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Investigations of soot combustion on Yttria-Stabilized Zirconia by Environmental Transmission Electron Microscopy (ETEM)

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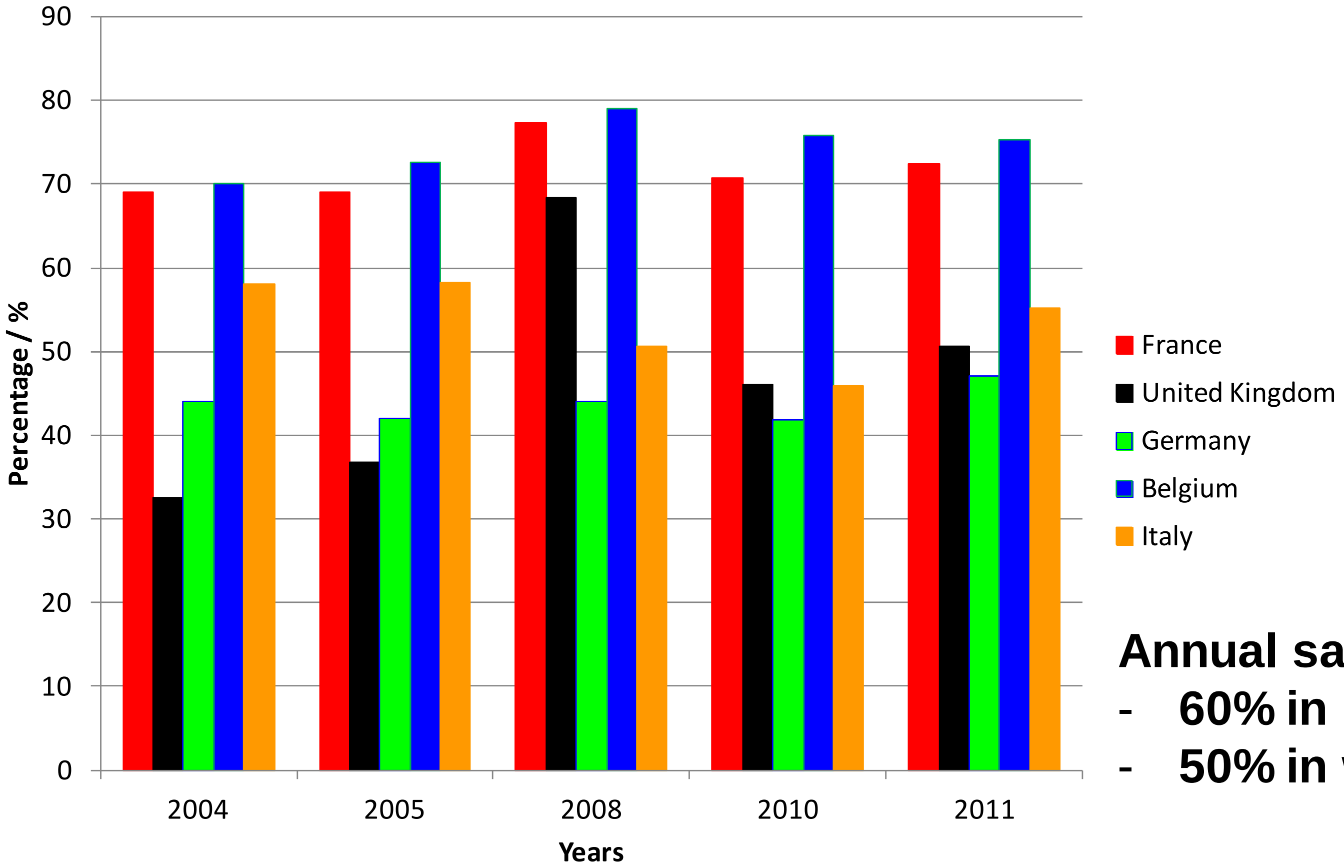
Important market share of Diesel cars in Europe



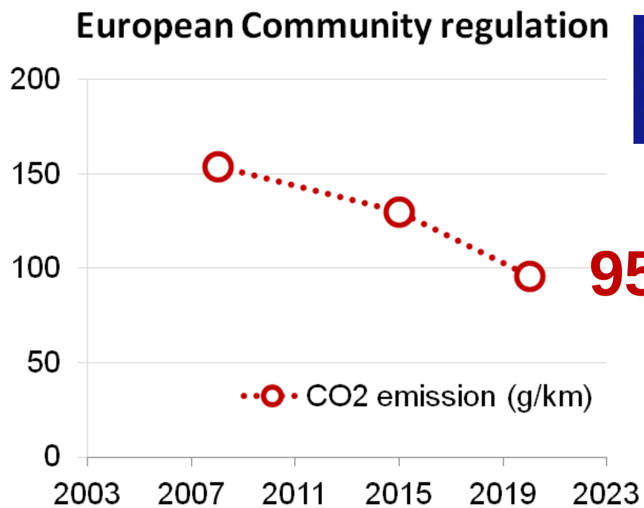
Annual sales of new Diesel cars:

- **60% in France,**
- **50% in western Europe.**

Comité des Constructeurs Français d'Automobiles in *Tableau de bord automobile*, *Vol.* http://www.ccfa.fr/Tableau-de-bord-automobile, **2004, 2005, 2008, 2010, 2011**

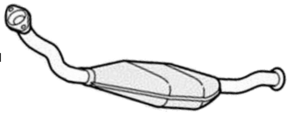
- **Diesel cars reduce the fuel consumption**

  – Participate to the CO_2 emission reduction:



95 g CO_2/km in 2020

- *But* **Diesel engines emit Particulate Matter**



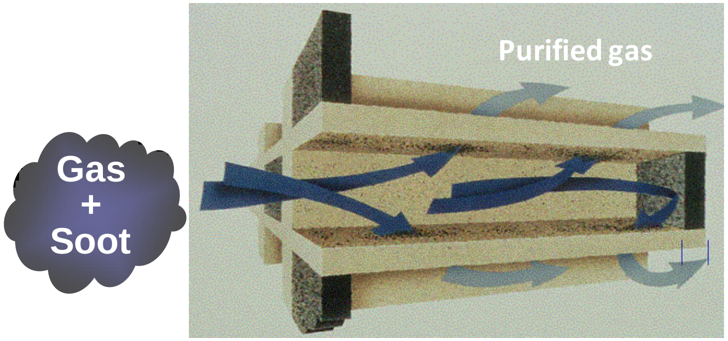
  – from 2014 *(Euro 6)*: PM emission limitation expressed in number of particulates besides mass!

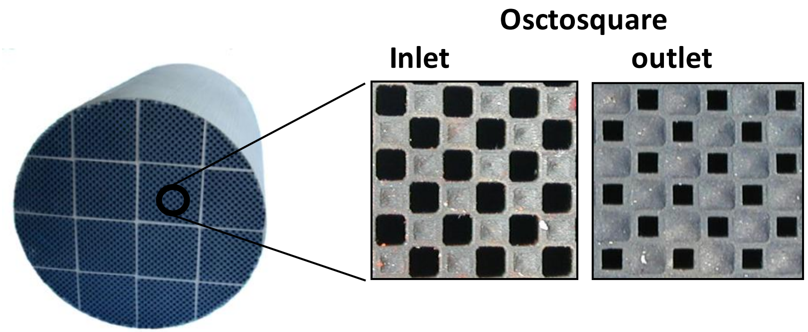
  6 10^{11} part/km *and* **4,5 mg/km in 2014**

  – PM abatement is OK but a continuous improvement of the global system is still required

Diesel Particulates Filters (DPF)

- From 2000 in France
- From October 2010: mandatory in all new Diesel cars *(EURO 5)*
- DPF, ceramic structures (cordierite, SiC) with:
  - alternately plugged channels at the inlet and outlet
  - porous filtering walls
- High filtering efficiency
- Need a regeneration: fuel post-inject ion (exhaust gas temperature increase)
- Regeneration = fuel over-consumption

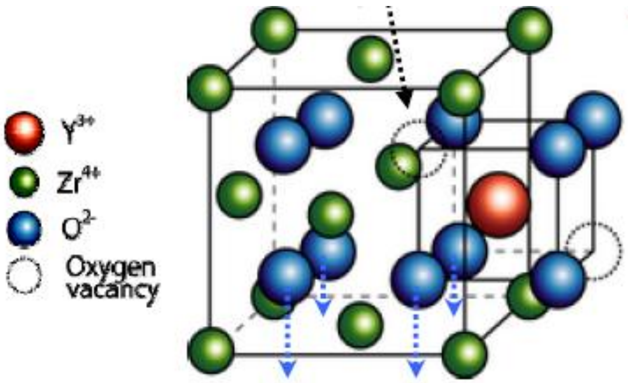


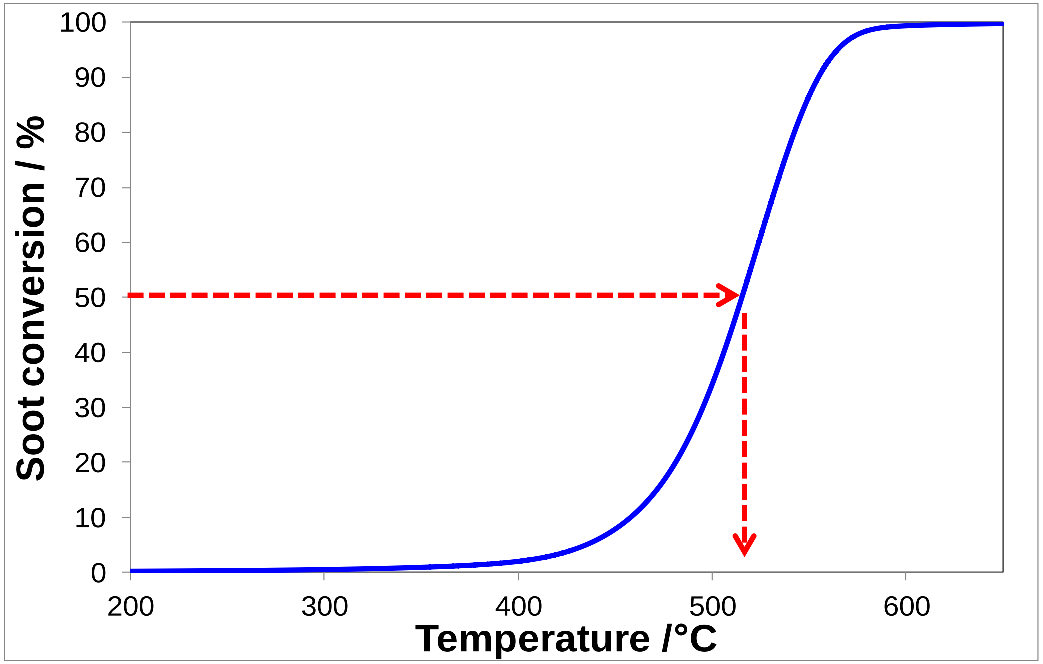


The aim: **produce a self regenerating DPF**

Yttria-Stabilized Zirconia (YSZ)

- High chemical and thermal stability (used as electrolyte in SOFCs)
- Fluorite structure
- No redox properties
- Bulk ionic oxygen conductivity
- YSZ Tosoh (13 m²/g) : $(ZrO_2)_{0.92}(Y_2O_3)_{0.08}$





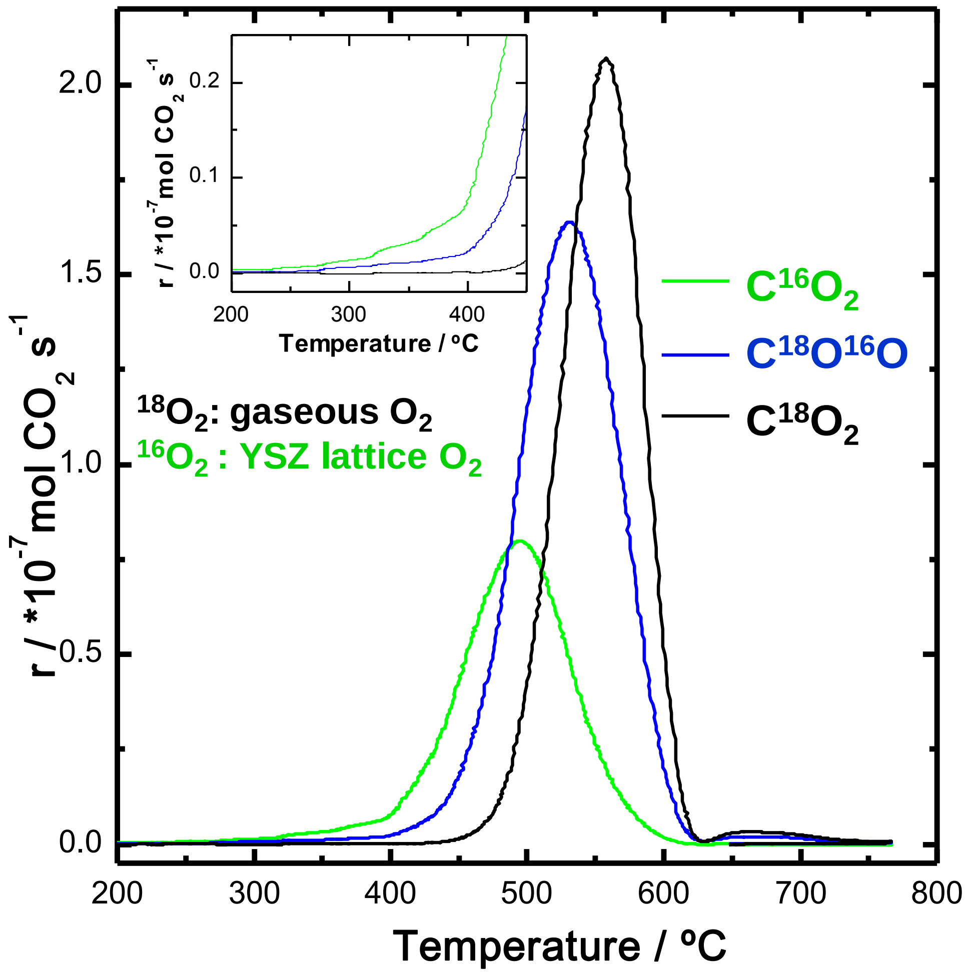
YSZ can oxidize soot

T50 = 680 °C soot without catalyst

T50 = 500 °C on commercial catalyst (Pt / $CeZrO_2$)

T50 = 520 °C on YSZ

Patent WO 2011098718 (A1),
G. BLANCHARD, S. ROUSSEAU, L. MAZRI, L. LIZARRAGA, A. GIROIR-FENDLER, B. D'ANNA, P. VERNOUX



E. OBEID et al., *Journal of Catalysis*, **309** (2014) 87-96

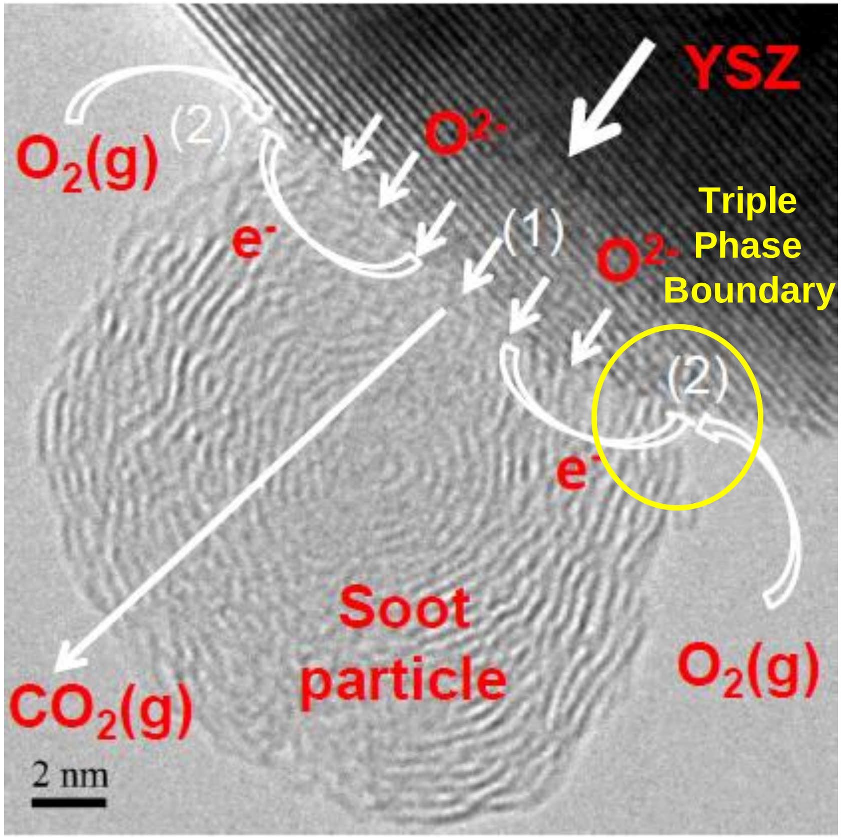
Soot oxidation starts from 270°C

Below 400°C, $C^{16}O_2$ is the only one product.

60% of O atoms in the overall CO_2 production are coming from the YSZ bulk

YSZ lattice oxygen species are clearly involved in the ignition of the soot oxidation process

Fuel-cell type electrochemical oxidation process



Soot: reactant and current collector

1. Electrochemical oxidation of soot:

$C + 2\,O^{2-}{}_{YSZ} \rightarrow CO_2 + 4\,e-$ (though the soot)

2. Electrochemical reduction of oxygen:

$2\,O_{ads} + 4\,e-$ (through the soot) $\rightarrow 2\,O^{2-}{}_{YSZ}$

ElectroMotive Force induced between the anode (soot / YSZ interface) and the cathode (TPB: O_2 / YSZ / soot)

Two key parameters:

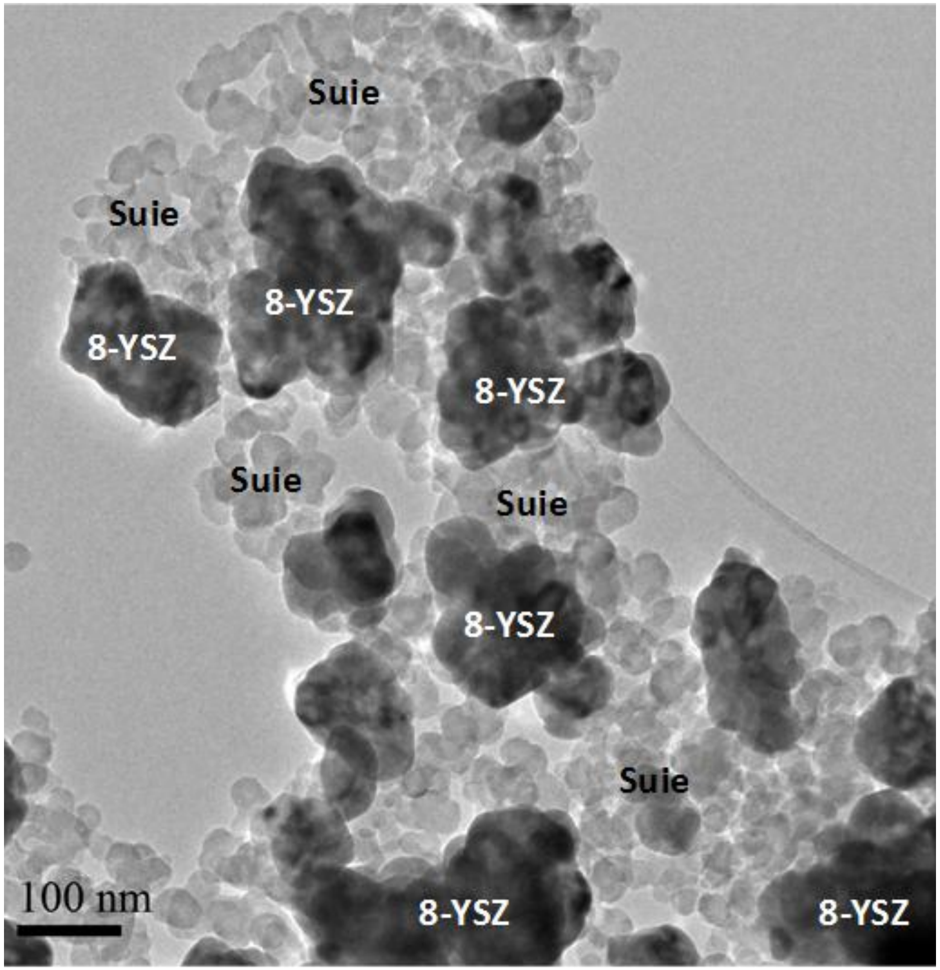
- **The oxygen partial pressure in the gas phase (EMF)**
- **The contact surface between soot and YSZ**

⇩

ETEM experiments to confirm the importance of the soot / YSZ contact points

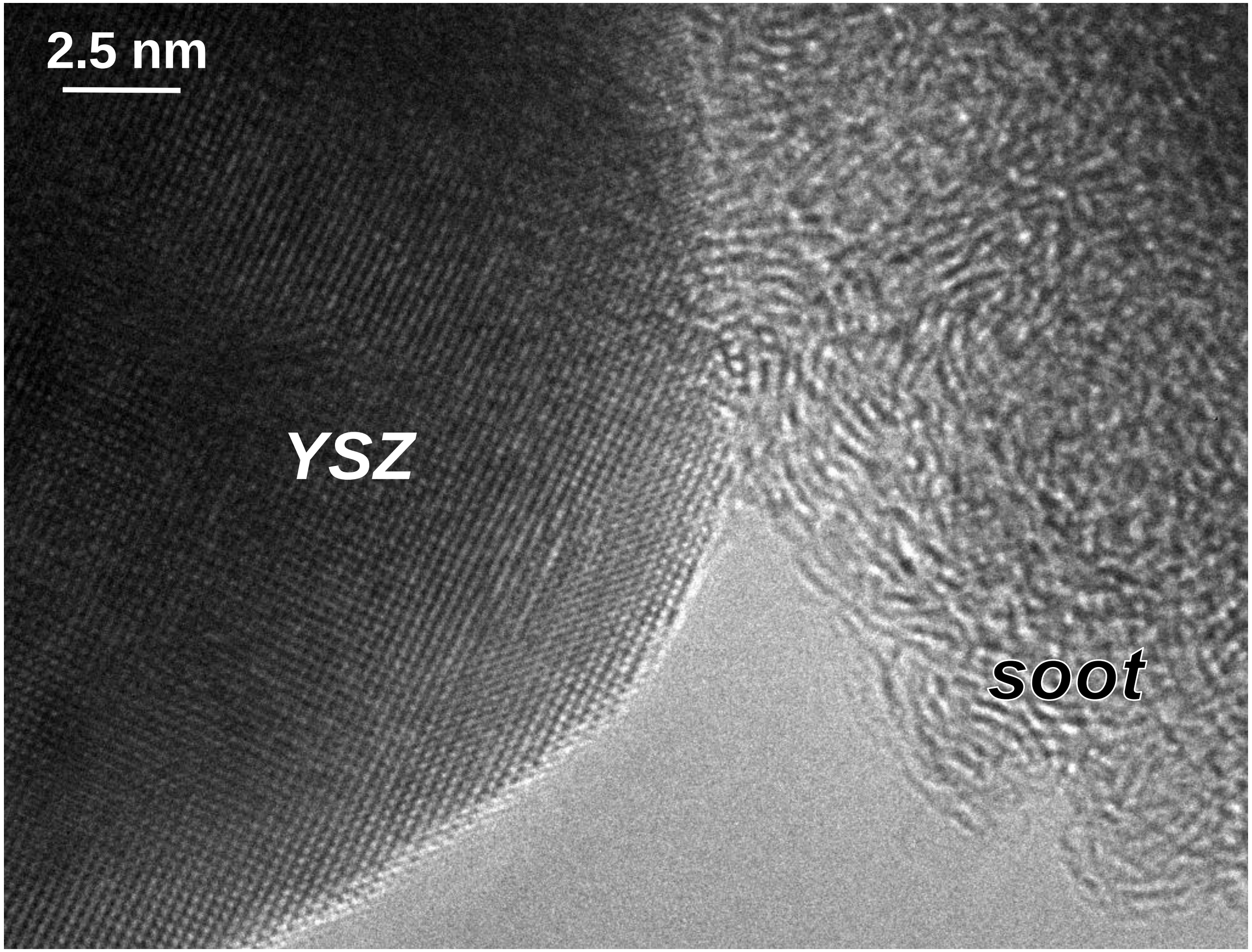
SOOT production

- Soot produced with a CAST burner (propane/air flame, O_2/propane = 5.16)
- Specific surface area: 140 $m^2\ g^{-1}$
- Mixture between collected soot and YSZ powder:
  - YSZ/soot = 4/1 (weight ratio)
  - Crushed in a mortar for 15 min



SOOT production

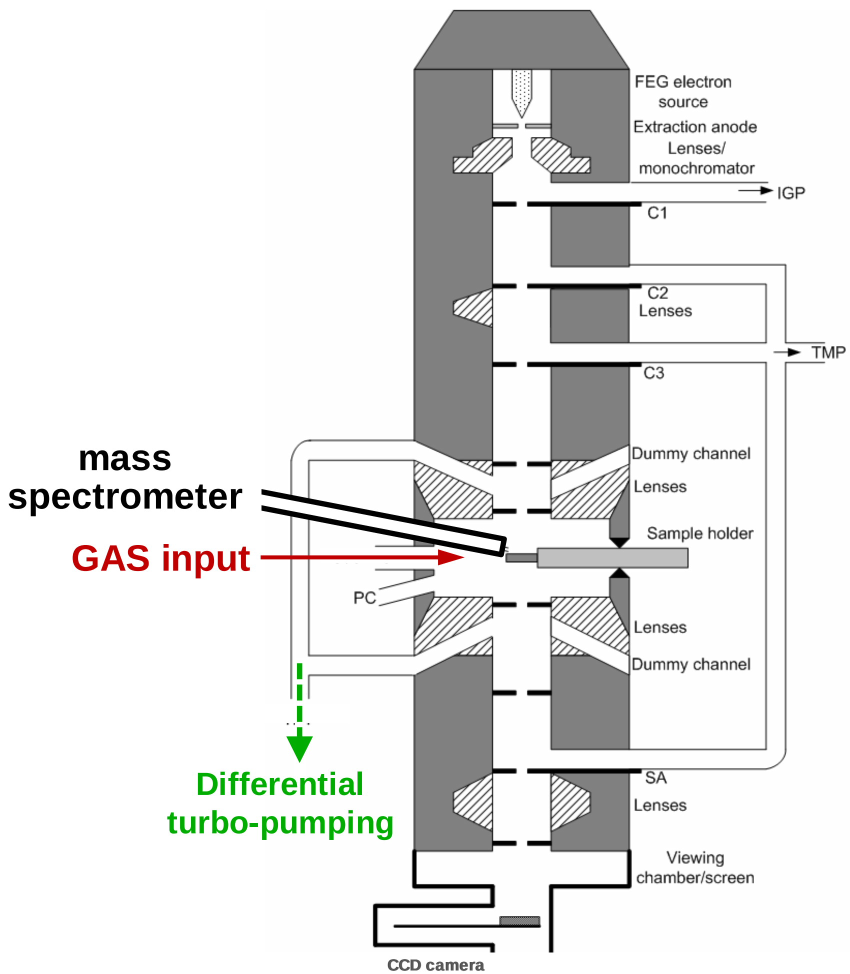
- Tight contact between soot particulates and YSZ grains

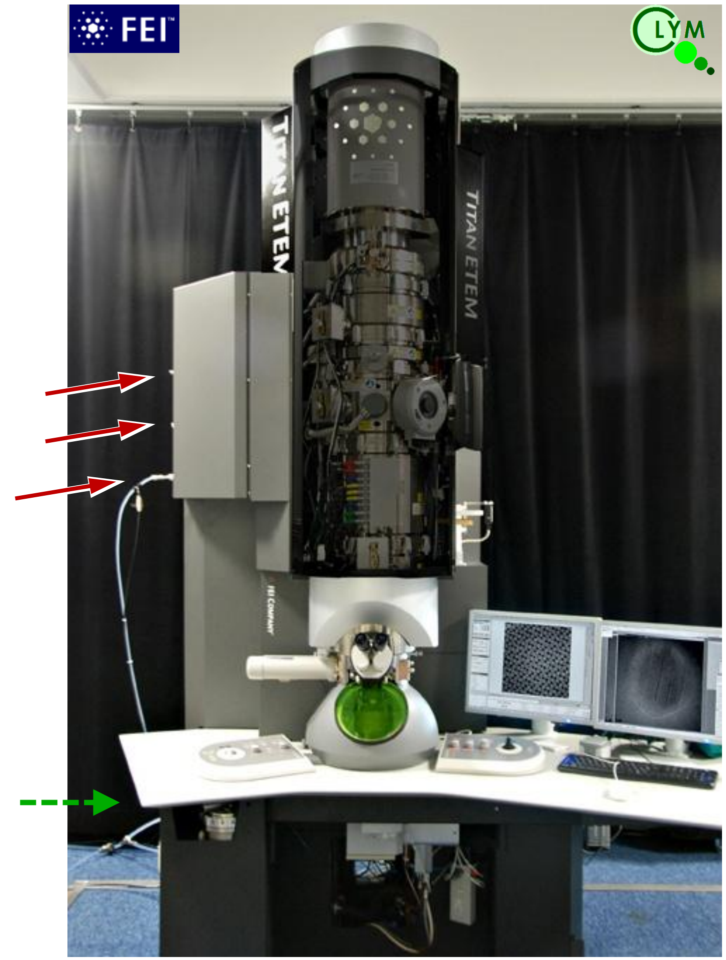


The Environmental TEM (ETEM) setup

ETEM: FEI TITAN 60-300 kV with an objective C_s aberration corrector

$P_{gaz} \leq$ 23 mbar, T ≈ 1000°C, HRTEM info limit = 0.085 nm, STEM resolution STEM = 0.13 nm





www.clym.fr

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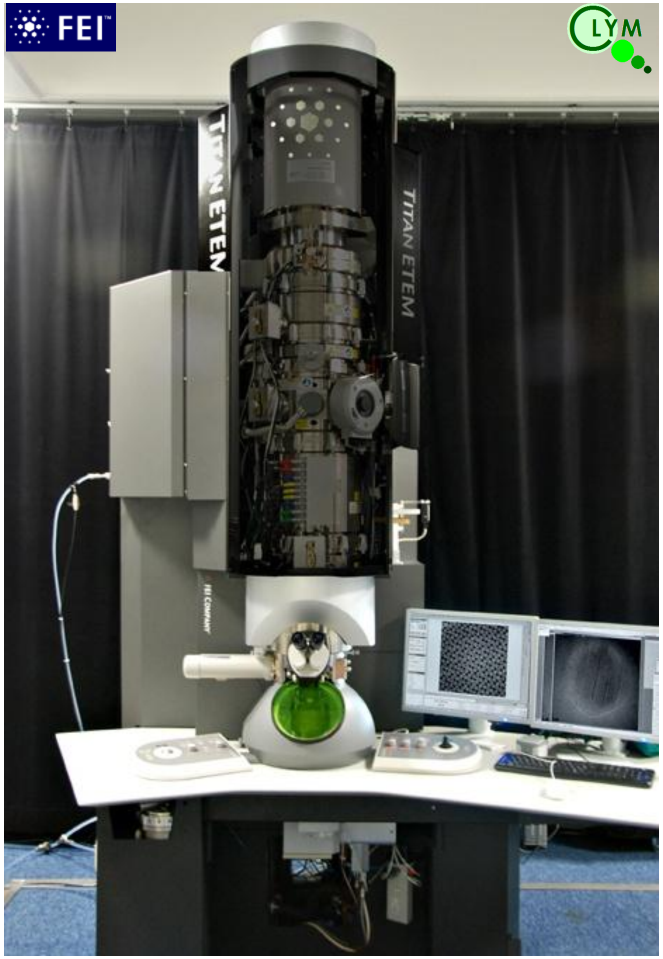
- Mixed soot/YSZ powders mounted on Titania grids with *or* without supporting film (C, SiO_x)
- Inconel heating TEM sample holder
- Pure Oxygen gas introduced up to 3 mbar and up to 550°C
- Observations performed at 300 kV *and* 80 kV (irradiation effects) with *and* without 'BEAM ON'



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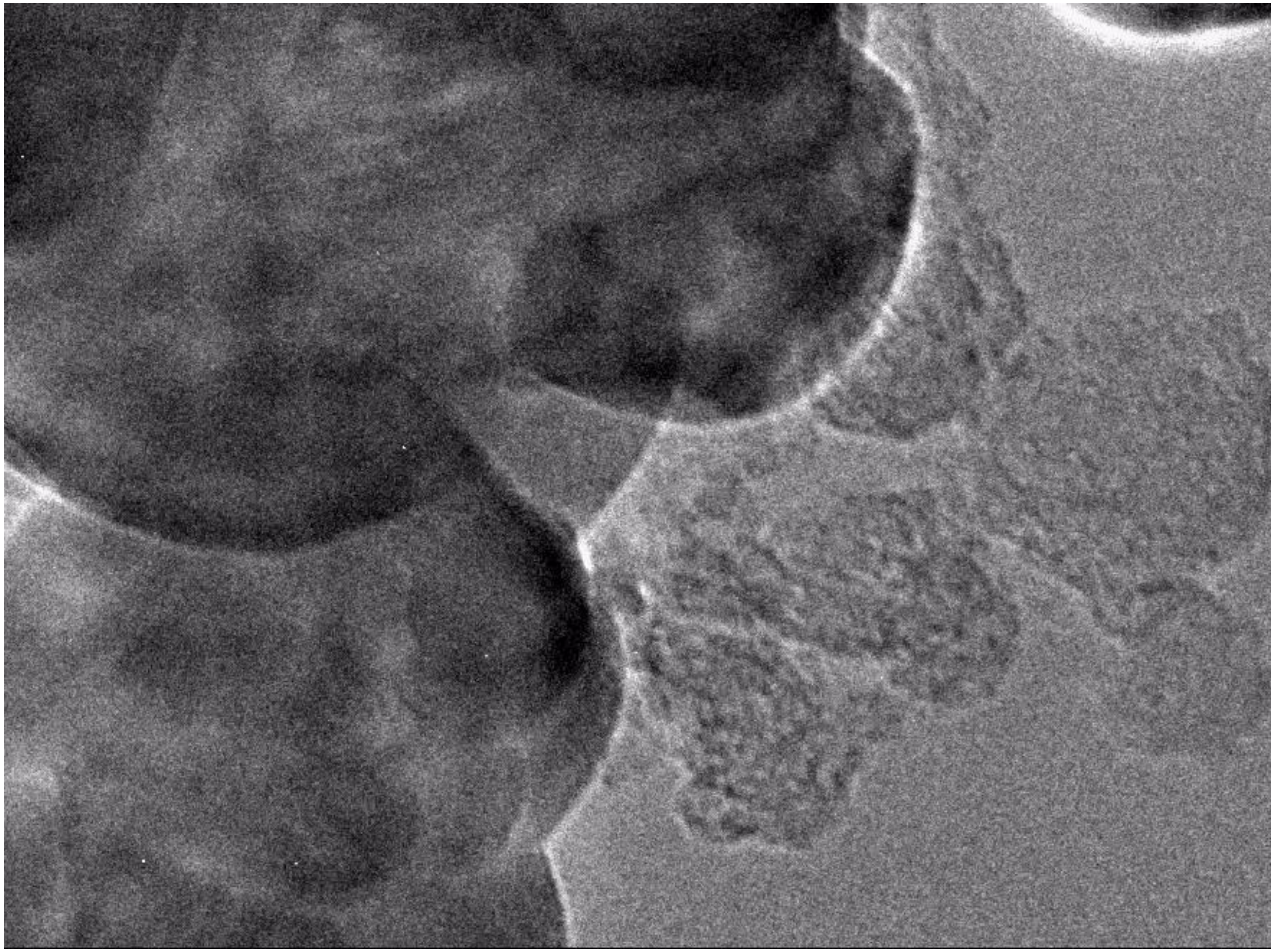
T° = 425 ± 25°C, 2 mbar O_2

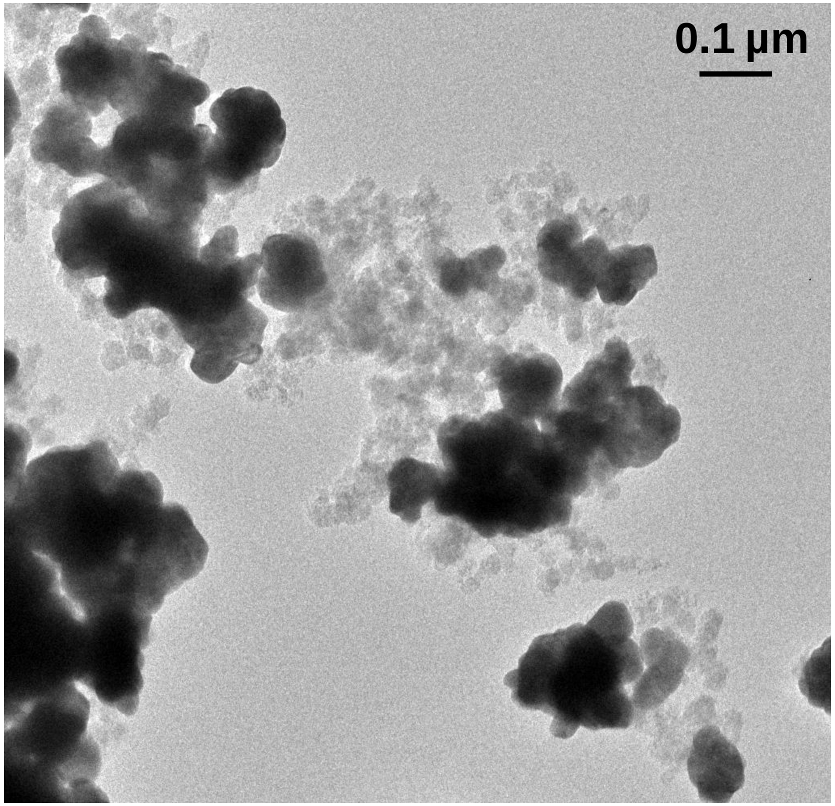
300 kV, SiO_x supporting film



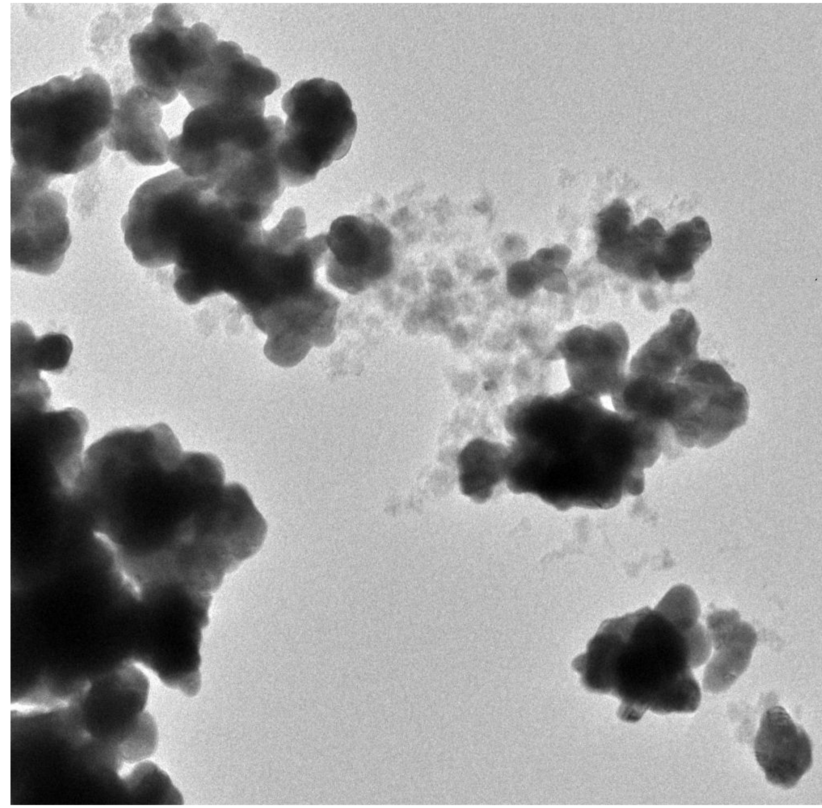
speed x4

T° = 475 ± 25°C, 1.7 10^{-1} mbar O_2

80 kV, SiO_x supporting film, t_0



After **5'**, **beam off**

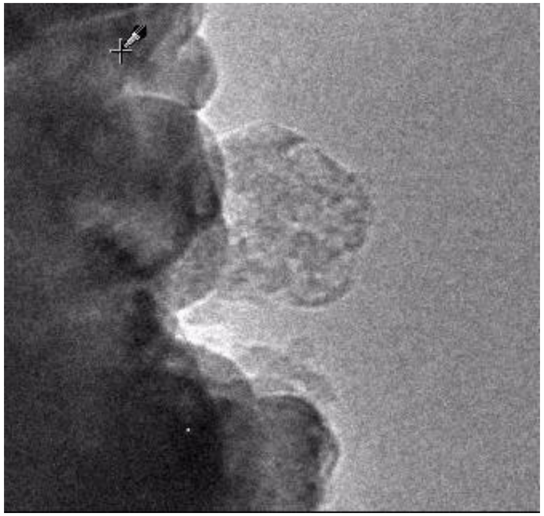


- Similar observations at 300 kV whatever the type or nature of support

NO intrinsic modification due to the electron beam (irradiation)

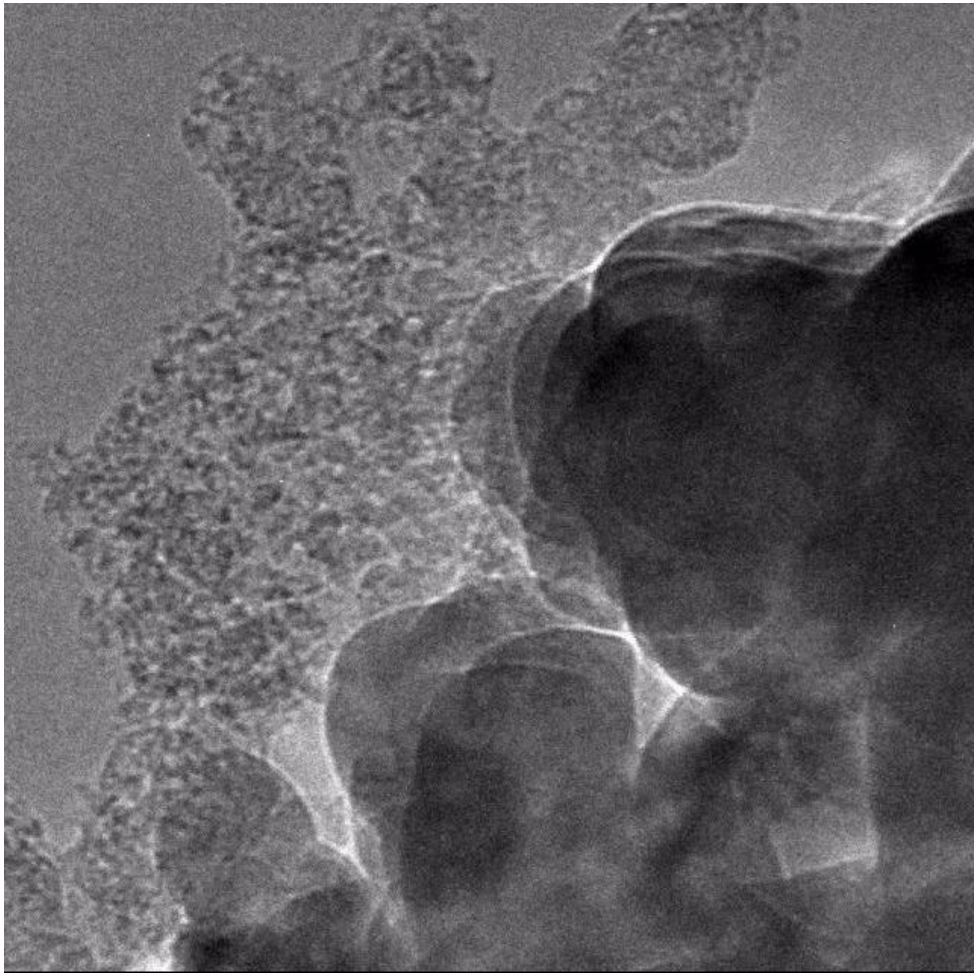
T° = 475 ± 25°C, 1.7 10^{-1} mbar O_2

80 kV, no supporting film



20 nm

300 kV, no supporting film



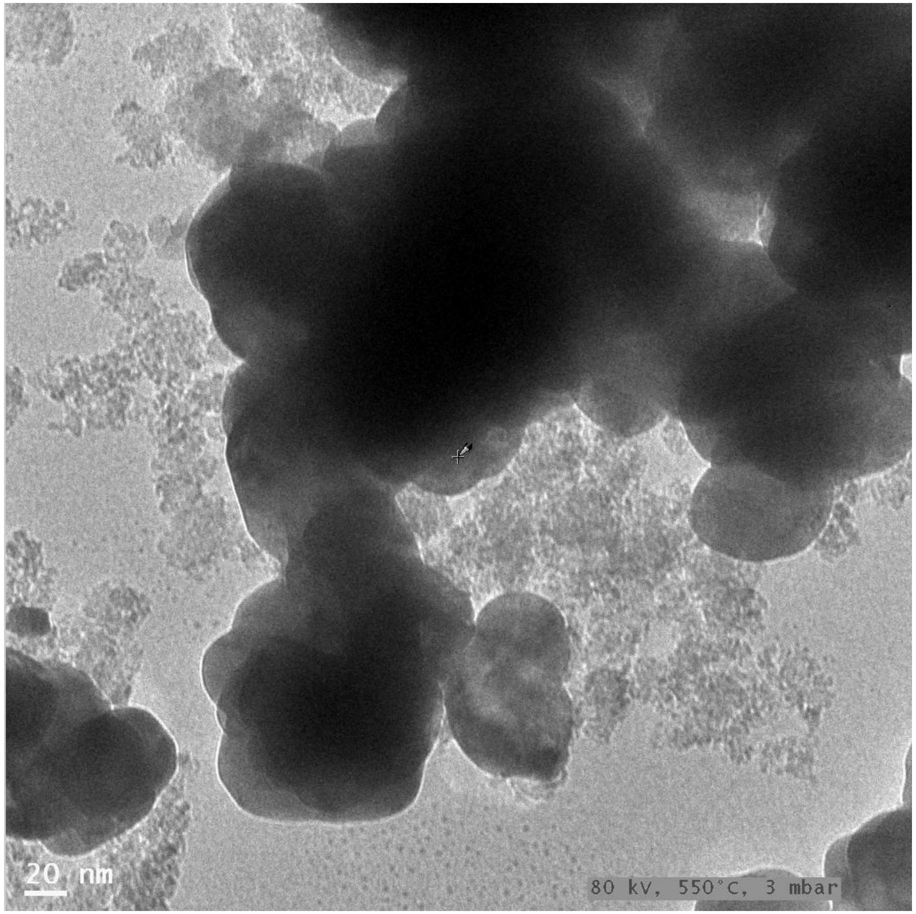
speed x2

20 nm

T° = 525 ± 25°C, 3 mbar O_2

80 kV, SiO_x supporting film

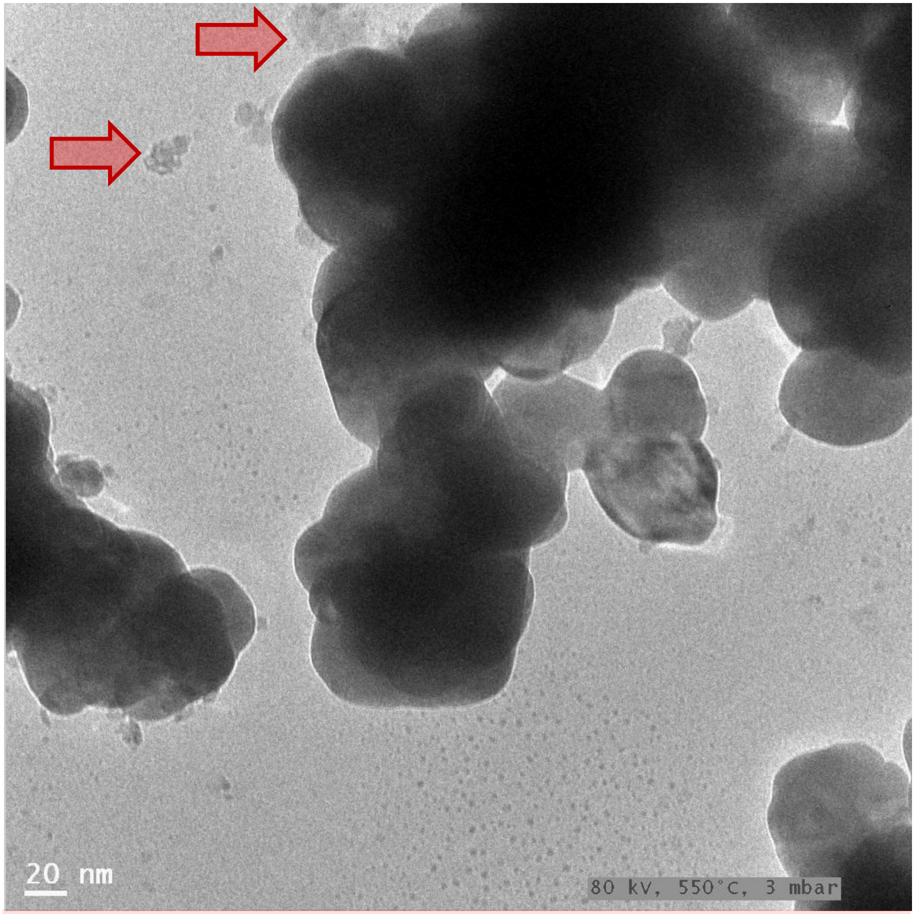
speed x4



T° = 525 ± 25°C, 3 mbar O_2

300 kV, SiO_x supporting film

speed x4

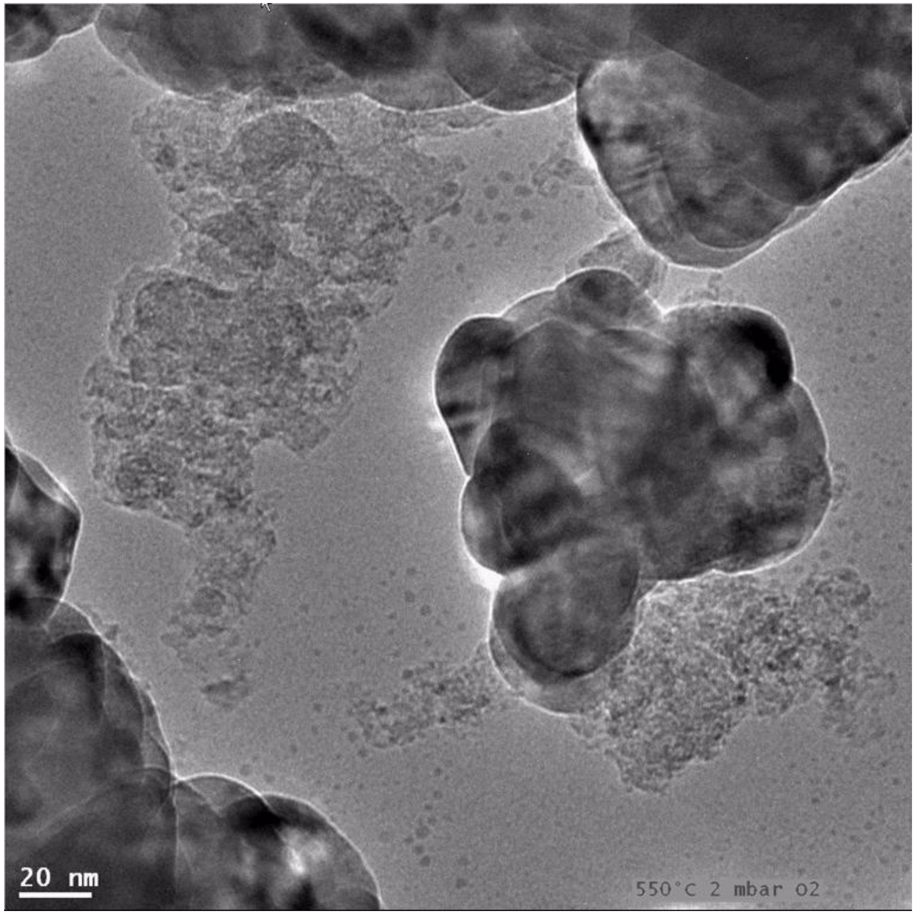


Soot particulates do not burn if not in (close) **contact with PSZ**

T° = 525 ± 25°C, 2 mbar O_2

300 kV, SiO_x supporting film

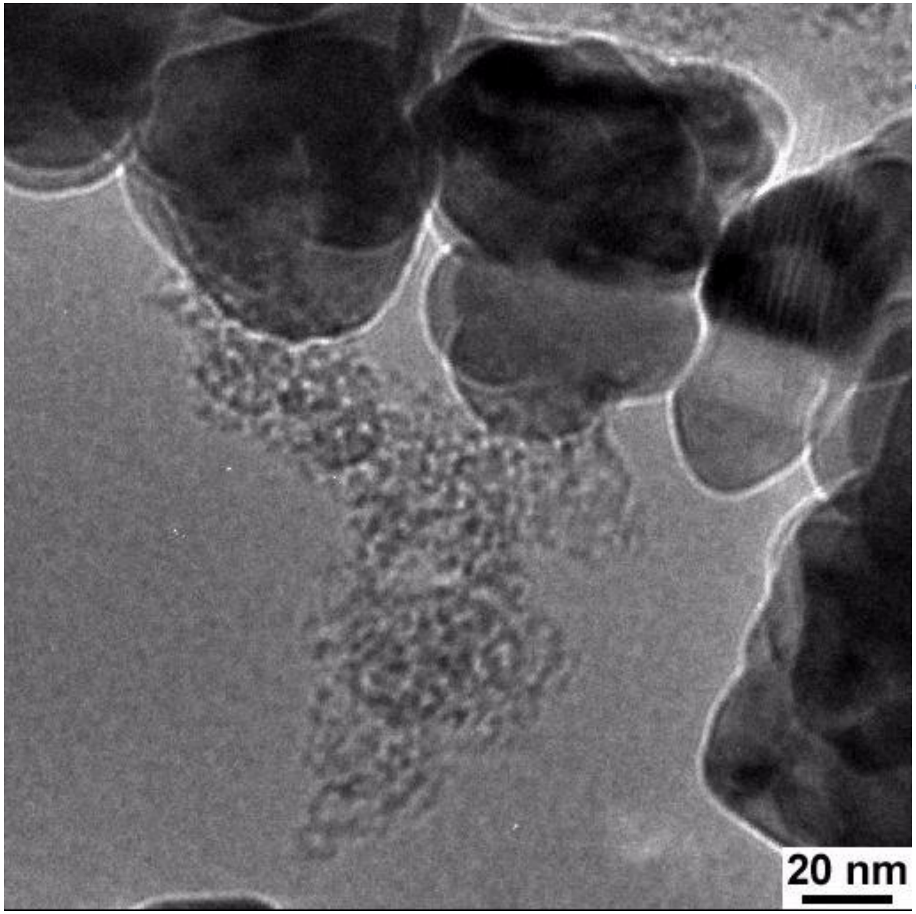
speed x4



T° = 525 ± 25°C, 2 mbar O_2

300 kV, SiO_x supporting film

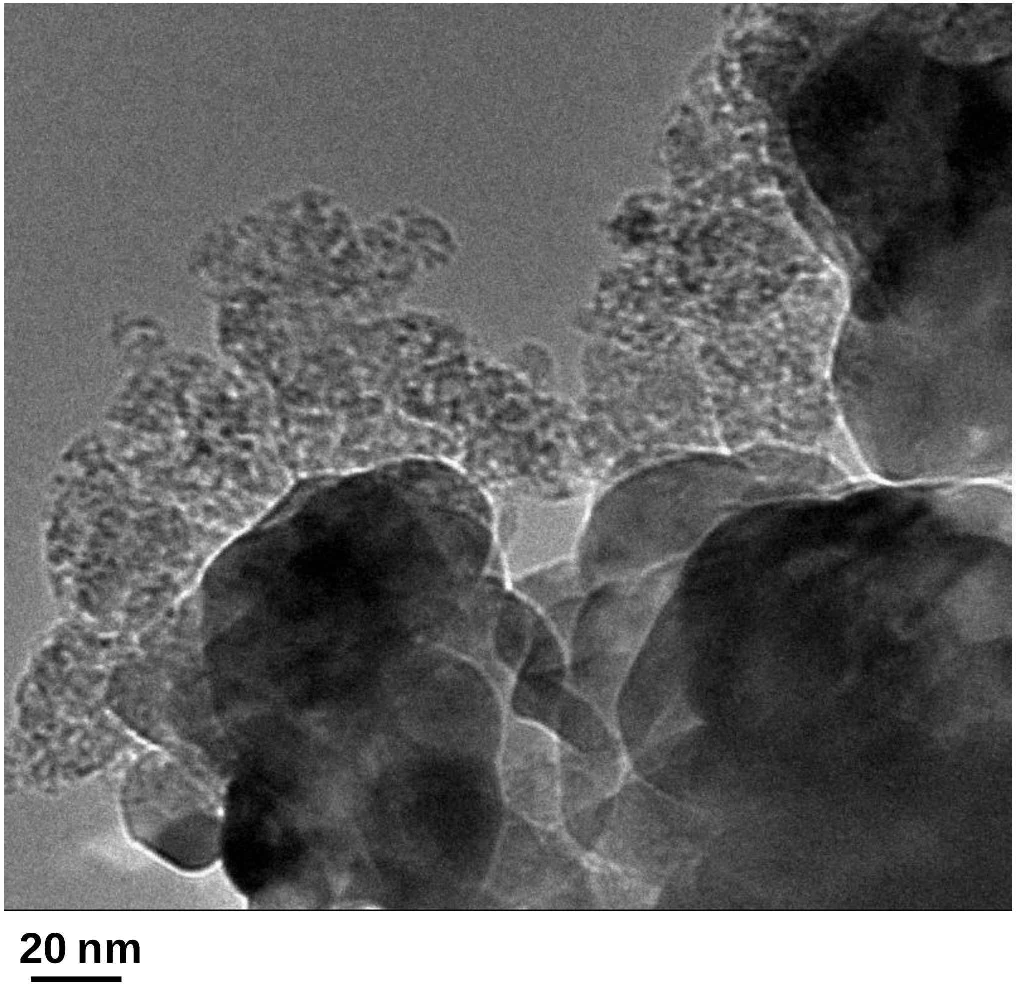
speed x2



T° = 475 ± 25°C, 2 mbar O_2

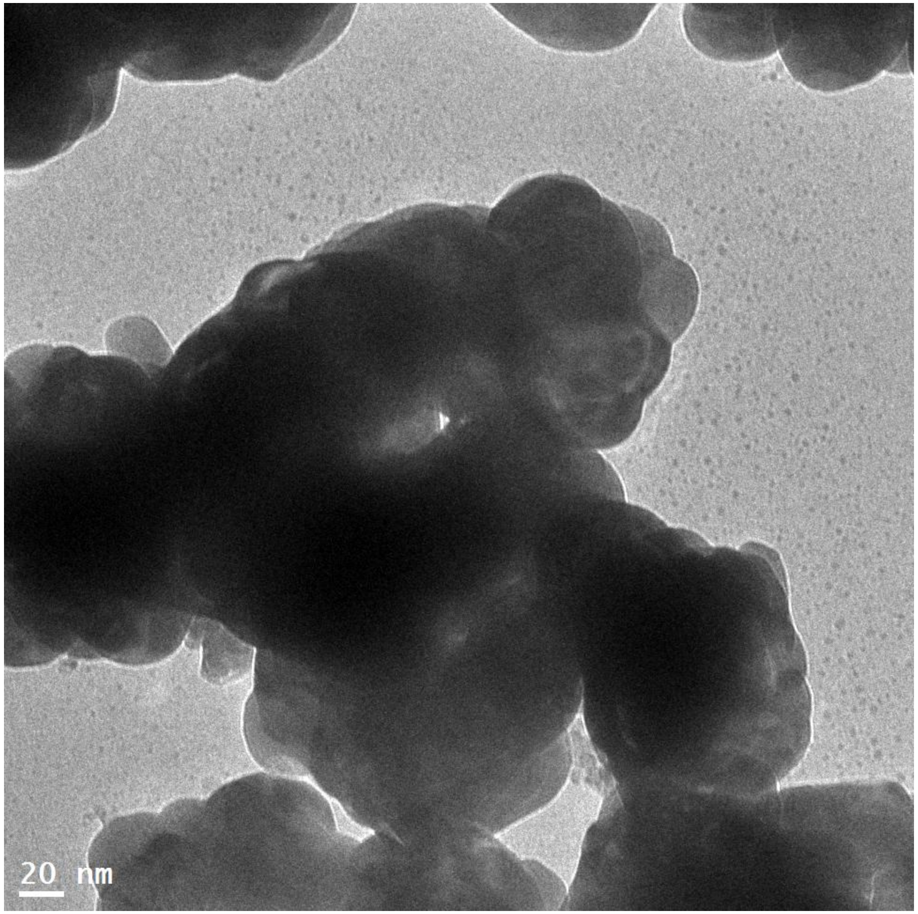
300 kV, no supporting film

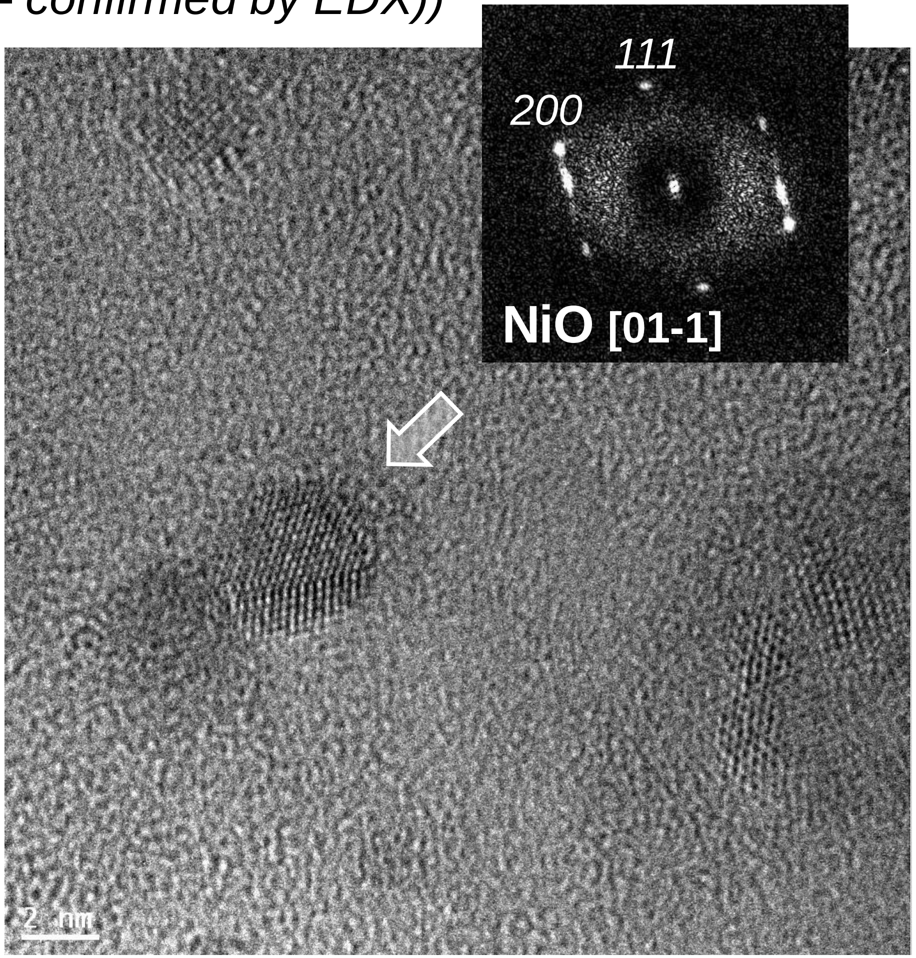
speed x1



Back to room temperature and High Vacuum

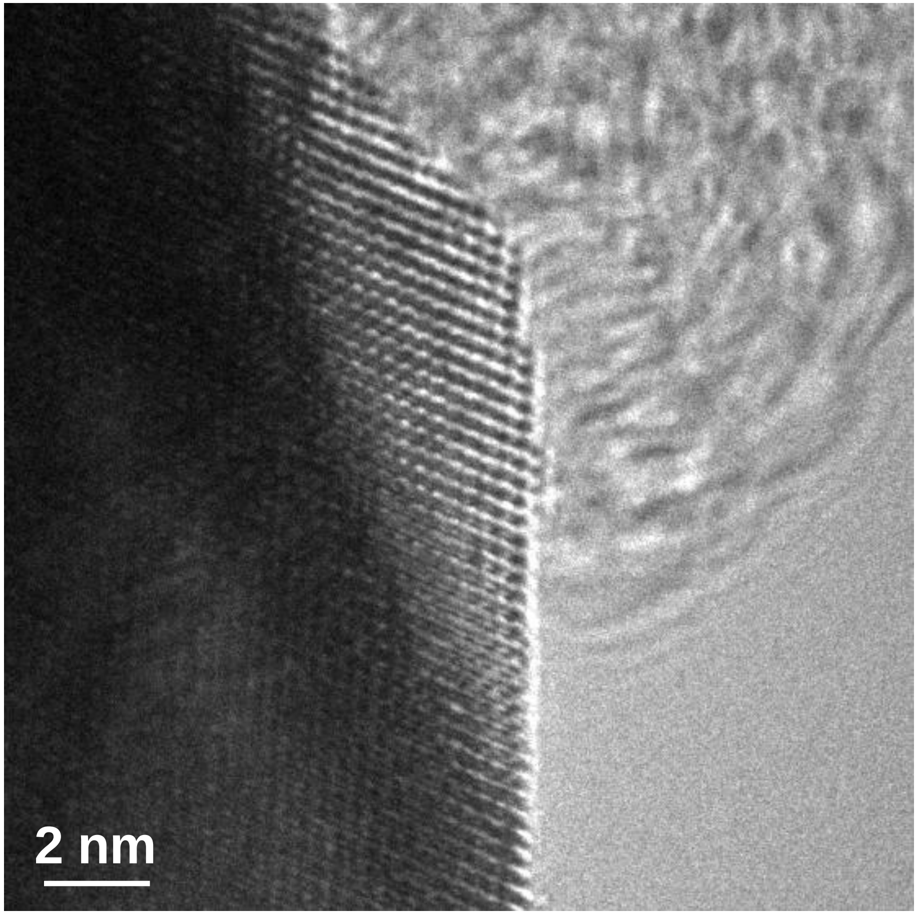
Left particles *(Ni impurities within the soot – confirmed by EDX))*

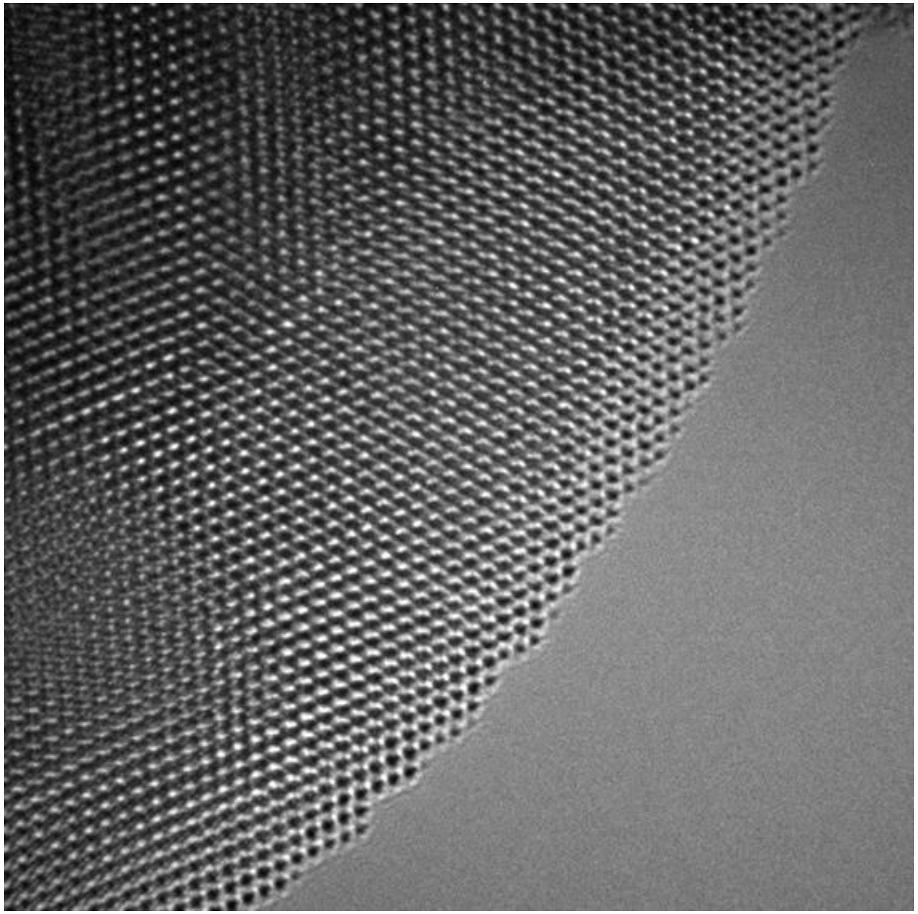




Back to room temperature and High Vacuum

YSZ grains surface BEFORE O_2 exposure **AFTER O_2 exposure at ≤ 550°C**





80 kV 300 kV

CONCLUSIONS

- **YSZ, a purely O^{2-} conductor, can oxidize soot without any noble metal.**

- **In-situ ETEM experiments in presence of O_2 confirm that:**
  - **bulk YSZ oxygens are the active species for soot oxidation at the soot/YSZ interface**
    (no oxidation takes place without contact)
  - The number of soot/YSZ contact points is the key parameter
  - Non linear soot oxidation rate : local thermal effect?
  - *CAST soot contains Ni as impurity (nanoparticles)*

ACKNOWLEDGMENTS

- French **National Research Agency** ANR for funding "PIREP2" *(Contract No. ANR-2010-VPTT-006-01)*
- PSA PEUGEOT CITROËN, ADEME — **PhD grant of Emil OBEID**
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