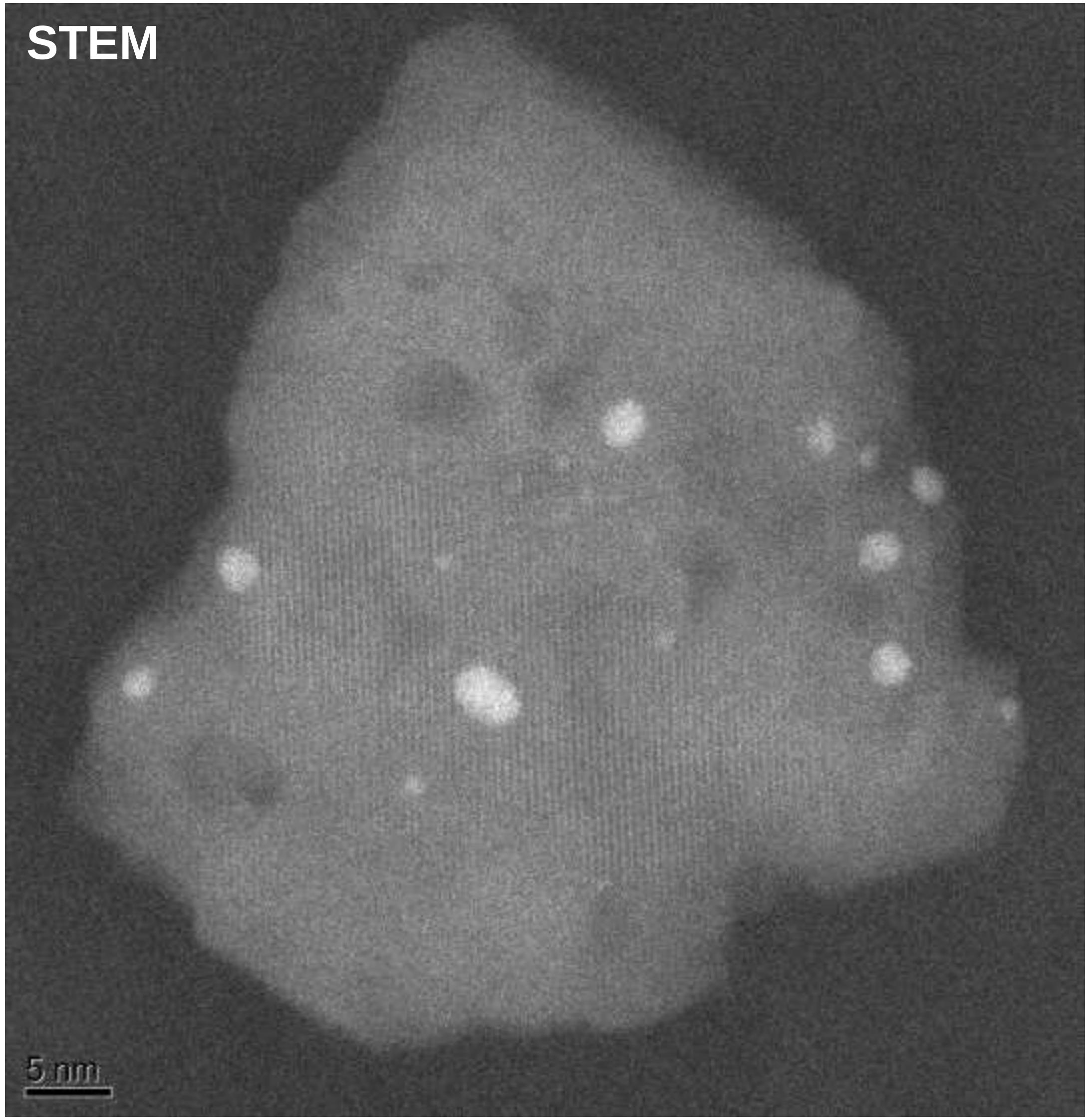



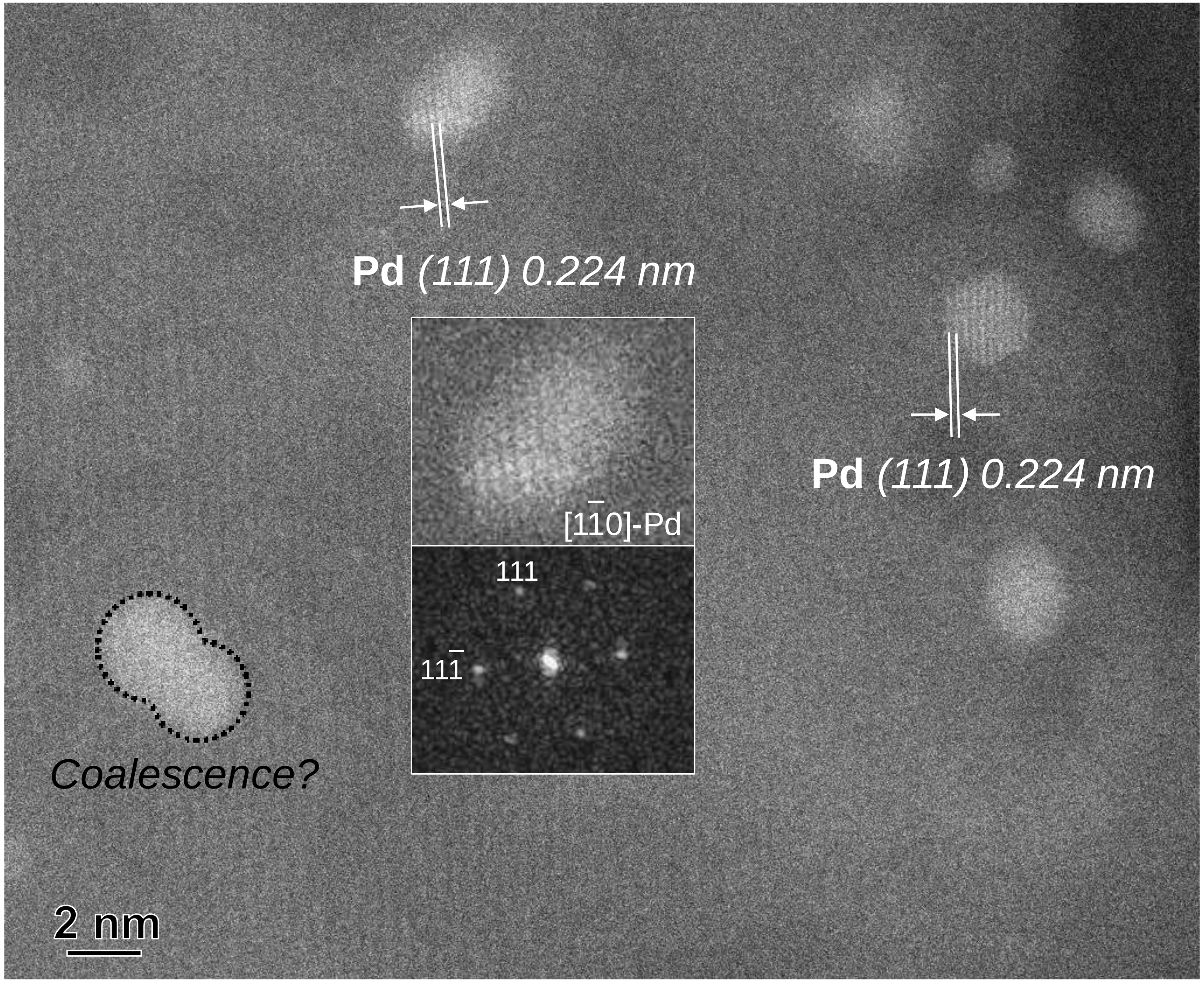

*STEM-(HA)ADF*

# Nature and Crystallography of Pd-based NPs

- **Reduced state** ***(systematically metallic fcc*** **Pd)**

**Reduction under $H_2$ 11 mbar at 200°C, 2h.**



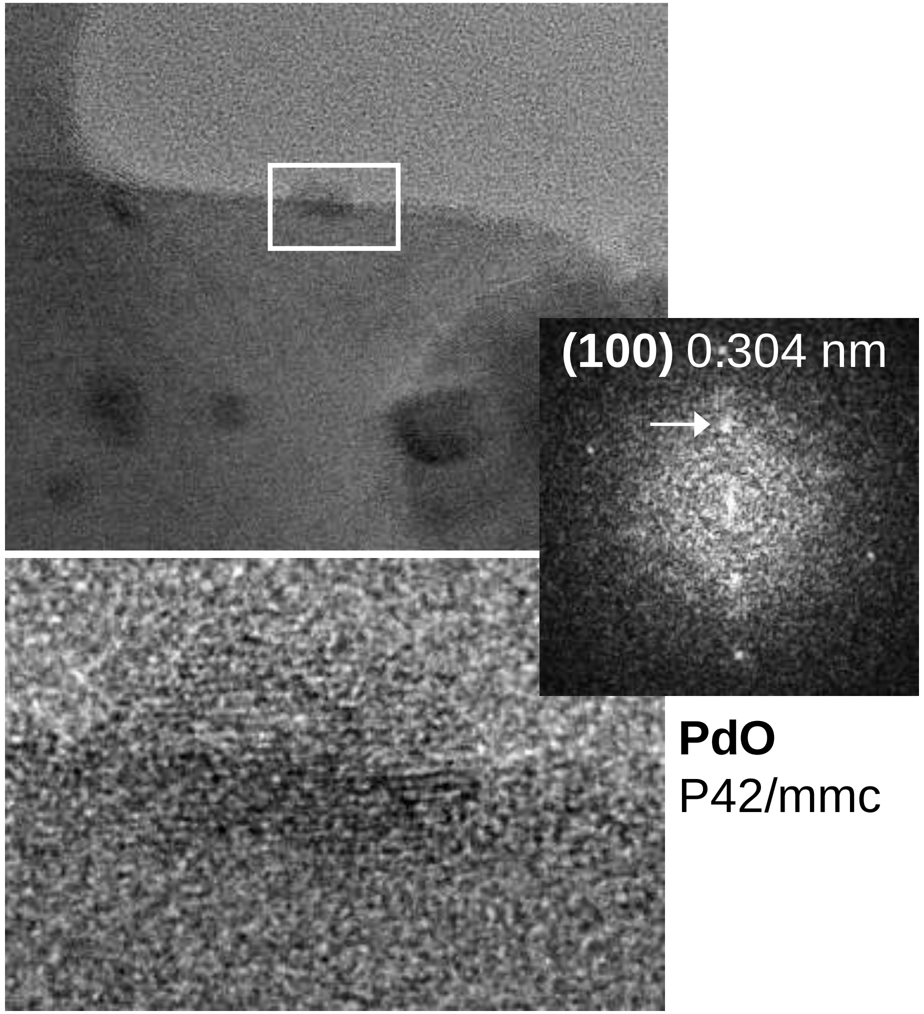



# Nature and Crystallography of Pd-based NPs

- **Reduction directly followed in the ETEM state** *(beam OFF between micrographs)*

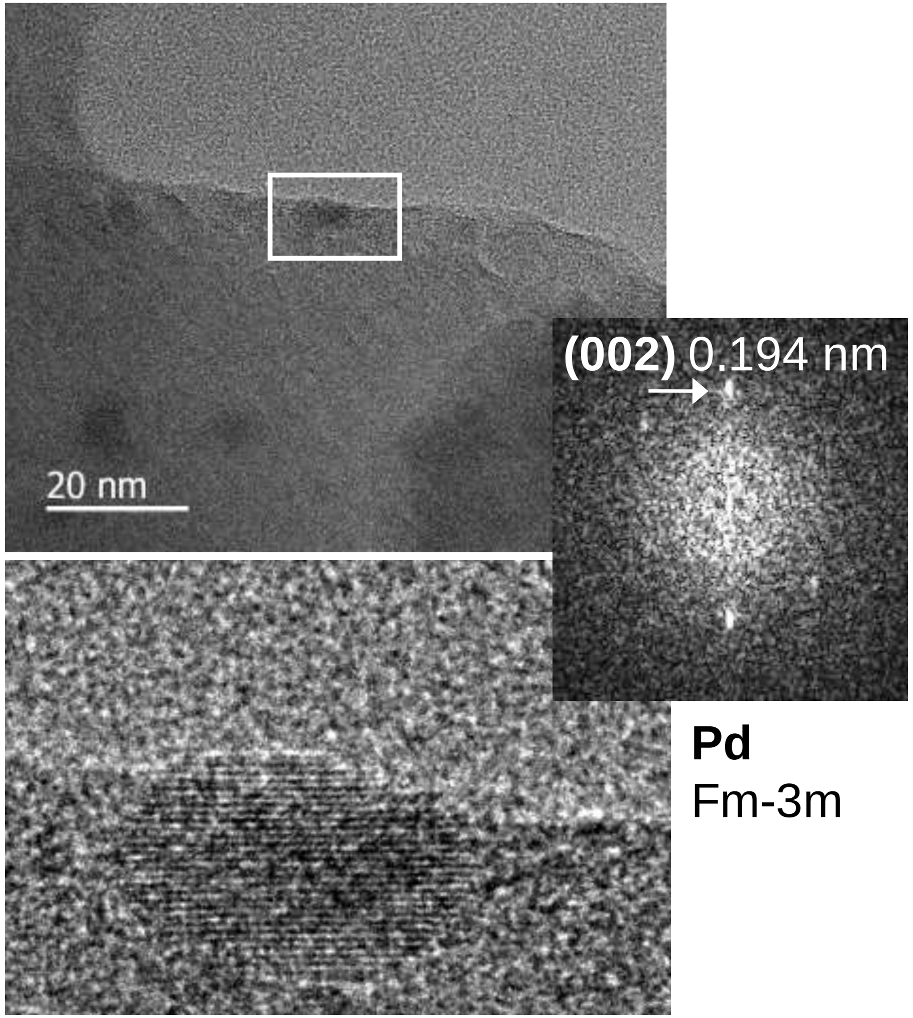
*Large Pd NPs,*
*$\alpha$-$Al_2O_3$*

**2 mbar $H_2$ at 150°C, *time $t_0$***




**PdO**
P42/mmc

**after 45' at 150°C**

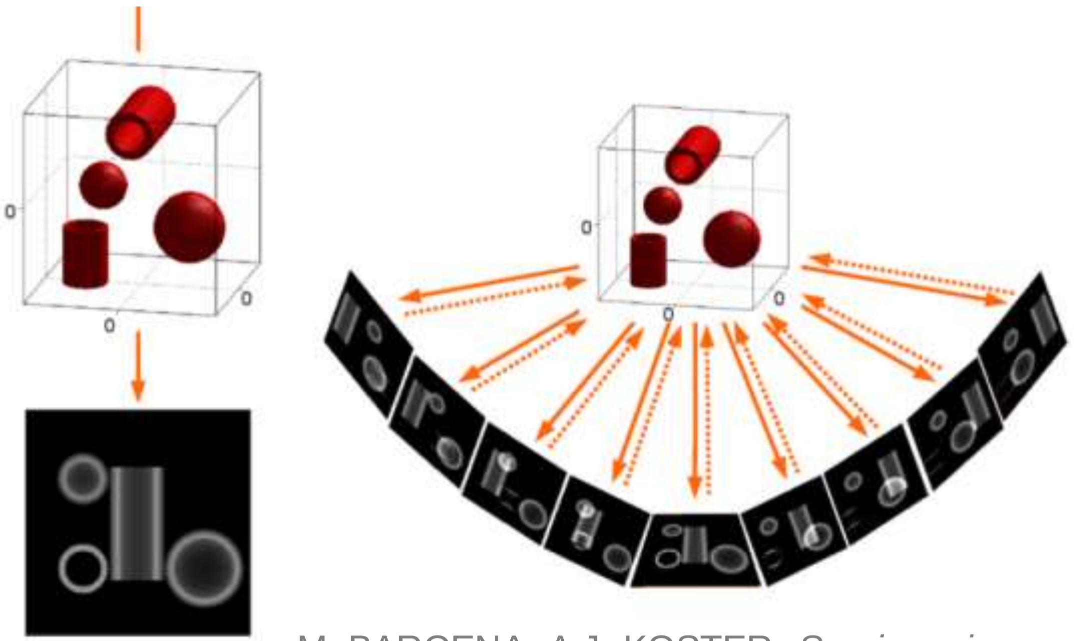



**Pd**
Fm-3m

# Attemps for *in situ* 3D characterization

- **Context: follow the evolution of nanomaterials in situ and *in 3D* under dynamic environmental conditions**

**- Principle of 'tilt electron tomography' in a TEM**



M. BARCENA, A.J. KOSTER, *Seminars in Cell & Developmental Biology*, **20** (2009) 920

**Classical step-by-step 'tilted'tomography in STEM**

| | |
|---|---|
| Rotation angular amplitude | ***140°*** |
| Angular step increment | ***2°*** |
| Pause at each tilt | ***30 sec*** |
| Exposure time of each image | ***40 sec*** |
| Time to proceed to the next tilt | ***0.5 sec*** |
| ***Total acquisition time*** | ***≈83 min*** |

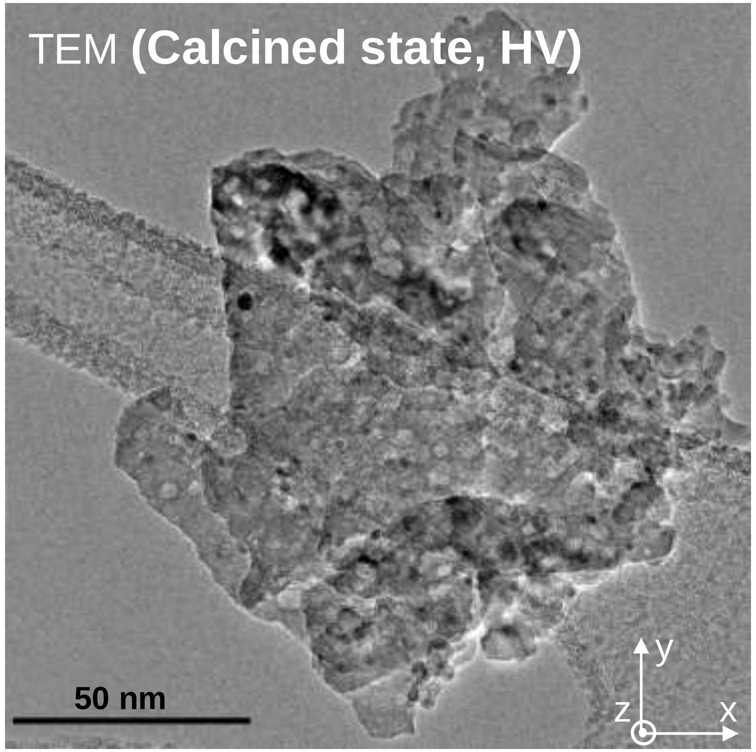
Re-centering, re-focusing…

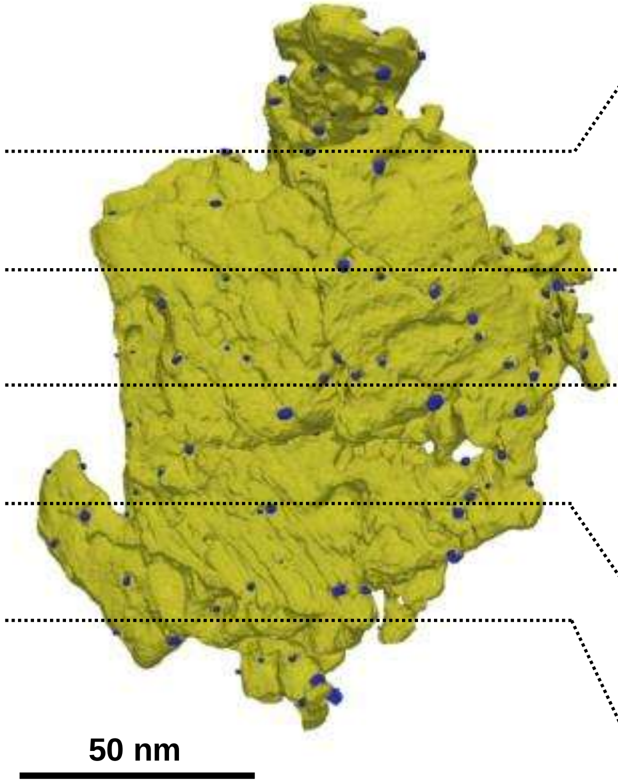
10 µs dwell time, 2K x 2K scan

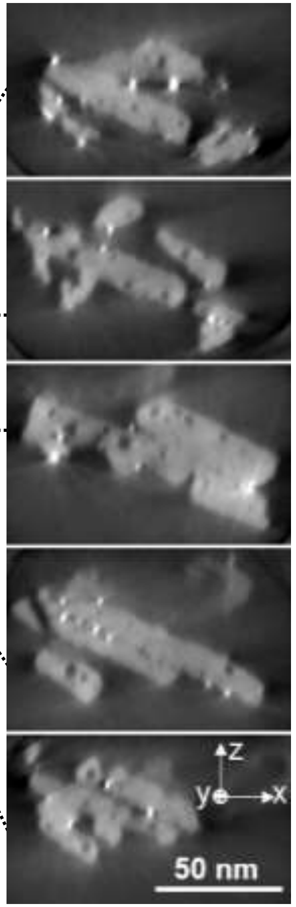
# Attemps for *in situ* 3D characterization

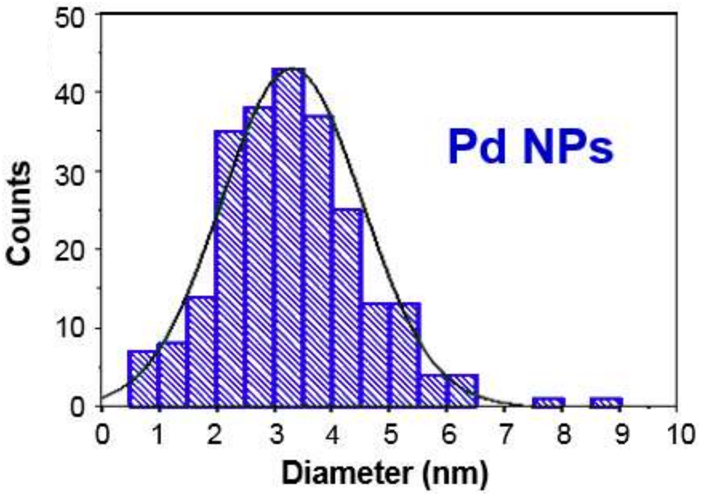
- **Context: follow the evolution of nanomaterials in situ and *in 3D* under dynamic environmental conditions**

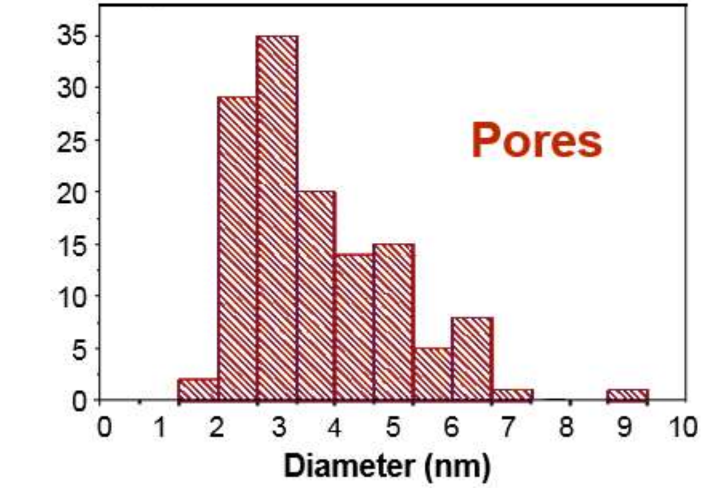
**- STEM tomography, +73 / -73°, step 2°, 100 min**



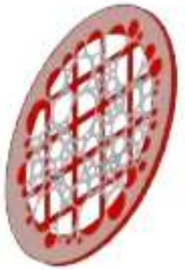



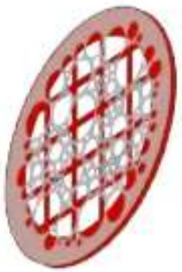



# Attemps for *in situ* 3D characterization

- **Towards real time tomography under environmental conditions**

**1) Speed up tilt tomography in Bright Field TEM**





**Classical step-by-step 'tilted'tomography in STEM**

| | |
|---|---|
| Rotation angular amplitude | *140°* |
| Angular step increment | *2°* |
| Pause at each tilt | *30 sec* |
| Exposure time of each image | *40 sec* |
| Time to proceed to next tilt | *0.5 sec* |
| ***Total acquisition time*** | *≈83 min* |

**Optimized step-by-step 'tilted'tomography in BF-TEM**

| | |
|---|---|
| Rotation angular amplitude | *140°* |
| Angular step increment | *2°* |
| Pause at each tilt | *0.5 sec* |
| Exposure time of each image | *0.1 sec* |
| Time to proceed to next tilt | *0.3 sec* |
| ***Total acquisition time*** | *≈1 min* |

L. ROIBAN et al., *Microsc. Microanal.* **22** 5 (2016) 8

L. ROIBAN et al., *J. of Microscopy,* **269**, 2 (2018), 117

**'tilted' tomography by continuous rotation in BF-TEM**

| | |
|---|---|
| Rotation angular amplitude | *140°* |
| **Total acquisition time** | *5 sec* |
| Angular rotation speed | *28°/sec* |
| *Number of frames per second* | *100* |
| *'Angular rotation 'blur' per frame* | *0.28°* |

H. BANJAK et al., *Ultramicroscopy,* **189**, (2018), 109

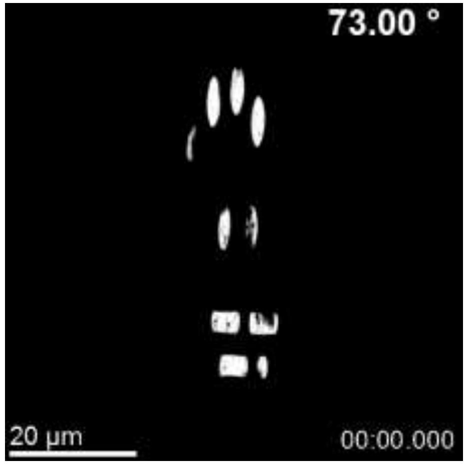
# Attemps for *in situ* 3D characterization

- **Towards real time tomography under environmental conditions**

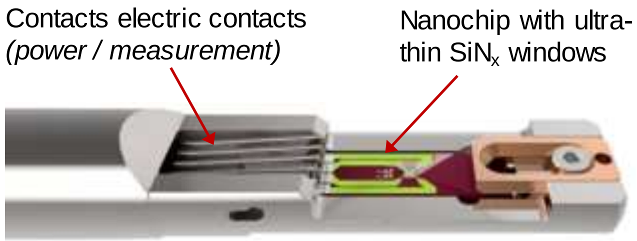
**2) Fast tomography under gas and in temperature at the level of *a few seconds***

**OneView camera**
**100 fps in 2Kx2K**
GATAN

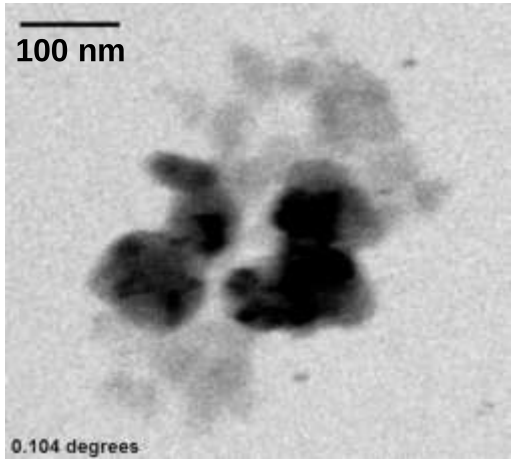
**LARGE TILT AMPLITUDE of a MEMS-based heating holder *±72° rotation***
DENS solutions

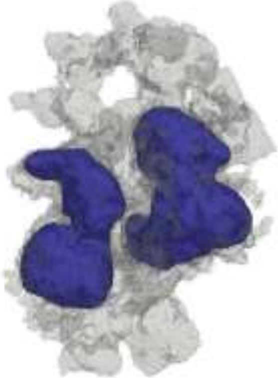


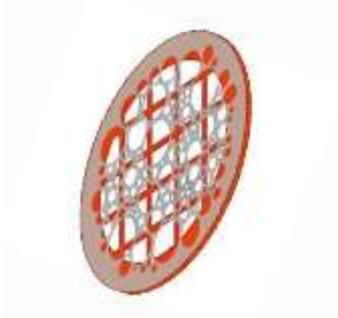

Total time 5.4''




***Example:* soot @ $ZrO_2$, 350°C, $O_2$ 5 $10^{-5}$ mbar**





**'tilted' tomography by continuous rotation in BF-TEM**

| | |
|---|---|
| Rotation angular amplitude | *140°* |
| **Total acquisition time** | *5 sec* |
| Angular rotation speed | *28°/sec* |
| *Number of frames per second* | *100* |
| *'Angular rotation 'blur' per frame* | *0.28°* |

H. BANJAK et al., *Ultramicroscopy,* **189**, (2018), 109

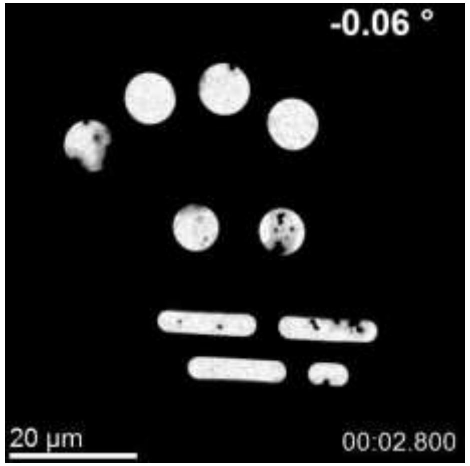
# Attemps for *in situ* 3D characterization

- **Towards real time tomography under environmental conditions**

## 2) Fast tomography under gas and in temperature at the level of *a few seconds*

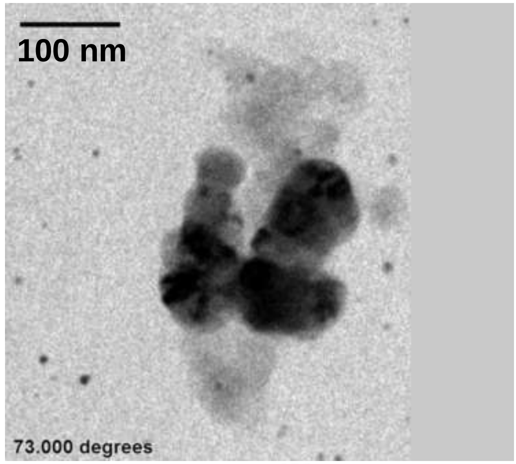
**OneView camera**
**100 fps in 2Kx2K**
GATAN

**LARGE TILT AMPLITUDE of a MEMS-based heating holder**
***±72° rotation***
DENS solutions

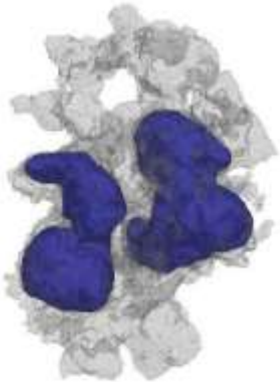


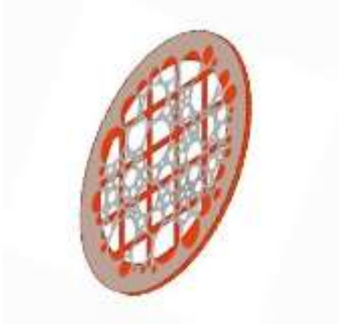

Total time 5.4''


***Example:* soot @ $ZrO_2$, 350°C, $O_2$ 5 $10^{-5}$ mbar**




Total time 5.1''





**'tilted' tomography by**
**continuous rotation in BF-TEM**

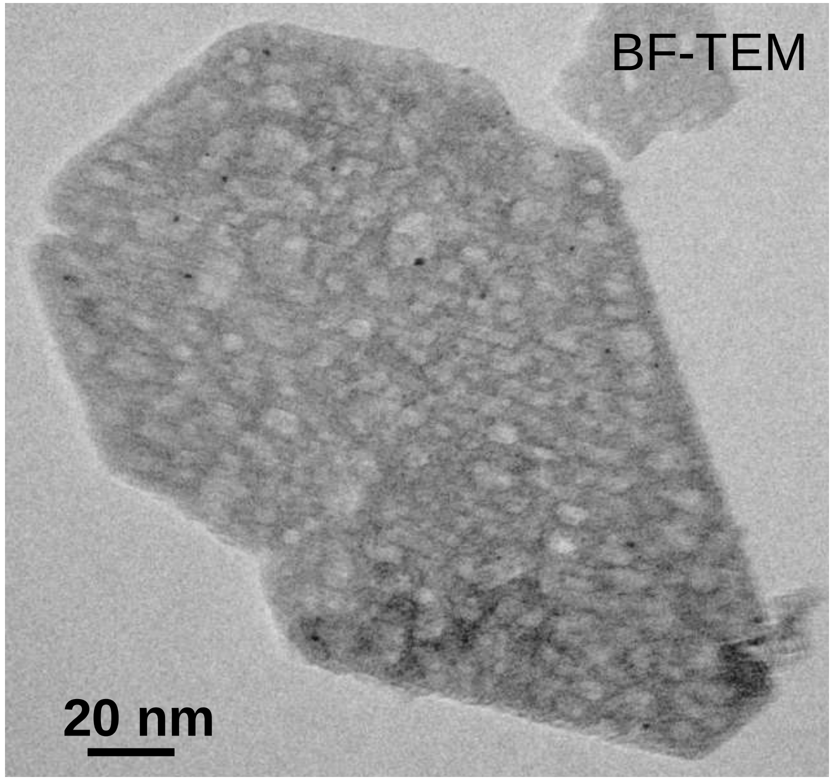
| | |
|---|---|
| Rotation angular amplitude | *140°* |
| **Total acquisition time** | ***5 sec*** |
| Angular rotation speed | *28°/sec* |
| *Number of frames per second* | *100* |
| *'Angular rotation 'blur' per frame* | *0.28°* |

H. BANJAK et al., *Ultramicroscopy*, **189**, (2018), 109

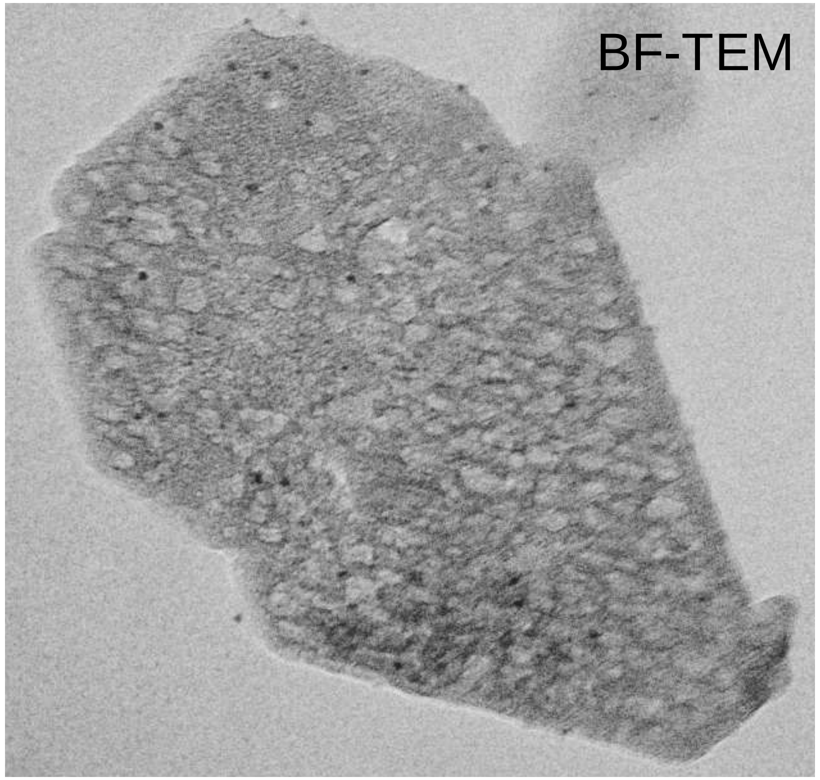
# Attemps for *in situ* 3D characterization

- **Semi-fast tomography of Pd@δ-$Al_2O_3$ during in situ ETEM calcination**

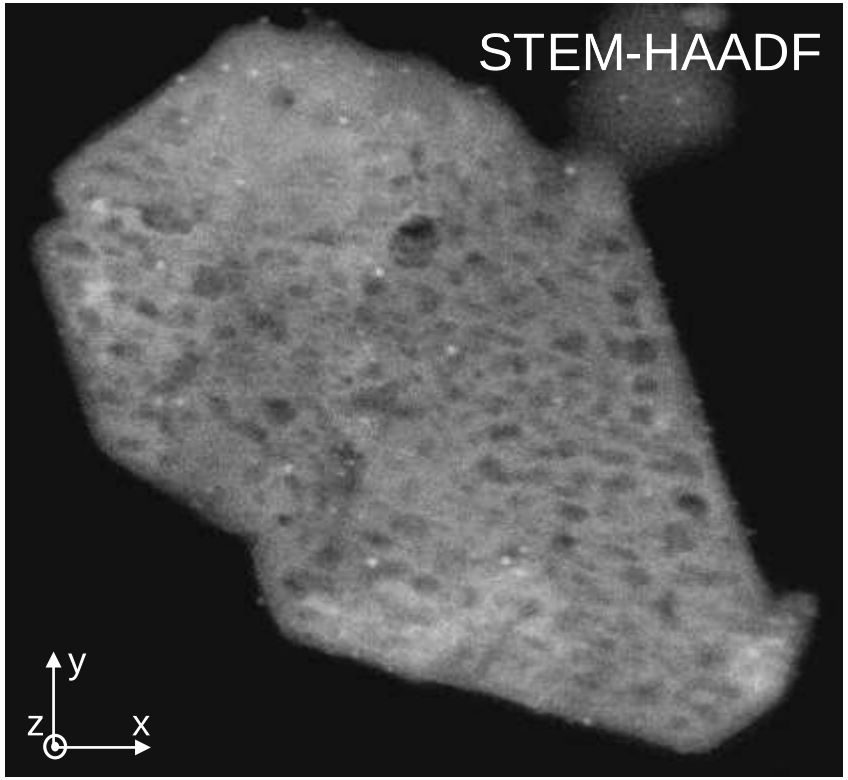
**20°C, High Vacuum**




**350°C, after 60', 2.6 mbar $O_2$**




Rapid cooling to **20°C, High Vacuum after 60' at 350°C, 2.6 mbar $O_2$**

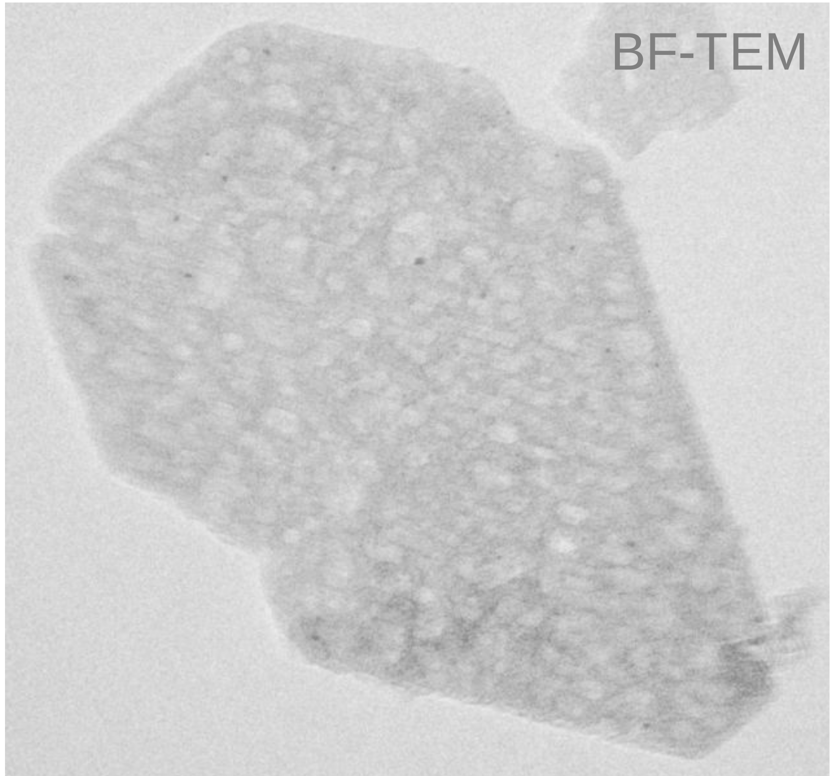



⇨ **LITTLE Visibility of Pd NPs** (low mag)

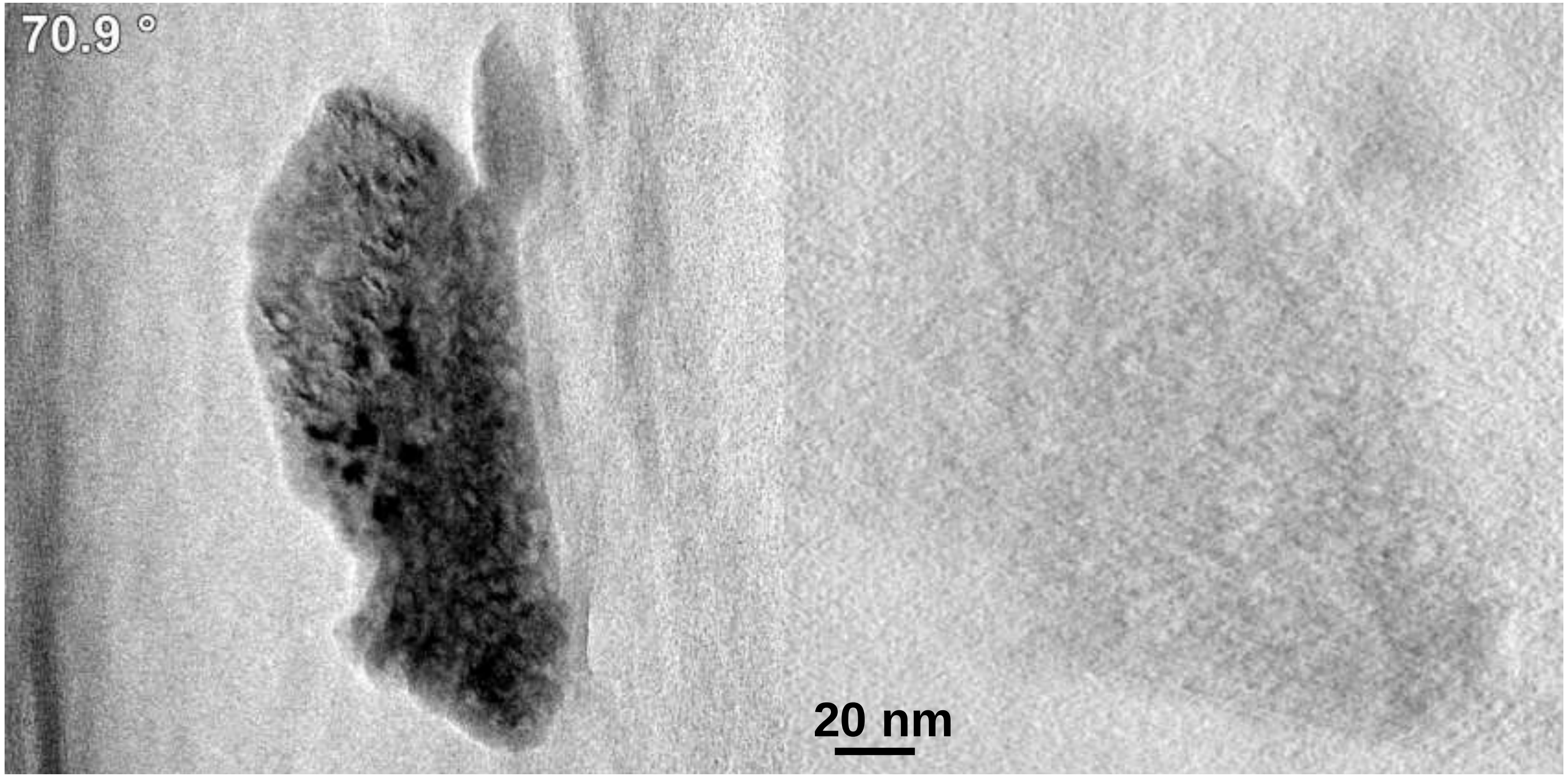
# Attemps for *in situ* 3D characterization

- **Semi-fast tomography of Pd@δ-$Al_2O_3$ during in situ ETEM calcination**

**20°C, High Vacuum**




**350°C, after 60', 2.6 mbar $O_2$**



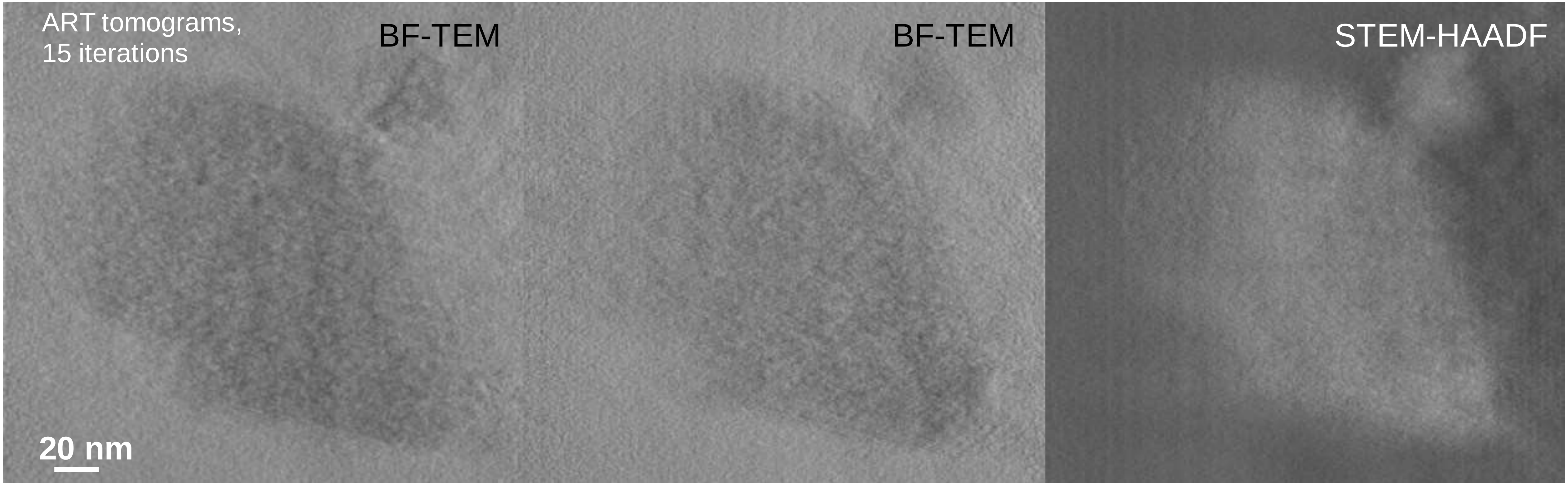

⇨ **Tomograms enhance the VISIBILITY of Pd NPs**

**Total Semi-Fast BF acquisition: 73.4° / -66.6°, step 2°, 2 min 42 sec**
**Reconstruction 15 ART iterations** (63 images between 70.9 and -63.1°)

# Attemps for *in situ* 3D characterization

- **Semi-fast tomography of Pd@δ-$Al_2O_3$ during in situ ETEM calcination**

**20°C, High Vacuum** | **350°C, after 60', 2.6 mbar $O_2$** | Rapid cooling to **20°C, High Vacuum after 60' at 350°C, 2.6 mbar $O_2$**



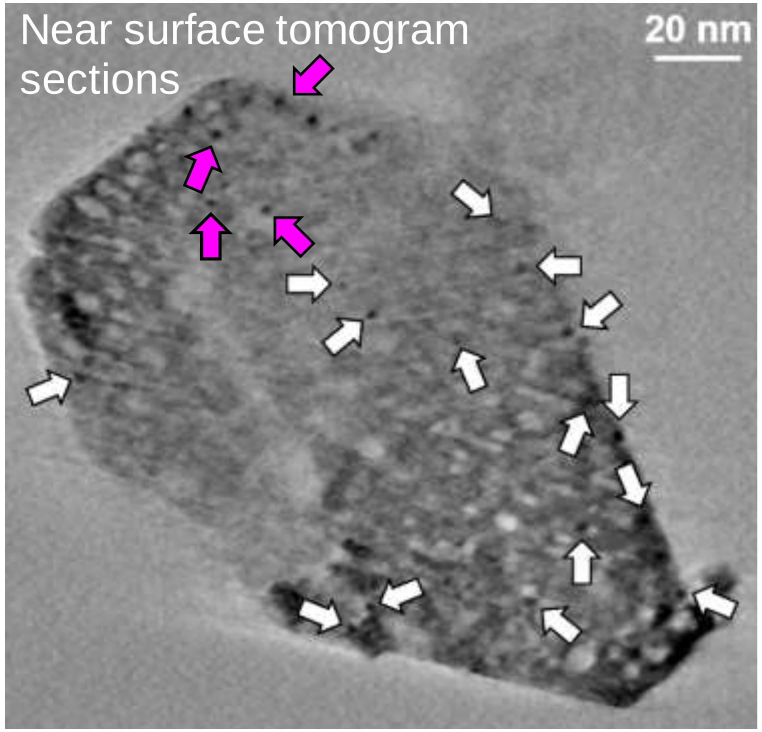

**Semi-Fast BF acquisitions: 73.4° / -66.6°, step 2°, 2 min 42 sec**

**STEM: 75° / -67.8°, step 2°, ≈ 90 min**

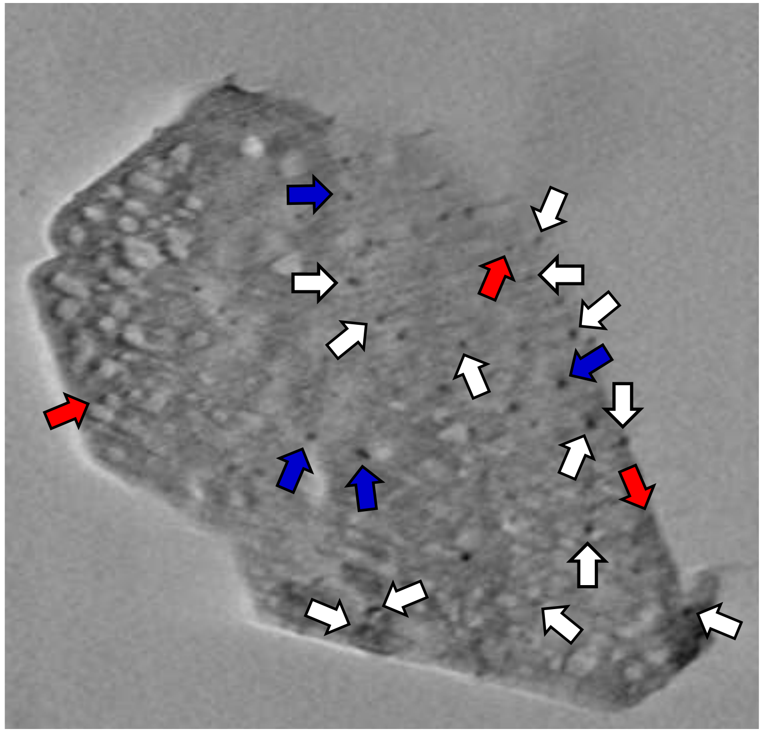
# Attemps for *in situ* 3D characterization

- **Semi-fast tomography of Pd@δ-$Al_2O_3$ during in situ ETEM calcination**

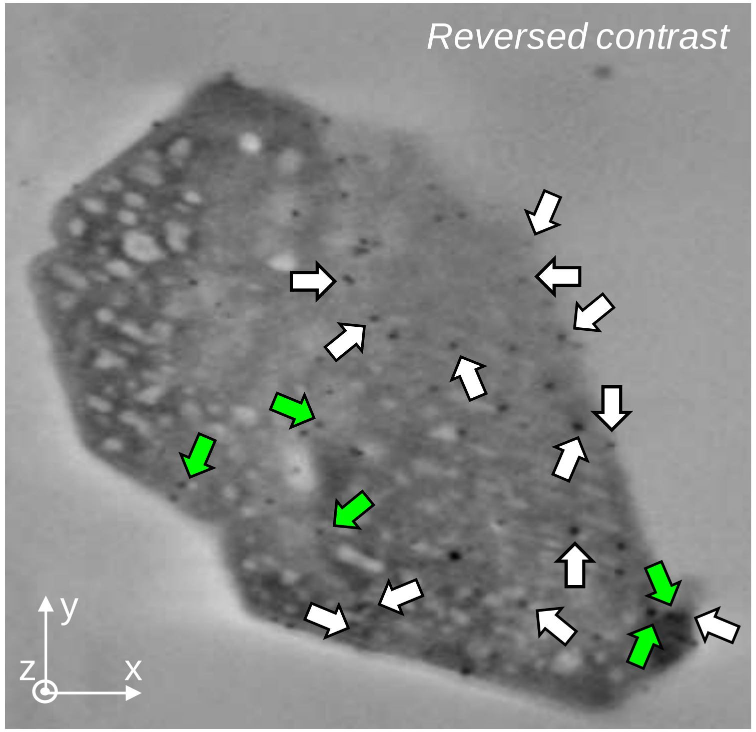
**20°C, High Vacuum**




**350°C, after 60', 2.6 mbar $O_2$**

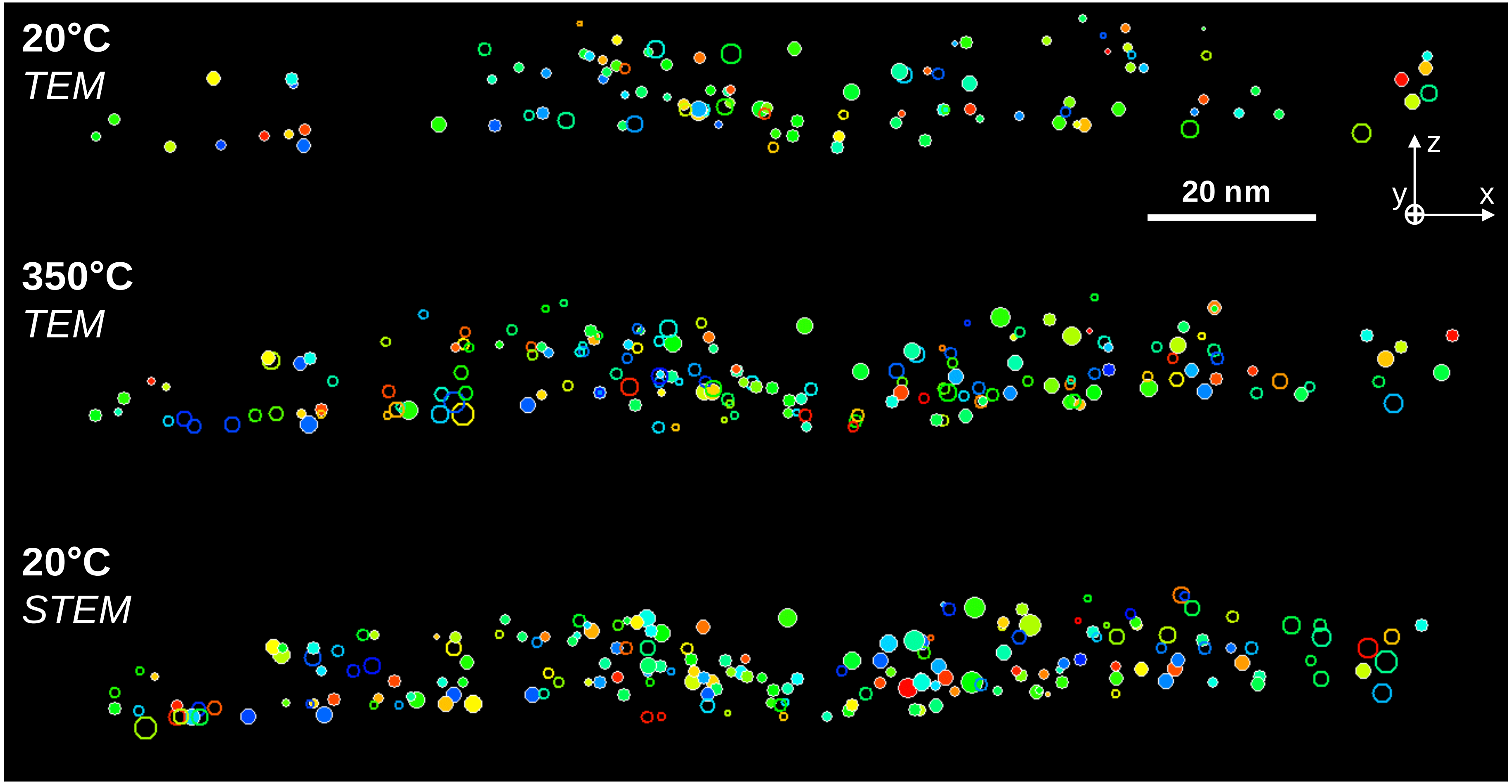


Rapid cooling to **20°C, High Vacuum after 60' at 350°C, 2.6 mbar $O_2$**




**Initial NPs at 20°C** | **Lost (not seen) NPs after heating at 350°C** | **'New' NPs after heating at 350°C** | **Lost (not seen) NPs when back to 20°C** | **'New' NPs when back to 20°C**

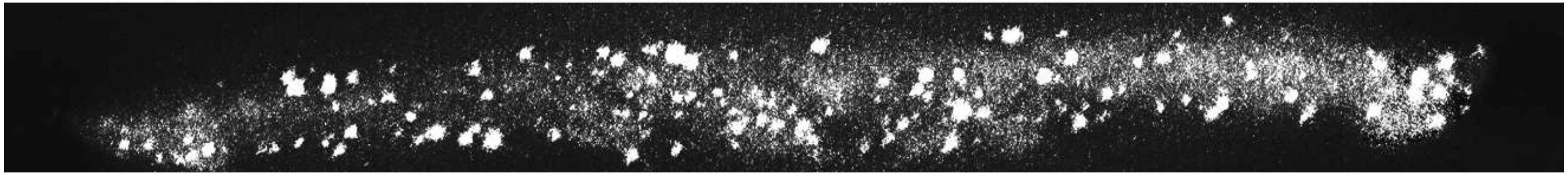
# Attemps for *in situ* 3D characterization




(x,z) projections

**Significant changes while heating at 350°C** (slight growth / coalescence) but **new NPs**

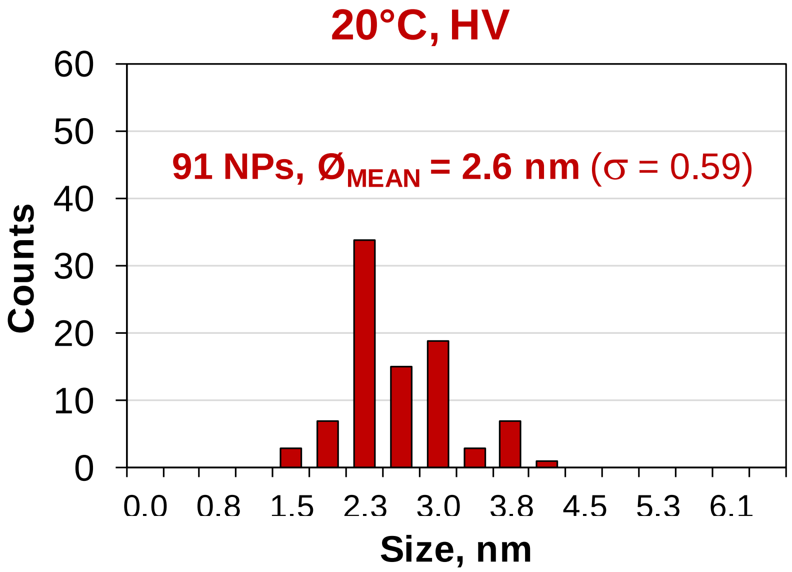
**Minor changes when cooling down to RT°** (few 'new' NPs - better resolution in STEM -)

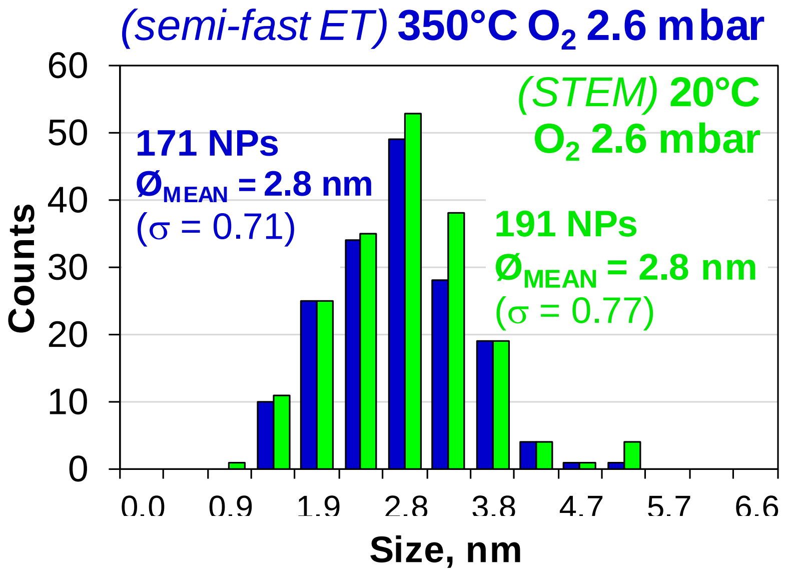


# Attemps for *in situ* 3D characterization

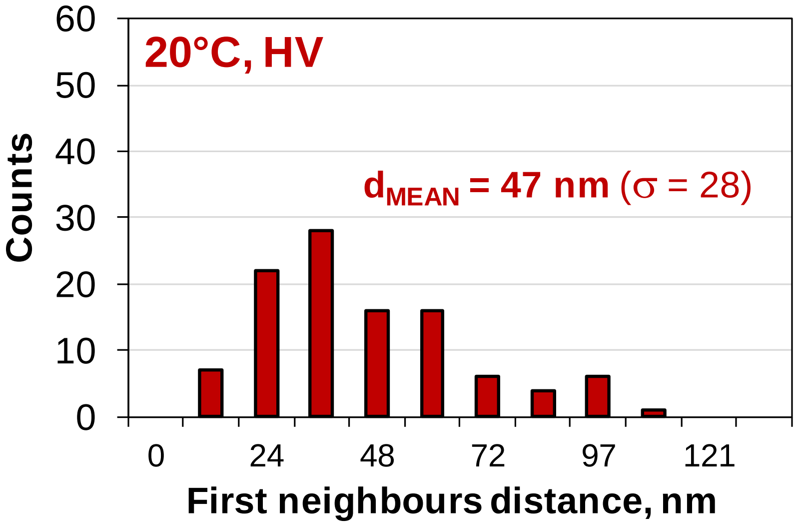
- **Statistics on the NPs population**

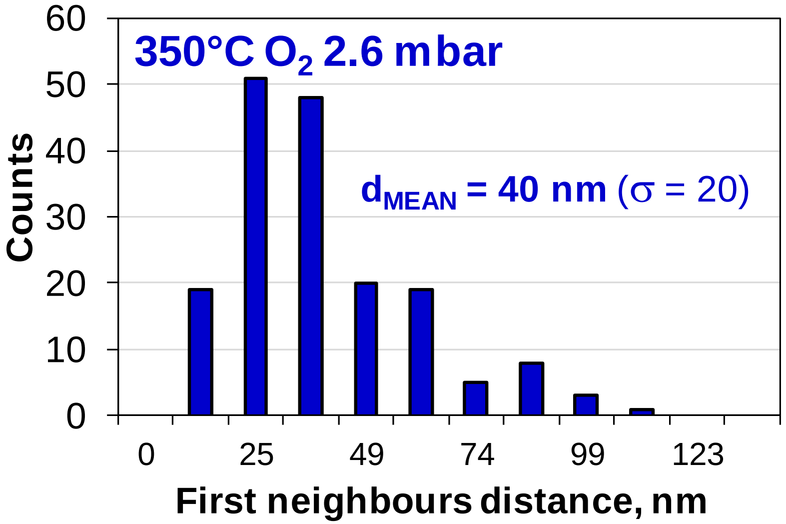
**Size histograms**




**First neighbours**



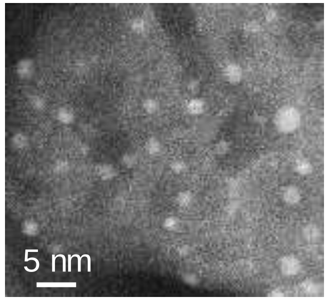



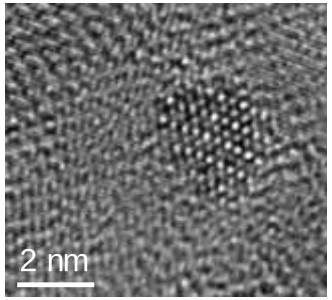
# CONCLUSIONS

- **Preparation (drying, calcination, reduction) of impregnated Pd @ $\delta$-$Al_2O_3$ nanocatalysts:**
  **efficient characterization in Environmental TEM (ETEM)**

  **- NP size below 4 nm** (3.41 ± 0.5 nm) **after the whole preparation process**

  **- Small growth essentially due to Ostwald Ripening before 450°C**



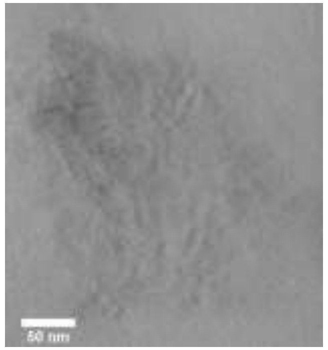

- **Probable instability of the PdO phase under High Vacuum in the TEM**
  **(reasonable behavior under a few mbar of oxygen / air)**

- **(semi) fast Electron Tomography is possible under environmental (gaz, temperature) conditions (acquisition time down to a few seconds)**

  **- *At the minute level:* snapshots at different stages of a reaction (kinetic studies?)**

  **- *At a few seconds level:* identification of fast evolving processes (sintering, facetting?)**

  - *Possible interest for electron beam sensitive materials (polymer / biological materials)*



Pd – $\delta$, tomogram (150'' acquisition)

**A few nm resolution *(so far)***

# ACKNOWLEDGEMENTS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  LabeX 'IMUST' Université de Lyon (ANR)
  IFPen
- *CPER 2007-2013*


- [www.metsa.fr](http://www.metsa.fr)

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**I.R. FR 3507**