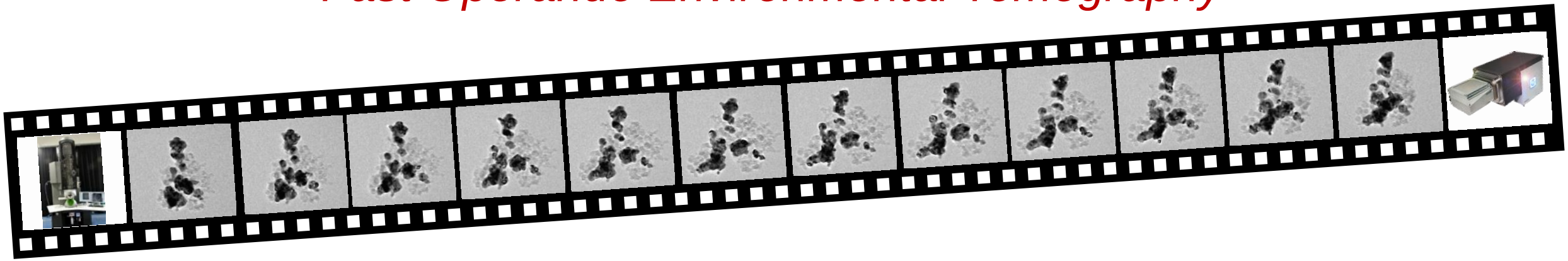
Real time 3D Environmental TEM in-depth study of catalytic soot combustion on Zirconia-based catalysts

Fast Operando Environmental Tomography



T. Epicier[1], S. Koneti[1], L. Roiban[1], H. Banjak[2], D. Lopez-Gonzalez[3], P. Vernoux[3]

[1]Univ Lyon, INSA-Lyon, CNRS, Université Claude Bernard Lyon 1, MATEIS, UMR 5510, 69621 Villeurbanne Cedex, France

[2]Univ Lyon, INSA-Lyon, CNRS, INSERM, CREATIS, UMR 5220, U1206, 69621 Villeurbanne Cedex, France

[3]Univ Lyon, Université Claude Bernard Lyon 1, IRCELYON, UMR 5256, CNRS, 69626 Villeurbanne, France

Fast tomography in Materials Science at the µm / sub-µm level by X-Ray µ-CT: *the current and in progress situation*

TOMOGRAPHY at SEVERAL Hertz for *in situ* HT° / straining / recrystallization / growth / matter (fluid) flow

Several hundreds of projections recorded in less than 10 s and even 1 s over continuously repeated sweeps of 180°

www.psi.ch *(P. Scherrer Inst., Switzerland)*

R. MOKSO et al., *Sci.Reports* **5** (2015) 8727

als.lbl.gov *(Advanced Light Source, USA)*

H.S. BARNARD et al., *J. Phys. Conf. Series* **849** (2017) 012043

www.diamond.ac.uk *(Diamond Light Source, UK)*

B. CAI et al., *Acta Mater* **105** (2016) 338-346

www.synchrotron-soleil.fr *(Soleil, France)*

K. MEDJOUB et al., *J. Synchr. Rad.* **20** (2013) 293-299

www.esrf.eu *(European SRF, Eu)*

J. VILLANOVA et al., *Mat. Today* (2017), on line, DOI/ 10.1016/j.mattod.2017.06.001

ssrf.sinap.ac.cn *(Shanghai SRF, China)*

L. XU et al., *J. Inst.* **10** (2015) C03010

www.riken.jp *(Spring8, Japan)*

K. UESUGI et al., *J. Synchr. Rad.* **13** (2006) 403-407

Fast tomography in Materials Science at the µm / sub-µm level by X-Ray µ-CT: *the current and in progress situation*

TOMOGRAPHY at SEVERAL Hertz for *in situ* HT° / straining / recrystallization / growth / matter (fluid) flow

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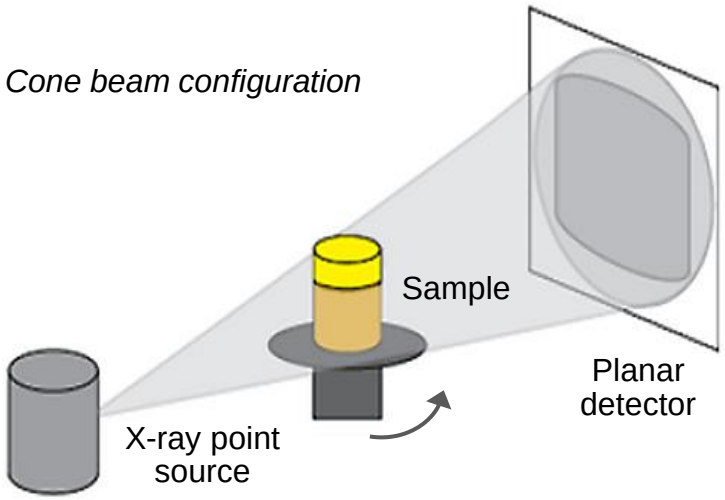
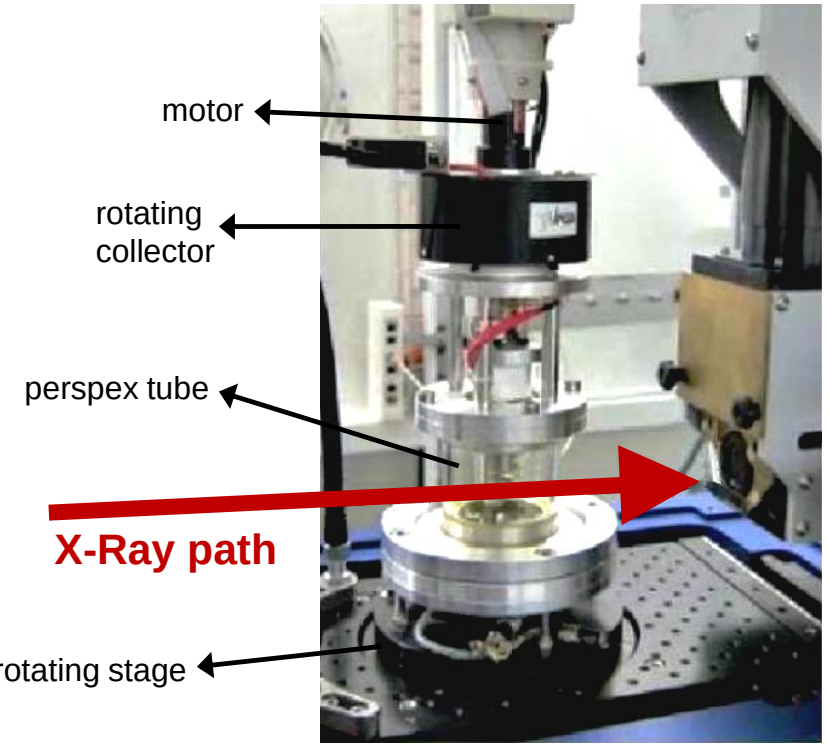


Tensile test (Al alloy)

10 rps (20 x 180° / s)



E. MAIRE et al., *Int. J. Fract.* (2016)

PAUL SCHERRER INSTITUT

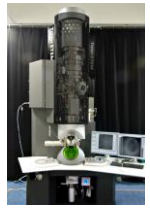
PSI

Fast tomography in Materials Science at the nm level in a TEM: *the current and in progress situation*

Bright Field CONTINUOUS ROTATION AND RECORDING ELECTRON TOMOGRAPHY in a FEW MINUTES

- **First attempts…** T. EPICIER et al., Prague IMC2014 (www.microscopy.cz/abstracts/2812.pdf)

TITAN ETEM FEI



www.clym.fr

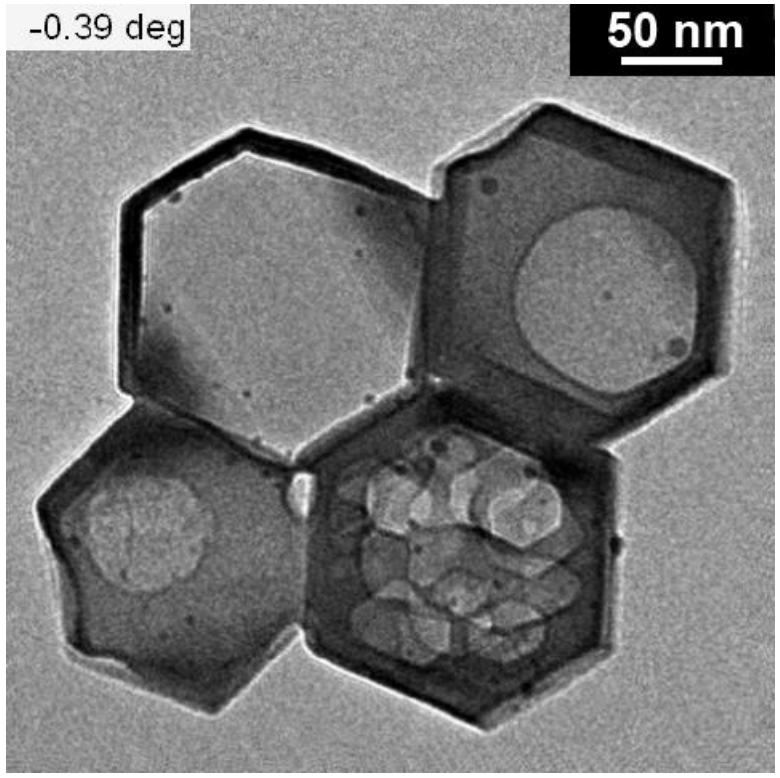
Manual continuous tilt from 78° to -38° in 3'40"

UltraScan 2K US1000XP-P Gatan CCD camera GATAN

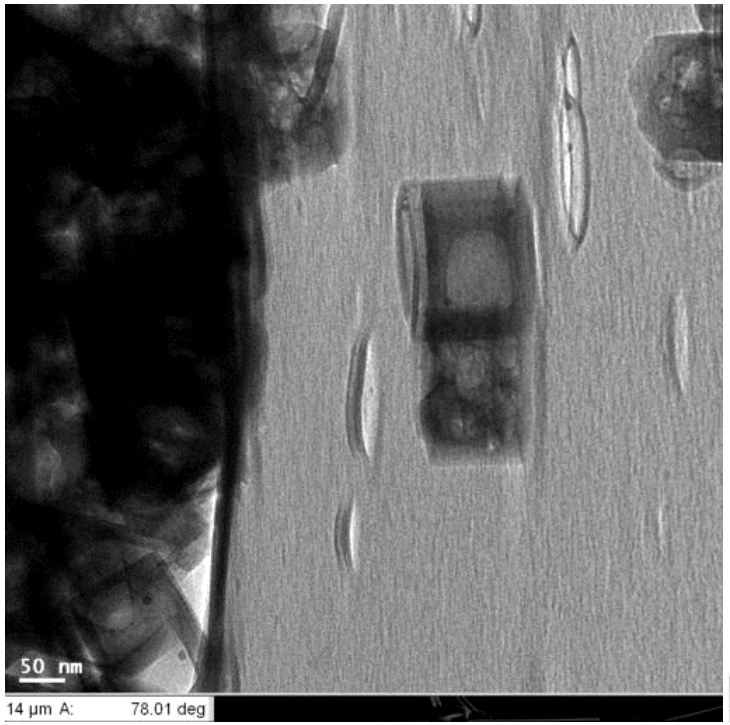
screen video capture

CamStudio

Ag@silicalites, High Vacuum at 20°C



328 *aligned* frames from a 1584 frames video sequence



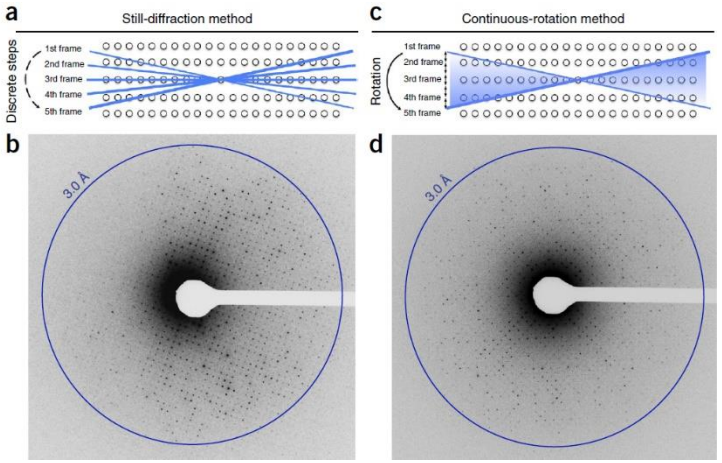
speed x20

Fast tomography in Materials Science at the nm level in a TEM: *the current and in progress situation*

Bright Field CONTINUOUS ROTATION AND RECORDING ELECTRON TOMOGRAPHY in a FEW MINUTES

- **Other applications in diffraction…**

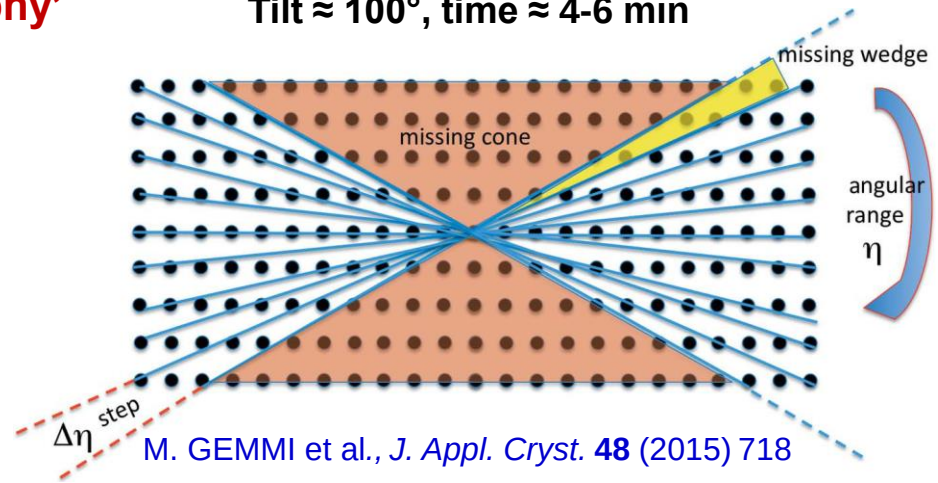
- continuous-rotation data collection in MicroED



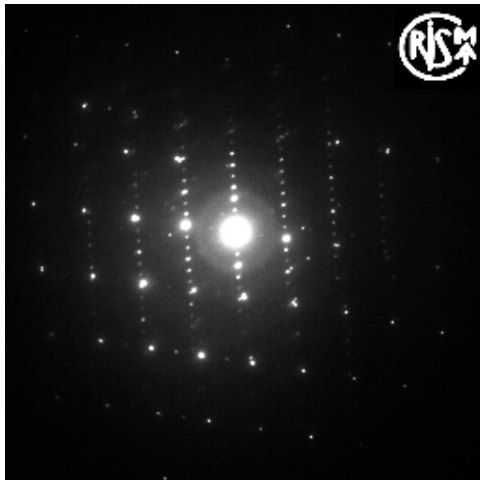
B.L. NANNENGA et al., *Nature Methods* **11** (2014) 927-930

- 'Fast diffraction tomography'

Tilt ≈ 100°, time ≈ 4-6 min



M. GEMMI et al., *J. Appl. Cryst.* **48** (2015) 718

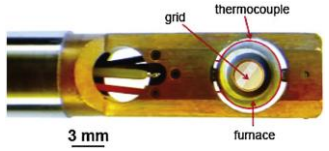


Courtesy Philippe Boullay, *ENSI Caen, F*

- **Other applications for *in situ* in Materials Science…**

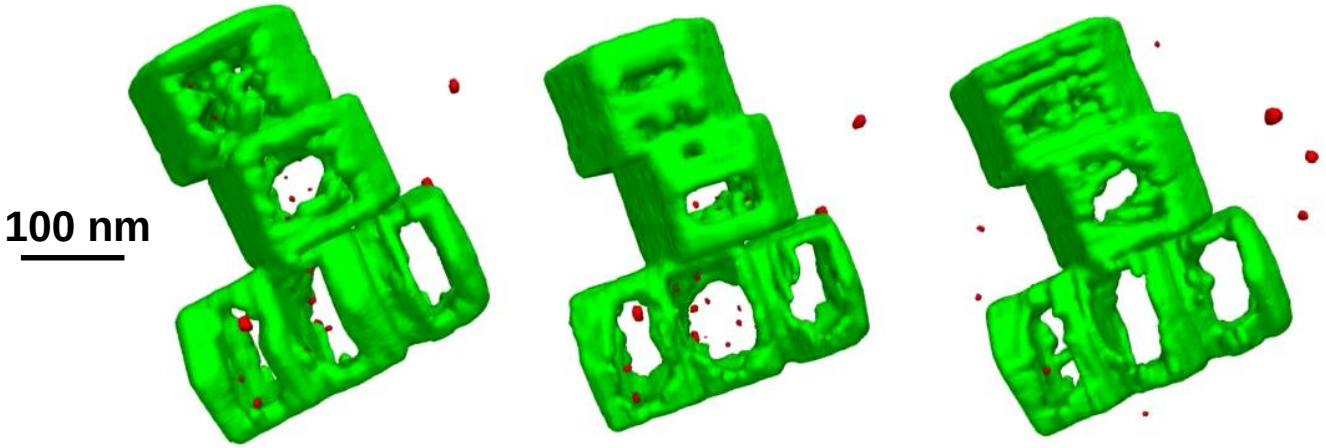
- Towards Operando ETEM:Calcination of Ag@silicalites nano-catalysts L. ROIBAN et al., *J. of Microscopy*, (2017)

***In situ* tilt series (-25° / +42°)**



Furnace based GATAN™ ***(900°C)***

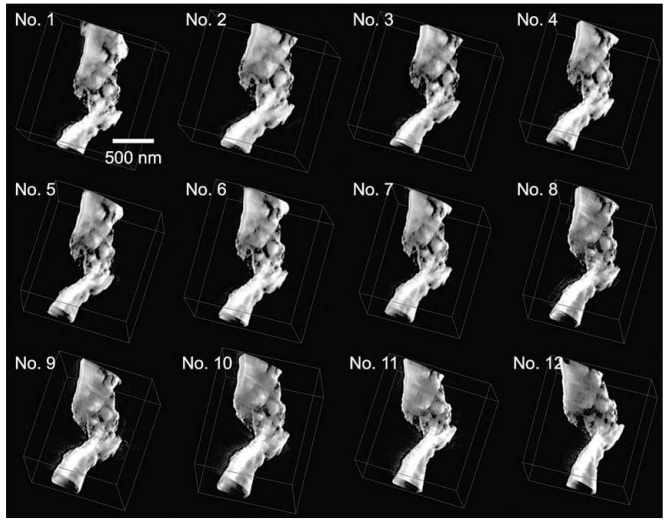
20°C, HV **280°C, 10^{-1} mbar O_2** **450°C, 10^{-1} mbar O_2**



Acquisition 2'01" ***1'46"*** ***1'56"***

- Towards in situ straining

Tilt up to ≈ ± 60°, time ≈ 2 min



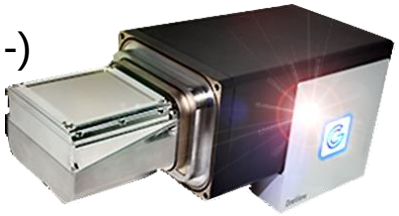
KYUSHU UNIVERSITY FACULTY OF ENGINEERING Mel-Build

S. HATA et al., *Microscopy* (2017) 143-153

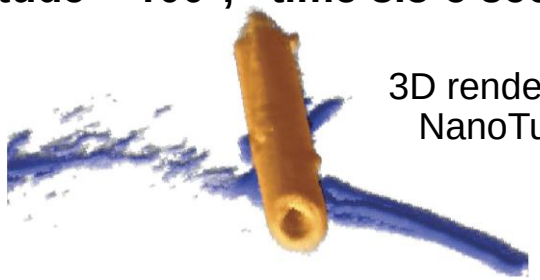
Development in progress; collaboration with **Research Center for Ultra High Voltage Electron Microscopy,** Osaka University
www.uhvem.osaka-u.ac.jp/en/what.html

- **Taking profit of FAST optimized CMOS or DIRECT ELECTRON detection cameras**

Oneview
(100 fps - 2K -)

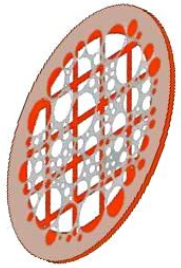


Tilt amplitude ≈ 100°, time 3.5-8 sec, frame acquisition time ≈ 1 µsec



3D rendering of a Carbon NanoTube on a C film

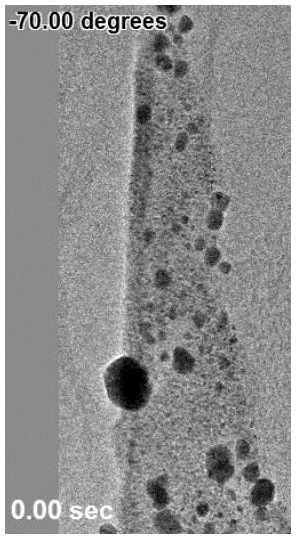
V. MIGUNOV et al., *Sci. Rep.*, **5** 14516 (2015)



Rotation angular amplitude: 2α	***140°***
Total acquisition time: t_{total}	***5 sec***
Angular rotation speed: $\omega = 2\alpha/t_{total}$	***28°/sec***
Number of frames per second: ***Fps***	***100***
Rotation blur / frame: $\Delta\alpha = \frac{2\alpha}{t_{total}.Fps}$	***0.28°***

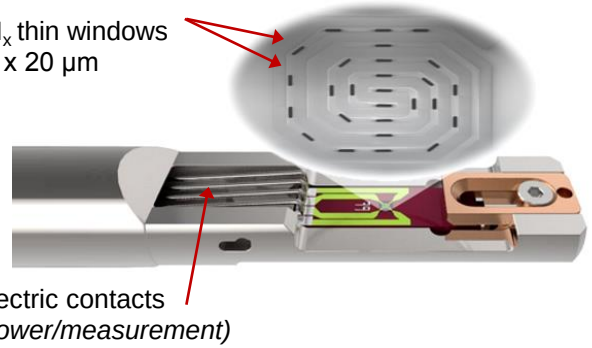
L. ROIBAN et al., *Microsc. Microanal.* **22** 5 (2016) 8

S. KONETI et al., *To be published*

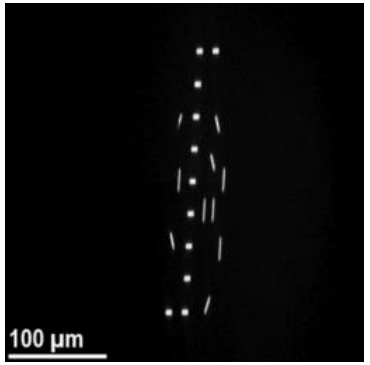


Au@TiO$_2$

tilt +70° / -70°,
time ≈ 5.2 sec.
2K, 513 images
$\Delta\alpha \approx 0.27°$/frame



MEMS-based heating holder Si/Pt/**SiN$_x$ nanochip 1300°C**
www.denssolutions.com

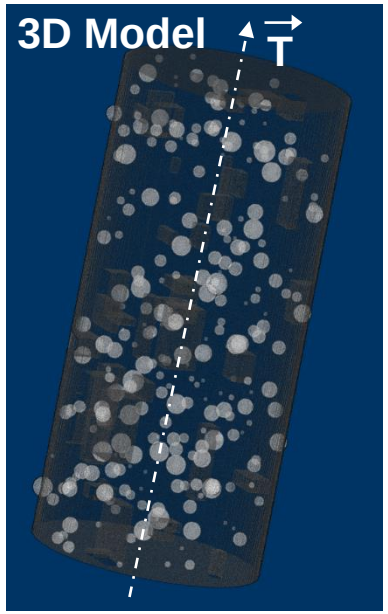


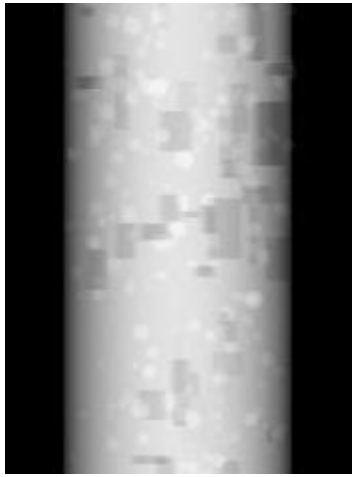
Wildfire™ S5 holder
±72° rotation

Continuous tilt and recording ET: *blur effects*

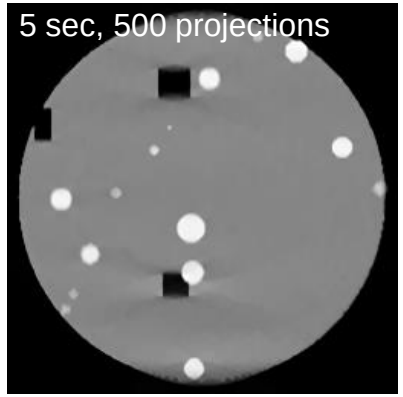
- **Evaluation of rotation-induced blur effects:** 2D and 3D ghosts approaches

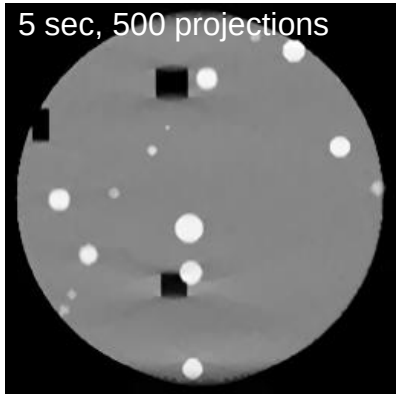
Rotation angular amplitude: 2α	*140°*	*140°*	*140°*	*140°*
Total acquisition time: t_{total}	*10 sec*	*5 sec*	*1 sec*	*0.3 sec*
Angular rotation speed $\omega = 2\alpha/t_{total}$	*14°/sec*	*28°/sec*	*140°/sec*	*467°/sec*
Number of frames per second: *Fps*	*100*	*100*	*100*	*100*
Rotation blur / frame: $\Delta\alpha = \frac{2\alpha}{t_{total}.Fps}$	*0.14°*	*0.28°*	*1.4°*	*4.7°*

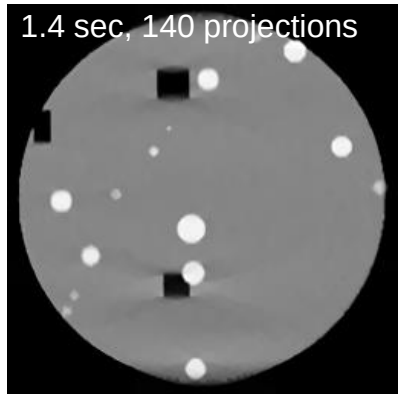


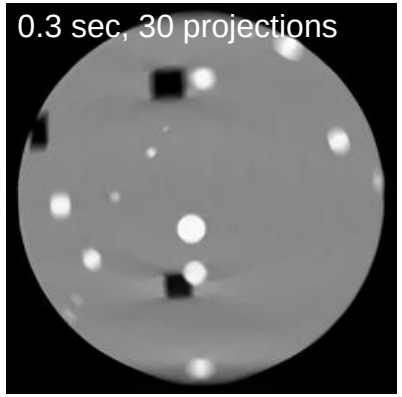


SIRT-based reconstructions

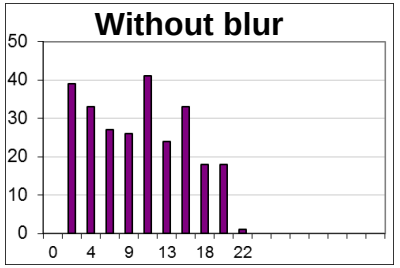


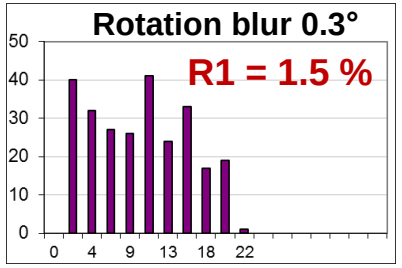


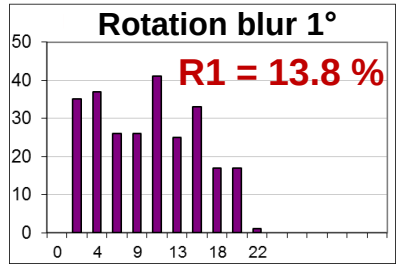


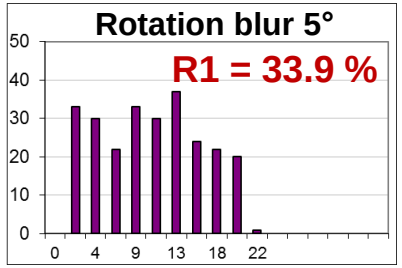


"NP" size histograms







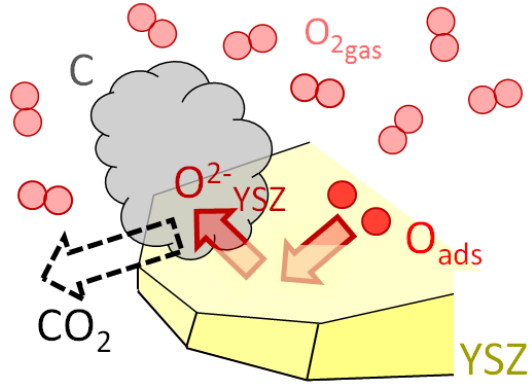


3D Operando electron tomography: soot oxidation on YSZ catalysts

- **Diesel motors**
  - **reducing the particulate emission *(~carbon soot)***
  - **Diesel Particulate Filter (DPF) : aims at burning the C particulates**

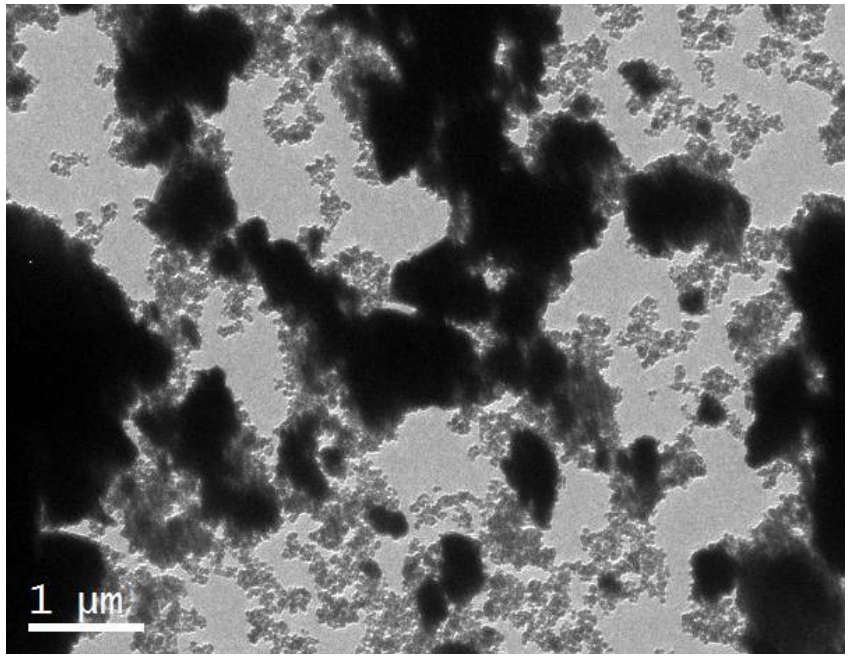
- **Use of ZrO_2 *(YSZ)* as a catalyst to promote an electrochemical oxidation** (like a fuel cell)

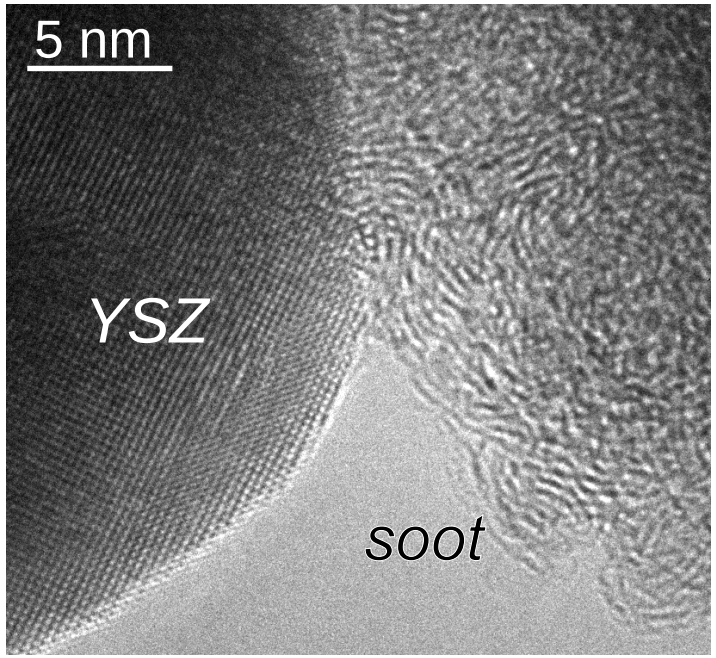
$$C + O_2 \rightarrow CO_2 \uparrow$$

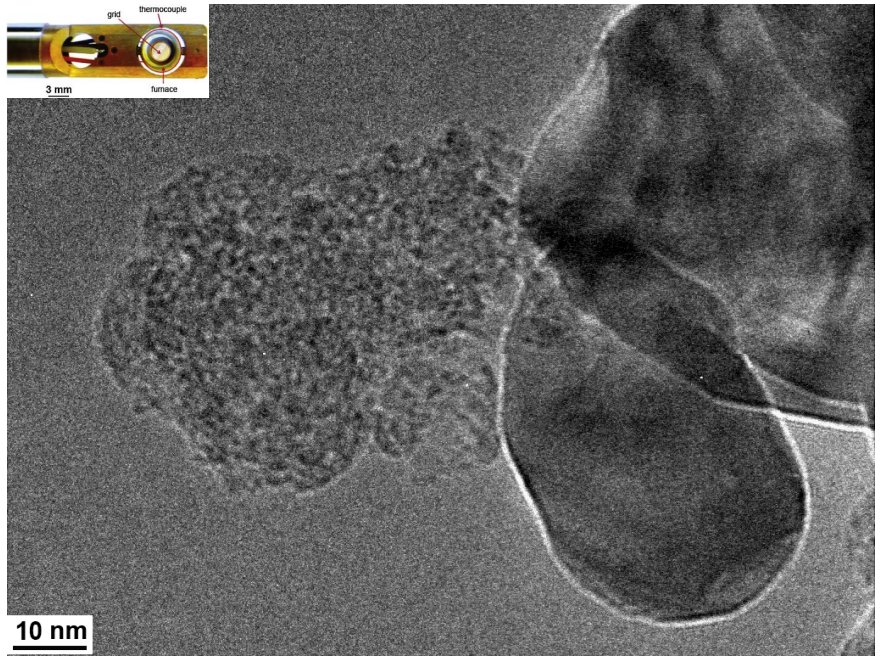


E. OBEID et al., *J. of Catalysis*, **309** (2014) 87-96; A. SERVE, *Appl. Catal. A*, **504** (2015) 74-80

T° = 495°C, 1.2 10^{-2} mbar O_2, 300 kV





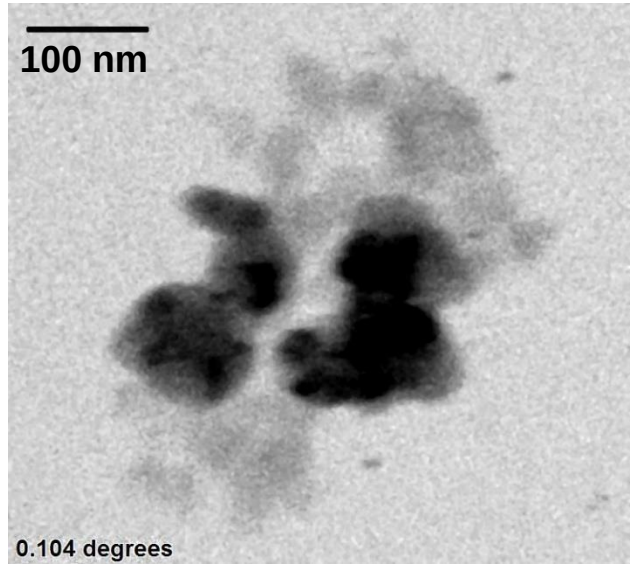


Thierry EPICIER, *Univ. Lyon*

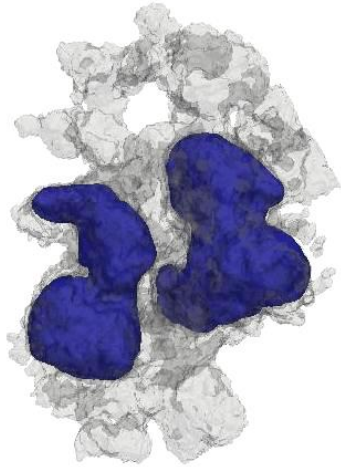
Speed x5, total time 4'13"

- **Test of continuous rotation and recording fast tomography under *quasi*-environmental conditions**

- T = 300°C, 5 10^{-5} mbar O_2
- Acquisition time: **5.1 seconds**
- Projections 2K, 100 fps
- Continuous tilt -69° to 71°, Wildfire S5 DENS solutions
- 309 ‘less-blurred’ aligned projections sorted out of 507



True speed, total time 5.1"



- Reconstruction 1024^3 Voxels

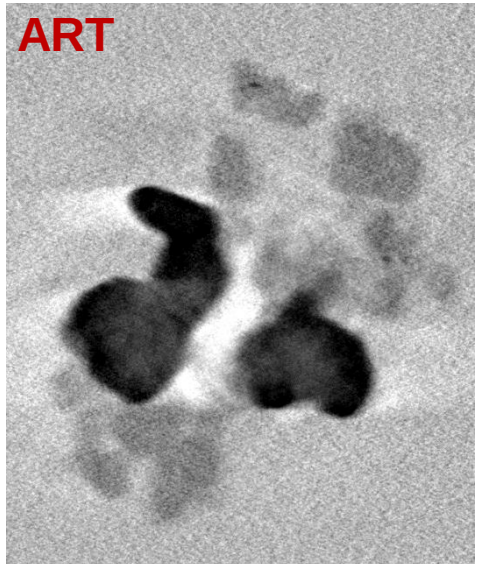
SIRT-FISTA-TV H. BANJAK et al, *to be published*

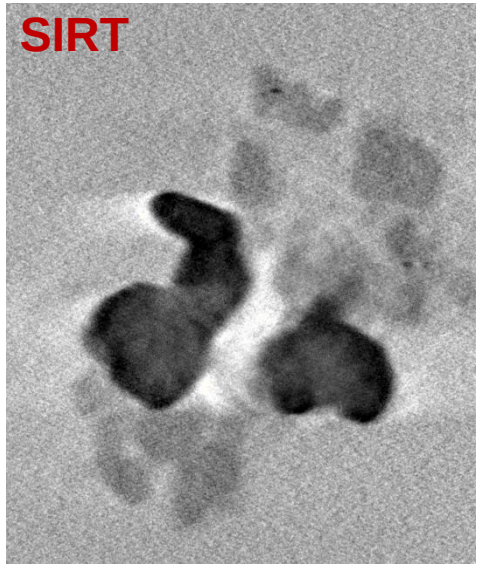
***TV**-minimization*

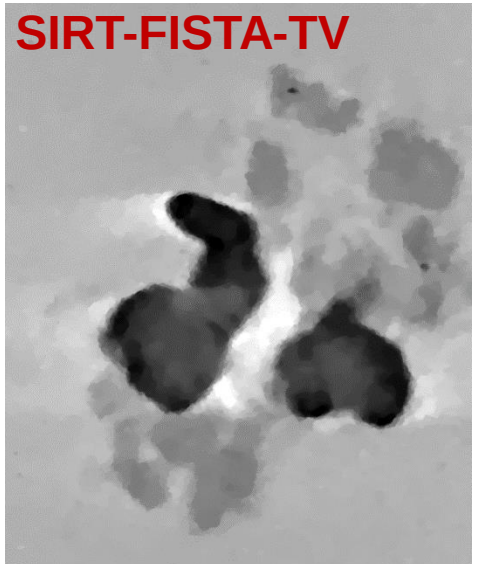
E.Y. SIDKY, X. PAN, *Phys. Med. Biol* **53** (2008) 4777

***FISTA** acceleration*

A. BECK, M. TEBOULLE, SIAM JIS **2** 1 (2009) 183)







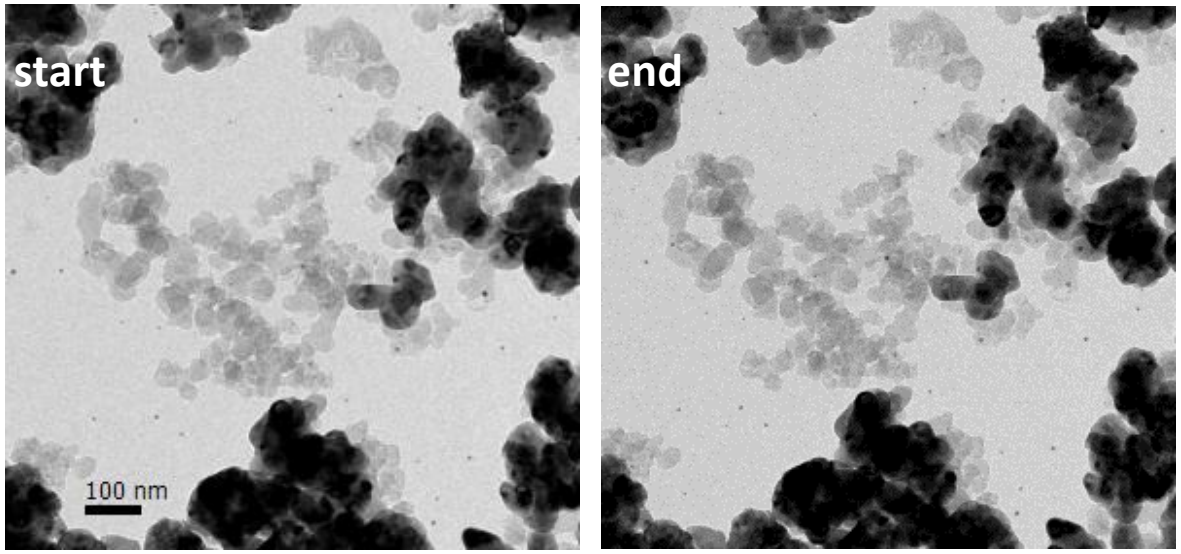
- **Towards 3D kinetic studies…**

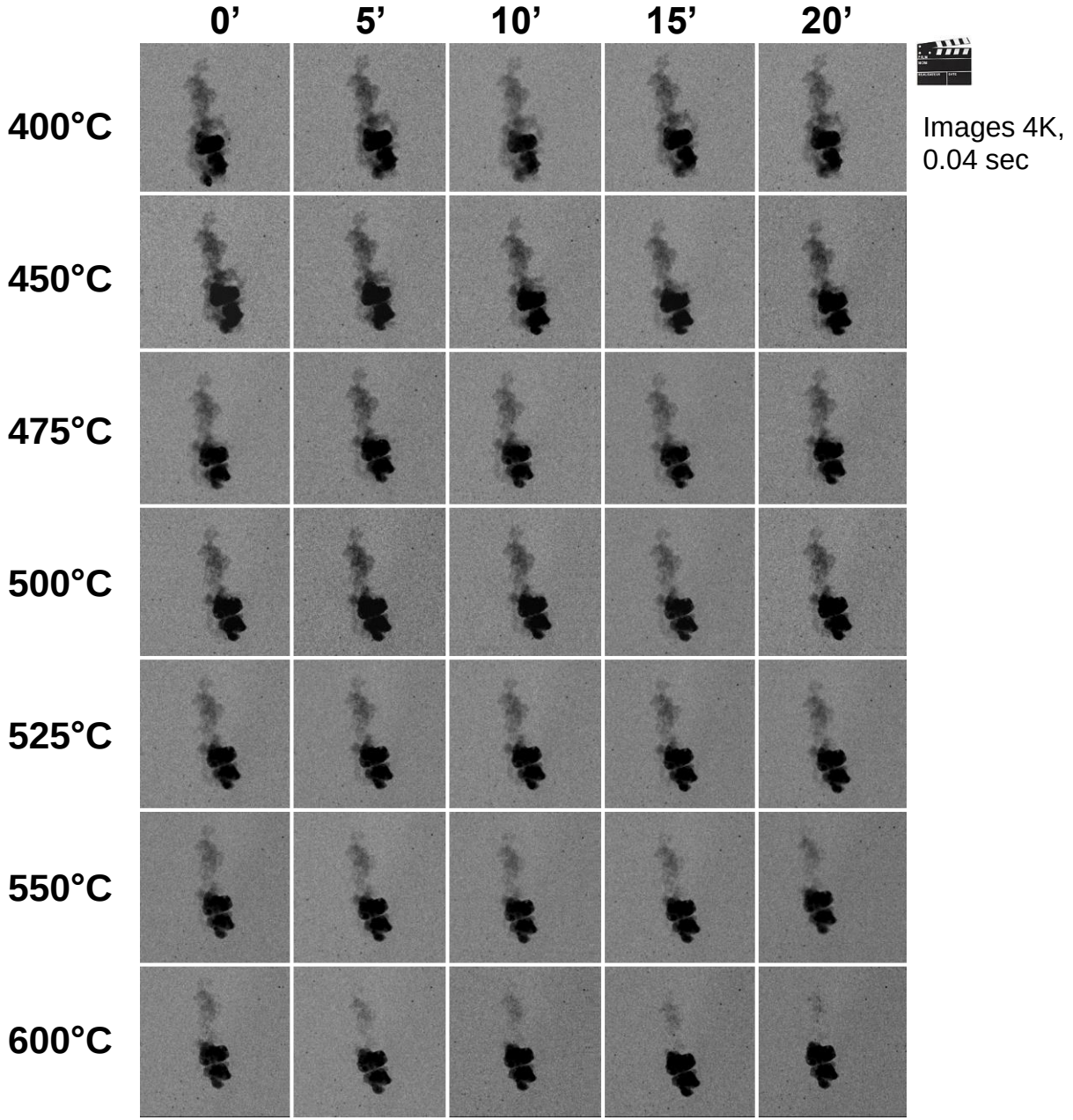
Activation energy of soot combustion on ZrO_2 in oxygen (ETEM 1.7 mbar)

Arrhenius plot $SPEED_{combustion} = S_0 \exp(-\Delta G/RT)$

Irradiation time ≈ 2 h 45 min
flux 1.7 $e^-.Å^{-2}.s^{-1}$, **total dose 1.7 10^4 $e^-.Å^{-2}$**

Irradiation test 5 min
flux 56 $e^-.Å^{-2}.s^{-1}$, **total dose 1.68 10^4 $e^-.Å^{-2}$**





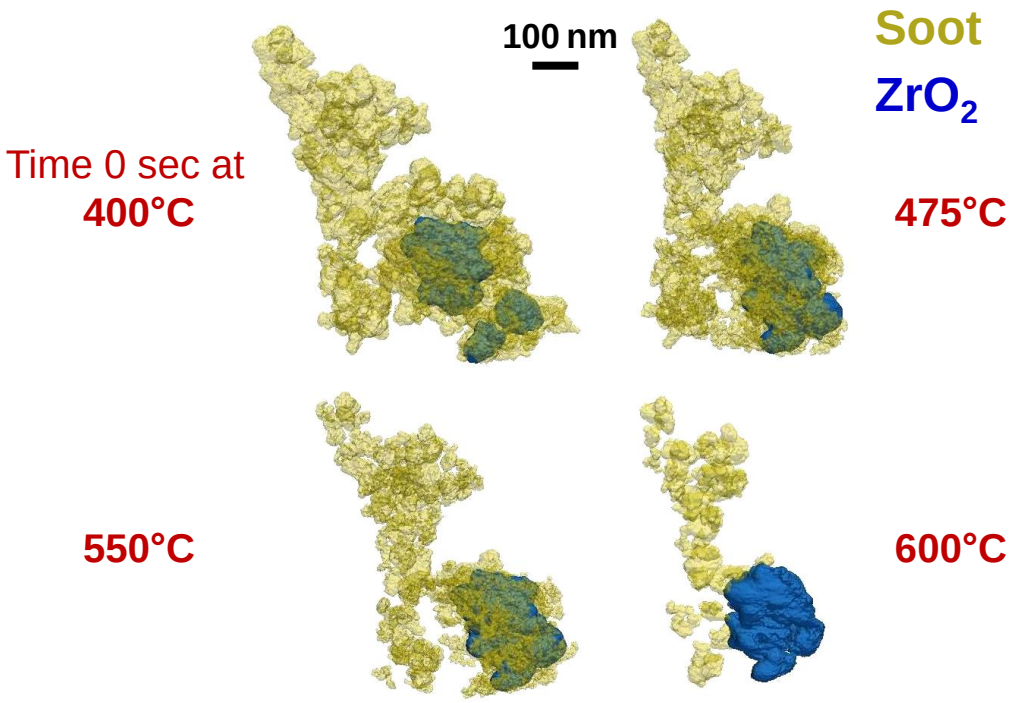
Images 4K, 0.04 sec

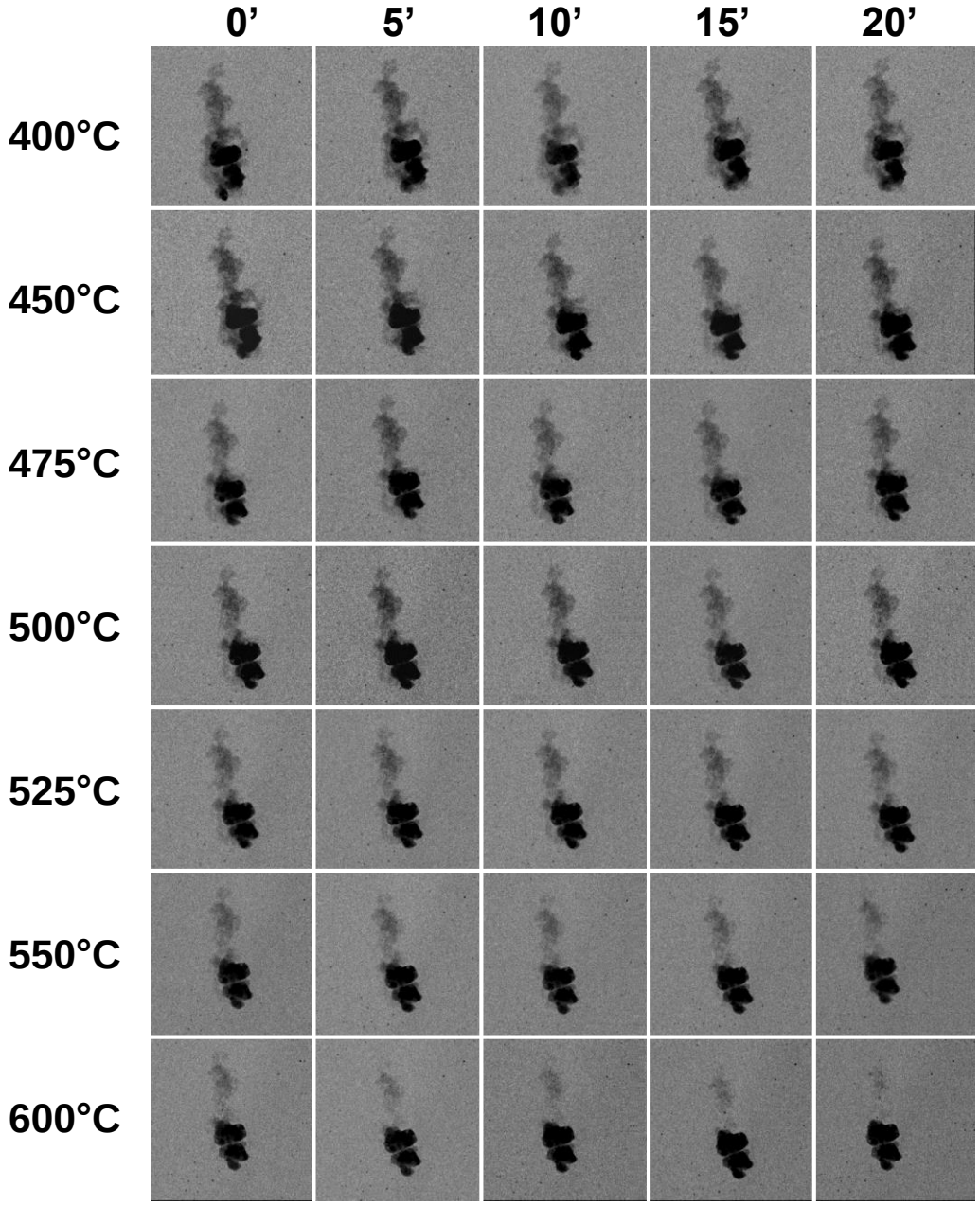
- **Towards 3D kinetic studies…**

Activation energy of soot combustion on ZrO_2 in oxygen (ETEM 1.7 mbar)

Arrhenius plot $SPEED_{combustion} = S_0 \exp(-\Delta G/RT)$

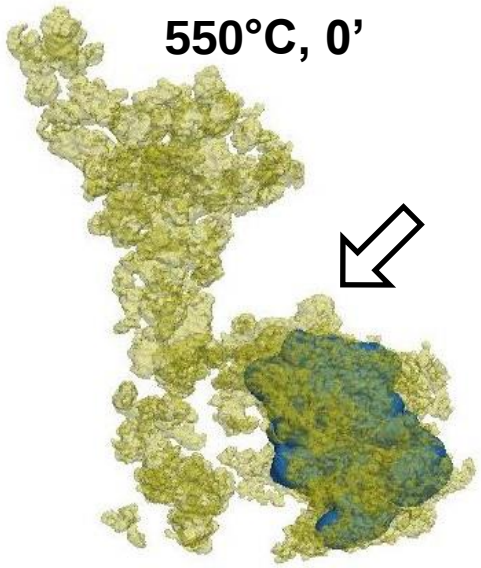
Tilting series +70° to -71° in 130'', one tilt series every 5' at **400°C, 450°C, 475°C, 500°C, 525°C, 550°C, 600°C under 1.7 mbar O_2** *(total 35 tilt series ≈ 2h45, irradiation controlled)*

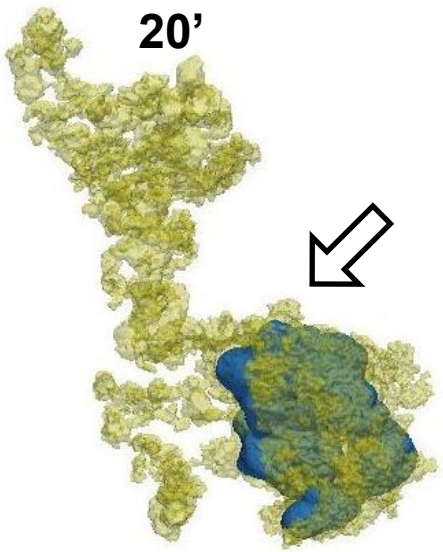


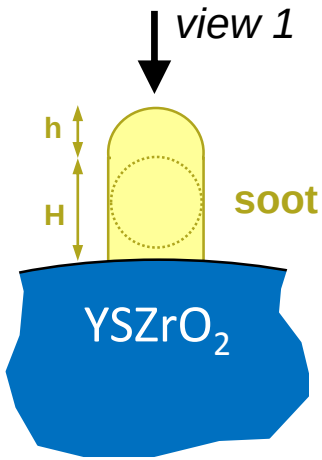


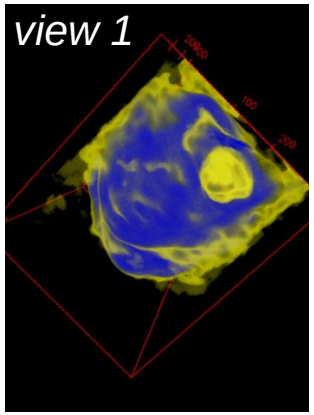
Images 4K, 0.04 sec

- **Soot on YSZ: 3D ETEM 400-550°C, 1.7 mbar O_2**

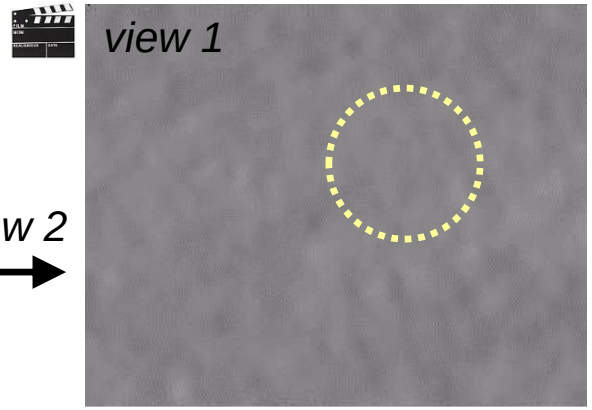




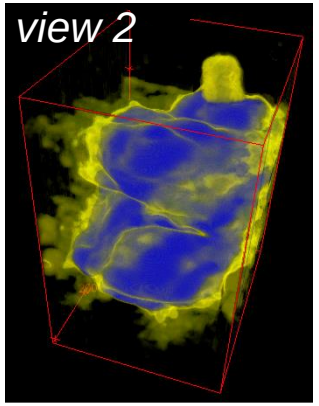




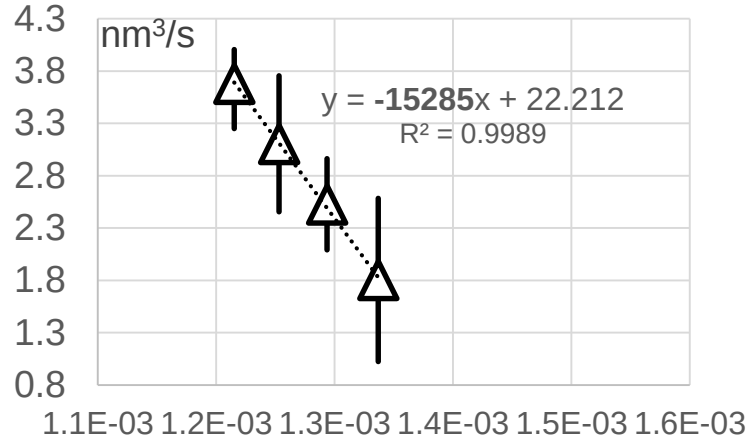
525°C, 0'



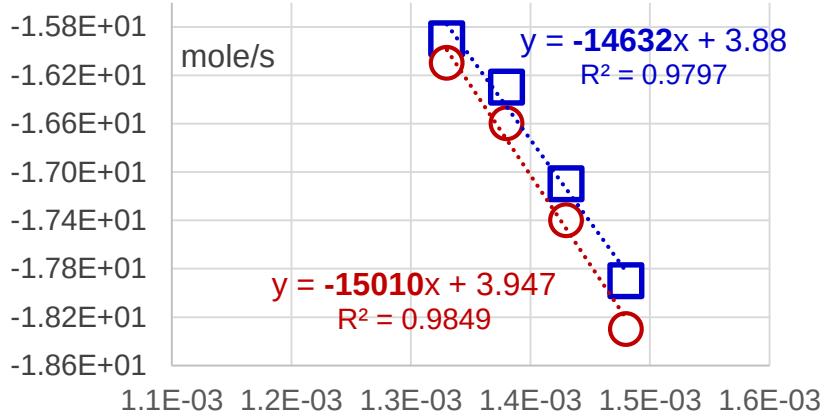
view 2



Burning Speed of Soot 'in contact' (ln(V) vs. 1/T)



CO_x production (IR spectroscopy / Micro-chromatography (ln(V) vs. 1/T)



ΔG ≈ 127.1 kJ/mole (*IR* 121.7, *MC* 124.8)

Soot oxidation below 527°C: 148 kJ/mole

H. Jung et al., *Combustion and Flame* **136** (2004) 445-456

Burning of Carbon black on Ceria: 133 kJ/mole

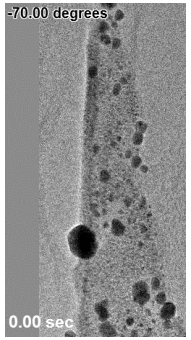
S.B. Simonsen et al., *J. Catalysis* **255** (2008)

Thierry EPICIER, *Univ. Lyon*

Conclusions and perspectives

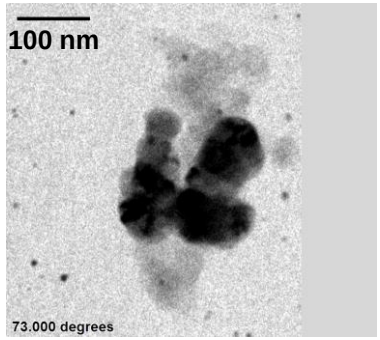
- **Bright Field TEM Electron Tomography is possible down to the few seconds range owing to fast CMOS and direct electron cameras**

NPs Au @ TiO_2, 20°C
High Vacuum
(deposition at 400°C)
P. VAZ et al., (2016)



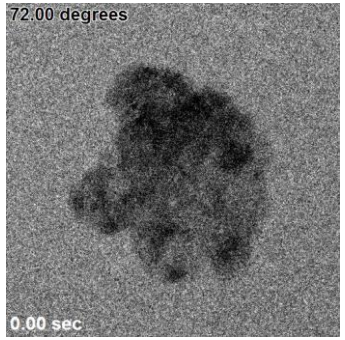
tilt series -70° / +70°,
Total time ≈ 5.2 sec.
2K, 513 images
$\Delta\alpha \approx 0.27°$/frame

Soot @ YSZ (ZrO_2),
5 10^{-5} mbar O_2, 300°C



tilt series +73° / -70°,
Total time ≈ 5.3 sec.
2K, 527 images
$\Delta\alpha \approx 0.27°$/frame

Pd @ δ-Al_2O_3,
600°C 0.4 mbar H_2
(after 20 min)

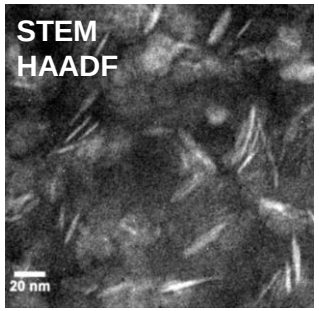


tilt series +72° / -79°,
Total time ≈ 3.4 sec.
2K, 338 images
$\Delta\alpha \approx 0.45°$/frame

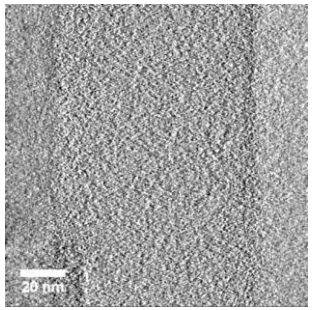
- **Rotation blur due to continuous rotation during video recording is not *strictly speaking* a limiting factor**

- **Even at a 1 or 2 minute(s) level, fast approaches offer advantages for beam sensitive samples (e.g. polymers) and to follow kinetics especially in the Environmental TEM**

POLYMER NANOCOMPOSITE:
Mg_3AlCO_3 Layer-**D**ouble **H**ydroxide **nanoplatelets in** P(MA-co-BA) **latex**



+70 to -70°,
Total time 200 sec.
(2K images, 0.2 sec,
total electron dose
≈ 2.4 10^4 $e^-/Å^2$ *validated by an irradiation test*)



3D model (Mg_3AlCO_3 LDH nanoplatelets)

F. DALMAS et al., *16th EPF Europ. Polymer Fed. Congress*, July 2017

- **Improvement of the goniometer rotation speed and stability is needed to achieve *sub-second* time resolution**

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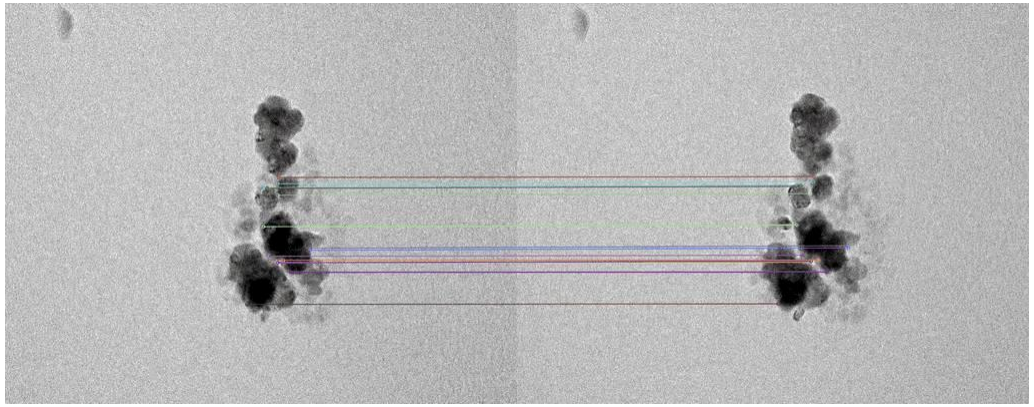
- **Voichita MAXIM, Thomas GRENIER, Khahn TRAN,** *CREATIS, INSA-Lyon*



Frame n Frame n+1

- ANR project ‘3DCLEAN’ n°15-CE09-0009-01, LabeX ‘IMUST’ University of Lyon
- GATAN