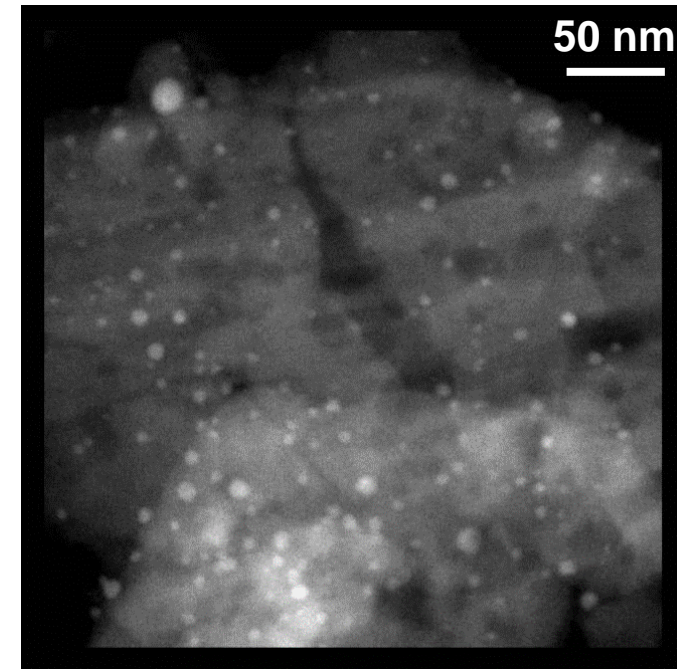


# 2D and Fast 3D in situ study of the calcination and reduction of Pd nanocatalysts supported on Alumina in Environmental Transmission Electron Microscopy (ETEM)



L. GRAMOLI,  
C. DUCOTTET,  
T. EPICIER



**Thierry Epicier<sup>1</sup>, Siddardha Koneti<sup>1</sup>, Lucian Roiban<sup>1</sup>,  
Anne-Sophie Gay<sup>2</sup>, Amandine Cabiach<sup>2</sup>, Priscilla Avenier<sup>2</sup>**



<sup>1</sup>Université de Lyon, MATEIS, INSA de Lyon, UCB Lyon 1, UMR 5510 CNRS, Villeurbanne Cedex, France

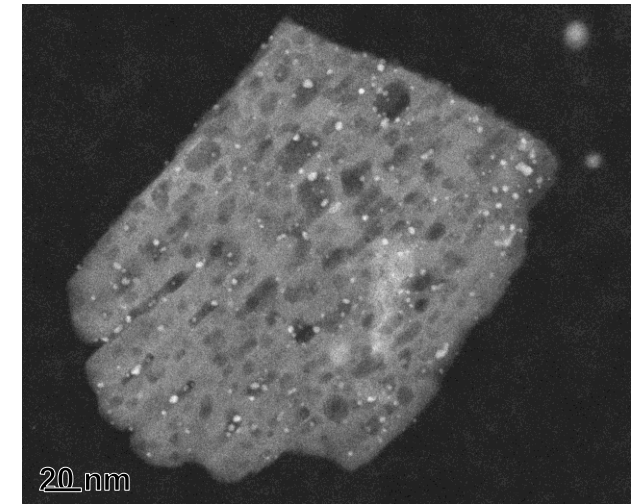
<sup>2</sup>IFP Energies Nouvelles, Solaize, France



# OUTLINE



- TEM beyond High Vacuum: Environmental TEM (ETEM)
- Preparation of Pd nanocatalysts supported on  $\delta\text{-Al}_2\text{O}_3$
- From 2D to 3D in situ analysis in ETEM
- Conclusion / Perspectives: Towards *real time Environmental Tomography*?



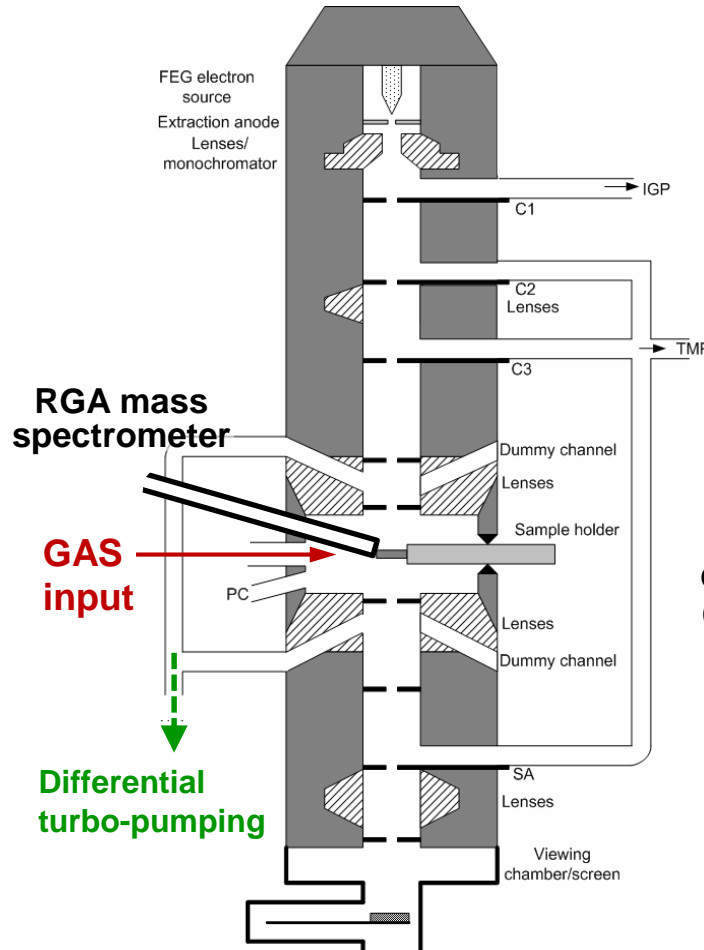
# TEM beyond High Vacuum: Environmental TEM (ETEM)



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



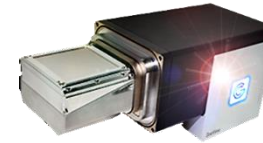
Controlled pressure range:  $\approx 10^{-8}$  mbar to  $\approx 20$  mbar



## Specific equipments

Fast 16 Mp CMOS camera OneView

100 fps in 2Kx2K

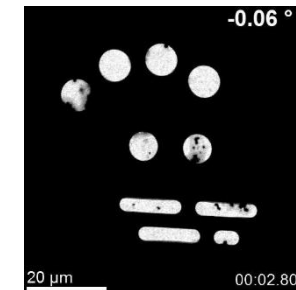
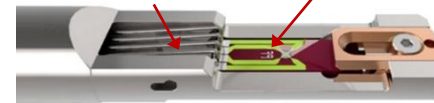


MEMS-based ( $\text{SiN}_x$  chip)

heating holder  $1100^\circ\text{C}$ ,  $\pm 72^\circ$  rotation

Contacts electric contacts (power / measurement)

Nanochip, ultra-thin  $\text{SiN}_x$  windows



[www.clym.fr/Ly-EtTEM\\_examples/Ly-EtTEM\\_examples.html](http://www.clym.fr/Ly-EtTEM_examples/Ly-EtTEM_examples.html)





# TEM beyond High Vacuum: Environmental TEM (ETEM)

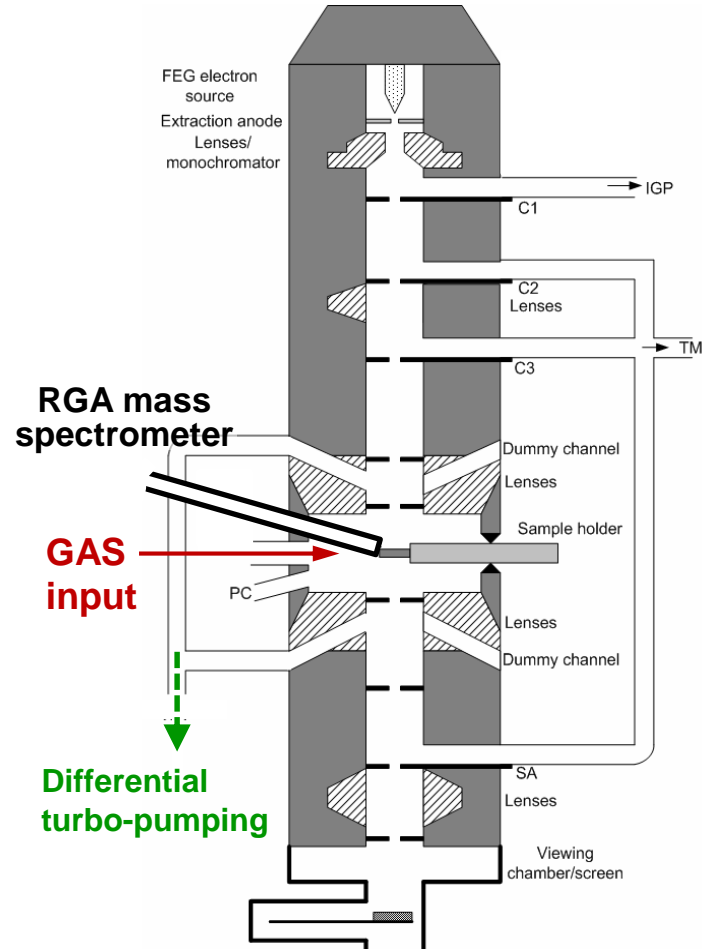


Aberration-corrected **FEI** TITAN ETEM, 80-300 kV at Univ. Lyon, F



[www.clym.fr/Ly-EtTEM\\_examples/Ly-EtTEM\\_examples.html](http://www.clym.fr/Ly-EtTEM_examples/Ly-EtTEM_examples.html)

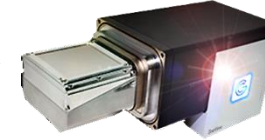
Controlled pressure range:  $\approx 10^{-8}$  mbar to  $\approx 20$  mbar



## Specific equipments

Fast 16 Mp CMOS camera OneView

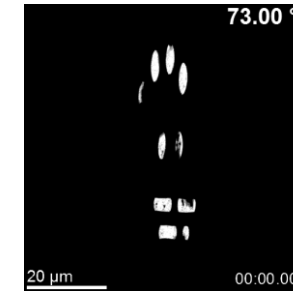
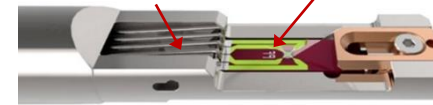
100 fps in 2Kx2K



MEMS-based ( $\text{SiN}_x$  chip) heating holder  $1100^\circ\text{C}$ ,  $\pm 72^\circ$  rotation

Contacts electric contacts (power / measurement)

Nanochip, ultra-thin  $\text{SiN}_x$  windows



Total time 5.4"

## Fast tomography

High speed acquisition of tilt series videos / continuous rotation of the goniometer

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

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

T. EPICIER et al., *Microsc. & Microanal.*, **24** (2018) 1814

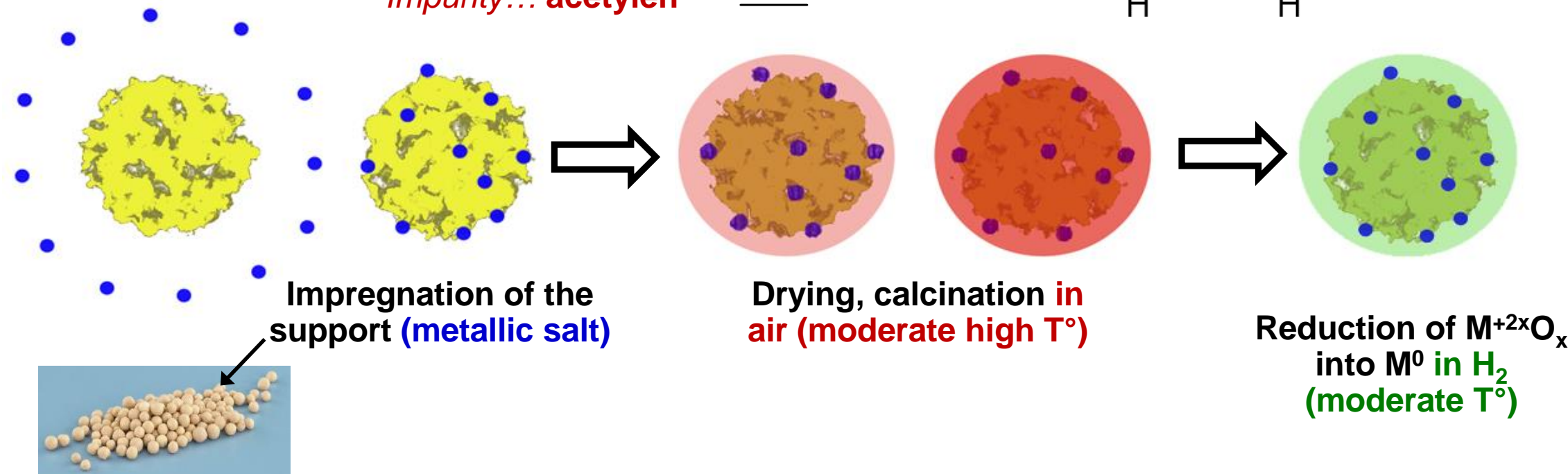
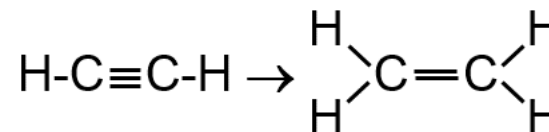
# Preparation of Pd nanocatalysts supported on $\delta\text{-Al}_2\text{O}_3$



## • Background (*selective hydrogenation in petrochemistry*)

Ex.: C2 cut

Looking for... ethylen  $\equiv\equiv$   
Impurity... acetylen  $\equiv\equiv\equiv$



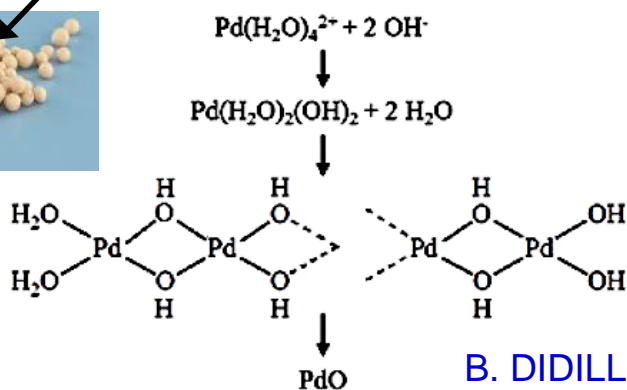
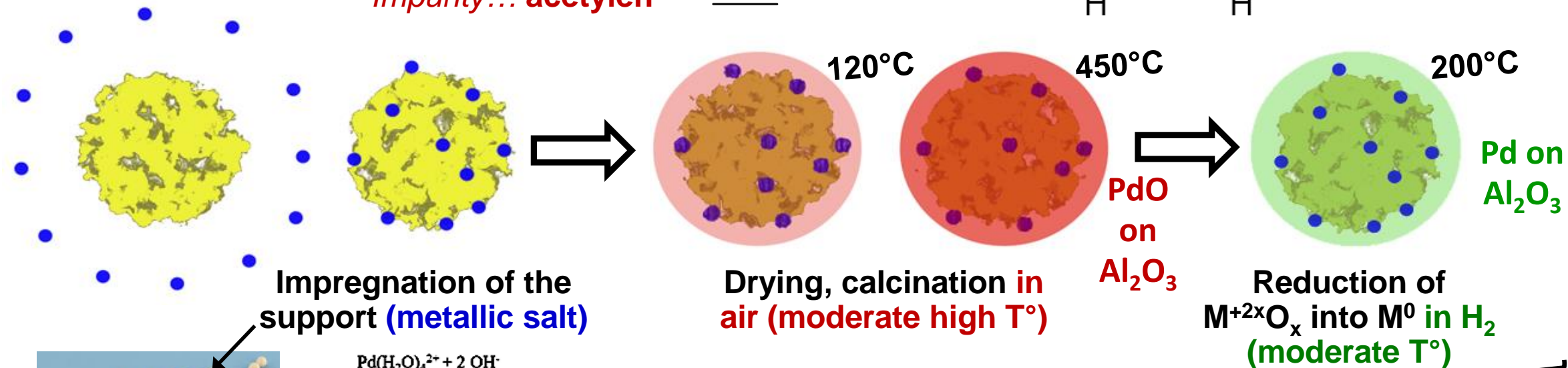
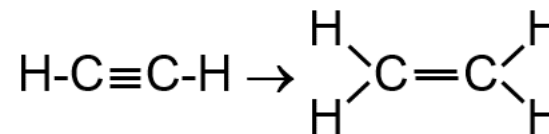
# Preparation of Pd nanocatalysts supported on $\delta\text{-Al}_2\text{O}_3$



## • Background (*selective hydrogenation in petrochemistry*)

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Looking for... ethylen  $\equiv\equiv$   
Impurity... acetylen  $\equiv\equiv\equiv$



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



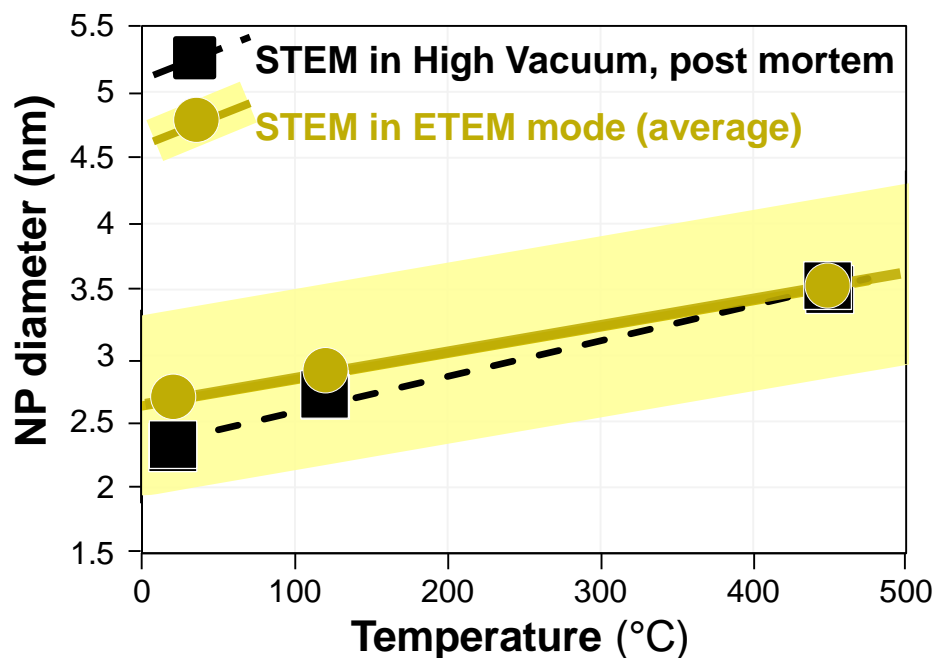




## • Checking NPs size and phase during and after in situ calcination in the ETEM

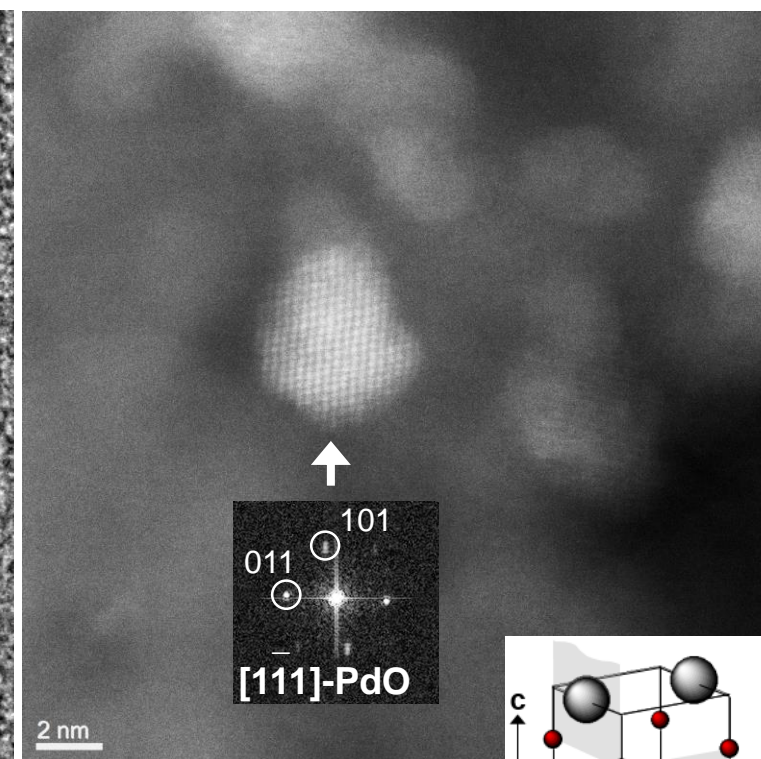
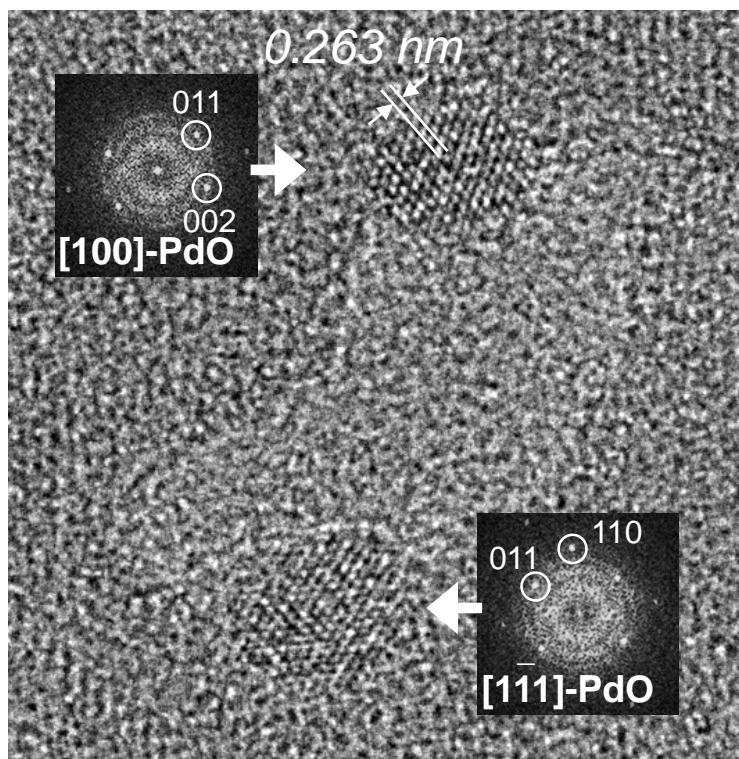
in situ ETEM: HRTEM after 2 hrs. at 450°C, 10 mbar O<sub>2</sub>

HRSTEM back to 20°C



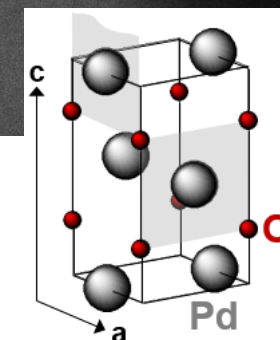
Final average sizes (nm):

Impregnated	Dried	Calcined
2.57 ± 0.5	3.0 ± 0.5	3.41 ± 0.5



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

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

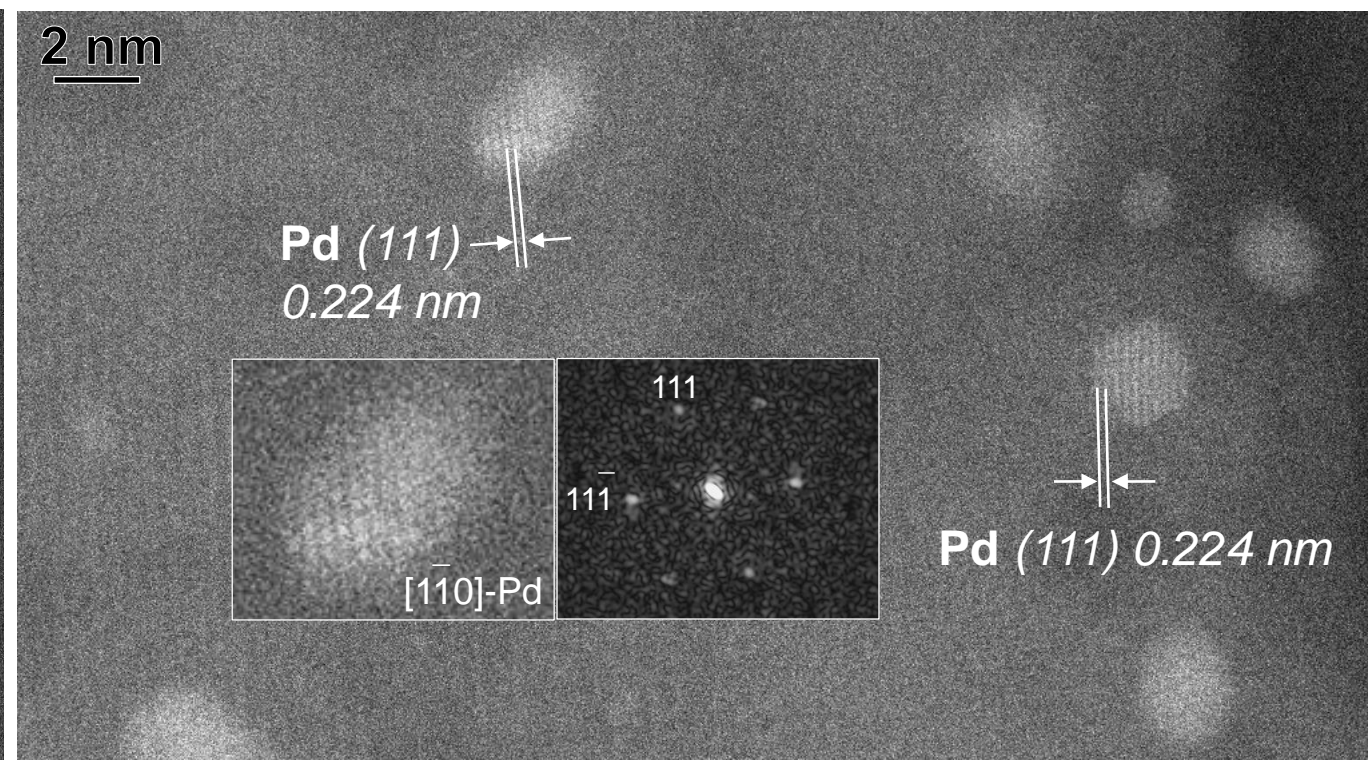
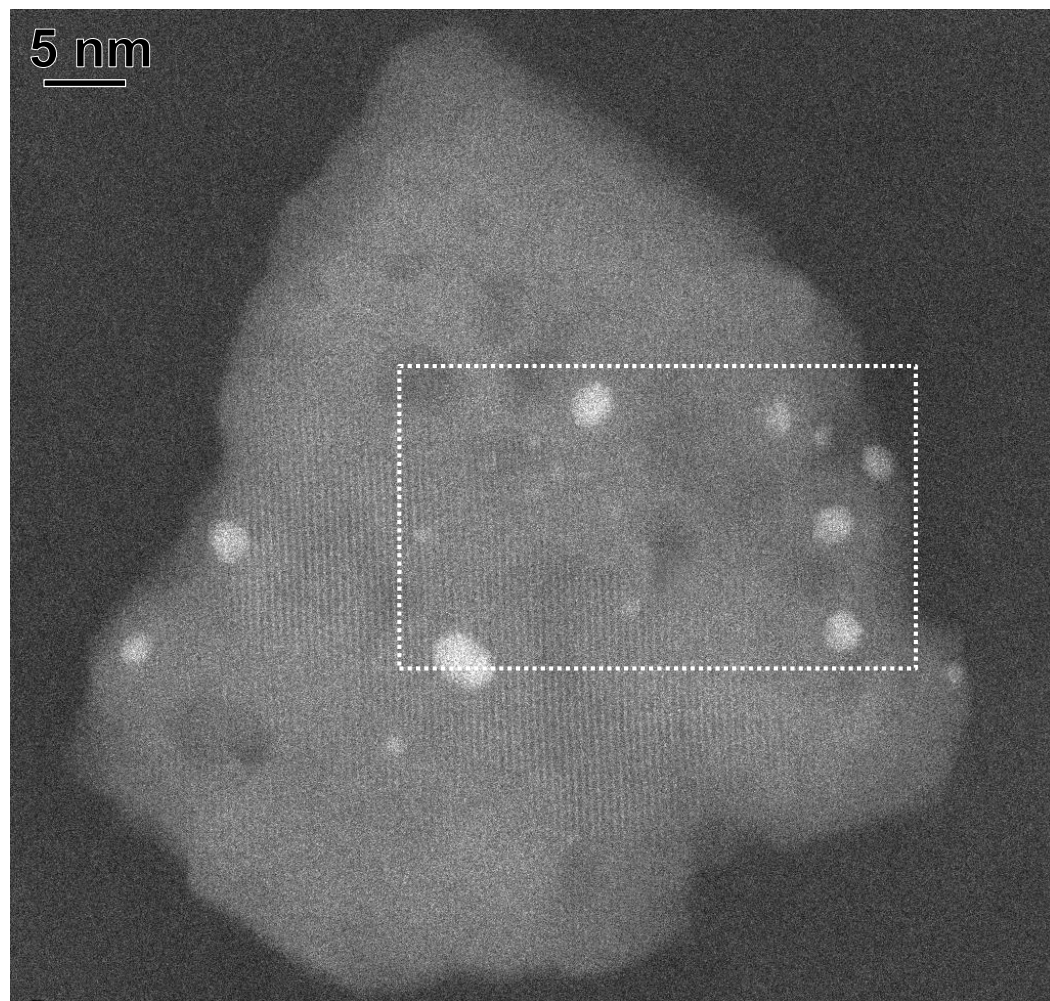






- Checking final state during and after in situ reduction in the ETEM

in situ ETEM: HRSTEM after 2 hrs. at 200°C, 11 mbar H<sub>2</sub>



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



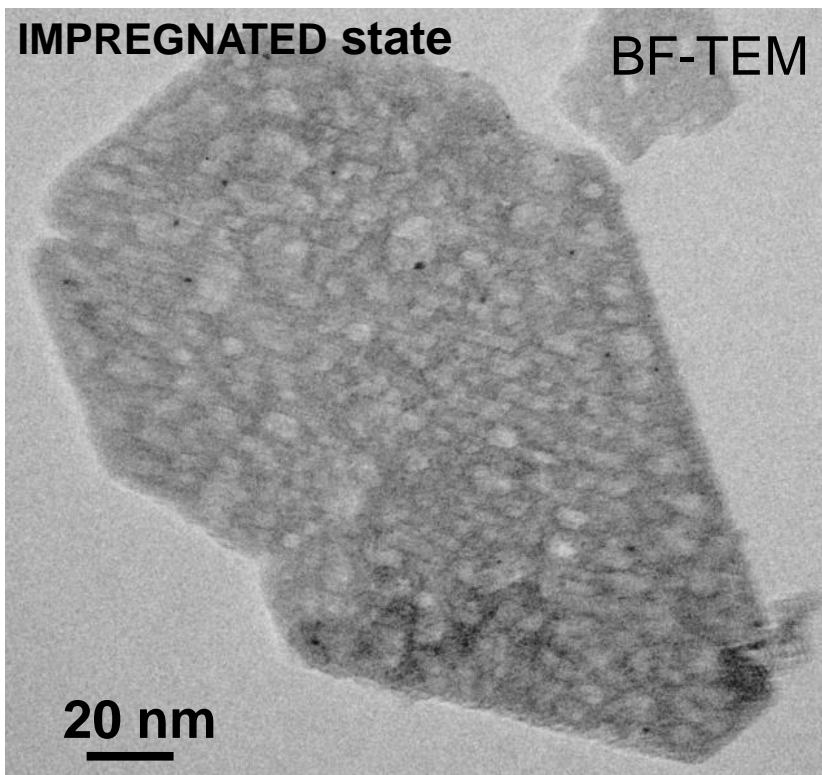


# From 2D to 3D in situ analysis in ETEM

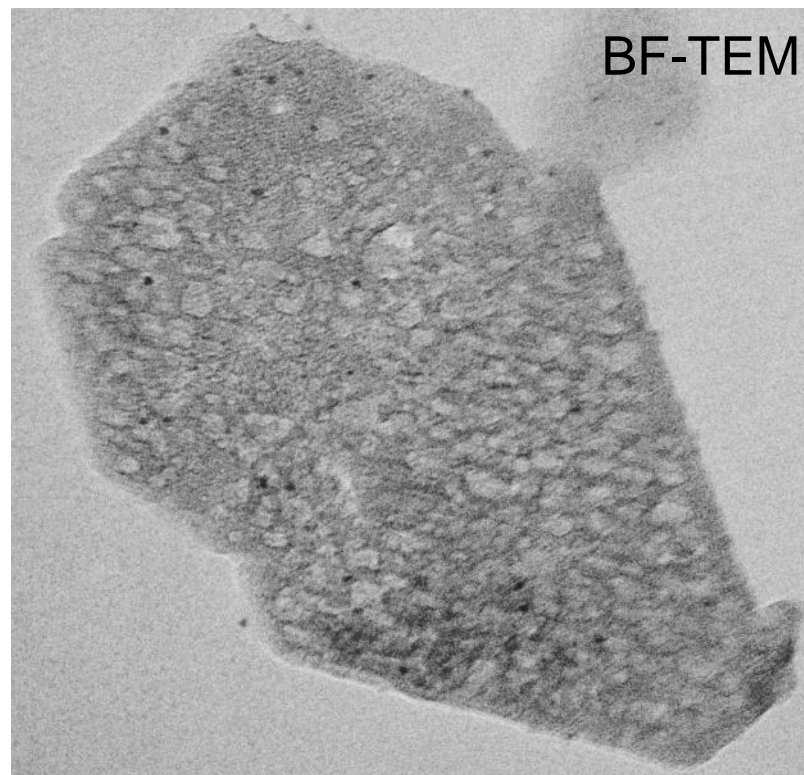


- Classical 2D imaging during in situ ETEM calcination

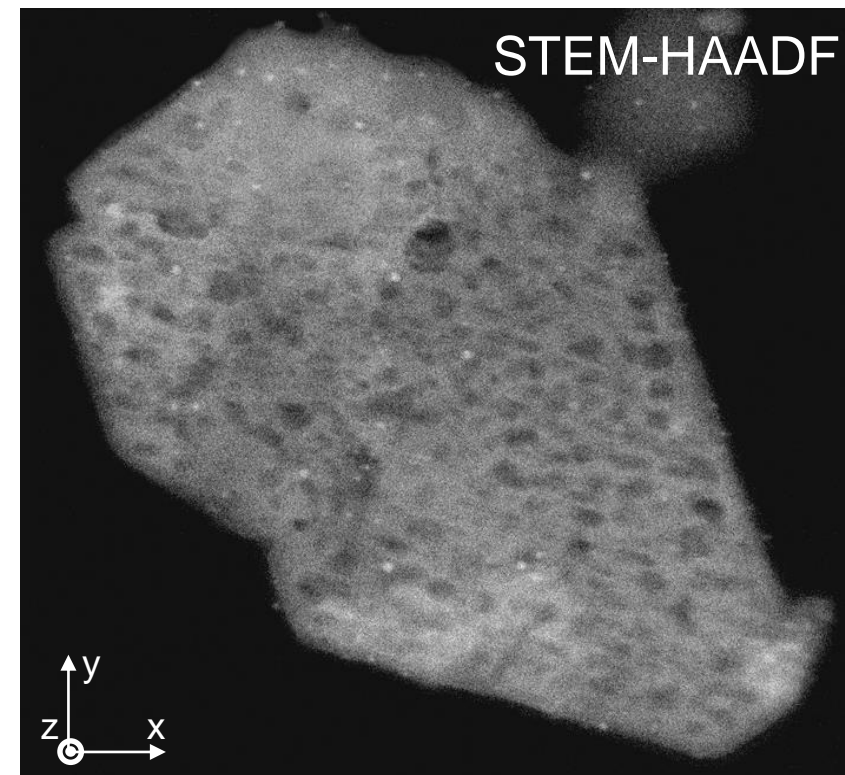
20°C, High Vacuum



350°C, 2.6 mbar O<sub>2</sub> after 60 min.



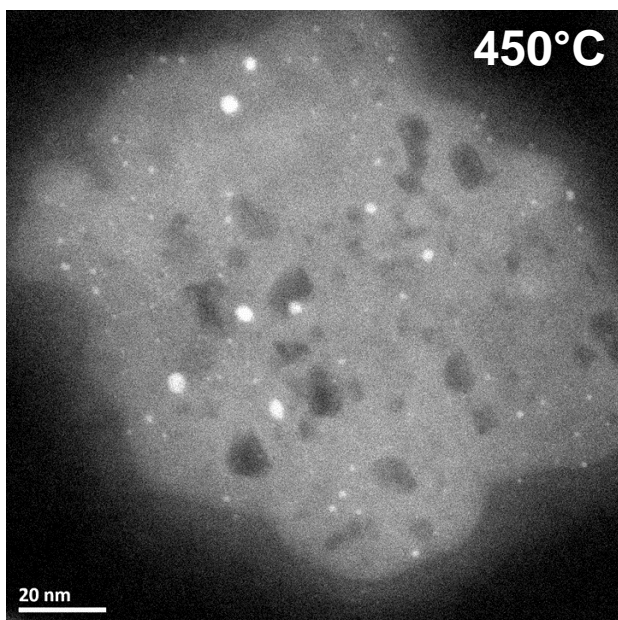
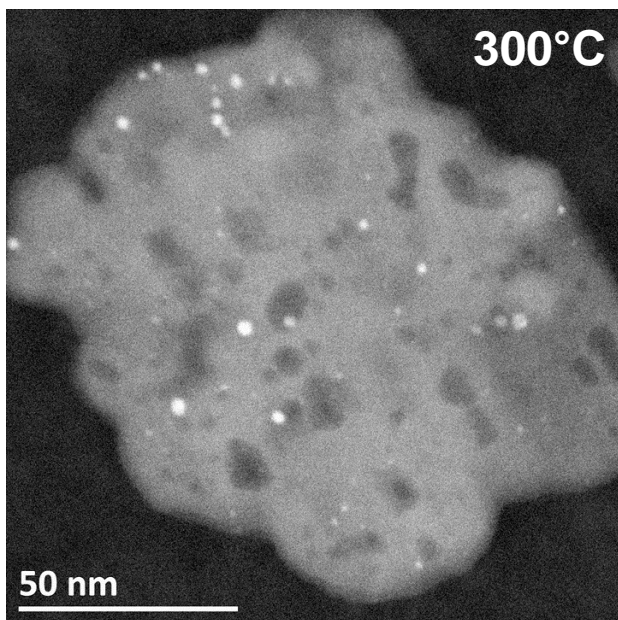
Rapid cooling to 20°C, High Vacuum



⇒ Clearly more NPs after heating at 350°C than initially at 20°C

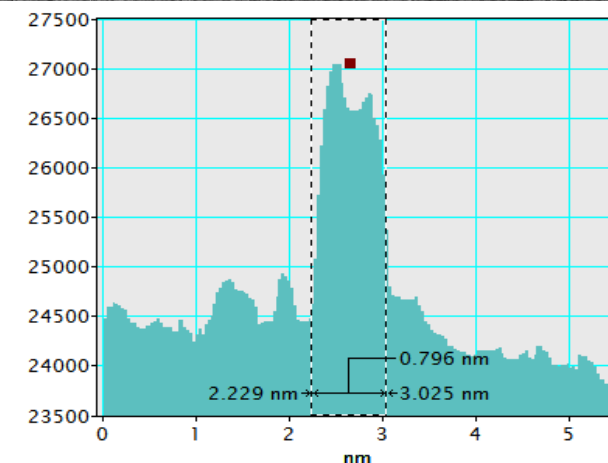
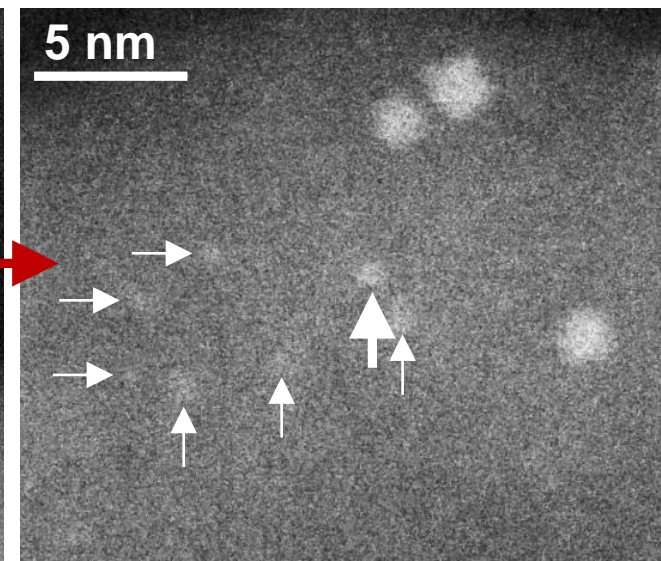
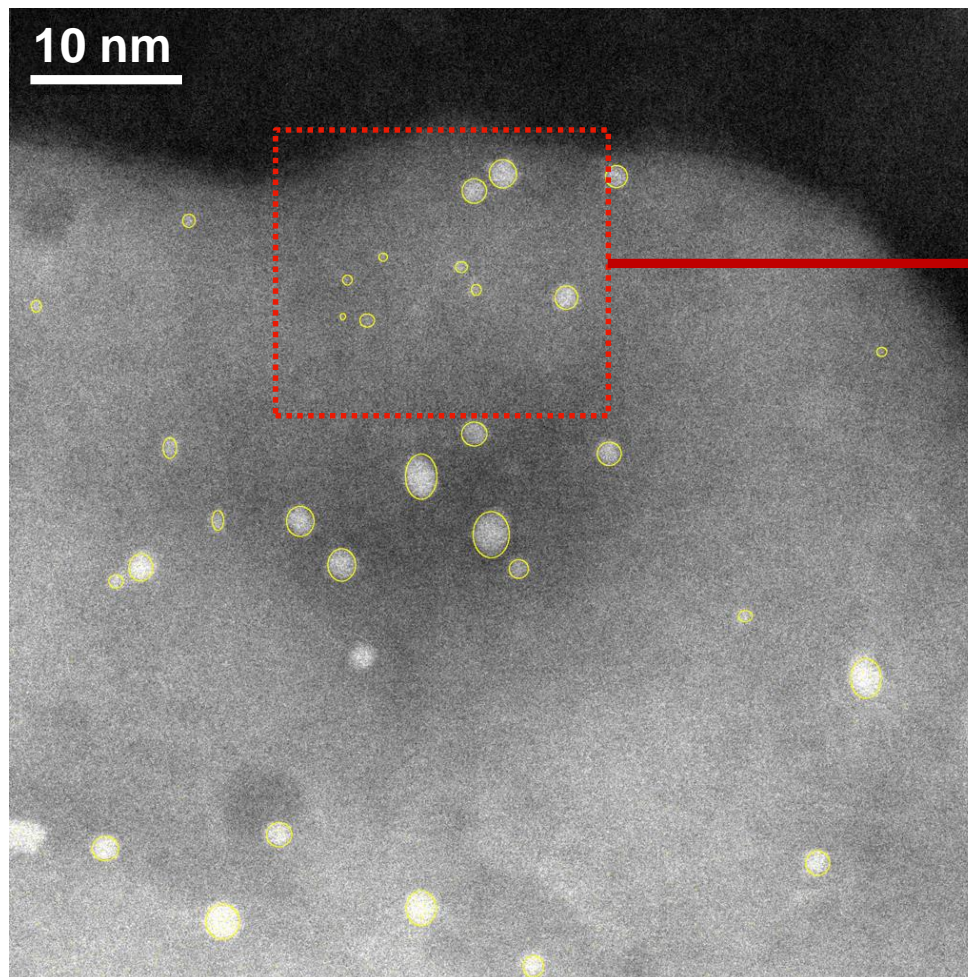






## Initial (Impregnated) state

Large reservoir of Pd clusters (isolated atoms?)





# From 2D to 3D in situ analysis in ETEM

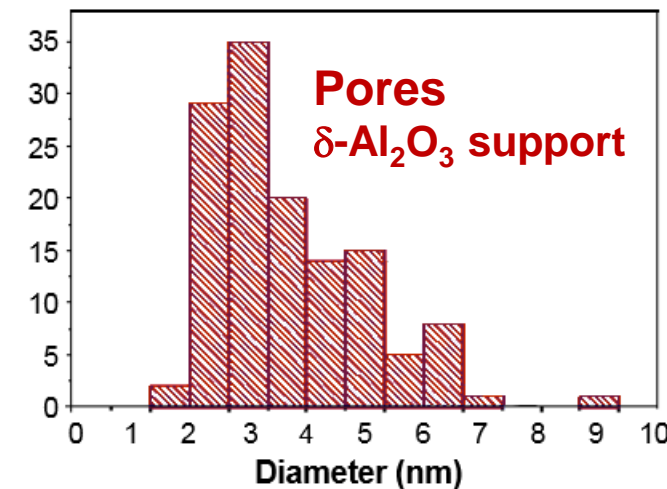
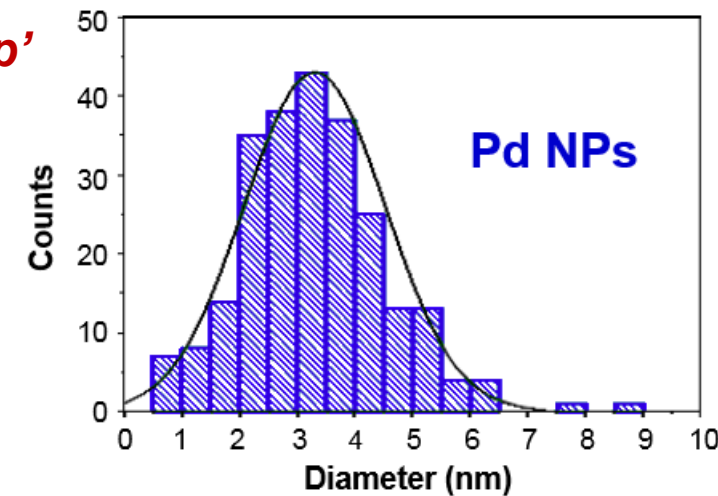
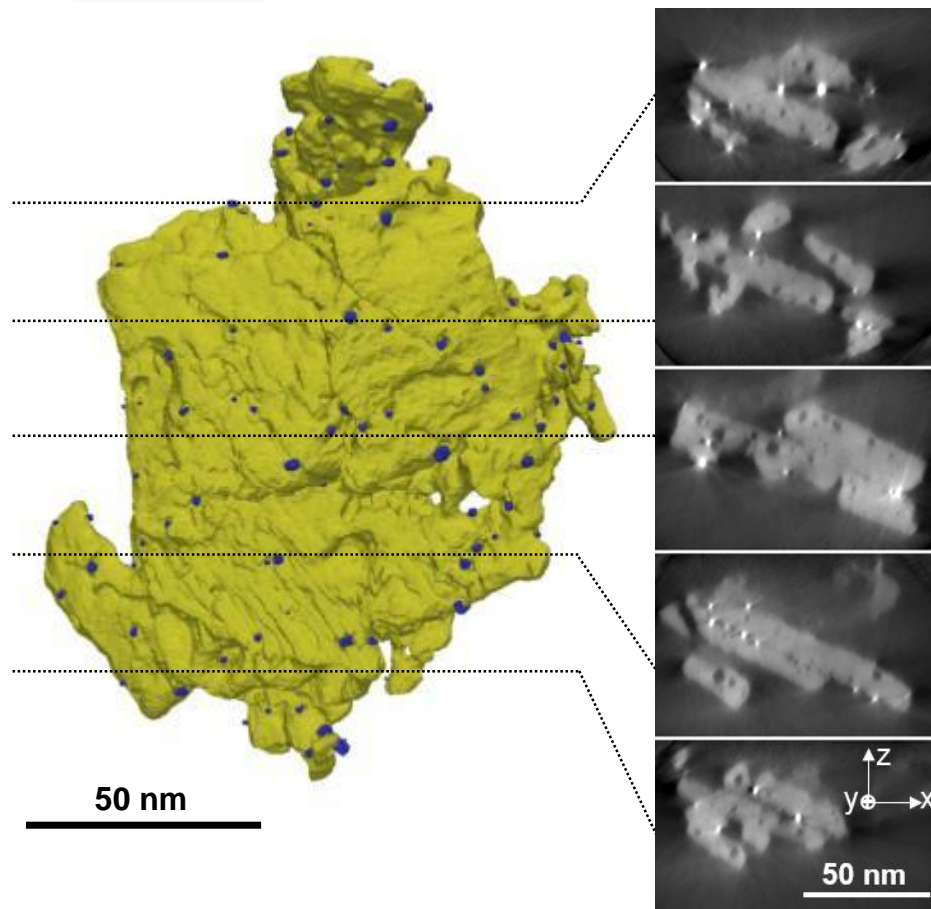
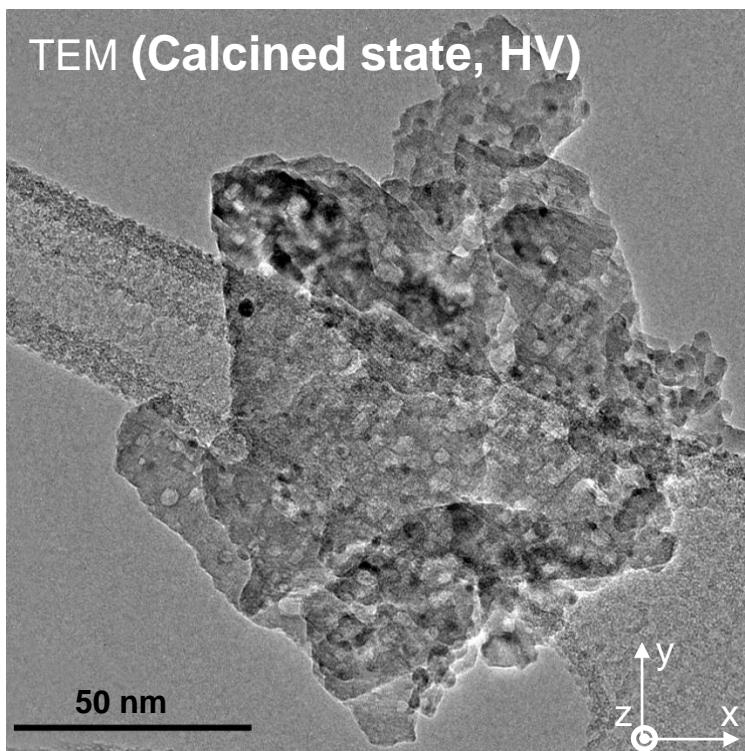


- Context: follow the evolution of nanomaterials in situ and *in 3D* under dynamic environmental conditions

STEM tomography, +73/-73°, step 2°, 100 min. ← Tilt series acquisition

Conventional 'step-by-step'

Tilt series acquisition





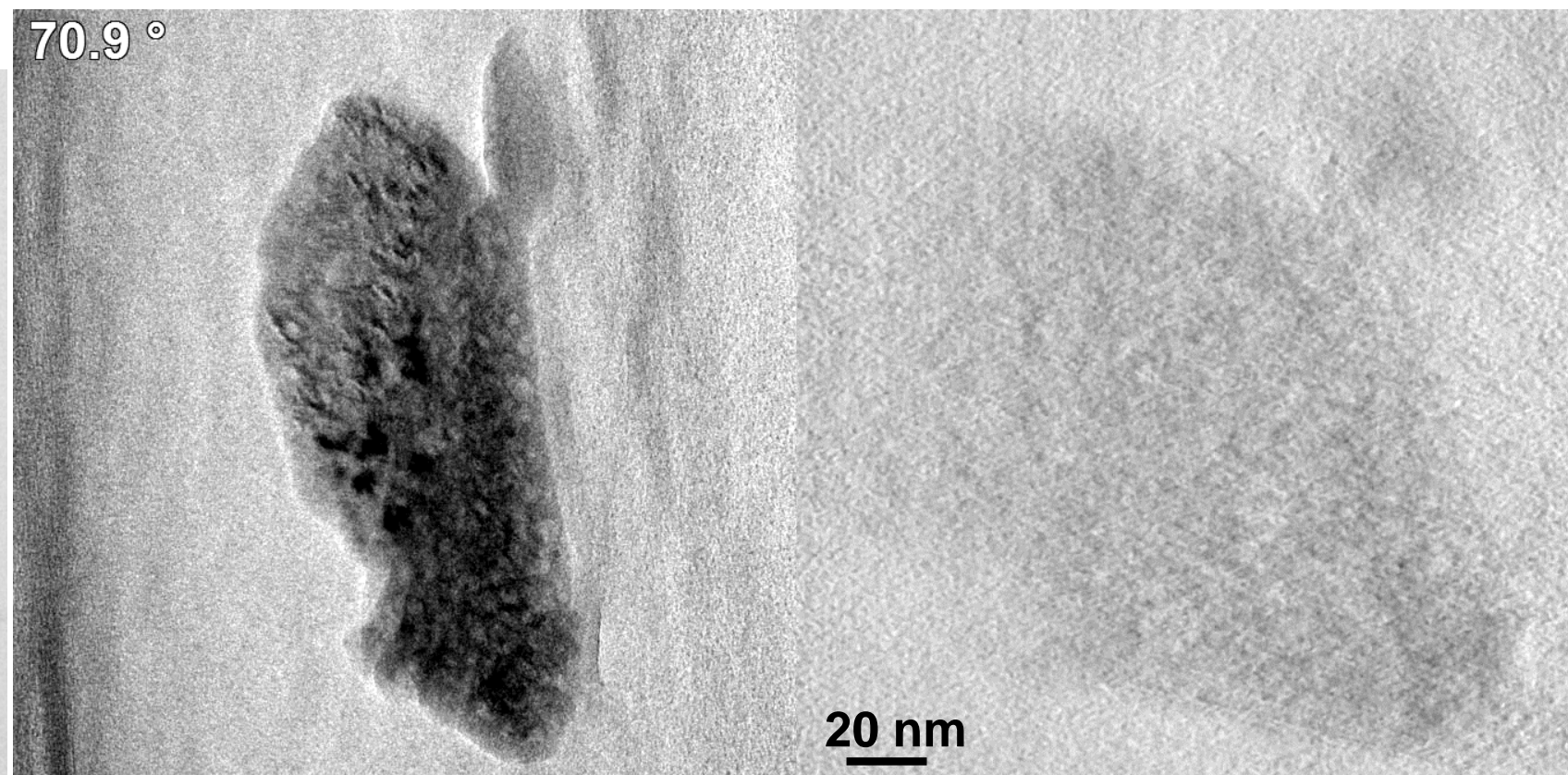
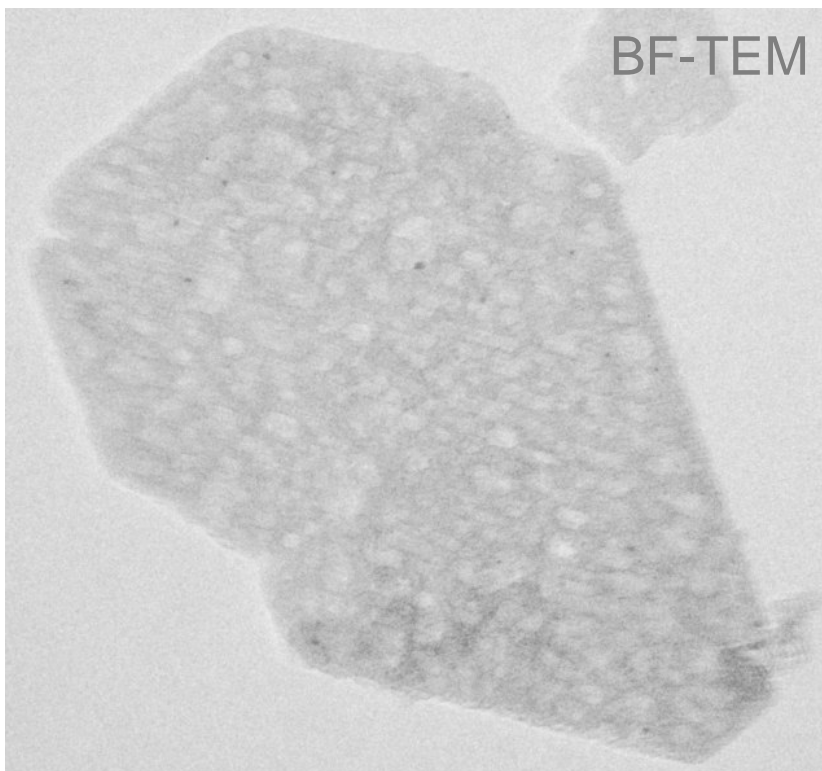
# From 2D to 3D in situ analysis in ETEM



- Accelerated 'step-by-step' *BF-TEM* tomography during in situ ETEM calcination

350°C, after 60 min., 2.6 mbar O<sub>2</sub>

20°C, High Vacuum



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

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





# From 2D to 3D in situ analysis in ETEM



- Accelerated 'step-by-step' *BF-TEM* tomography during in situ ETEM calcination

20°C, High Vacuum

350°C, 2.6 mbar O<sub>2</sub> after 60 min.

Rapid cooling to 20°C, High Vacuum

ART tomograms,  
15 iterations

BF-TEM

BF-TEM

STEM-HAADF

20 nm

Accelerated BF acquisition: 73.4° / -66.6°, step 2°, **2 min 42 sec**

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

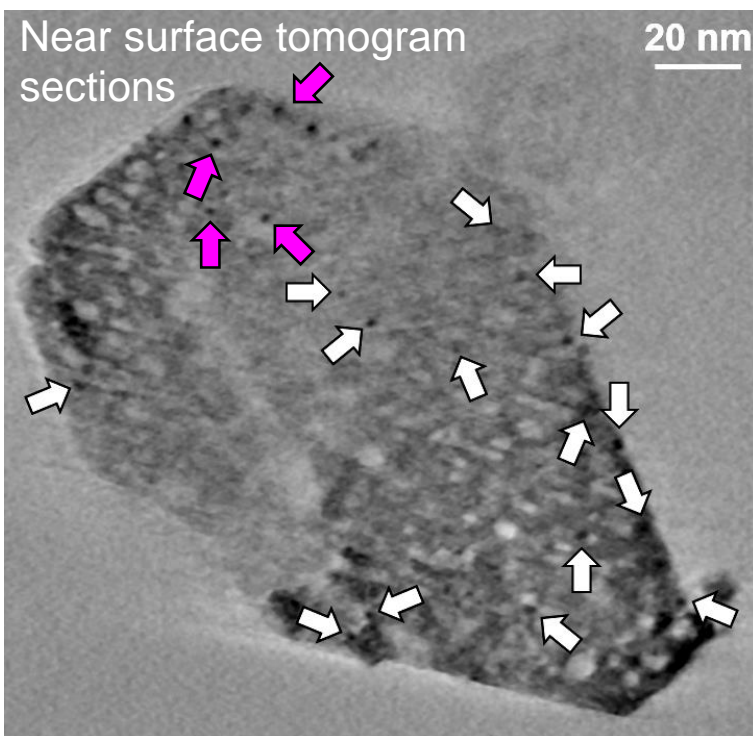


# From 2D to 3D in situ analysis in ETEM

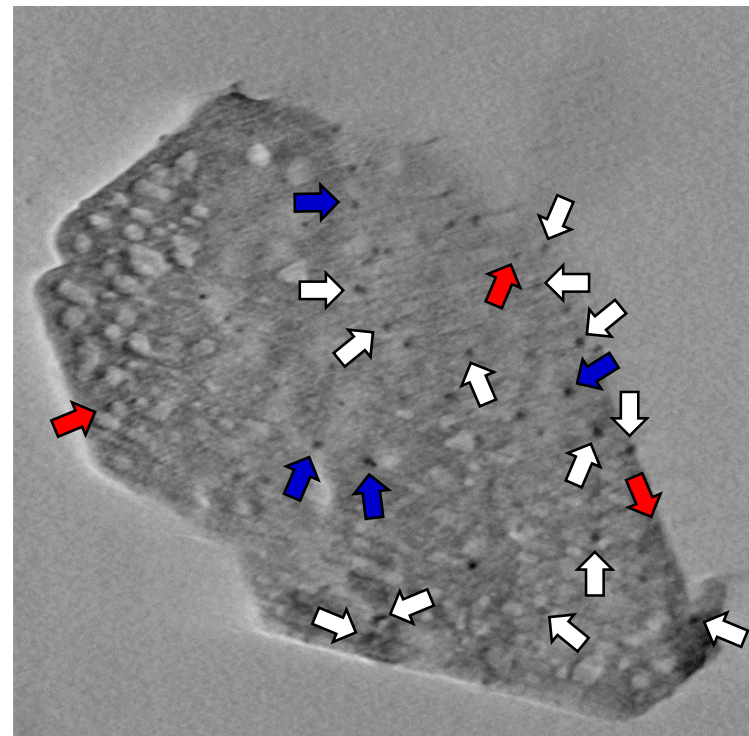


- Accelerated 'step-by-step' *BF-TEM* tomography during in situ ETEM calcination

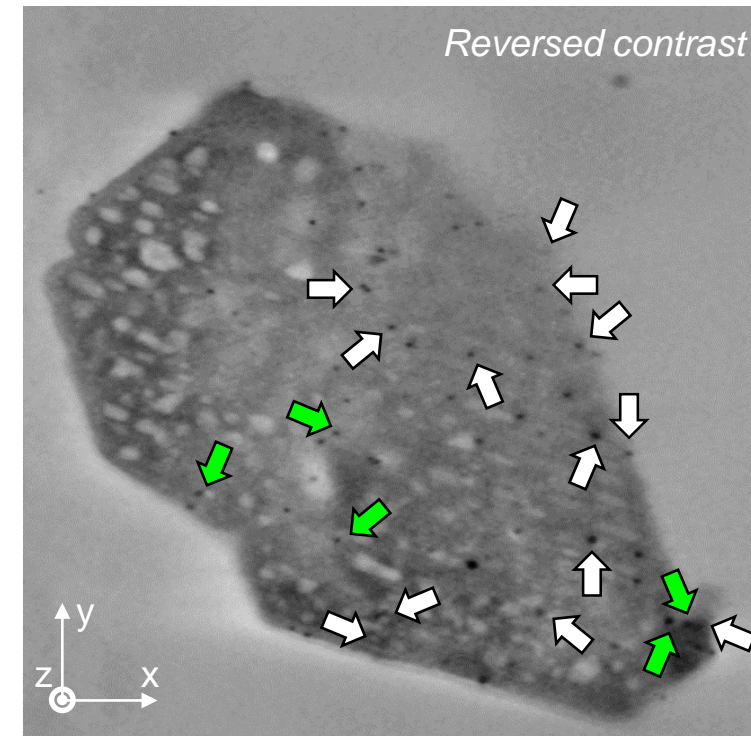
20°C, High Vacuum



350°C, 2.6 mbar O<sub>2</sub> after 60 min.

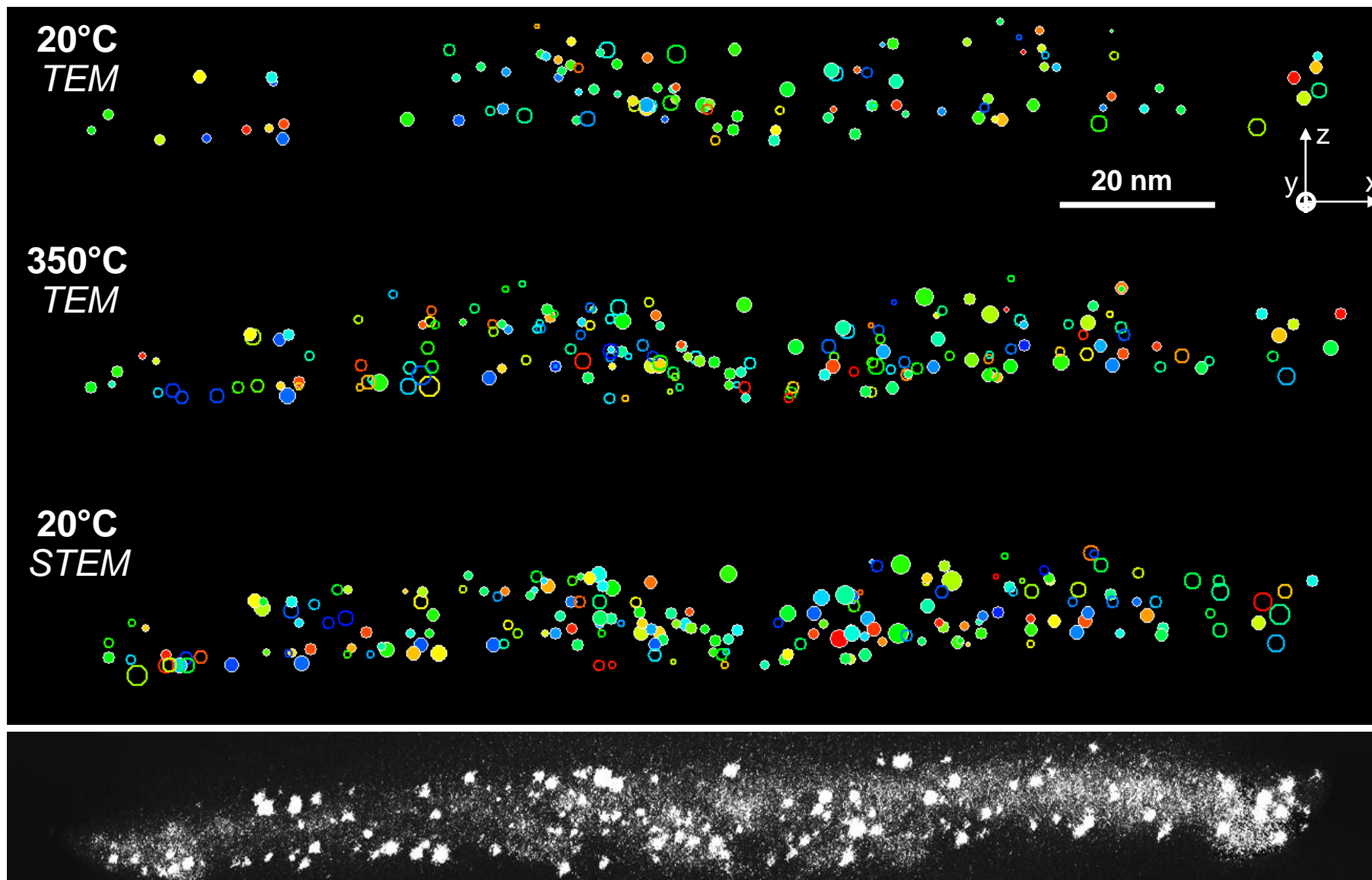


Rapid cooling to 20°C, High Vacuum





# From 2D to 3D in situ analysis in ETEM



(x,z) projections

Changes while heating at 350°C: minor growth / calescence but **new NPs**

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

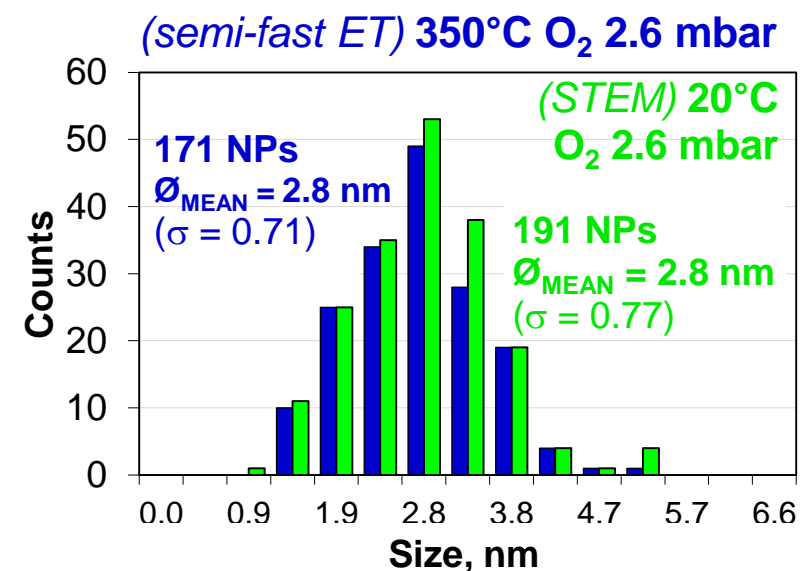
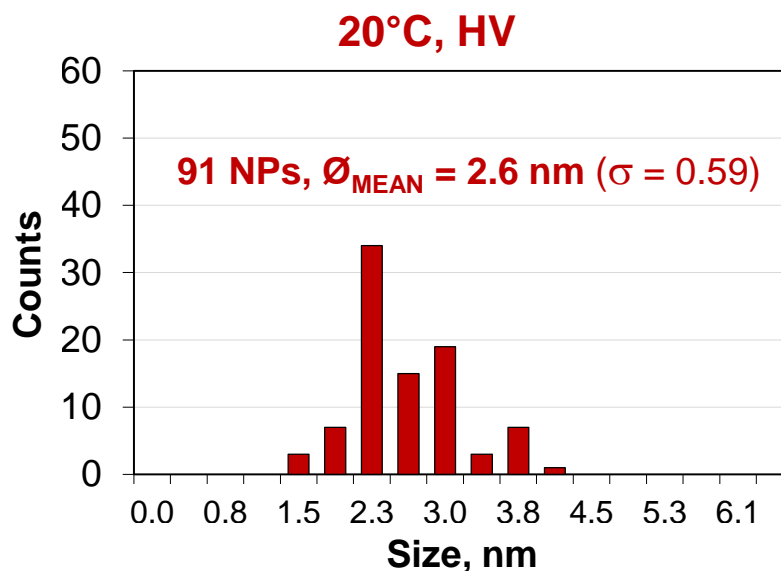


# From 2D to 3D in situ analysis in ETEM

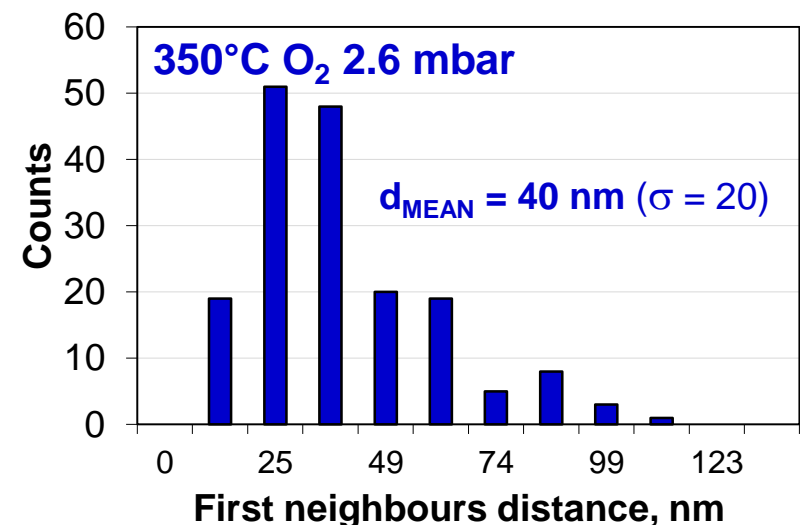
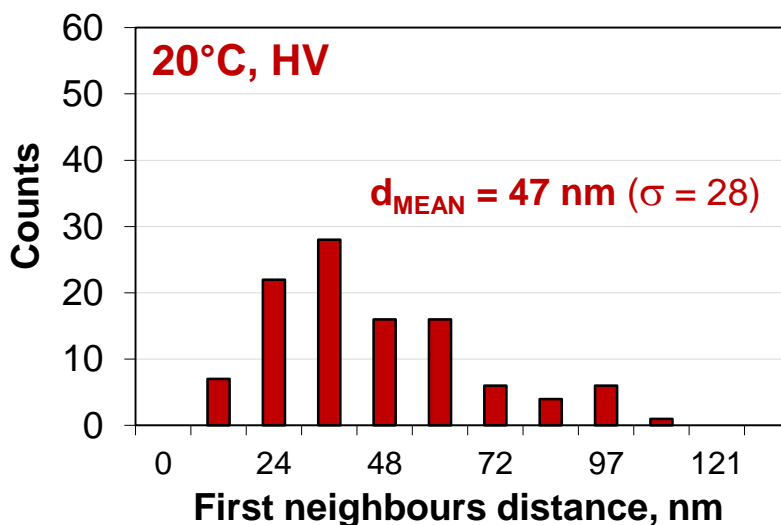


- Statistics on the NPs population

Size histograms



First neighbours

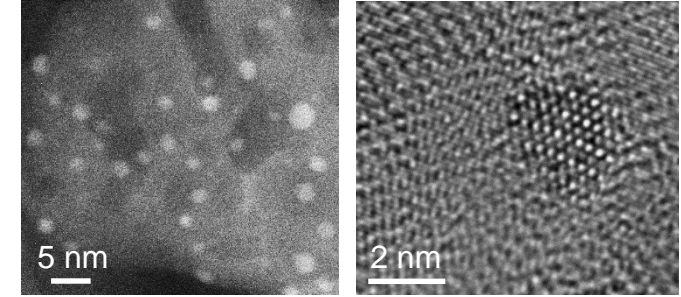




# Conclusion / Perspectives: *Towards real time Environmental Tomography?*

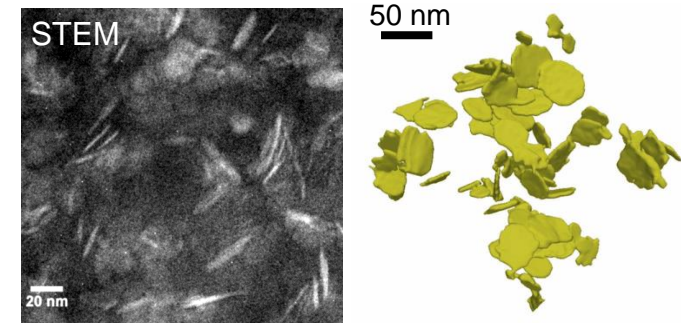
- Preparation (drying, calcination, reduction) of impregnated Pd @  $\delta$ -Al<sub>2</sub>O<sub>3</sub> nanocatalysts:  
**efficient characterization in Environmental TEM (ETEM)**

- NP size below 4 nm ( $3.41 \pm 0.5$  nm) after the whole preparation process
- Minor growth essentially due to Ostwald Ripening before 450°C



- Fast Electron Tomography is possible under environmental conditions (gas and T°)

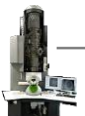
- **At the minute level:**  
snapshots at various stages of a reaction (kinetic studies are possible)
- **Possible application to electron beam sensitive materials** →  
(polymer / biological materials)



LDH (Mg<sub>3</sub>AlCO<sub>3</sub>) platelets in a Latex-based nanocomposite (P(MA-co-BA))

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

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



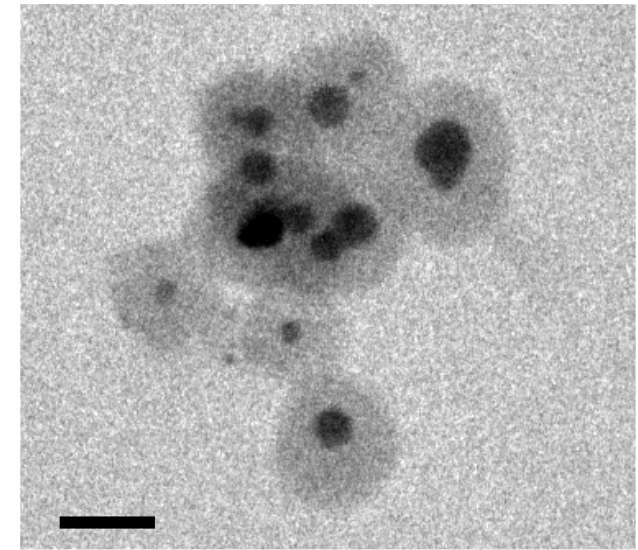
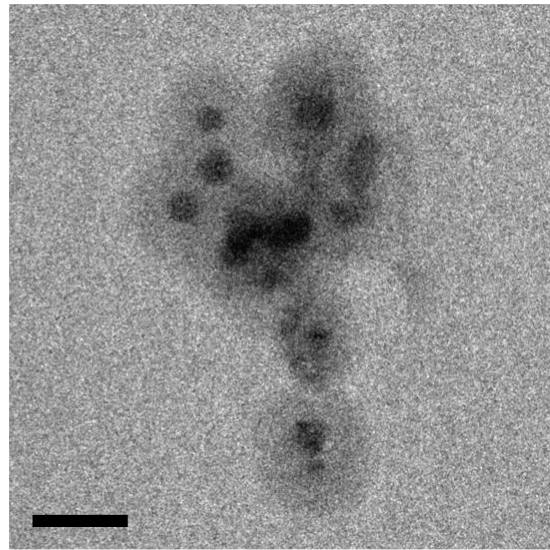
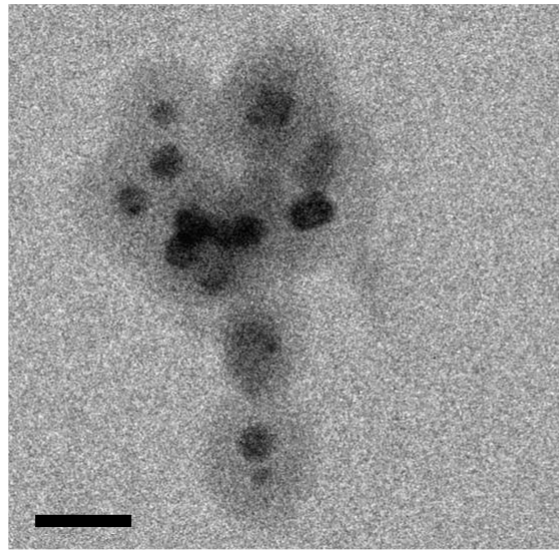
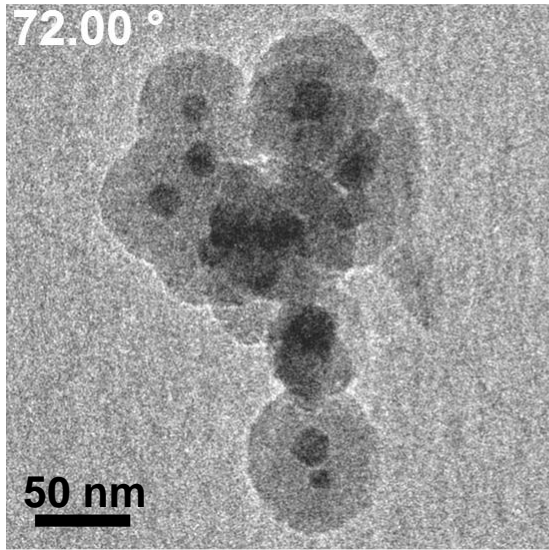
# 3D-ETEM study of the sintering resistance of Pd@SiO<sub>2</sub> nanocatalysts

20°C, 6 10<sup>-7</sup> mbar (HV)

after 35' at 400°C, H<sub>2</sub> 4 mbar

after 60' at 500°C, H<sub>2</sub> 4 mbar

after 60' at 800°C, H<sub>2</sub> 4 mbar



acquisition ≈ 6 s

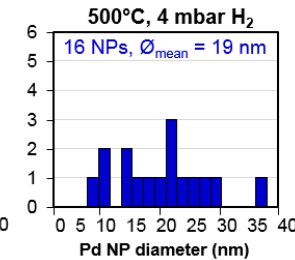
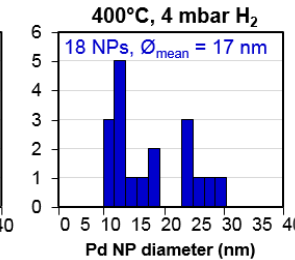
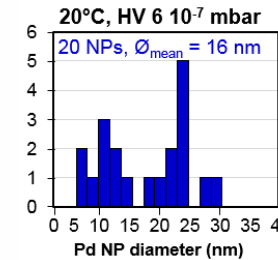
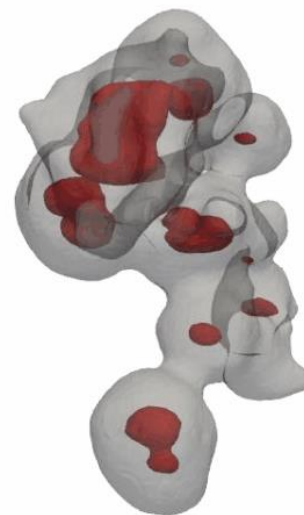
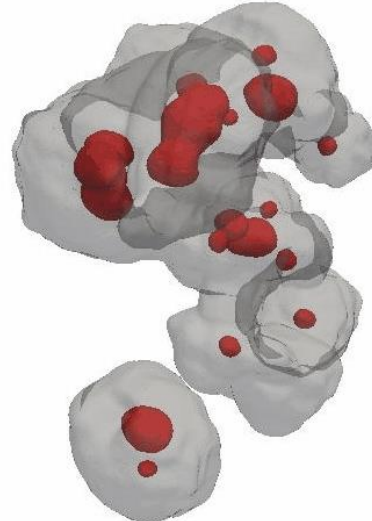
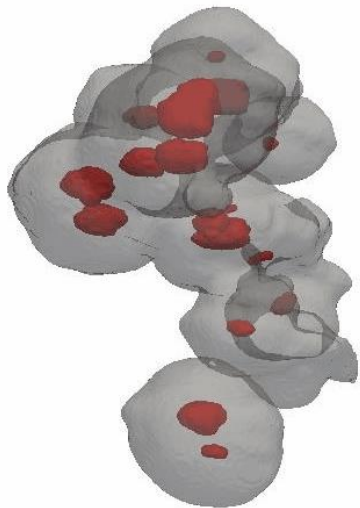
acquisition ≈ 8 s

acquisition ≈ 7 s

acquisition ≈ 9 s

Total Exposure time: ...62 s.....149 s.....167 s.....≈ 2 min 20 s

cumulative dose = 1.9 10<sup>6</sup> e-/nm<sup>2</sup>





S. KONETI et al., submitted to *Mat. Charact.*, (2018)





# ACKNOWLEDGEMENTS



- **Matthieu BUGNET, Philippe STEYER, MATEIS INSA-Lyon** 
- **Mimoun AOUINE, Francisco J. CADETE SANTOS AIRES, IRCELYON, University Lyon I** 
- ANR project '3DCLEAN' n° 15-CE09-0009-01, LabeX 'IMUST' Université de Lyon (ANR) IFPen



- **CPER 2007-2013 Rhône-Alpes GRAND LYON**   



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



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**I.R. FR 3507**  

