

***In situ* Environmental HRTEM Discloses Low Temperature Carbon Soot Oxidation by Ceria-zirconia at Nanoscale**

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Sample preparation

Ce_{0.8}Zr_{0.2}O₂ was prepared by precipitation using a solution of cerium nitrate with aqueous ammonium hydroxide in presence of H₂O₂. The precipitate formed after titrating with NaOH was filtered and dried at 100 °C for 15h, and then calcined under static air at 500°C for 3 h. The sample was characterized by X-ray diffraction, BET N₂ adsorption, temperature-programmed reduction, and high resolution transmission electron microscopy.

Catalytic measurements

Conventional catalyst/soot mixtures were obtained under loose contact mode by mixing the Ce_{0.8}Zr_{0.2}O₂ with soot (Printex U by Degussa) with a spatula in a ratio C/CZ80=1:20. Improved contact was achieved in a high energy Spex mill equipped with 9 zirconia balls (Φ= 10 mm) and a 50 ml jar. In a typical experiment 1.2 g of ceria-zirconia was milled with 0.06 g of soot (C/CZ80=1:20) corresponding to a ball to powder ratio of 22.1. Milling time was set to 8 hours.

Soot oxidation activity was measured under O₂/N₂ mixtures by running with a Temperature Programmed Oxidation ramp measurements. In this procedure, 20 mg of the CZ-soot mixtures were heated at a constant rate (10 °C/min) in a quartz reactor under O₂ gas flow (10% O₂ v/v, balance N₂; total flow 0.5 l/min). The catalyst temperature was measured by a chromel-alumel thermocouple, located on the catalyst bed. The outlet gas composition (CO, CO₂) was monitored by FT-IR gas analyzer (MultiGas 2030, MKS).

Catalyst characterization

Textural characteristics of the samples were measured according to the B.E.T. method by N₂ adsorption at -196°C, using a Tristar 3000 gas adsorption analyzer (Micromeritics). Structural features of the catalysts were investigated by powder X-ray diffraction analysis (XRD). Diffractograms were recorded on a Philips X'Pert diffractometer (equipped with a real time multiple strip detector) operated at 40kV and 40mA using Ni-filtered Cu-Kα radiation, using a step size of

0.02° and a counting time of 40 s per angular abscissa in the 2θ range 20°-140°. The Philips X'Pert HighScore software was used for phase identification. The mean crystalline size was estimated from the full width at the half maximum (FWHM) of the main diffraction peak using the Scherrer equation with a correction for instrument line broadening. Rietveld refinement of XRD spectra was performed by means of GSAS-EXPGUI program¹. Temperature-programmed reduction (TPR) experiments with an AutoChem II 2920 instrument (Micromeritics) have been used to measure the redox behavior of the catalytic materials. Samples (50-60 mg) were heated from room temperature to 800°C at a constant rate (10°C/min) in a U-shaped quartz reactor, under a flowing hydrogen/nitrogen mixture (30 ml/min, 4.6% H₂ in N₂) while monitoring the hydrogen consumption with a TCD detector. For ex-situ high-resolution transmission electron microscopy studies (HRTEM), a JEOL JEM 2010F electron microscope equipped with a field emission gun was used working at an accelerating voltage of 200 kV. Samples were dispersed in ethanol and a drop of supernatant suspension was poured onto a holey carbon coated grid and dried completely before measurements.

In situ ETEM

In-situ Electron microscopy was performed with an image Cs aberration corrected FEI-Titan ETEM (80-300 kV). Samples were suspended in ethanol and transferred on the heating nanochips (Wildfire, DENSSolutions) and dried at room temperature. The DENSSolution nanochip include a Pt heating spiral (20 μm width, ~150 nm thick) embedded in a 400 nm thick SiN sandwich. Samples can be easily placed on the EMwindows, ultra thin (<20 nm) electron transparent SiN membranes, in between the windings of heating spiral. Due to the small dimensions of heating element, the nanochip require less than 10 mW of power for reaching a temperature of 1100 °C. TEM images were acquired at 300 kV. Mass flow controllers (Brooks) were used to premix gases using a dedicated, home-made designed gas mixing system (Serv'Instrumentation), which were then dosed into the microscope at the sample stage by controlling the pressure close to the sample.

First series of experiments were performed in ultra-high vacuum conditions to test the stability of CZ80 and of the two different soot/CZ80 mixtures in both supertight and loose contact modes under the electron beam at room temperature without any oxygen. The two contact configurations were in-situ observed in presence of 1 mbar of O₂ only room temperature for the supertight one and from RT up to 600°C for the loose contact mode.

XPS

Surface characterization was done with X-ray photoelectron spectroscopy (XPS) on a SPECS system equipped with an Al anode XR50 source operating at 150 mW and a Phoibos MCD-9 detector. The pass energy of the hemispherical analyzer was set at 25 eV and the energy step was set at 0.1 eV.

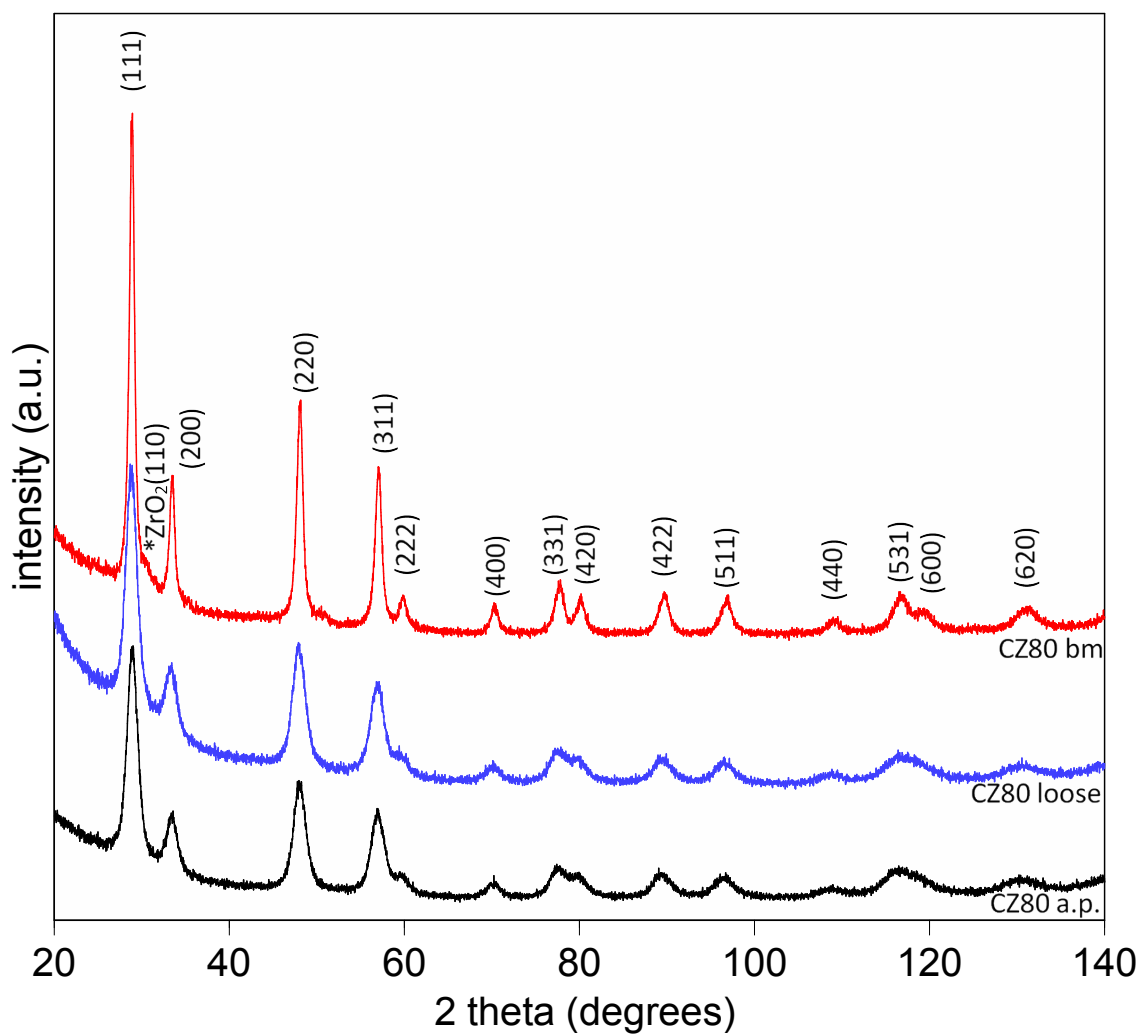


Figure 1S: XRD profiles of $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ as prepared (black line) and C/CZ80 mixtures mixed under loose conditions (blue line) and under high-energy milling for 8 h (red line).

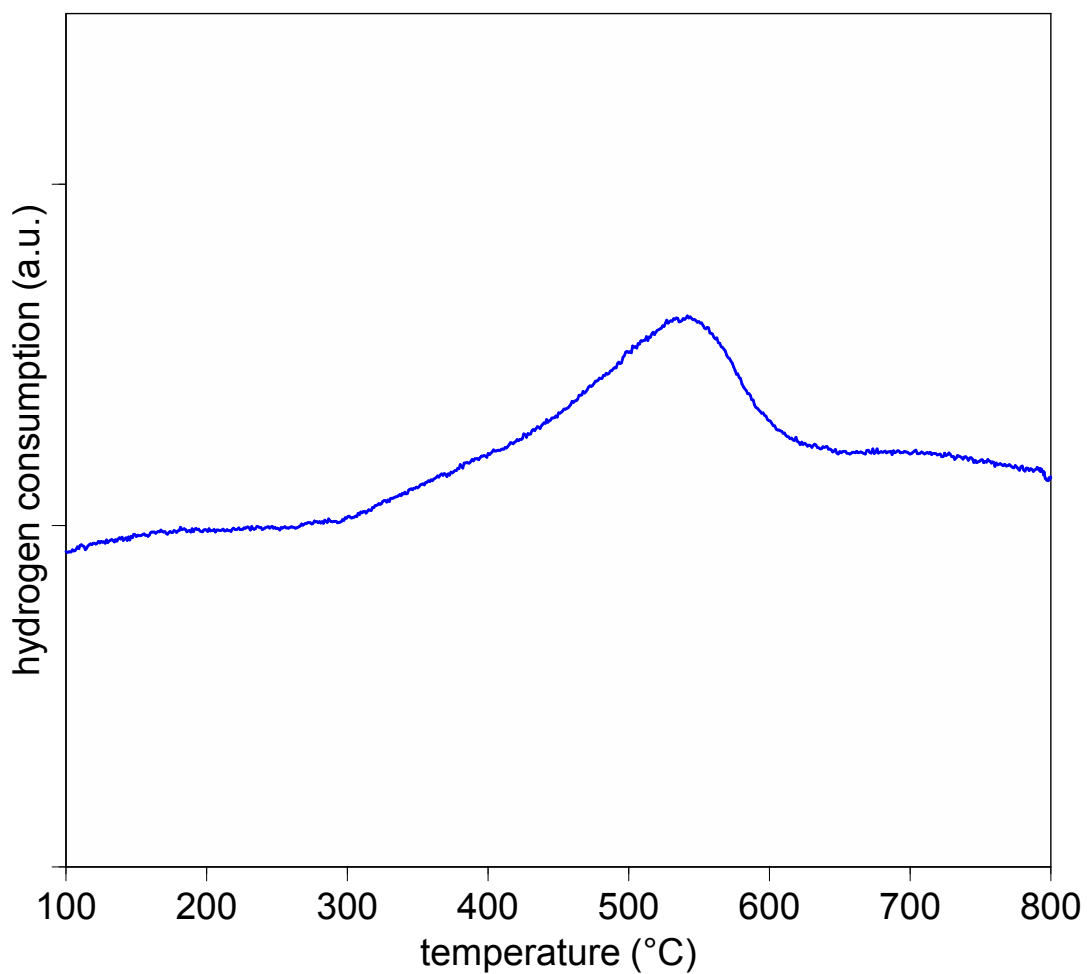


Figure 2S: Temperature programmed reduction (TPR) profile for bare $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$. The profile is characterized by one broad hydrogen uptake peak centered at around 550°C due to reduction of surface and bulk Ce^{4+} cations. Overall hydrogen consumption is consistent with a reduction degree of ca. 40% @800°C

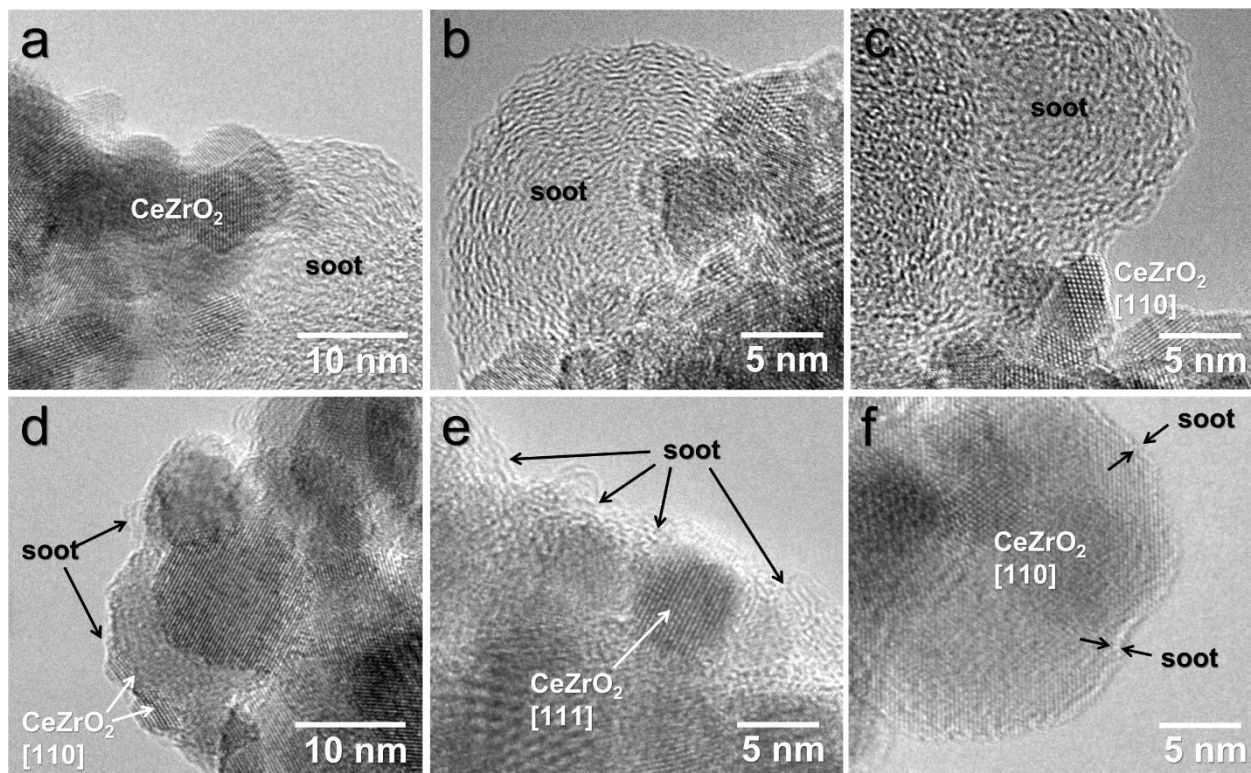


Figure 3S: Representative HRTEM images of $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ and soot mixed in loose contact mode (a-c) and after milling for 8 h (d-f).

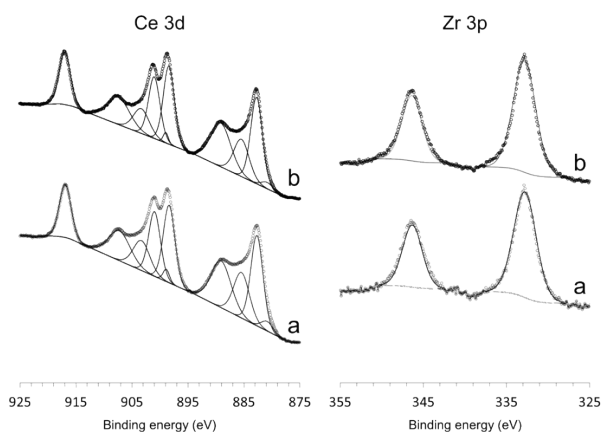


Figure 4S: XP spectra of Ce3d and Zr3p photoelectrons of (a) $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ and (b) $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ milled for 8h.

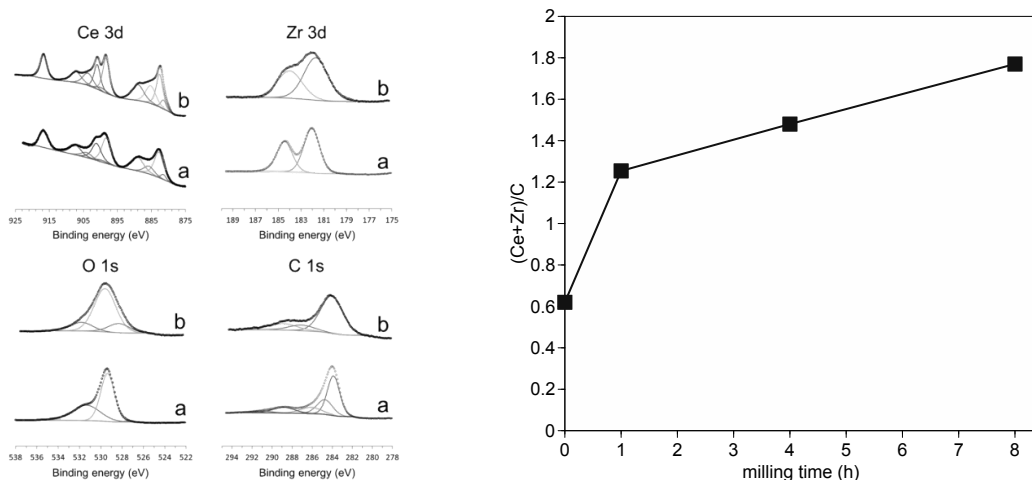


Figure 5S: Left, XPS spectra of Ce3d, Zr3d, O1s and C1s photoelectrons of (a) $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ mixed with soot and (b) $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ mixed with soot and milled for 8h. Broadening of C1s and O1s peaks following the milling of $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ with carbon is ascribed to the large structural disorder characterizing different carbon species at the interface strongly interacting with the ceria-zirconia catalyst.

Right, (Ce+Zr)/C atomic ratio against milling time from XPS analysis. The ratio increases with milling time as carbon develops a thin wrapping shell around the ceria-zirconia nanoparticles². This is consistent with a gradual substitution of localized large carbon clusters in poor contact with ceria-zirconia, that are typical of loosely mixed samples, with an interface comprised by a thin carbon layer distributed over the ceria-zirconia surface, typical of high energy milled samples; this newly created configuration permits the photoemitted electrons from underneath Ce and Zr atoms to reach the surface.

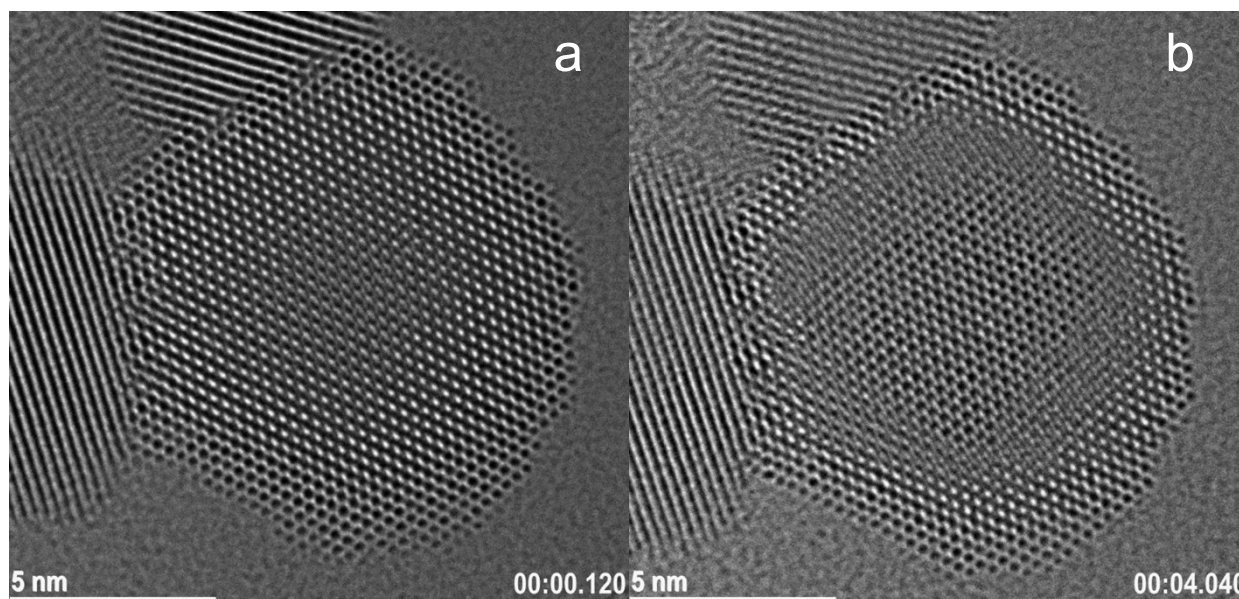


Figure 6S: ETEM images extracted from video 1 recorded under UHV at RT. Beam voltage = 300 kV; a) starting time t0, b) t0 +4s. Stability under the electron beam of a CZ80 crystallite.

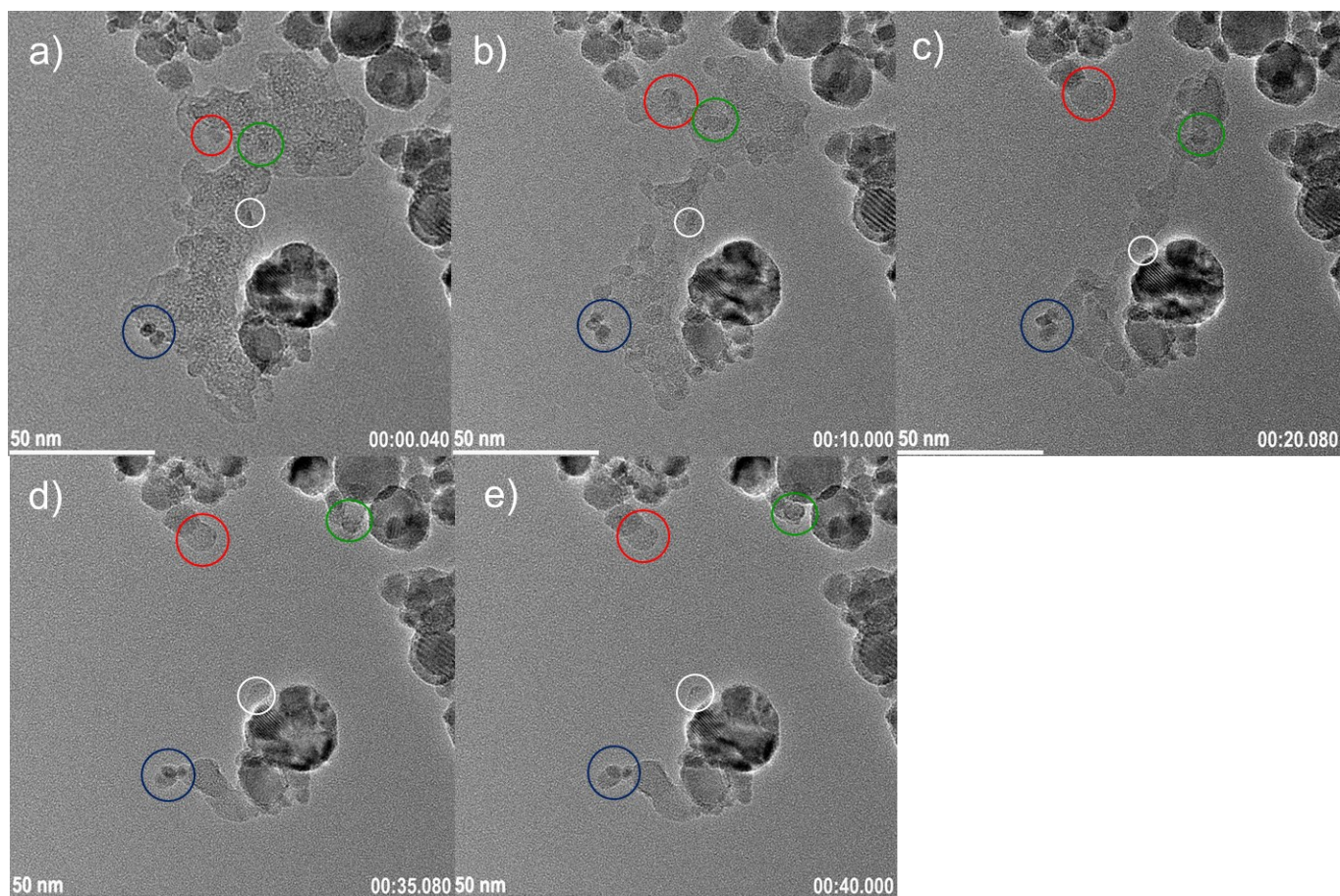


Figure 7S : ETEM images extracted from video 6 recorded at room temperature under 0.37 mbar of O_2 . Beam voltage = 300 kV; a) starting time t_0 , b) $t_0 + 10s$, c) $t_0 + 20s$, d) $t_0 + 35s$ and e) $t_0 + 40s$. Coloured circles indicate the positions of CZ80 nanoparticles embedded into the carbon soot.

Table S1: characteristics of $Ce_{0.8}Zr_{0.2}O_2$ and soot mixtures

sample	Surface Area (m^2/g)	Crystallite size (nm)	Cell parameter ^a
CZ80	79	6.4	5.3596 (5)
CZ80 loose	78	6.4	5.3589 (4)
CZ80 bm8h	29	13.6	5.3492 (3)

^a cell parameter obtained by Rietveld refinement. Abrasion during milling is responsible for the small decrease of the lattice parameter (from 5.3596 to 5.3492Å) due to inclusion of Zr into $Ce_{0.8}Zr_{0.2}O_2$ solid solution³. According to this, the stoichiometry of solid solution changes to $Ce_{0.78}Zr_{0.22}O_2$ after 8 hours of milling.

References

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- [2] E. Aneggi, V. Rico-Perez, C. de Leitenburg, S. Maschio, L. Soler, J. Llorca, A. Trovarelli, *Angewandte Chemie International Edition* **2015**, *54*, 14040-14043.
- [3] A. Trovarelli, F. Zamar, J. Llorca, C. de Leitenburg, G. Dolcetti, J. T. Kiss, *Journal of Catalysis* **1997**, *169*, 490-502.